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Ligand Additivity Effects and Periodic Trends in the Stability and Acidity of Octahedral η^2-Dihydrogen Complexes of d^6 Transition Metal Ions

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An original approach for predicting the properties of η^2-dihydrogen complexes $M(H_2)L_5$ is described based on additive electrochemical parameters for the ligands and Lever's correlations for transition metals of groups 6–8. A correlation for group 9 is also reported. On the basis of the properties of the ~70 known d^6 octahedral dihydrogen complexes, it is concluded that there is a narrow range of possible energies of the $d_\pi(t_{2g})$ electrons where stable bonding of the η^2-H_2 ligand is possible at 25 °C. This range, defined in terms of electrochemical potentials $E_{1/2}(d^5/d^6)$ of corresponding dinitrogen complexes $M(N_2)L_5$, appears to depend on the ligand trans to N_2 but is independent of the metal and of the charge on the complex. This means that progressively more electron-donating ligand sets are needed to stabilize η^2-H_2 (or N_2) complexes on going from group 6 metals to group 9 d^6 metal ions. Complexes $M(N_2)L_5$ with potentials above 2.0 V vs NHE correspond to $M(H_2)L_5$ species that lose H_2 irreversibly at 25 °C whereas complexes with potentials below 0.5 V correspond to dihydrides, $M(H)_2L_5$. Even if the energetics of the d electrons are correct, intramolecular homolytic splitting of dihydrogen might still occur if the product dihydride is especially stable. The potentials, $E_{1/2}(d^5/d^6)$, that limit stability are more negative when the η^2-H_2 ligand is trans to CO than to a σ-donor ligand. A ligand additivity model provides a guide to the combinations of ligands which are likely to produce stable dihydrogen complexes. The narrow range of electrochemical potentials for stable η^2-H_2 complexes translates into a possible range of pK_a values of about 0–40 for complexes $M(\eta^2\text{-}H_2)L_5$. Very acidic dihydrogen complexes ($pK_a < 0$) will be very labile with respect to H_2 loss at 25 °C. Dihydrogen complexes are proposed as intermediates in some previously reported reactions, and the predicted properties of postulated dihydrogen complexes are shown to be consistent with the reactivity observed. The dinitrogen stretching frequency of corresponding complexes $M(N_2)L_5$ can also be predicted fairly reliably.

Introduction

Enough examples of d^6 octahedral η^2-dihydrogen complexes[1] have now appeared to enable a correlation between structure and reactivity. The reactions of interest refer to the decomposition of the dihydrogen complex by homolytic or heterolytic splitting of the H-H bond or by loss or substitution of the labile η^2-H_2 group.

It was postulated in an earlier paper that stable octahedral complexes with the metal in the d^6 configuration are obtained in two instances.[2] First complexes that have the η^2-H_2 ligand trans to CO will be stable when they form derivatives *trans*-$M(N_2)(CO)L_4$ or *trans*-$M(CO)_2L_4$ with electrochemical potentials $E_{1/2}(d^5/d^6)$ of about 0.0 V vs SCE (0.2 V vs NHE). Second, complexes that have the η^2-H_2 group trans to a good σ-donor like H^- will be stable when they form derivatives *trans*-$M(N_2)HL_4$ or *trans*-$M(CO)HL_4$ with $E_{1/2}(d^5/d^6)$ of about 1.0 V vs SCE (1.2 V vs NHE). There is a linear relationship between $E_{1/2}$ values and ionization energies from photoelectron spectroscopy and this indicates that electrochemistry gives a good measure of the energy of the $t_{2g}{}^6$ electrons in the complex. The more negative the $E_{1/2}$, the more back-bonding there will be to the π-acid ligand (N_2, CO, or H_2). A certain amount of back-bonding is necessary for stable M–(η^2-H_2) bonding at 25 °C but too much back-bonding (too negative a $E_{1/2}$) will result in homolytic cleavage of the H–H bond to give a dihydride. Back-bonding to dihydrogen is reduced when the ligand is trans to CO instead of a σ-donor ligand. For a stable dihydrogen binding site, the critical amount of back-bonding was proposed to occur when the dinitrogen stretching frequency of the complex with N_2 substituted for H_2 falls in the range of dinitrogen stretching frequencies $\nu(N_2)$ = 2060–2150 cm^{-1}. This present paper examines the properties of dihydrogen complexes prepared since this original range of stability was proposed in order to see how this prediction has held up.

A recent development is the additive ligand approach for the estimation of electrochemical potentials $E_{1/2}(d^5/d^6)$ for six-coordinate complexes.[3,4] This work was founded on extensive evidence that simple additive schemes for explaining and/or predicting the properties of complexes are valid and very useful.[5] The current paper shows how this approach reveals periodic trends in the stability of η^2-dihydrogen complexes and how it can be used to predict which combinations of ligands might give stable complexes.

A second advance is the correlation of electrochemical parameters with the acidity of dihydrogen complexes (eq 1).[6–8] The

$$1.37(pK_a\{M(\eta^2\text{-}H_2)\}) = \Delta H_{BDE}\{M(\eta^2\text{-}H_2)\} - 23.1E_{1/2}(MH/MH^-) - 59 \quad (1)$$

pK_a of a dihydrogen complex $M(\eta^2\text{-}H_2)L_5$ can be calculated if the ΔH_{BDE} and $E_{1/2}$ terms can be evaluated. The constant 59 in eq 1 has been estimated for pK_a values determined in non-aqueous solution and then extrapolated to the aqueous pK_a scale and for the $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$ reference potential.[7,8] The electrochemical potential $E_{1/2}(MH/MH^-)$ for the oxidation of the complex ($MHL_5{}^-$) which results from the deprotonation of the dihydrogen complex can be estimated by the ligand additivity method.[3,4,6] Little is known about the bond dissociation enthalpy, $\Delta H_{BDE}\{M(\eta^2\text{-}H_2)\}$, which is the energy required to take a hydrogen atom from the η^2-H_2 ligand (eq 2).

$$\Delta H_{BDE}\{M(\eta^2\text{-}H_2)L_5\} = \Delta H_f\{H^\bullet\} + \Delta H_f\{MHL_5{}^\bullet\} - \Delta H_f\{M(\eta^2\text{-}H_2)L_5\} \quad (2)$$

If there is enough back-bonding to the dihydrogen in the complex so that it is in equilibrium with a dihydride tautomer, then ΔH_{BDE} is expected to be close to a metal–hydride bond energy (60–75 kcal mol^{-1}). One example is the series of complexes $[Ru(C_5R_5)H_2(\text{bidentate phosphine})]^+$ which display this tautomerism and probably have ΔH_{BDE} close to a typical Ru–H bond energy of 65 kcal mol^{-1}.[6] If there is little back-bonding to the dihydrogen and significant H–H bond energy, then ΔH_{BDE} might be as large as 83.5 kcal mol^{-1} for the postulated species $[Mn(H_2)(CO)_5]^+$[9] as deduced from earlier proton affinity data for $MnH(CO)_5$.[10] Complexes $[Ru(H)(\eta^2\text{-}H_2)$(bidentate phos-

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Table I. Lever's Additive Electrochemical Parameters, E_L (in V)

ligand[a]	type	E_L	ligand[a]	type	E_L
NO^+	$L^{\pi+}$	~1.9	1/2 dmpe	L^{σ}_2	0.28
CO	L^{π}	0.99	1/2 depe	L^{σ}_2	0.27
H_2	L^{π}	~0.8	1/2 bpy	L^{σ}_2	0.27
C_2H_4 (olefin)	L^{π}	0.76	thf	L^{σ}	~0.2
N_2	L^{π}	0.68	NH_3	L^{σ}	0.07
CNBu	L^{σ}	0.45	1/3 $C_5H_5^-$ (Mn)	$X^{\sigma-}L^{\sigma}L^{\pi}$	~0.3
1/2 dppm	L^{σ}_2	0.43	1/3 $C_5H_5^-$ (Ru)	$\chi^{\sigma-}L^{\sigma}_2$	0.03
$P(OEt)_3$	L^{σ}	0.42	$HB(3,5Me_2pz)_3^-$	$X^{\sigma}L^{\sigma}_2$	~0
PPh_3	L^{σ}	0.39	1/2 bq^-	$L^{\sigma}(N)X^{\sigma-}(C)$	~0
$PEtPh_2$	L^{σ}	0.36	1/4 oep^{2-}	$X^{\sigma-}_2L^{\sigma}_2$	~0
1/2 dppe	L^{σ}_2	0.36	μ-Cl^-	$X^{\sigma-}L^{\sigma}$	~0
1/4 meso-tet	L^{σ}_4	~0.36	μ-H^-	$X^{\sigma-}$	~0
1/2 dppp, 1/2 dppb	L^{σ}_2	0.36	1/2 OAc^-	$X^{\sigma-}L^{\sigma}$	~−0.05
1/2 binap	L^{σ}_2	0.36	1/3 $C_5Me_5^-$ (Ru)	$X^{\sigma-}L^{\sigma}_2$	~−0.09
PMe_2Ph	L^{σ}	0.34	Cl^-	$X^{\sigma-}$	−0.24
CH_3CN	L^{σ}	0.34	H^-	$X^{\sigma-}$	−0.4
1/3 cyttp	L^{σ}_3	~0.32	μ-S^{2-}	$X^{\pi-}X^{\sigma-}$	~−0.35
1/4 PP_3	L^{σ}_4	~0.30	S^tBu^-	$X^{\pi-}$	−0.55
PBu_3	L^{σ}	0.29	OH^-	$X^{\pi-}$	−0.59
PPr^i_3	L^{σ}	~0.29	NR_2^-	$X^{\pi-}$	~−0.6
PCy_3	L^{σ}	~0.29			

[a] Abbreviations: dppm = $PPh_2CH_2PPh_2$, dppe = $PPh_2CH_2CH_2PPh_2$, meso-tet = $\{PPh_2CH_2CH_2PPhCH_2-\}_2$, PP_3 = $P(CH_2CH_2PPh_2)_3$, depe = $PEt_2CH_2CH_2PEt_2$, dmpe = $PMe_2CH_2CH_2PMe_2$, bq^- = cyclometalated benzoquinolato, oep^{2-} = octaethylporphyrinato, dppp = $PPh_2CH_2CH_2CH_2PPh_2$, dppb = $PPh_2CH_2CH_2CH_2CH_2PPh_2$, binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, cyttp = $(PCy_2CH_2CH_2CH_2)_2PPh$, $HB(3,5Me_2pz)_3^-$ = tris-(3,5-dimethylpyrazolyl)hydroborato.

Table II. Equations for Calculating $E_{1/2}(d^5/d^6)$ (V vs NHE) for Metal Complexes in Organic Solvents[a]

Cr(I)/Cr(0)	$E_{1/2} = 0.52\sum E_L - 1.75$	(3)
Mo(I)/Mo(0)	$E_{1/2} = 0.74\sum E_L - 2.25$	(4)
W(I)/W(0)	$[E_{1/2} = 0.6\sum E_L - 2]$	(5)
Mn(II)/Mn(I)	$E_{1/2} = 0.81\sum E_L - 1.76$	(6)
Re(II)/Re(I)	$E_{1/2} = 0.76\sum E_L - 0.95$	(7)
Fe(III)/Fe(II)	$E_{1/2} = 1.10\sum E_L - 0.43$	(8)
Ru(III)/Ru(II)	$E_{1/2} = 0.97\sum E_L - 0.03$	(9)
Os(III)/Os(II)	$E_{1/2} = 1.01\sum E_L - 0.40$	(10)
Rh(IV)/Rh(III)	$[E_{1/2} = 0.7\sum E_L + 1.3 + 0.5]$	(11)
Ir(IV)/Ir(III)	$[E_{1/2} = 0.7\sum E_L + 1.3]$	(12)

[a] From Lever[3,4] excepting the equations in brackets (see text).

phine)$_2$]$^+$ are thought to have ΔH_{BDE} near 80 kcal mol^{-1}.[7] However there is still uncertainty as to how the energy $\Delta H_f\{MHL_5^{\bullet}\}$ in eq 2 varies with the metal and ligands and also whether a correction based on the kinetics of electron transfer[11] needs to be made to account for the irreversibility of oxidation of many metal hydride complexes. Nevertheless a rough estimate of the pK_a of a dihydrogen complex can be obtained by use of eq 1 and predicted $E_{1/2}$ values.

Results

Ligand Additivity. Tables I and II present ligand parameters, E_L, and equations for d^6 metal complexes, respectively, as proposed primarily by Lever. Also included in Table I are the parameters for the η^2-H_2 ligand[12,13] and the $C_5H_5^-$ ligand on Ru and Mn.[8] A value of −0.3 V was proposed for H^- on the basis of one measurement.[3] A value of −0.4 V appears to give more reasonable $E_{1/2}$ values for the variety of hydrides discussed here. The parameters for NO^+, CO, H_2, $C_5H_5^-$, H^-, $P(OR)_3$, and olefin ligands may well vary depending on the metal and the nature of the other ligands because of the high polarizability of these ligands. This problem makes a quantitative treatment difficult. However the simplicity of the approach and the surprisingly good agreement with observed properties justifies the qualitative treatment presented here. Several dihydrogen complexes have the ligands PPr^i_3 or PCy_3; these are assumed to have the same E_L value as PBu_3 (0.29 V). Common ligands with the most positive potentials (apart from NO^+) are neutral π-acid ligands (denoted L^{π}); next are neutral σ-donor ligands (L^{σ}); next are anionic σ-donor ligands ($X^{\sigma-}$); the most negative are anionic π-donor ligands ($X^{\pi-}$). The π-donor ligands raise the energy of the d^6 metal HOMO electrons by significant repulsion between the nonbonding d electrons and lone pairs on the ligands. Parameters for the $X^{\pi-}$ ligands OH^- and S^tBu^- were provided by Lever[3] (on the basis of the work of Pickett and co-workers).[14] The values for the NR_2^- ligand and μ-S^{2-} ligand are estimated from these values for use later in the discussion. The π-acid ligands have a variable effect on lowering the energy of the HOMO depending on which isomer and which combination of types of ligands are involved (see below). The more complicated ligands of unknown E_L were first classified according to the donor atoms (e.g. cyclometalated benzoquinolato as L^{σ} for the N donor and $X^{\sigma-}$ for the C^- donor atom). Then an averaged E_L value was calculated (e.g. the E_L for a N-donor ligand, L^{σ}, is approximately 0.2 V and E_L for $X^{\sigma-}$ is approximately −0.2 V so that the averaged value for bq^- is 0 V).

The equations for calculating the electrochemical potential $E_{1/2}(d^5/d^6)$ for low-spin, d^6 octahedral complexes are listed in Table II as provided primarily by Lever. The equation for W(0) is tentative since it is based on only a few points.[2,15] The $E_{1/2}$ values for the Cr complexes are corrected according to the number of carbonyl groups and the isomer present.[5] Lever obtained eq 4 for Mo without correcting for the effect of carbonyl isomers but noted that ignoring the correction still gave reasonable agreement with observed electrochemical potentials. A similar approach of correcting Cr values but not Mo or W is followed here. Little is known about the oxidation of electron-rich complexes of the Co group with the metal in the d^6 configuration. There is a cluster of data for iridium complexes of the type $IrCl_4L_2^-$[16] and $Ir(Et_2NCS_2)_3$[17] with $\sum E_L$ values around −0.35 ± 0.15 V and with $E_{1/2}$ values near 0.9 ± 0.2 V vs SCE or 1.1 V vs NHE,[18] but these do not give a linear correlation. The only complex to be examined with a reversible oxidation and a $\sum E_L$ = −1.44 V which is out of this cluster of data is $IrCl_6^{3-}$ with $E_{1/2}$ near 0.3 ± 0.2 V vs NHE (values of −0.02[19] and 0.23 V[16] vs SCE have been reported). From these values a tentative correlation is proposed for the Ir(IV/III) couple (eq 12, Table II). This eq gives $E_{1/2}$ = 1.5 V for the complex $[IrH_2(bpy)_2]^+$ while the observed peak potential for oxidation is 1.4 V vs NHE.[20] Equation 11 for Rh complexes is based on the observation that peak potentials for some complexes $RhCl_4L_2^-$ are ~0.5 V more positive than isostructural Ir complexes.[16] A comparison of eqs 9 and 10 reveals that $E_{1/2}$(Ru(III/II)) values are 0.4 V more positive than $E_{1/2}$(Os(III/II)) values for analogous complexes.

Table III classifies the structures of known d^6, octahedral dihydrogen complexes $M(\eta^2\text{-}H_2)L_5$ according to the class of ligands (L^{π}, L^{σ}, $X^{\sigma-}$) and gives the sum of E_L values ($\sum^5 E_L$) for the five ligands excluding the dihydrogen ligand.[21] Table III starts with group 6 metal complexes and ends with those of group 9. This list is not exhaustive. It only includes a few representatives of the class of complexes $Ru(C_5R_5)L_2(H_2)^+$ and it does not include some complexes such as $Cr(C_6R_6)(CO)_2(H_2)$[22] where the E_L value

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(21) The bold numbers in the tables refer to the ML_5 fragments; e.g. **1** for $Cr(CO)_5$. A dihydrogen complex, e.g., $Cr(H_2)(CO)_5$, is then referred to as **1**(H_2).

Table III. Properties of η^2-Dihydrogen and Dinitrogen Binding Sites, ML_5

ML_5[a]						
no.[21]	formula	ligand set[a]	$\sum^5 E_L$,[b] V	calcd $E_{1/2}$[c] for N_2ML_5, V	observed stability[d] of H_2ML_5	ref
1	$Cr(CO)_5$	L^{π}_5	5.4	1.4	loses H_2	40, 41
2	$Cr(CO)_4(H_2)$	L^{π}_5	5.21	1.3	loses H_2	42
3	$Cr(olefin)(CO)_4$	L^{π}_5	5.17	1.3	loses H_2	43
4	$Cr(CO)_4(C_2H_4)$	L^{π}_5	5.17	1.3	loses H_2	44
5	$Cr(CO)_3(PCy_3)_2$	$L^{\pi}_3L^{\sigma}_2$	3.70	0.5	labile/loses H_2	45
6	$Mo(CO)_5$	L^{π}_5	4.95	1.9	loses H_2	42
7	$Mo(CO)_4(C_2H_4)$	L^{π}_5	4.72	1.7	loses H_2	44
8	$Mo(CO)_3(PPr^i_3)_2$	$L^{\pi}_3L^{\sigma}_2$	3.55	0.9	labile	26
9	$Mo(CO)_3(PCy_3)_2$	$L^{\pi}_3L^{\sigma}_2$	3.55	0.9	labile	26
10	$Mo(CO)(dppe)_2$	$L^{\pi}L^{\sigma}_4$	2.43	0.1	labile	46
11	$W(CO)_5$	L^{π}_5	4.95	1.4	loses H_2	42, 47
12	$W(CO)_4(C_2H_4)$	L^{π}_5	4.72	1.2	loses H_2	44
13	$W(CO)_3(PCy_3)_2$	$L^{\pi}_3L^{\sigma}_2$	3.55	0.5	labile, $(H)_2$	26
14	$W(CO)_3(PPr^i_3)_2$	$L^{\pi}_3L^{\sigma}_2$	3.55	0.5	labile, $(H)_2$	26
15	$Mn(C_5H_5)(CO)_2$	$X^{\sigma-}L^{\pi}L^{\sigma}_3$	2.97	1.2	labile	2, 22
16	$ReCl(PMePh_2)_4$	$X^{\sigma-}L^{\sigma}_4$	1.26	0.5	stable, $(H)_2$?	48
17	$FeH(P(OEt)_3)_4^+$	$X^{\sigma-}L^{\sigma}_4$	1.28	1.7	stable	27
18	$FeH(dppe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	1.04	1.5	stable	33
19	$FeH(meso\text{-}tet)^+$	$X^{\sigma-}L^{\sigma}_4$	1.04	1.5	stable	49
20	$FeH(PP_3)^+$	$X^{\sigma-}L^{\sigma}_4$	0.80	1.2	stable	50, 51
21	$FeH(depe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	0.68	1.1	stable	33
22	$FeH(dmpe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	0.72	1.1	stable	30, 31
23	$FeH_2(PEtPh_2)_3$	$X^{\sigma-}_2L^{\sigma}_3$	0.28	0.6	labile	52
24	$Ru(C_5Me_5)(CO)_2^+$	$X^{\sigma-}L^{\sigma}_4$	1.71	2.4	loses H_2	34
25	$Ru(C_5H_5)(CO)(PCy_3)^+$	$X^{\sigma-}L^{\pi}L^{\sigma}_3$	1.37	2.0	labile	53
26	$Ru(C_5H_5)(CNBu)(PPh_3)^+$	$X^{\sigma-}L^{\sigma}_4$	0.93	1.6	labile	54
27	$Ru(C_5H_5)(dppm)^+$	$X^{\sigma-}L^{\sigma}_4$	0.95	1.6	stable	6, 55
28	$RuH(dppe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	1.04	1.6	labile	33
29	$RuH(binap)_2^+$	$X^{\sigma-}L^{\sigma}_4$	1.04	1.6	labile	56
30	$RuH(dppp)_2^+$	$X^{\sigma-}L^{\sigma}_4$	1.04	1.6	stable	57
31	$RuH(PP_3)^+$	$X^{\sigma-}L^{\sigma}_4$	0.80	1.4	stable	35
32	$RuCl(depe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	0.84	1.4	labile	58
33	$RuH_2(H_2)(PCy_3)_2$	$X^{\sigma-}_2L^{\pi}L^{\sigma}_2$	0.58	1.2	labile	59
34	$RuH(depe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	0.68	1.3	stable	33
35	$Ru(\mu\text{-}Cl)_3(dppb)$[e]	$X^{\sigma-}_2L^{\sigma}_3$	0.72	1.3	labile	60
36	$RuH_2(PPh_3)_3$	$X^{\sigma-}_2L^{\sigma}_3$	0.37	1.0	labile	61
37	$RuH_2(Cyttp)$	$X^{\sigma-}_2L^{\sigma}_3$	0.17	0.8	labile	62
38	$Ru(\mu\text{-}H)_3(PCy_3)_2$[e]	$X^{\sigma-}_2L^{\sigma}_3$	0.38	1.0	stable	59
39	$OsH(dppe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	1.04	1.3	stable	63
40	$Os(OAc)(PPh_3)_3^+$	$X^{\sigma-}L^{\sigma}_4$	1.07	1.4	stable, $(H)_2$?	64
41	$OsHCl(CO)(PPr^i_3)_2$	$X^{\sigma-}_2L^{\pi}L^{\sigma}_2$	0.93	1.2	labile	65
42	$OsCl(depe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	0.84	1.1	stable, $(H)_2$?	58
43	$OsH(depe)_2^+$	$X^{\sigma-}L^{\sigma}_4$	0.68	1.0	stable, $(H)_2$	63
44	$Os(NH_3)_5^{2+}$	L^{σ}_5	0.35	0.6	stable, $(H)_2$?	36
45	$Os(thf?)(oep)$	$L^{\sigma}X^{\sigma-}_2L^{\sigma}_2$	0.2	0.5	stable, $(H)_2$?	66a
46	$Rh(HB(3,5Me_2pz)_3)H_2$	$X^{\sigma-}_3L^{\sigma}_2$	−0.8	1.6	stable	67
47	$IrH_2(H_2)(PCy_3)_2^+$	$X^{\sigma-}_2L^{\pi}L^{\sigma}_2$	0.58	2.2	labile	68
48	$IrH_2(PMe_2Ph)_3^+$	$X^{\sigma-}_2L^{\sigma}_3$	0.22	1.9	labile	69
49	$Ir(bq)H(PCy_3)_2^+$	$X^{\sigma-}_2L^{\sigma}_3$	0.18	1.9	labile	28
50	$IrHCl_2(PPr^i_3)_2$	$X^{\sigma-}_3L^{\sigma}_2$	−0.30	1.6	labile	70
51	$IrH_2Cl(PPr^i_3)_2$	$X^{\sigma-}_3L^{\sigma}_2$	−0.46	1.5	labile	71

[a] The formulas ML_5 and ligand set are written so that the ligand that is trans to η^2-H_2 in $(\eta^2\text{-}H_2)ML_5$ or trans to N_2 in $(N_2)ML_5$ comes first in the list. [b] The sum of the ligand parameters for the *five* ligands (not including H_2 or N_2). [c] $E_{1/2}(d^5/d^6)$ (in V vs NHE) for MN_2L_5 in organic solvents calculated from eq 13 and one of the equations eqs 3–12. [d] See text for description of categories. [e] This is part of a bimetallic complex.

of C_6R_6 is not known. The $E_{1/2}(d^5/d^6)$ value for the corresponding dinitrogen complex, $M(N_2)L_5$ (whether or not it actually exists), has been calculated by use of the equations in Table II and the sum of parameters, $\sum E_L$, which includes the E_L value for N_2, 0.68 V:

$$\sum E_L(MN_2L_5) = \sum^5 E_L + 0.68 \tag{13}$$

Also provided in Table III is a comment regarding the observed stability of the dihydrogen complex. *Stable* indicates that the complex is stable in solution under Ar at 25 °C. Dihydrogen complexes which are close in energy to their seven-coordinate dihydride tautomeric forms are noted as $(H)_2$ (or $(H)_2$? for suspected cases). *Labile* means that the complex is fully formed only under 1 atm of H_2. *Loses H_2* means that the complex in solution is only stable at low temperature or under high H_2 pressure.

There is a linear correlation between $E_{1/2}$ and force constant $k(N_2)$ for the dinitrogen complexes once the effects of the trans ligand and the metal (3d or 4d versus 5d) are taken into account.[2] In fact a simple equation relating $\nu(N_2)$ in cm^{-1} and $E_{1/2}$ (in V vs NHE) for dinitrogen complexes (of 3d or 4d metals in this case) can be derived on the basis of this work:[18]

$$\nu(N_2) = 492.55[-2\Delta k_L + (E_{1/2} + 7.54)/0.434]^{0.5} \tag{14}$$

A similar equation is obtained for 5d metals, where an additional correction of −0.26 V is introduced to account for the much lower stretching frequencies of 5d metal complexes compared to the 3d or 4d analogues:[2]

$$\nu(N_2) = 492.55[-2\Delta k_L + (E_{1/2} + 7.54 - 0.26)/0.434]^{0.5} \tag{15}$$

The term Δk_L corrects the force constant for the effect of the trans ligand. It was determined empirically to be about 0.9 for a halide,

(22) Howdle, S. M.; Healy, M. A.; Poliakoff, M. *J. Am. Chem. Soc.* **1990**, *112*, 4804–4813.

Table IV. Calculated and Observed Stretching Frequencies $\nu(N_2)$ (cm^{-1}) for Complexes $M(N_2)L_5$

ML5				
no.	formula	$\nu(N_2)_{calcd}$[a]	$\nu(N_2)_{obsd}$	ref
1	$Cr(CO)_5$	2235	2237	72
2	$Cr(CO)_4(H_2)$	2223	2230	42
3	$Cr(olefin)(CO)_4$	2223	2219	43
4	$Cr(CO)_4(C_2H_4)$	2223	2223	44
5	$Cr(CO)_3(PCy_3)_2$	2120	2128	45
6	$Mo(CO)_4(C_2H_4)$	2278	2229	44
8	$Mo(CO)_3(PCy_3)_2$	2172	2159	73
10	$Mo(CO)(dppe)_2$	2067	2120	74
	$Mo(CO)(depe)_2$	2024	2050	46
12	$W(CO)_4(C_2H_4)$	2183	2204	44
13	$W(CO)_3(PCy_3)_2$	2090	2120	73
15	$Mn(C_5H_5)(CO)_2$	2161	2169	75
16	$ReCl(PMePh_2)_4$	1966	1925	76
18	$FeH(dppe)_2^+$	2188	2120	33
19	$FeH(meso\text{-}tet)^+$	2188	2130	77
20	$FeH(PP_3)^+$	2142	2100	78
21	$FeH(depe)_2^+$	2137	2090	33, 79
22	$FeH(dmpe)_2^+$	2143	2094	30
23	$FeH_2(PEtPh_2)_3$	2079	2058	80
31	$RuH(PP_3)^+$	2181	2182	35
34	$RuH(depe)_2^+$	2166	2163	33, 79
35	$Ru(\mu\text{-}Cl)_3(dppb)$	2168	2175	60
36	$RuH_2(PPh_3)_3$	2127	2147	81
37	$RuH_2(Cyttp)$	2102	2100	62
38	$Ru(\mu\text{-}H)_3(PCy_3)_2$	2128	2145	59
	Ru(thf)(oep)	2081	2110	66b
43	$OsH(depe)_2^+$	2091	2136	63, 79
44	$Os(NH_3)_5^{2+}$	2004	2035	82
45	Os(thf?)(oep)	2026	2030	66b

[a] Calculated by use of eq 1 or 2, the Δk_L values of ref 2, and the $E_{1/2}$ values of Table III.

Table V. Calculated and Observed $E_{1/2}(d^5/d^6)$ Values (V vs NHE) for the Dinitrogen Complexes $M(N_2)L_5$

ML5				
no.	formula	$E_{1/2}$(calcd)[a]	$E_{1/2}$(obsd)[b]	ref
10	$Mo(CO)(dppe)_2$	0.1	0.09	14
16	$ReCl(PMePh_2)_4$	0.5	>0.25[c]	
18	$FeH(dppe)_2^+$	1.5	1.11	14
20	$FeH(PP_3)^+$	1.2	1.07[d]	51
21	$FeH(depe)_2^+$	1.1	0.91	12
44	$Os(NH_3)_5^{2+}$	0.6	0.58	82

[a] Values from Table III. [b] Conversion of data according to footnote 18. [c] Complex $Re(N_2)(Cl)(PMe_2Ph)_4$, which is more reducing than **16**(N_2), has $E_{1/2}$ = 0.25 V.[83,84] [d] Irreversible oxidation.

0.9 for nitrogen σ-donors, 0.5 for P donors, 0.5 for hydrides, alkyls, and η^5-C_5H_5, and 0 for CO and carbenes.[2]

A similar equation relates force constants k(CO) and $E_{1/2}(M\text{-}(CO)L_5)$,[2] but this article will concentrate on dinitrogen complexes and their relationship to dihydrogen complexes. It was pointed out earlier that the ligating properties of dinitrogen parallel those of dihydrogen.[2,23] However dinitrogen complexes of the late transition metals are expected to be less stable than analogous dihydrogen complexes; for example dihydrogen complexes **46**(H_2) to **51**(H_2) in Table III are not expected to have dinitrogen analogues. The N_2 ligand is much more sensitive to effects of the trans ligand than the CO ligand.[2] In addition the high stretching frequency of N_2 is less susceptible than CO stretches to coupling with other vibrational modes. It is better to compare force constants k(CO) than frequencies ν(CO) for carbonyl derivatives.

Tables IV and V list observed properties of *dinitrogen* complexes and those predicted on the basis of eqs 14 and eq 15 and the equations of Table II. There is fairly good agreement (±29 cm^{-1} average deviation) between predicted and observed dinitrogen stretching frequencies (Table IV). A reviewer suggested that inserting a constant value of $E_{1/2}$ = 1 V in eq 14 or 15 might give just as good agreement; this is not true because this assumption leads to a much larger average deviation from $\nu(N_2)_{obs}$ of ±46 cm^{-1}. The large error for complexes **7**(N_2) and **10**(N_2) might be due to coupling of CO and N_2 vibrations. Predicted frequencies for the iron complexes are too high. Similarly the observed electrochemical potentials for the iron dinitrogen complexes (Table V) are lower than those predicted on the basis of eq 8 from Table II. Work in progress suggests that the slope of eq 8 varies depending on the chelating phosphine ligand for iron complexes and so there will be a large error in the predicted $E_{1/2}$ value.

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Table VI. Properties of Hypothetical or Known Dinitrogen Complexes $M(N_2)L_5$ Related to Known Seven-Coordinate Dihydride (or Polyhydride) Complexes $M(d^4)(H)_2L_5$

ML5				
no.	formula	$E_{1/2}$[a]	$\nu(N_2)$[b]	ref
	$Cr(P(OMe)_3)_5$	(−0.3)	(1950)	85
	$Mo(CO)(depe)_2$	(−0.2)	2050	46
	$Mo(P(OMe)_3)_5$	(−0.2)	(1966)	86
	$Mo(PMe_3)_5$	(−0.7)	1950	87
13	$W(CO)_3(PCy_3)_2$	(0.5)	2120	73
	$W(P(OMe)_3)_5$	(−0.3)	(1913)	86
	$Re(C_5H_5)(CO)_2$	(1.2)	2147	22
	$ReH(dppe)_2$	0.2	2006	33
	$Ru(C_5H_5)(dppe)^+$	(1.5)	(2193)	6, 55
	$OsH(PMe_3)_4^+$	(1.1)	(2107)	88
43	$OsH(depe)_2^+$	1.0	2136	63, 79
	$OsH_2(PPh_3)_3$	(0.7)	(2048)	61
	$IrH_3(PPr^i_3)_2$	(1.3)	(2139)	89

[a] Values in V vs NHE. Calculated values are in parentheses. [b] Values in cm^{-1}. Calculated values are in parentheses.

Table VI lists observed or calculated properties of dinitrogen complexes which correspond to some known seven-coordinate, d^4, dihydride or polyhydride complexes. In other words, this table lists complexes where homolytic cleavage of dihydrogen takes place. Some of the dinitrogen complexes have not yet been prepared or discovered. There are many other examples of complexes containing more electron-donating ligands. The ones in Table VI are chosen to show how the original range of dinitrogen frequencies for stable H_2 coordination (2060–2150 cm^{-1}) is not always valid (see below).

Dihydrogen Acidity. Equation 1 may be used to predict the pK_a of the η^2-H_2 ligand in the complex $M(H_2)L_5$. However it is necessary to obtain the electrochemical potential, $E_{1/2}(MH/MH^-)$, for the oxidation of the complex MHL_5^-, which is the conjugate base of $M(H_2)L_5$. This is done by use of eqs 3–12 (Table II) and the sum, $\sum E_L(MHL_5^-)$, from eq 16 where the parameter for the hydride ligand is assumed to remain the constant value of −0.4 V:

$$\sum E_L(MHL_5^-) = \sum^{5} E_L - 0.4 \qquad (16)$$

There is a constant difference of 1.08 V between $\sum E_L(MN_2L_5)$ and $\sum E_L(MHL_5^-)$. Table VII lists the calculated electrochemical potentials for selected hydride complexes.

As mentioned in the introduction, the energy term $\Delta H_{BDE}\{M\text{-}(\eta^2\text{-}H_2)\}$ of eq 1 might vary between 60 and 85 kcal mol^{-1}. Thus it is only possible to predict the limits of dihydrogen acidity for a complex with a given electrochemical potential (in V vs NHE):

$$pK_a(\text{lower limit}) = 60/1.37 - 16.9E_{1/2}(MH/MH^-) - 33 \qquad (17)$$

$$pK_a(\text{upper limit}) = pK_a(\text{lower limit}) + 85/1.37 - 60/1.37 \qquad (18)$$

The possible range spans 18 pK_a units! Our ability to estimate pK_a values will only improve once more is known about the term $\Delta H_{BDE}\{M(\eta^2\text{-}H_2)\}$ (see the Discussion). Table VII lists the pK_a range for the most reducing complex and the least reducing complex of each metal (and hence the extremes in expected pK_a values). The pK_a values for other complexes are also provided

Table VII. Calculated Acidity Ranges of Dihydrogen Complexes and Observed pK_a Values

ML$_5$ no.	ML$_5$ formula	calcd[a] $E_{1/2}$ of HML$_5$, V	calcd[b] pK_a range of $(H_2)ML_5$	obsd[c] pK_a of $(H_2)ML_5$	ref
1	$Cr(CO)_5$	0.9	−3 to 15	<7? (HCO_3^-)	24
5	$Cr(CO)_3(PCy_3)_2$	0.0	11 to 29		
6	$Mo(CO)_5$	1.1	−8 to 10	<7? (HCO_3^-)	24
10	$Mo(CO)(dppe)_2$	−0.8	24 to 42		
11	$W(CO)_5$	0.7	−2 to 16	<7? (HCO_3^-)	24
13	$W(CO)_3(PCy_3)_2$	−0.1	13 to 31	10 to 18 ($CuOBu^t$)	25
15	$Mn(C_5H_5)(CO)_2$	0.4	4 to 22		
16	$ReCl(PMePh_2)_4$	−0.3	16 to 34		
17	$FeH(P(OEt)_3)_4^+$	0.5	2 to 20	<11 (NEt_3)	27
18	$FeH(dppe)_2^+$	0.3	6 to 24	12	7
22	$FeH(dmpe)_2^+$	0.0	11 to 29	~16 (OEt^-)	30, 31
23	$FeH_2(PEtPh_2)_3$	−0.5	18 to 36	<18 ($CuOBu^t$)	25
24	$Ru(C_5Me_5)(CO)_2^+$	1.2	−10 to 8	−2 (ether)	34
27	$Ru(C_5H_5)(dppm)^+$	0.5	2 to 20	7.5	6
28	$RuH(dppe)_2^+$	0.6	1 to 19	14.1	7
31	$RuH(PP_3)^+$	0.4	4 to 22	<18 (OBu^t)	35
36	$RuH_2(PPh_3)_3$	−0.1	12 to 30	17 (OCy^-)	32
39	$OsH(dppe)_2^+$	0.2	7 to 25	12.6	7
43	$OsH(depe)_2^+$	0.0	10 to 28	~16 (OEt^-)	33
44	$Os(NH_3)_5^{2+}$	−0.4	19 to 37	>15 (not OMe^-)	36
47	$IrH_2(H_2)(PCy_3)_2^+$	1.4	−13 to 5	<11 (NEt_3)	28
48	$IrH_2(PMe_2Ph)_3^+$	1.2	−9 to 9	<11 (NEt_3)	29
49	$Ir(bq)H(PCy_3)_2^+$	1.1	−8 to 10	<40 (BuLi)	28
51	$IrH_2Cl(PPr^i_3)_2$	0.7	−1 to 17		

[a] Calculated by use of eq 16. [b] Calculated by use of eq 17 and 18. [c] Observed pK_a (extrapolated to aqueous scale). The base that deprotonates the complex $(H_2)ML_5$ is given in parentheses; see also the Results.

when there is information from the literature about their acidic behavior.

Table VII also provides pK_a values based on experimental observations. The complexes $[M(CO)_5Cl]^-$ (M = Cr, Mo, W) catalyze the conversion of CO_2, H_2, and alkyl halides to alkyl formates.[24] A key step in the mechanism is the reaction of H_2 with $[M(CO)_5Cl]^-$ in the presence of sodium bicarbonate (pK_a of H_2O/CO_2 is 6.4). Since dihydrogen complexes $M(H_2)(CO)_5$, **1**(H_2), **6**(H_2), and **11**(H_2)[21] are well characterized, it is logical to propose the following steps in the mechanism:

$$H_2 + [M(CO)_5Cl]^- + Na^+ \rightarrow M(H_2)(CO)_5 + NaCl \quad (19)$$

$$M(H_2)(CO)_5 + HCO_3^- \rightarrow MH(CO)_5^- + H_2O/CO_2 \quad (20)$$

Thus the pK_a of the dihydrogen complexes are proposed to be less than 6.4, a value which fits into the predicted ranges for **1**(H_2), **6**(H_2), and **11**(H_2) (Table VII). Complexes **13**(H_2) and **23**(H_2) are deprotonated by copper *tert*-butoxide.[25] Since the pK_a of $HOBu^t$ is approximately 18, the pK_a of these complexes should be less than this. Attempted reactions of the dihydrogen complexes **13**(H_2) and **14**(H_2) with NHR_2, NR_3, PPr^i_3, and PCy_3[26] gave no evidence for proton transfer, and so the pK_a of **13**(H_2) is likely to be greater than 10 (which is approximately the pK_a of $HPCy_3^+$ or HNR_3^+). Complexes **17**(H_2),[27] **47**(H_2),[28] and **48**(H_2)[29] react with NEt_3 to give the conjugate base hydride and $HNEt_3^+$ (pK_a = 10.8), and so their values must be less than 11. Complex **18**(H_2) has a value near 12 since it transfers protons reversibly and is in equilibrium with protonated Proton Sponge (pK_a = 12.4) or $[Ru(C_5Me_5)(PMePh_2)_2(H)_2]^+$ (pK_a = 12.2) although in each case some decomposition occurs.[7] Complexes **22**(H_2),[30,31] **36**(H_2),[32] and **43**(H_2)[33] are reversibly deprotonated by alkoxides of the alcohols HOEt (pK_a = 16), HOCy (pK_a = 17), and HOEt, respectively. Complex **24**(H_2) is exceedingly acidic and protonates ether; its pK_a must be near −2.[34] The pK_a determinations of **27**(H_2) have been described.[6] Complex **28**(H_2) is reversibly deprotonated by $Ru(C_5Me_5)(H)(PMe_2Ph)_2$ (pK_a of acid form, $[Ru(C_5Me_5)(PMe_2Ph)_2(H)_2]^+$, is 14.3).[7] The p$K_a$ of **39**(H_2) was found by a similar equilibrium.[7] Upper limits can be placed on the acidity of complexes **31**(H_2)[35] and **49**(H_2)[28] on the basis of their reactions with strong bases. Similarly a lower limit is placed on the pK_a of **44**(H_2) since it failed to react with methoxide.[36]

Table VIII. Summary of Properties of Dihydrogen Complexes as a Function of the Trans Ligand, the Period of the Metal, and $E_{1/2}(d^5/d^6)$ (in V vs NHE) for the Corresponding Dinitrogen Complex

η^2-H_2 Trans to CO on a Cr Group Metal

M	$(N_2)M(CO)L_4$ $E_{1/2}$ range	$(H_2)M(CO)L_4$ stability	$(H_2)M(CO)L_4$ acidity range (pK_a)
3d	>0.5	loss of H_2	<25
4d,5d	>1.0	loss of H_2	<17
3d	0–0.5	stable H_2	21 to 39
4d,5d	0–1	stable H_2	2 to 37
3d	<0	splitting of H_2	>19
4d,5d	<0	splitting of H_2	>19

η^2-H_2 Trans to $X^{\sigma-}$ (or L^σ) on a Group 7, 8, or 9 Metal

M	$(N_2)M(X)L_4$ $E_{1/2}$ range	$(H_2)M(X)L_4$ stability	$(H_2)M(X)L_4$ acidity range (pK_a)
3d	>1.7	loss of H_2	<20
4d,5d	>2.0	loss of H_2	<14
3d	0.5–1.7	stable H_2	2 to 34
4d,5d	0.5–2.0	stable H_2	−9 to 34
3d	<0	splitting of H_2	>25
4d,5d	<0.5	splitting of H_2	>16

Discussion

The electrochemical potentials $E_{1/2}(d^5/d^6)$ for the oxidation of dinitrogen complexes, $M(N_2)L_5$, that are predicted by use of additive ligand parameters and Lever's equations of Table II are useful in understanding and predicting the stability and acidity of corresponding dihydrogen complexes $M(\eta^2\text{-}H_2)L_5$. The $E_{1/2}$ value for the dinitrogen complex is used in preference to that of the dihydrogen complex itself when discussing stability and acidity for two reasons. First some reversible oxidations of dinitrogen complexes have been observed (Table V) whereas none have been found for dihydrogen. Second the E_L value for dinitrogen is not known to deviate from 0.68 V. By contrast the E_L value for dihydrogen is likely to change as the H–H distance and other factors that influence bonding vary.[12,13] The good agreement between observed and calculated frequencies $\nu(N_2)$ displayed in Table IV attests to the validity of the calculated $E_{1/2}$ values, upon which the calculated $\nu(N_2)$ values are based. Nevertheless the additive approach is only qualitatively correct because of the problems mentioned above, which include the variability of E_L parameters for polarizable ligands and changes in the slopes of the equations in Table II due to the presence of polarizable ligands.

Range of Stability of Dihydrogen Complexes. Table VIII organizes the information about known dihydrogen and dihydride complexes obtained from Tables III, VI, and VII first according to the ligand trans to η^2-H_2, then by row of the metal and then by ranges of the $E_{1/2}(d^5/d^6)$ values of $M(N_2)L_5$. The most numerous type of complex has H_2 trans to a σ-donor like L^σ or $X^{\sigma-}$

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Table IX. Postulated Dihydrogen Complexes[a]

dihydrogen complex							
no.	formula	type	$\sum E_L(N_2)$, V	$E_{1/2}(N_2)$, V	stability	pK_a range	ref
52(H_2)	$[(H_2)Os(bpy)_2(CO)]^{2+}$	$L^{\sigma}_4L^{\pi}$	2.7	2.4	loss of H_2	−11 to 7	90
53(H_2)	$[(H_2)Os(bpy)(PPh_3)_2(CO)]^{2+}$	$L^{\sigma}_4L^{\pi}$	3.0	2.6	loss of H_2	−15 to 3	38
54(H_2)	$[\{(H_2)Rh(P_3)\}_2(\mu\text{-}S)_2]^{2+}$	$L^{\sigma}_3X^{\sigma}X^{\pi}$	1.1	2.4	loss of H_2	−12 to 6	91
55(H_2)	$(H_2)IrH_2(OCH_2CF_3)(PPr^i_3)_2$	$X^{\sigma}_2L^{\sigma}_2X^{\pi}$	0.1	1.1	stable	9 to 27	92
56(H_2)	$(H_2)IrH_2(pnp)$	$X^{\sigma}_2L^{\sigma}_2X^{\pi}$	0.2	1.2	stable	7 to 25	93
57(H_2)	$(H_2)Ru(PPh_3)(pnp)Cl$	$L^{\sigma}_3X^{\sigma}X^{\pi}$	0.95	1.0	stable	13 to 31	94

[a] $P_3 = (PPh_2CH_2)_3CMe$; pnp = $(PPh_2CH_2SiMe_2)_2N^-$.

(the bottom half of Table VIII), and so these will be considered first.

A striking observation is that a complex with H_2 trans to a σ-donor must have an $E_{1/2}$ of MN_2L_5 between 0.5 and about 1.8 V, irrespective of the metal or charge of the complex, for stable H_2 binding. Since the $E_{1/2}$ value reflects the energy of the HOMO t_{2g} electrons, this condition means that the electrons must be energetic enough for $t_{2g}(M) \rightarrow \sigma^*(H_2)$ back-bonding but not so energetic as to completely split the H–H bond. An $E_{1/2}$ value in the range 0.5–1.8 V is a necessary but not sufficient condition since homolytic splitting of the H_2 may still occur for reasons other than d electron energy (see below). The $E_{1/2}$ range is consistent with the range of frequencies $\nu(N_2)$ = 2060–2150 cm^{-1} for the dinitrogen complexes that was originally proposed.[2] Equations 14 and 15 can be used to translate these stretching frequencies into $E_{1/2}$ values to give the range 0.7–1.4 V assuming that the trans ligand is hydride (Δk_L 0.5). Thus the original proposal is still valid, but the limits have been expanded somewhat.

It is possible that this range shifts to more positive potentials on going from Re (0.5–1.5 V) to Ir (1.0–2.2 V), since Ir allows stable H_2 binding at more positive potentials (see complexes **47**(H_2) to **49**(H_2)). However more information on the electrochemistry of iridium complexes is required to verify this. Certainly metal–hydride bond energies appear to increase in hydride complexes on going from Re(I) to Ir(III) on the basis of the increase in IR frequencies, ν(MH). If dihydrogen–iridium σ-bonding can benefit from this increase in covalent/ionic bond energy, then perhaps there can be stable bonding where there is very little π-back-bonding (at 2.2 V). Another possible explanation for the anomalously positive range for iridium complexes is that all of these complexes contain hydrides and the E_L value of the hydride may not be constant, but instead decrease on going from Re to Ir. That is, the hydride leaves more electron density on Ir than Re. This interpretation is supported by the observation that the addition of dihydrogen to Ir(I) appears to be reductive instead of oxidative.[37]

The constant range of HOMO energies (from 0.5 to about 1.8 V), regardless of the metal in the complex, is achieved by the coordination of ligand sets with appropriate net electron-donating ability. A set of electron-withdrawing ligands (not including H_2) with $\sum^5 E_L \sim 3$ is needed for W(0), whereas a more electron donating set of ligands with $\sum^5 E_L \sim 2.0$ is required by Re(I). An even more electron rich set is needed for Os(II) with $\sum^5 E_L \sim 1.0$, and the most electron-donating ligands with $\sum^5 E_L \sim 0.0$ are found on Ir(III). To obtain stable complexes on Pt(IV), a very electron-donating ligand set (by extrapolation $\sum^5 E_L \sim -1.0$) that would include $X^{\pi-}$ ligands would be required. The $X^{\pi-}$ ligand in such a Pt(IV) complex would very likely promote the heterolytic cleavage of dihydrogen and would make the observation of a stable dihydrogen complex exceedingly difficult (see below for examples of such a reaction).

Examples of formulas of neutral complexes with $E_{1/2}$ values that fall in the critical range would be $(H_2)WL^{\pi}{}_2L^{\sigma}{}_3$, $(H_2)ReX^{\sigma-}L^{\sigma}{}_2L^{\pi}{}_2$, $(H_2)OsX^{\sigma-}{}_2L^{\sigma}{}_2L^{\pi}$, and $(H_2)IrX^{\sigma-}{}_3L^{\sigma}{}_2$ (the first ligand in the list is situated trans to η^2-H_2). There could be up to 18 complexes, some isomeric, of Re or Os with combinations of just three types of ligands ($E_L(X^{\sigma-}) = -0.2$ V, $E_L(L^{\sigma}) = 0.25$ V, $E_L(L^{\pi}) = 0.8$ V) that would have $E_{1/2}$ values in the required range. Fewer (about 10) are possible for W and Ir. If $X^{\pi-}$ ligands are also included, then Ir(III) provides the greatest number of possible isomers of stable dihydrogen complexes. However as noted above the $X^{\pi-}$ ligand would promote heterolytic splitting of dihydrogen, and this is probably why no stable dihydrogen complexes containing an $X^{\pi-}$ ligand have yet been prepared. If the NO^+ ligand is included in the list of possible ligands, then the number of isomers possible for the group 6 metals increases. Nitrosyl complexes of group 8 and 9 metals will be too electron poor to form stable dihydrogen complexes at room temperature.

Dihydrogen complexes having the H_2 ligand trans to CO have only been found so far with the chromium group metals. Stable complexes *trans*-$M(H_2)(CO)L_4$ were proposed to occur when $E_{1/2}$ for the complex *trans*-$M(N_2)(CO)L_4$ was near 0 V vs SCE (or 0.2 V vs NHE).[2] Table VIII gives a more precise range of values. The range may be more narrow for Cr than for Mo or W. As noted previously, complexes with η^2-dihydrogen trans to CO have to have a more electron-donating ligand set than those with η^2-H_2 trans to a σ-donor because CO competes more effectively for d_{π} electrons from the metal than does the η^2-H_2 ligand.

There is now enough information to set the limit of $E_{1/2}$ values where irreversible loss of H_2 occurs at 25 °C as defined in Table VIII. Certainly complexes with $E_{1/2}$ greater than 2.0 V (H_2 trans to σ donor) or greater than 1.0 V (H_2 trans to CO) will be unstable except perhaps for Ir as noted above.

Complexes with $E_{1/2}$ values at the more positive end of the range of stability will have labile H_2 ligands. Complexes with low $E_{1/2}$ might be labile for other reasons (H_2 trans to a high trans influence ligand or stabilization of the resulting five-coordinate complex by dimerization or agostic interaction as in the case of the Cr complex **5**(H_2)).

The prediction of sets of ligands that prevent homolytic cleavage of the H_2 ligand is complicated because information on both the reactant and product of eq 21 is needed. The additivity approach

$$M(\eta^2\text{-}H_2)L_5 \rightarrow M(H)_2L_5 \tag{21}$$

provides the HOMO energy of the reactant at which homolytic cleavage should be very favorable (corresponding to an $E_{1/2}$ of less than 0 V). However there are many d^4 dihydrides or polyhydrides with $E_{1/2}$ values considerably more positive than this (see Table VI). Application of the rule that homolytic splitting of dihydrogen should not occur if $\nu(N_2)$ is greater than 2060 cm^{-1} shows that there are several complexes which should be dihydrogen complexes when they are actually dihydrides: $Re(C_5H_5)(H)_2(CO)_2$, $Os(H)_3(PMe_3)_4{}^+$, and $Ir(H)_5(PPr^i_3)_2$. The product of reaction 21 is favored by 5d metals, and particularly Ir, because of their high metal–hydride bond energies. It is also apparently favored by combinations of small ligands such as hydrides or a C_5R_5 ligand (equivalent to three small ligands) in structures like $[M(C_5R_5)(L)_2(H)_2]^{n+}$.

Range of Acidities of Dihydrogen Complexes. Only broad generalizations can be made with the current information. Table VIII verifies that dihydrogen complexes with a wide range of pK_a values (~0–40) can be stable at 25 °C. However very acidic dihydrogen complexes (pK_a < 0) are not likely to be stable at room temperature because they correspond to N_2 complexes with $E_{1/2}$ > 2.0 V (H_2 trans to $X^{\sigma-}$). Iridium complexes appear to be potentially the most acidic complexes. Determining the pK_a of very acidic dihydrogen complexes will be challenging because of their high lability (see complexes **47**(H_2) to **51**(H_2) in Table III).

(37) Crabtree, R. H.; Quirk, J. M. *J. Organomet. Chem.* **1980**, *199*, 99–106.

A strength of this additive ligand approach is that it allows the contributions to the acidity of the H_2 ligand from the overall charge on the complex and from the ligands in the complex to be qualitatively evaluated. Usually cationic complexes are more acidic than neutral complexes of the same metal ion. However it is interesting that the dicationic complex $Os(H_2)(NH_3)_5^{2+}$, **44**(H_2), is *less* acidic than monocationic osmium(II) complex $Os(H_2)H(dppe)_2^+$, **39**(H_2) (see Table VII). The reason for this is that the pentammine ligand set with a $\sum^5 E_L$ value of 0.35 V is clearly more electron-donating than the ligand set of complex **39**(H_2) ($\sum^5 E_L$ value of 1.04 V as noted in Table III).

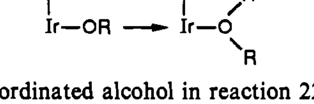
The agreement of prediction with experiment in Table VII suggests that when more is learned about the ΔH_{BDE} term of eq 1, the ligand additivity approach will be very useful in explaining the acid–base reactions of dihydrogen in a transition metal complex. One possibility is that dihydrogen complexes with electron-donating ligand sets ($E_{1/2} \sim 0.5$ when N_2 is trans to a σ-donor ligand) will have ΔH_{BDE} values typical of metal hydrides (60–75 kcal mol^{-1}) because the dihydrogen complexes will be so close in energy to the dihydride tautomer. Complexes with electron-withdrawing sets of ligands and very labile H_2 ligands ($E_{1/2} \sim$ 1.7 V) will have high ΔH_{BDE} values of ~80 kcal mol^{-1}. Complexes with labile dihydrogen ligands might have this high ΔH_{BDE} because of the high energy of the H–H bond (free H_2 has a ΔH_{BDE} of 104 kcal mol^{-1}). This would help to improve our predictive power, but remains to be proved.

Some Applications of the Additivity Method. It is interesting to analyze reactions found in the literature for which dihydrogen complexes are probable intermediates. Table IX gives a few examples.

The complexes $[OsH(CO)(bpy)_2]^+$ and $[OsH(CO)(bpy)(PPh_3)_2]^+$ are protonated by acids stronger than CF_3COOH to give, at least for the latter example, complexes thought to be unstable dihydrides. The $E_{1/2}$ values calculated for these complexes suggest that they would be dihydrogen complexes that are unstable with respect to loss of dihydrogen, $[Os(\eta^2\text{-}H_2)(CO)(bpy)_2]^{2+}$ (**52**(H_2)) and $[Os(\eta^2\text{-}H_2)(CO)(bpy)(PPh_3)_2]^{2+}$ (**53**(H_2)), respectively. Their pK_a values are expected to be very low (less than 7 for **52**(H_2) and less than 3 for **53**(H_2)), and this explains why **53**(H_2) protonates diethyl ether.[38]

The complex $[Rh\{(PPh_2CH_2)_3CMe\}]_2(\mu\text{-}S)_2^{2+}$ reacts with dihydrogen to give a dimeric hydrido μ-sulfhydryl complex $[RhH\{(PPh_2CH_2)_3CMe\}]_2(\mu\text{-}SH)_2^{2+}$. This reaction can be reversed. A dihydrogen complex $[Rh(\eta^2\text{-}H_2)\{(PPh_2CH_2)_3CMe\}]_2(\mu\text{-}S)_2^{2+}$ (**54**(H_2)) is a likely intermediate as shown in Scheme I. The predicted $E_{1/2}$ value for the N_2 complex suggests that the dihydrogen complex would be unstable with respect to loss of dihydrogen (Table IX). However its pK_a is predicted to be less than 6, and this is certainly acidic enough to generate a μ-SH group (p$K_a \sim 7$) by heterolytic splitting of a dihydrogen in an unstable intermediate. Thus the additivity method is of use in predicting when such intramolecular heterolytic cleavage of dihydrogen will occur.

Many other examples of this type of reaction can be found in the literature. The five-coordinate complex $Ir(H)_2(OCH_2CF_3)(PPr^i_3)_2$ reacts with H_2 to produce $HOCH_2CF_3$ and $IrH_5(PPr^i_3)_2$. The dihydrogen complex $Ir(\eta^2\text{-}H_2)(H)_2(OCH_2CF_3)(PPr^i_3)_2$ (**55**(H_2)) with properties as postulated in Table IX would be a stable intermediate in this reaction if it were not for the proton transfer reaction to coordinated alkoxide:

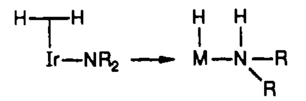


(22)

The pK_a of the coordinated alcohol in reaction 22 is estimated to be 11 and the range of acidity calculated for the dihydrogen ligand in this complex includes this value. Therefore proton transfer could be favored.

(38) Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1247–1252.

Heterolytic cleavage of dihydrogen by coordinated amide is a similar reaction.



(23)

Fryzuk and co-workers have reported that five-coordinate, d[6] complexes $IrH_2\{(PPh_2CH_2SiMe_2)_2N\}$ and $RuCl\{(PPh_2CH_2SiMe_2)_2N\}(PPh_3)$ as well as related complexes react with dihydrogen according to eq 23. Table IX indicates that dihydrogen complexes $Ir(\eta^2\text{-}H_2)H_2\{(PPh_2CH_2SiMe_2)_2N\}$ (**56**(H_2)) and $Ru(\eta^2\text{-}H_2)Cl\{(PPh_2CH_2SiMe_2)_2N\}(PPh_3)$ (**57**(H_2)) would be stable if it were not for the deprotonation of dihydrogen by the amide $X^{\leftarrow}$ ligand (pK_a($MNHR_2$) > 10). The pK_a of the H_2 for **56**(H_2) and **57**(H_2) could be low enough for a favorable proton transfer to occur.

Finally it is important to note that this approach is also applicable to the prediction of the acidity of seven-coordinate hydride complexes, MHL_6^{n+}, where all six L are not necessarily the same. The pK_a values of the M–H bond of some carbonyl metal hydride complexes[39a] have recently been related by use of thermodynamic

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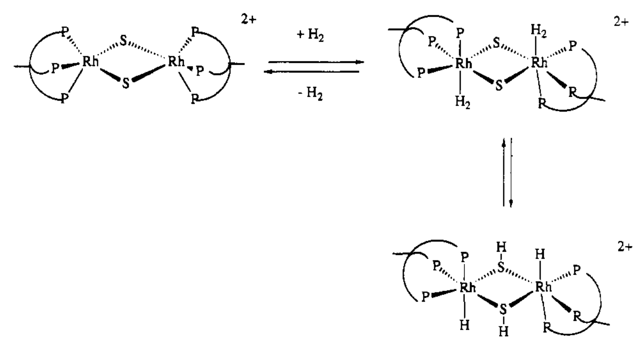
cycles to the dissociation energy of the metal hydride bond, $\Delta H_{BDE}(MH)$, and to electrochemical potentials, $E_{1/2}(M/M^-)$, for the oxidation of the deprotonated species:[11]

$$\Delta H_{BDE}(MH) = 1.37[pK_a(MH)] + 23.1E_{1/2}(M/M^-) + \text{constant} \quad (24)$$

Since the constant in eq 24 can be determined and the $E_{1/2}$ value of the complex $ML_6^{(n-1)+}$, the conjugate base of the hydride MHL_6^{n+}, can be predicted by Lever's method, then the pK_a of MHL_6^{n+} is predictable if the metal-hydride bond energy, $\Delta H_{BDE}(MH)$, can be estimated. This will be the subject of a future study. However the method cannot account for changes in acidity caused by changes in stereochemistry of the seven-coordinate hydride.[39b]

Scheme I



Conclusions

The additive ligand approach, despite its flaws, is shown to be very useful in understanding and predicting the chemistry of dihydrogen complexes. Predicted electrochemical potentials of dinitrogen complexes provide good indicators for choosing binding sites capable of stabilizing the η^2-dihydrogen ligand. Since the pK_a of coordinated dihydrogen is linked to electrochemical potentials that are predictable by the ligand additivity method, estimating pK_a values can lead to a better understanding of the acidity of the η^2-H_2 ligand. In the light of this new information, it will be interesting to review the literature for reactions which might involve η^2-dihydrogen coordination. This work also provides guidelines for future synthetic efforts in preparing stable dihydrogen complexes, especially acidic ones, and also shows that there is a limit to the strength of the acid produced. It also suggests that the electrochemistry of more electron-rich complexes of Rh(III) and Ir(III) should be examined. More information is needed on the energy terms of eq 2. The estimation of the acidity of seven-coordinate hydrides should also be possible by the same method that has been applied to six-coordinate dihydrogen complexes.

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