An Acidity Scale for Phosphorus-Containing Compounds Including Metal Hydrides and Dihydrogen Complexes in THF: Toward the Unification of Acidity Scales

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Abstract: More than 70 equilibrium constants K between acids and bases, mainly phosphine derivatives, have been measured in tetrahydrofuran (THF) at 20 °C by ^1H and/or ^{31}P NMR. The acids were chosen or newly synthesized in order to cover the wide pK_α^{THF} range of 5−41 versus the anchor compound [HPCy$_3$]BPh$_4$ at 9.7. These pK_α^{THF} values are approximations to absolute, free ion pK_a^{THF} and are obtained by crudely correcting the observed K for 1:1 ion-pairing effects by use of the Fuoss equation. The acid/base compounds include 14 phosphonium/phosphine couples, 17 cationic hydride/neutral hydride couples, 9 neutral polyhydride/anionic hydride couples, 14 dihydrogen/hydride couples, and 4 other nitrogen- and phosphorus-based acids. The effects on pK_α of the counterions BAr$'_4{}^-$ and BF$_4^-$ vs BPh$_4^-$ and [K(2,2,2-crypt)]$^+$ versus [K(18-crown-6)]$^+$ are found to be minor after correcting for differences in inter-ion distances in the ion-pairs involved. Correlations with ν(M−H) noted here for the first time suggest that destabilization of M−H bonding in the conjugate base hydride is an important contributor to hydride acidity. It appears that Re−H bonding in the anions [ReH$_6$(PR$_3$)$_2$]$^-$ is greatly weakened by small increases in the basicity of PR$_3$, resulting in a large increase in the pK_α of the conjugate acid ReH$_7$(PR$_3$)$_2$. Correlations with other scales allow an estimate of the pK_α^{THF} values of more than 1000 inorganic and organic acids, 20 carbonyl hydride complexes, 46 cationic hydrides complexes, and dihydrogen gas. Therefore, many new acid−base reactions can be predicted and known reactions explained. THF, with its low dielectric constant, disfavors the ionization of neutral acids HA over HB$^+$, and therefore separate lines are found for pK_α^{THF}(HA) and pK_α^{THF}(HB$^+$) when plotted against pK_a^{DMSO} or pK_a^{MeCN}. The crystal structure of [Re(H)$_2$(PMe$_3$)$_5$]BPh$_4$ is reported.

Introduction

Acidity scales of organic compounds in nonaqueous solvents are used extensively to understand and predict reactivity. For example, a scale of acid dissociation constants, K_a^{DMSO}(AH → H(DMSO)$_x^+$ + A$^-$), for over 1000 compounds in dimethyl sulfoxide (DMSO) have been determined by Bordwell's group by use of electronic spectroscopy.[1]

We are interested in measuring the widest possible range of transition metal hydride and dihydrogen acid strengths and relating them to acid dissociation constants for organic compounds so that new acid−base reactions can be predicted. Tetrahydrofuran (THF) is the best solvent for our studies. Potentially, pK_a^{THF} values can range from approximately 0 for H(THF)$_x^+$ to greater than 50 for the deprotonation of THF. There are only limited pK_a scales for transition metal hydride complexes, despite the fact that they often mediate organometallic reactions; these were reviewed in 1991.[2] Most of these complexes contain carbonyl and/or phosphine ligands and are usually insoluble in water, except for a few acidic compounds such as HCo(CO)$_4$ with p$K_a^{aq} \approx 0$ (p$K_a^{MeCN} = 8.4$).[2] A precise scale for about 20 neutral hydrido-carbonyl compounds in acetonitrile (MeCN) was reported by Norton and co-workers on the basis of NMR and IR measurements.[3−5] Metal hydride acid strengths in the range $10 <$ p$K_a^{MeCN} < 27$ have been determined. However, MeCN is not useful for some weakly acidic neutral hydride complexes which we show in this work to have p$K_a^{MeCN} > 34$; therefore, the conjugate base form deprotonates CH$_3$CN (p$K_a^{MeCN} = 44$),[6] and thus the base strength is leveled by the solvent. It is also not useful for many η^2-dihydrogen complexes because CH$_3$CN is a better ligand than η^2-H$_2$. Nevertheless, the first pK_a determination of a dihydrogen complex was done in this solvent.[7] Similarly, DMSO is a medium strength ligand and can substitute H$_2$. It can also undergo reduction and be deprotonated by strong bases. We and others have found that CH$_2$Cl$_2$ is an excellent solvent for acidic dihydrogen and dihydride compounds but that it tends to react with hydride compounds when their conjugate acid forms have p$K_a^{aq} > 15$ on a pseudoaqueous scale.[8] Several pK_a^{aq} values of metal hydride complexes in CH$_2$Cl$_2$ anchored to the pK_a^{aq} of phosphonium salts have been reported; these are actually ion-pair pK values because the effects of ion-pairing

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have not been considered.[8−13] Angelici and co-workers have ranked the acidity and the bond dissociation energies of about 50 cationic hydrides by protonating neutral metal complexes in CH_2ClCH_2Cl with triflic acid ($HOSO_2CF_3$) and measuring the enthalpy of the reaction.[14,15] These fall in the range of 10−40 kcal/mol (or approximately $5 < pK_a^{THF} < 13$; see below). Again, the solvent CH_2ClCH_2Cl is incompatible with the very basic conjugates of weakly acidic hydrides.

A problem with THF is the low dielectric constant (7.6) and therefore the complication of ion-pairing; ionic equilibria in CH_2Cl_2 and CH_2ClCH_2Cl also have this complication. Solvents such as DMSO and acetonitrile have high enough dielectric constants (46.6 and 36.0, respectively) that ion-pairs are usually completely dissociated and the pK_a^{DMSO} or pK_a^{MeCN} values are independent of the nature of the cation M^+ of eq 1. A pK value, where K is the constant for eq 1, is determined in the reaction of a reference acid A_1H with the conjugate of the unknown acid A_2H in order to determine the pK_a^{DMSO} value of A_2H according to eq 2.

$$A_1H + M^+A_2^- \overset{K}{\rightleftharpoons} A_2H + M^+A_1^- \quad (1)$$

$$pK_a^{DMSO}(A_2H) = pK_a^{DMSO}(A_1H) - pK \quad (2)$$

Streitwieser and co-workers[16,17] and Antipin and co-workers[18,19] have determined free ion pK_{fi}^{THF} values of neutral hydrocarbon acids AH in THF by use of dissociation constants, $K_d(\{M^+,A^-\} \rightarrow M^+ + A^-)$, for the ion-pairs $\{M^+,A^-\}$ formed by the conjugate bases. Therefore, eq 2 can be corrected for ion-pairing as in eq 3.[17] They found that, when the pK_a^{DMSO} of

$$pK_{fi}^{THF}(A_2H) = pK_{fi}^{THF}(A_1H) - pK - \log(K_d(\{M^+,A_2^-\})/K_d(\{M^+,A_1^-\})) \quad (3)$$

fluorene at 22.9 (per hydrogen) is used as the anchor for the THF scale (i.e., $pK_{fi}^{THF}(\text{fluorene}) = 22.9$), the pK_a^{DMSO} and pK_{fi}^{THF} values coincide for a variety of unsaturated hydrocarbon acids.[17] However, the absolute pK_a^{THF} values are likely to be quite different from the pK_{fi}^{THF} and pK_a^{DMSO} values. The pK_a^{THF} for picric acid of 11.6 has been determined potentiometrically by Coetzee et al.[20] This is the only experiment we have found that attempts to establish an absolute pK_a^{THF} value. This value is different from the pK_a^{DMSO}(picric acid) of 0.[1]

The 1:1 ion-pair dissociation constants are determined by use of conductivity measurements or are estimated theoretically, for example, by use of the Fuoss model of ion-pairs (eq 4),[21] where

$$K_d = 3000e^b/(4\pi Na^3) \quad (4)$$

$b = -e^2/(a\epsilon kT)$, $N = 6.02 \times 10^{23}$ mol^{-1}, a is the inter-ion distance, which is equal to $r^+ + r^-$ in centimeters, $e = 4.80 \times 10^{-10}$ esu, ϵ is the dielectric constant, $k = 1.38 \times 10^{-16}$ erg/deg, and T is the temperature in kelvin.

In THF, monocations with Fuoss ion-pair radius r^+ and monoanions with radius r^- exist almost completely as 1:1 ion-pairs,[22] with K_d in the range 10^{-8}−10^{-4} M when the salt concentrations are less than 0.01 M.[17,18,23] Typically at concentrations greater than 0.01 M, the concentrations of triple ions (MA_2^-,M_2A^+) and quadrupoles (M_2A_2) become important, particularly when specific hydrogen-bonding or covalent interactions or short inter-ion distances are possible.[24] We find that eq 4 agrees within an order of magnitude with the K_d^{THF} that have been measured conductometrically[17,18,23,25] when crystallographically derived values of r^+ and r^- are used. The Fuoss equation was derived for spherical ions, so its application to nonsymmetrical ions is somewhat problematic.

Substitution of eq 4 for each salt into eq 3 yields eq 5, where the correction eq 6 is based on inter-ion-pair distances a in angstroms for the two salts MA_1 and MA_2. In eq 5, pK_α^{THF} is used instead of pK_a^{THF} because, although these quantities should be equal, there may be some disagreement because of errors in the corrections for ion-pairing which must be addressed in future work.

$$pK_\alpha^{THF}(A_2H) = pK_\alpha^{THF}(A_1H) - pK + \Delta pK_d \quad (5)$$

$$\Delta pK_d = -33.5(1/a_{MA_1} - 1/a_{MA_2}) + 3\log(a_{MA_2}/a_{MA_1}) \quad (6)$$

Equations 5 and 6 show the importance of utilizing salts of similar inter-ion-pair separation in order to minimize this correction in the construction of a pK_a^{THF} scale. Small ions with localized charge should be avoided to minimize ion-pair aggregation.

We are using for synthetic, practical, and solubility reasons the large, non-hydrogen-bonding anions BPh_4^- or $BAr'_4{}^-$, Ar′ = C_6H_3-3,5-$(CF_3)_2$, or cations $[K(Q)]^+$, Q = 18-crown-6 or $[K(Z)]^+$, Z = 2,2,2-crypt. The ability of such counterions to effect changes in the pK_a scale needs to be studied because these are common, weakly ion-pairing counterions used by organometallic chemists.

Since 1990, the Morris group [8,10−12,26] and other groups [27−29] have been working on determining the relative acidity of cationic dihydrogen and dihydride complexes by measuring by use of quantitative $^{31}P\{$gated $^1H\}$ and ^1H NMR spectroscopy the constants for equilibria with phosphonium salts, $[HPR_3]BF_4$ or $[HPR_3]BPh_4$, of known pK_a^{aq}. Our earlier acidity scales covered smaller pK_a ranges than the current work and were not corrected for ion-pairing effects as in eq 5. The use of a variety of pK_a^{aq} references for our nonaqueous scales introduced some errors. Also, the pK_a of many neutral hydrides could not be determined by use of phosphonium acids because they are much greater than that of $[HP^tBu_3]^+$, the weakest common phosphonium

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Table 1. ^{31}P NMR Chemical Shifts of Phosphines and Phosphonium Salts in THF

bases	δ ^{31}P	acids[a]	δ ^{31}P
P^tBu_3	63.4	$[HP^tBu_3]^+$	57.9[b]
PCy_3	10.9	$[HPCy_3]^+$	32.4[b,c]
P^tBu_2Me	12.1	$[HP^tBu_2Me]^+$	42.2[b]
P^iPr_3	20.7	$[HP^iPr_3]^+$	44.3[b]
PMe_3	−61.5	$[HPMe_3]^+$	−0.6[b]
PEt_3	−18.8	$[HPEt_3]^+$	23.7[b]
P^nBu_3	−31.7	$[HP^nBu_3]^+$	11.4;[d] 14.4[b]
P^iPr_2Me	−9.7	$[HP^iPr_2Me]^+$	30.8[b]
P^tBu_2Ph	39.6	$[HP^tBu_2Ph]^+$	50.3
P^nBu_2Ph[e]	−25.3	$[HP^nBu_2Ph]^+$ [e]	−2.6
PCy_2Ph	2.5	$[HPCy_2Ph]^+$	26.8
PEt_2Ph[e]	−16.1	$[HPEt_2Ph]^+$ [e]	1.3
$PMePh_2$[e]	−26.9	$[HPMePh_2]^+$ [e]	−6.6
$PEtPh_2$[e]	−11.5	$[HPEtPh_2]^+$ [e]	−2.3
$[K(crypt)][PO(OEt)_2PhN]$	4.4	$PO(OEt)_2PhNH$	2.6

[a] BPh_4^- salts, if not mentioned otherwise. [b] $[B(C_6H_3(CF_3)_2)_4]^-$ salt. [c] δ 29.95 reported for the corresponding BPh_4^- salt.[47] [d] In agreement with reported δ 11.9 for the BPh_4^- salt.[47] [e] These acids and bases are in fast exchange on the NMR time scale in solution, and single averaged chemical shifts are observed for their mixtures.

acid.[30] However, our earlier acidity measurements were useful in explaining the relative strengths of proton−hydride bonds,[31,32] understanding H/D exchange reactions, and predicting reactivity, such as the protonation of coordinated dinitrogen.[33,34] They assisted us in understanding the bond dissociation energies and bonding of the $M(\eta^2\text{-}H_2)$ unit and in finding complexes that displayed, for the first time, proton transfer between dihydrogen and a thiolate ligand ($[M(H_2)(SR)L_n]^+ \rightleftharpoons [M(H)(SHR)L_n]^+$)[35,36] and between dihydrogen and a cyanide ligand ($[M(H_2)(CN)L_n]^+ \rightleftharpoons [M(H)(CNH)L_n]^+$).[37−39]

Now many neutral dihydrogen and polyhydride complexes are available for study, partly because of a high-yield, general method for the synthesis of the conjugate base anionic hydrides. This involves the reaction of KH and crown or crypt with $MH_lCl_x(PR_3)_2$ starting materials in THF.[31,32] Therefore, we undertook the creation of a continuous acidity scale in THF to better understand the acid/base behavior of cationic and neutral metal hydride and dihydrogen complexes.

Experimental Section

General. If not specified otherwise, all manipulations and NMR sample preparations were carried out under N_2 with the use of standard Schlenk and glovebox techniques in dry, oxygen-free solvents. ^1H and ^{31}P NMR measurements were done on a Varian Gemini 300 spectrometer; spectral data are reported in Tables 1 and 2.

The phosphine and amine compounds were received from commercial suppliers (Aldrich Chemical Co., Organometallics, Inc.) and used without further purification. Rhenium powder, KH, 2,2,2-crypt, $[N^nBu_4]BH_4$, and $NaBPh_4$ were supplied by Aldrich Chemical Co. OsO_4 was obtained from Johnson Matthey. $Fe(C_5Me_5)(CO)_2H$ and $Mo(C_5H_5)(CO)_3H$ were provided by Dr. Morris Bullock, Brookhaven National Laboratory. The compounds $Ru(H_2)_2H_2(P^iPr_3)_2$ and $[K(18\text{-crown-}6)][RuH_5(P^iPr_3)_2]$,[40] $[K(18\text{-crown-}6)][RuH_3(CO)(P^iPr_3)_2]$,[32] $[K(18\text{-crown-}6)][RuH_3(PPh_3)_3]$,[32] $[K(18\text{-crown-}6)][OsH_3(CO)(P^iPr_3)_2]$,[32] $[K(2,2,2\text{-crypt})][OsH_3(CO)(P^iPr_3)_2]$,[32] $[K(18\text{-crown-}6)][OsH_5(P^iPr_3)_2]$,[31] $OsH_4(CO)(P^iPr_3)_2$,[32] $ReOCl_3(PPh_3)_2$,[41] $[K(18\text{-crown-}6)][ReH_3(NO)(P^iPr_3)_2]$,[32] $[K(18\text{-crown-}6)][ReH_6(PPh_3)_2]$,[42] $ReH_7(PPh_2C_6H_4F)_2$,[43] $ReOCl_3(PCy_3)_2$,[44] $RuH(C_5H_5)(dppe)$ and $RuH(C_5H_5)(dppm)$,[11,45] $K_2[OsO_2(OMe)_4]$,[46] $[OsH_3(PMe_3)_4]BPh_4$, $[OsH_3(PEt_3)_4]BPh_4$,[47] $ReH(PMe_3)_5$,[48] and $NaBAr'_4$[49] were prepared according to literature procedures. Aniline, morpholine, and 4-aminobenzotrifluoride were dried over KOH and distilled under Ar before use. The nitrogen-donor bases were converted to the HBF_4 salts by dropwise addition of $HBF_4 \cdot Et_2O$ to ether solutions of the nitrogen-donor bases under Ar. The protonated bases were carefully crystallized and characterized by ^1H NMR. Protonated salts that have not already been reported in the literature have been found to have the correct elemental analyses by the Guelph Microanalytical Laboratory.

$[HNEt_3]BPh_4$. NEt_3 (100 mg, 1 mmol) and CF_3COOH (225 mg, 2 mmol) were added to 1.5 mL of ethanol and mixed with another solution containing $NaBPh_4$ (338 mg; 1 mmol) in 3 mL of ethanol, affording a precipitate. It was separated by filtration, washed with 4 × 2 mL of ethanol, and dried in vacuo, giving the product in 82% yield (340 mg).

$[HPR_3]BPh_4$. All phosphonium salts $[HPR_3]BPh_4$ ($PR_3 = P^nBu_3$, P^tBu_2Ph, PCy_2Ph, P^nBu_2Ph, PEt_2Ph, $PMePh_2$) were isolated according to the reported preparation of $[HNEt_3]BPh_4$, with typical yields of 80−90%. The ^{31}P NMR chemical shifts are reported in Table 1.

$[HPR_3]BAr'_4$. When the BPh_4^- salts proved insoluble in THF ($PR_3 = P^tBu_2Me$, P^iPr_3, PMe_3, PEt_3, P^iPr_2Me), the isolation of $[HPR_3]BAr'_4$ ($BAr'^-_4 = [B(C_6H_3(CF_3)_2)_4]^-$) was employed. In a typical preparation, PR_3 (0.32 mmol) was protonated by $[HOEt_2]BAr'_4$ (300 mg, 0.32 mmol) in 1.5 mL of THF. The product was precipitated by addition of hexanes (10 mL), filtered, washed with 3 × 2 mL of hexanes, and dried in vacuo to give a white solid. Typical yield: 80%.

$[HOEt_2]BAr'_4$. This is a more convenient method than the original.[49] A 1 M solution of anhydrous HCl (1 mL, 0.1 mmol) in Et_2O (Aldrich) was added to a solution of $NaBAr'_4$ (715 mg, 0.08 mmol) in 1.5 mL of Et_2O. NaCl precipitated and was filtered off. The filtrate was mixed with 15 mL of hexane, and an oily residue formed in the vial. After triturating with a spatula, the oily residue afforded a precipitate. It was filtered, washed with 3 × 2 mL of hexanes, and dried in vacuo. Yield: 733 mg (96%).

$ReH_3(PMePh_2)_4$. H_2O_2 (30%, 3 mL) was cautiously (strongly exothermic reaction) added dropwise to rhenium powder (417 mg, 2.24 mmol), and the mixture was stirred for 15 min. Stirring was continued at 60 °C for an additional 15 min to give a clear grayish solution. The solvent was removed in vacuo at 40−60 °C. By use of a pipet, 1.5 mL of HCl (37%) was added to the orange residue, and the resulting solution was added against a flow of N_2 to a solution of $PMePh_2$ (2.7 g, 13.5 mmol) in 20 mL of ethanol. This was repeated with two more batches of 1.5 mL of HCl until all of the residue was washed from the flask. The mixture was stirred for 20 h at 75 °C. The golden-yellow precipitate

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(45) Abbreviations: $PPh_2CH_2PPh_2$ (dppm), $PR_2CH_2CH_2PR_2$ (R = Ph (dppe), R = $C_6H_4CF_3$ (dtfpe), R = C_6H_4OMe (dape), R = $PPh_2CH_2CH_2CH_2PPh_2$ (dppp); $Q^+ = [K(18\text{-crown-}16)]^+$, and $Z^+ = [K(2,2,2\text{-crypt})]^+$.

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Table 2. NMR Data for the Hydride Complexes in THF or THF-d_8

formula	δ ^{31}P	pattern	J_{PP}	δ ^1H	pattern[a]	J_{HP}	J_{HH}
$Mo(C_5H_5)(CO)_3H$				−5.6	s		
$Re(H)_7(PCy_3)_2$	48.5	s		−6.4	t	18.9	
$[Re(H)_6(PCy_3)_2][K(2,2,2\text{-crypt})]$	65.9	s		−9.62	t	18.9	
$Re(H)_7(PPh_3)_2$	31.3	s		−4.9	t	18.5	
$[Re(H)_6(PPh_3)_2][K(18\text{-crown-}6)]$	44.5	s		−7.37	t	14.7	
$Re(H)_7(PPh_2C_6H_4F)_2$	30.4	s		−4.92	t	18.5	
$[Re(H)_6(PPh_2C_6H_4F)_2][K(18\text{-crown-}6)]$	43.6	s		−7.37	t	14.7	
$Re(H)_4(NO)(P^iPr_3)_2$	55.2	s		−2	br s		
				−7.4	br s		
mer-$[Re(H)_3(NO)(P^iPr_3)_2][K(18\text{-crown-}6)]$	66.7	s		−8.3	tt	33.5	8.3
				−5.6	dt	16	8.3
$[Re(H)_4(PMe_3)_4]BPh_4$	−42.1	s					
$Re(H)_3(PMe_3)_4$	−42	s		−7.76	p	20.6	
$[Re(H)_4(PMe_2Ph)_4]BPh_4$	−27	s		−4.17	m		
$Re(H)_3(PMe_2Ph)_4$	−19.9	s		−6.8	p	20	
$[Re(H)_4(PMePh_2)_4]BPh_4$	−9.7	s					
$Re(H)_3(PMePh_2)_4$	−1.7	s		−6.1	p	20	
$[Re(H)_2(PMe_3)_5]BPh_4$	−46.3	s		−7.63	h	29.3	
$ReH(PMe_3)_5$	−44.6	d	12.1				
	−52.4	br	12.1				
$FeH(C_5Me_5)(CO)_2H$				−11.8	s		
$Ru(H_2)_2(H)_2(P^iPr_3)_2$	88	s		−8.11	t	8.1	
$[RuH_5(P^iPr_3)_2][K(18\text{-crown-}6)]$	106.3	s		−9.25	t	18.8	
$Ru(H_2)(CO)(H)_2(P^iPr_3)_2$	83.7	s		−7.7	br		
mer-$[Ru(H)_3(CO)(P^iPr_3)_2][K(18\text{-crown-}6)]$	101.3	s		−9.97	tt	28	6.5
				−9.1	dt	20.9	6.5
mer-$[Ru(H)_3(CO)(P^iPr_3)_2][K(2,2,2\text{-crypt})]$	101.5	s		−10	tt	28	6.6
				−9.1	dt	21	6.6
$Ru(H_2)(H)_2(PPh_3)_3$	58	s		−7.6	br		
$[Ru(H)_3(PPh_3)_3][K(18\text{-crown-}6)]$	59.9	s		−9.95	AA′A″br		
$[Ru(H)_2(C_5Me_5)(PMe_3)_2]BPh_4$	14.4	s		−10	t	32.4	
$RuH(C_5Me_5)(PMe_3)_2$	6.3	s		−13.8	t	38	
$[Ru(H_2)(C_5Me_5)(PMe_2Ph)_2]BPh_4$	25	s		−9.3	t	30.1	
$RuH(C_5Me_5)(PMe_2Ph)_2$	26.4	s		−13.2	t	36.8	
$[Ru(H)_2(C_5Me_5)(PMePh_2)_2]BF_4$	41.4	s		−8.1	t	28.2	
$RuH(C_5Me_5)(PMePh_2)_2$	46.2	s		−12.5	t	35.3	
$[Ru(H)_2(C_5Me_5)(PPh_3)_2]BF_4$	61.8	s		−7.3	t	26.5	
$RuH(C_5Me_5)(PPh_3)_2$	69.2	s		−11.9	t	33.6	
$[Ru(H_2)(C_5Me_5)(dppm)]BF_4$	23.4	s		−6.8	br		
$[Ru(H)_2(C_5Me_5)(dppm)]BF_4$	4.9	s		−6.1	t	28.8	
$RuH(C_5Me_5)(dppm)$	17.5	s		−10.6	dt	32	3.5
$[Ru(H)_2(C_5H_5)(PPh_3)_2]BPh_4$	58.6	s		−7.44	t		
$RuH(C_5H_5)(PPh_3)_2$	67.6	s		−11.1	t		
$[Ru(H_2)(C_5H_5)(dppe)]BF_4$	79.6	s		−9.02	br		
$[Ru(H)_2(C_5H_5)(dppe)]BPh_4$	68.5	s		−8.8	t		
$RuH(dppe)(C_5H_5)$	92.5	s		−13.7	t		
$[Ru(H_2)(C_5H_5)(dppm)]BPh_4$	5	s		−6.89	br		
$RuH(C_5H_5)(dppm)$	20.7	s		−11	dt	31.3	3.8
$Os(H)_6(P^iPr_3)_2$	58.5	s		−10.4	t	9.45	
$[OsH_5(P^iPr_3)_2][K(18\text{-crown-}6)]$	63.7	s		−12.42	t	14.9	
$Os(H_2)(H)_2(CO)(P^iPr_3)_2$	50	s		−10.4	t	9.45	
mer-$[Os(H)_3(CO)(P^iPr_3)_2]K(18\text{-crown-}6)]$	61.3	s		−11.56		25.5	6.3
				−11.77		17.1	6.3
$[Os(H)_3(PEt_3)_4]BPh_4$	−11.6	s		−12.05	p	15.4	
$Os(H)_2(PEt_3)_4$	−18.8	t	13.4	−13.08	m		
	−11.7	t	13.4	−13.08	m		
$[Os(H)_3(PMe_3)_4]BPh_4$	−54.6	s		−9.73	p	5	
$Os(H)_2(PMe_3)_4$	−52.8	t	18	−11.26	m		
	−47.2	t	18	−11.26	m		
$[Os(H)_3(PMe_2Ph)_4]BPh_4$	−34.2	s		−7.7	p	9.9	
$Os(H)_2(PMe_2Ph)_4$	−30.3	t	15.5	−10.7	m		
	−32.7	t	15.5	−10.7	m		
$[Os(H)_3(PMePh_2)_4BPh_4$	−20	s		−6.7	p	9.2	
$Os(H)_2(PMePh_2)_4$	−9.4	m	11.4	−10.5	m		
	−13.9	m	11.4	−10.5	m		
$Ir(H)_5(PCy_3)_2$	32.5	s		−11	t	12	
cis-$[IrH_4(PCy_3)_2][K(18\text{-crown-}6)]$	28.5	s		−14.04	tt	13.5	4.5
				−15.43	BB′		
$Ir(H)_5(P^iPr_3)_2$	46.2	s		−11.29	t	12.3	
cis-$[IrH_4(P^iPr_3)_2][K(18\text{-crown-}6)]$	42.6	s		−14.95	tt	13.4	4.9
				−15.51	BB′	120	4.9

[a] p = pentet.

was separated by filtration and then washed with 2 × 5 mL of ethanol, 3 × 3 mL of diethyl ether, and again with 2 × 5 mL of ethanol. Yield: 1.75 g. In the product, the complexes $ReCl_3(PMePh_2)_3$ (70%) and $ReCl_4(PMePh_2)_2$ could be identified by use of ^1H NMR.[50,51] This mixture cleanly afforded the trihydride $ReH_3(PMePh_2)_4$ in an NMR tube reaction with BH_4^- and $PMePh_2$, and the trihydride was used in the preparative-scale reaction as follows.

Crude $ReCl_3(PMePh_2)_3$ (400 mg, ca. 0.45 mmol), $[^nBu_4N]BH_4$ (403 mg, 1.57 mmol), and $PMePh_2$ (448 mg, 2.24 mmol) were dissolved in 5 mL of THF. After 2 h, addition of 5 mL of ethanol caused precipitation of a yellow solid. The precipitate was filtered, washed with 3 × 3 mL of ethanol, and dried in vacuo. Yield: 300 mg (68%). The identity of this spectroscopically pure product was established by comparison to the literature NMR data.[51]

$ReH_3(PMe_2Ph)_4$ and $[ReH_4(PMe_2Ph)_4]BPh_4$. From rhenium powder (527 mg, 2.83 mmol) and H_2O_2 (3 mL), the orange product was prepared as described above for $ReCl_3(PMePh_2)_3$. It was extracted from the flask with 3 × 1.5 mL of HCl (37%) in ethanol (1:2), and the washings were added, in turn, against a flow of N_2 to a solution of PMe_2Ph (2.35 g, 17 mmol) in 7 mL of ethanol. The mixture was stirred for 18 h at 75 °C, cooled, and left at −30 °C overnight. The yellow precipitate was filtered and washed with 4 × 3 mL of ethanol, 3 mL of diethyl ether, and 2 × 3 mL of hexanes. Yield: 1.2 g. In the product, the complexes $ReCl_3(PMe_2Ph)_3$ and $ReCl_4(PMe_2Ph)_2$ could be detected by ^1H NMR.[50,52]

The crude $ReCl_3(PMe_2Ph)_3$ was successfully used in the preparation of $ReH_3(PMe_2Ph)_4$, as reported,[50] from pure $ReCl_3(PMe_2Ph)_3$. This method was employed to isolate $[ReH_4(PMe_2Ph)_4]BPh_4$ as well. Following the reported synthesis, the bright yellow suspension in ethanol was cooled to room temperature. The yellow precipitate of $ReH_3(PMe_2Ph)_4$ was filtered and washed with ethanol. From the filtrate, the cationic tetrahydride $[ReH_4(PMe_2Ph)_4]BPh_4$ could be precipitated further by the addition of a solution of $NaBPh_4$ in ethanol. The identity of this spectroscopically pure product was established by comparison to the literature NMR data.[53]

$ReH_3(PMe_3)_4$. A mixture of $ReOCl_3(PPh_3)_2$ (1.92 g, 2.3 mmol) and PMe_3 (1.83 g, 24 mmol) in THF (10 mL) was stirred for 16 h at 70 °C. Stirring continued for 2 h at 70 °C after addition of $[N^nBu_4]BH_4$ (2.16 g, 8.4 mmol). The reaction mixture was evaporated to dryness under vacuum at 75 °C (0.5 h), and the residue was extracted with hexanes. The solvent was removed under vacuum, and the solids were sublimed to afford 154 mg of $ReH_3(PMe_3)_4$ contaminated with 10% of $ReH(PMe_3)_5$.[48] ^1H NMR (C_6D_6): δ 1.56 (m, 36H, CH_3), −7.76 (q, ^2J(H−P) = 20.6 Hz, 3H, ReH). ^{31}P NMR (C_6D_6): δ −41.3. ^{31}P NMR (THF): δ −42.0.

$[ReH_2(PMe_3)_5]BPh_4$. THF (4 mL) was added to a mixture of $[HNEt_3]BPh_4$ (223 mg, 0.53 mmol) and crude $ReH(PMe_3)_5$ (300 mg, 0.53 mmol),[48] and the resulting solution was stirred for 1 h. Diethyl ether (15 mL) was then added, and colorless, air-stable crystals of $[ReH_2(PMe_3)_5]BPh_4$ precipitated. Yield: 442 mg, 94%. ^1H NMR (THF-d_8): δ −7.57 (sxt, ^2J(H,P) = 28.5 Hz, 2H, ReH), 1.64 (d, ^2J(H,P) = 7.32 Hz, 45H, CH_3), 6.77−7.34 (m, 20H, Ph). $^{31}P\{^1H\}$ (THF-d_8): δ −45.2 (s). IR (Nujol): 1852 cm^{-1} (νRe−H). Anal. Calcd for $C_{39}H_{67}BP_5Re$: C, 52.76; H, 7.61. Found: C, 52.79; H, 7.32.

$ReH(PMe_3)_5$. THF (10 mL) was added to a mixture of $[ReH_2(PMe_3)_5]BPh_4$ (250 mg, 0.28 mmol), 18-crown-6 (5 mg, 0.28 mmol), and KH (11 mg, 0.28 mmol), and the resulting suspension was stirred overnight and then evaporated to dryness. The solids were extracted with 3 × 3 mL of a hexane/diethyl ether mixture (1:1). The combined extracts were filtered and evaporated to dryness, to give a spectroscopically pure sample of $ReH(PMe_3)_5$.[48] Yield: 146 mg, 91%. ^1H NMR (C_6D_6): δ −8.77 (qui of d, ^2J(H,P) = 23.0 and 12.4 Hz, 1H, ReH), 1.55 (br, 36H, CH_3), 1.44 (d, ^2J(H,P) = 4.98 Hz, 9H, CH_3). $^{31}P\{^1H\}$ (C_6D_6): δ −45.0 (d), −52.6 (qi), ^2J(P,P) = 10.7 Hz. IR (Nujol) 1757 cm^{-1} (νRe−H).

$ReH_7(PCy_3)_2$. The following is a simplified version of the reported preparation. $ReOCl_3(PCy_3)_2$ (400 mg, 0.48 mmol) and $[N^nBu_4]BH_4$ (494 mg, 1.92 mmol) were slurried in 10 mL of ethanol. Stirring was continued for 20 h. Solids were collected by filtration, washed with 3 × 3 mL of ethanol, and dried in vacuo. Yield: 253 mg, 73%. Product identity was established by a comparison to the literature NMR data.[44]

$OsH_2(PMePh_2)_4$. $PMePh_2$ (566 mg, 2.83 mmol) was added to $K_2[OsO_2(OMe)_4]$ (200 mg, 0.47 mmol), and the mixture was dissolved in 6 mL of ethanol. Stirring continued for 20 h. The amorphous $OsH_2(PMePh_2)_4$ precipitated and was isolated by filtration, washed with 4 × 1.5 mL of ethanol, and dried in vacuo. Yield: 261 mg (56%). Product identity was established by a comparison to the literature NMR data.[54]

$OsH_2(PMe_2Ph)_4$. This complex was prepared as described above for $OsH_2(PMePh_2)_4$ using PMe_2Ph (683 mg, 4.94 mmol) and $K_2[OsO_2(OMe)_4]$ (300 mg, 0.71 mmol). Although the PMe_2Ph product is poorly soluble in ethanol, it did not precipitate from the reaction solution with stirring. Precipitation was achieved at −30 °C, and the solid was treated as above. Yield: 365 mg (70%). Product identity was established by a comparison to the literature NMR data.[55]

$[OsH_3(PMePh_2)_4]BPh_4$. $OsH_2(PMePh_2)_4$ (200 mg, 0.2 mmol) was dissolved in 7.5 mL of a mixture of ethanol and THF (4:1) containing CF_3COOH (70 mg, 0.61 mmol). The product was then precipitated by addition of $NaBPh_4$ (69 mg, 0.20 mmol) in 2 × 1.5 mL of ethanol. It was separated by filtration, washed with 3 × 3 mL of ethanol, and dried in vacuo. Yield: 245 mg (86%). Product identity was established by a comparison to the literature NMR data.[56]

$[OsH_3(PMePh_2)_4]BAr'_4$. The method above was utilized with $NaBAr'_4$ in place of $NaBPh_4$. Yield: 80%. Anal. Calcd for $C_{84}H_{67}BF_{24}OsP_4$: C, 54.32; H, 3.64. Found: C, 54.52; H, 3.66.

$[OsH_3(PMe_2Ph)_4]BPh_4$. $OsH_2(PMe_2Ph)_4$ (200 mg, 0.27 mmol) completely dissolved in 5 mL of ethanol upon addition of CF_3COOH (61 mg, 0.53 mmol). The product was then precipitated by addition of $NaBPh_4$ (92 mg, 0.27 mmol) in 2 × 1.5 mL of ethanol. It was separated by filtration, washed with 3 × 3 mL of ethanol, and dried in vacuo. Yield: 245 mg (86%). Product identity was established by a comparison to the literature NMR data.[56]

$OsH_6(P^iPr_3)_2$. $[K(18\text{-crown-}6)][OsH_5(P^iPr_3)_2]$ (360 mg, 0.44 mmol) was dissolved in 3 mL of ethanol at 20 °C and left at −30 °C for 20 h. The white crystalline precipitate was isolated by filtration while cold, washed with 2 × 1.5 mL of cold (−30 °C) ethanol, and dried under vacuum to give 125 mg (55%) of the product. Despite the almost quantitative formation of $OsH_6(P^iPr_3)_2$ in this reaction (confirmed by ^{31}P NMR; a trace impurity was $Os(H_2)H_2(CO)(P^iPr_3)_2$), the isolated yield is relatively low on account of the high solubility. Product identity was established by a comparison to the literature NMR data.[57]

[K(crypt)][NCCHCN]. [K][NCCHCN] (40 mg, 0.38 mmol)], prepared from KOH and $NCCH_2CN$ in MeOH, was added to a solution of 2,2,2-crypt (144 mg, 0.38 mmol) in THF (10 mL). The reaction was stirred for 24 h, and the solvent was removed by vacuum. The resulting pale pink powder was washed with 20 mL of diethyl ether to yield a white powder. Yield: 116 mg, 63%. ^1H NMR (CD_2Cl_2): δ 3.6 (s, 12H), 3.5 (m, 12H), 2.55 (m, 12H).

$[K(18\text{-crown-}6)][Ph_3C]$. A mixture of Ph_3CH (0.161 g, 0.659 mmol), KH (0.042 g, 1.7 mmol), 18-crown-6 (0.192 g, 0.726 mmol), and THF (5 mL) was stirred under 1 atm of N_2 for 12 h. The mixture changed from colorless to red within the first 5 min of the reaction. The solids were removed by filtration (glass frit) and washed with THF (3 × 1.5 mL). The combined filtrate and washings was evaporated to dryness under reduced pressure, and the resulting residue was extracted with 5 mL of hexanes. The red solids were collected by filtration (glass frit), washed with hexanes (3 × 1.5 mL), and dried under reduced pressure. Yield: 36%. ^1H NMR (THF-d_8): δ 7.29 (m, 6H, phenyl H), 6.50 (m, 6H, phenyl H), 5.93 (m, 3H, phenyl H), 3.55 (s, 24H, crown H).

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Reaction of [K(18-crown-6)][Ph_3C] with $IrH_5(P^iPr_3)_2$. A mixture of [K(18-crown-6)][Ph_3C] (0.009 g, 0.013 mmol) and $IrH_5(P^iPr_3)_2$ (0.009 g, 0.017 mmol) was dissolved in THF (0.65 mL). The resulting solution changed from red to colorless within 10 s. This indicates complete conversion of Ph_3C^- to Ph_3CH. The $^{31}P\{^1H\}$ NMR spectrum exhibited resonances for *cis*- and *trans*-$[IrH_4(P^iPr_3)_2]^-$ and $IrH_5(P^iPr_3)_2$.

Attempted Reaction of Ph_3CH with [K(18-crown-6)][$IrH_4(P^iPr_3)_2$]. A mixture of Ph_3CH (0.004 g, 0.02 mmol), [K(18-crown-6)][$IrH_4(P^iPr_3)_2$], and THF-d_8 was flame-sealed in an NMR tube under 1 atm of N_2. After 5 days there was still no sign of reaction on the basis of the ^1H NMR spectrum and the lack of color of the solution.

Determination of Equilibrium Constants in THF or THF-d_8. Samples were mixed as described in Table 3 and then flame-sealed under Ar. Solutions containing labile dihydrogen complexes were sealed under H_2 (1 atm). In general, equilibrium constants were determined by ^1H and gated-decoupled ^{31}P NMR (in nondeuterated THF for the majority of the ^{31}P measurements). The recycling time (D1 + AT) was set to more than $3T_1$ in the ^1H and ^{31}P measurements, employing 90° pulses. The time D1 + AT = 50 s was used in the ^{31}P measurements when no experimental T_1 information was available since, generally, the T_1 times were in the range of 2−8 s for the complexes of this work.

Usually, signals for all of the species in equilibrium could be located and integrated in the $^{31}P\{\text{gated } ^1H\}$ NMR and, in the case of hydride complexes, in the ^1H NMR spectra as well. The phosphonium compounds with $pK_a < 5$ were found to transfer protons faster than the phosphorus chemical shift difference in hertz so that only one averaged peak for each acid/base pair is observed in the $^{31}P\{\text{gated } ^1H\}$ spectrum and averaged resonances are also observed in the ^1H NMR spectra. In these cases, the limiting chemical shifts for the pure phosphines and phosphonium salts (Table 1) were used to determine the ratio of their concentrations from the weighted average chemical shifts. Mass-balance arguments can also be used to estimate the equilibrium concentration of the species from their starting concentrations.

Determination of Equilibrium Constants in CH_3CN. The following equilibria were studied:

$$PPh_3 + CF_3\text{-}4\text{-}C_6H_4NH_3^+ \rightleftharpoons HPPh_3^+ + CF_3\text{-}4\text{-}C_6H_4NH_2 \quad (7)$$

$$P(C_6H_4\text{-}4\text{-}OMe)_3 + C_6H_5NH_3^+ \rightleftharpoons HP(C_6H_4\text{-}4\text{-}OMe)_3^+ + C_6H_5NH_2 \quad (8)$$

$$PMePh_2 + C_6H_5NH_3^+ \rightleftharpoons HPMePh_2^+ + C_6H_5NH_2 \quad (9)$$

$$P^tBu_3 + O(CH_2CH_2)_2NH_2^+ \rightleftharpoons HP^tBu_3^+ + O(CH_2CH_2)_2NH \quad (10)$$

Each equilibrium was established in a 5-mm NMR tube containing a sealed glass capillary with $P(OMe)_3$ in C_6D_6 as a reference, sealed with a rubber septum and Parafilm, under an inert atmosphere. The ^{31}P and ^1H NMR spectra of the reaction mixtures and the separate components of each equilibrium were recorded.

Determination of the pK_a^{MeCN} of $HPPh_3^+$ by Use of Protonated *p*-Trifluoromethylaniline, CF_3-4-$C_6H_4NH_3BF_4$ (Eq 7). A solution consisting of 20 mg of PPh_3 (0.076 mmol) and 19 mg of $CF_3C_6H_4NH_3BF_4$ (0.076 mmol) in 0.8 mL of CD_3CN was prepared. After 0.5 h, the ^1H and ^{31}P NMR spectra were recorded. The ^1H NMR chemical shifts of the aromatic protons of $CF_3C_6H_4NH_2$ in the reaction mixture were 7.70 and 7.35 ppm. Relating these values to those of the aromatic protons of $CF_3C_6H_4NH_3^+$ (7.85, 7.60 ppm) and to those of $CF_3C_6H_4NH_2$ (7.35, 6.69 ppm), we determined the mole fractions of $CF_3C_6H_4NH_3^+$ to be 0.71 ± 0.01 and the ratio $[CF_3C_6H_4NH_2]/[CF_3C_6H_4NH_3^+]$ to be 0.40 ± 0.02. Similarly, the ratio $[HPPh_3^+]/[PPh_3]$ of 0.6 ± 0.2 was determined by use of the following ^{31}P NMR chemical shifts: δ −4.5 (PPh_3), 6.5 ($HPPh_3^+$), and −0.46 (reaction mixture). From the two ratios, the equilibrium constant for eq 7 (0.24 ± 0.05) can be calculated, which in turn was used in conjunction with the pK_a^{MeCN} of the protonated nitrogen-donor base (8.6) to calculate the pK_a^{MeCN} of $HPPh_3^+$ (8.0 ± 0.1).

Determination of the pK_a^{MeCN} of $HP(C_6H_4\text{-}4\text{-}OMe)_3^+$ by Use of Protonated Aniline, $C_6H_5NH_3BF_4$ (Eq 8). A solution was prepared from 13 mg of $P(C_6H_4\text{-}4\text{-}OMe)_3$ (0.038 mmol) and 6.7 mg of $C_6H_5NH_3BF_4$ (0.037 mmol) in 1.0 mL of CD_3CN. The NMR spectra were recorded after 1.5 h. ^{31}P NMR chemical shifts of phosphines used are as follows: δ 4.3 ($HP(C_6H_4\text{-}4\text{-}OMe)_3^+$), −9.4 ($P(C_6H_4\text{-}4\text{-}OMe)_3$), and −5.2 (reaction mixture). The ^1H NMR chemical shifts for the methyl protons of the phosphines were as follows: δ 3.89 ($HP(C_6H_4\text{-}4\text{-}OMe)_3^+$), 3.76 ($P(C_6H_4\text{-}4\text{-}OMe)_3$), and 3.80 (reaction mixture). The mole fraction of $[HP(C_6H_4\text{-}4\text{-}OMe)_3^+]$ was determined to be 0.3 ± 0.1, and the ratio $[HP(C_6H_4\text{-}4\text{-}OMe)_3^+]/[P(C_6H_4\text{-}4\text{-}OMe)_3]$ was 0.4 ± 0.2. The ratio $[C_6H_5NH_2]/[C_6H_5NH_3^+]$ could not be directly determined since the resonances in the ^1H NMR spectrum were not well resolved. Since the reaction was performed with the reactants in a 1:1 mole ratio, the mole fractions $[C_6H_5NH_2]$ and $[C_6H_5NH_3^+]$ are assumed to be equal to those of the phosphines, 0.3 ± 0.1 and 0.7 ± 0.1, respectively. The equilibrium constant for eq 8 is therefore 0.2 ± 0.2. The pK_a^{MeCN} of the amine is 10.6,[58] and the pK_a^{MeCN} of $HP(C_6H_4\text{-}4\text{-}OMe)_3^+$ is thus determined to be 9.8 ± 0.4.

Determination of pK_a^{MeCN} of $HPMePh_2^+$ by Use of Protonated Aniline, $C_6H_5NH_3BF_4$ (Eq 9). In 1.0 mL of CD_3CN, a solution was prepared consisting of 20 mg of $PMePh_2$ (0.10 mmol) and 18 mg of $C_6H_5NH_3BF_4$ (0.10 mmol). After 1.5 h, the NMR spectra were recorded. ^{31}P NMR chemical shifts of phosphines used are as follows: δ 4.2 ($HPMePh_2^+$), −26.0 ($PMePh_2$), and −18.2 (reaction mixture). The ^1H NMR chemical shifts for the methyl protons of the phosphines were as follows: δ 2.49 ($HPMePh_2^+$), 1.60 ($PMePh_2$), and 1.82 (reaction mixture). The mole fraction $[HPMePh_2^+]$ was determined to be 0.25 ± 0.01, and the average ratio $[HPMePh_2^+]/[PMePh_2]$ was 0.34 ± 0.01. The ratio $[C_6H_5NH_2]/[C_6H_5NH_3^+]$ was estimated on the basis of mass balance as above. The equilibrium constant is therefore 0.11 ± 0.01. The pK_a^{MeCN} of the amine is 10.6,[58] and the pK_a^{MeCN} of $HPMePh_2^+$ is therefore determined to be 9.6 ± 0.1.

Determination of the pK_a^{MeCN} of $HP^tBu_3^+$ by Use of Protonated Morpholine, $O(CH_2CH_2)_2NH_2BF_4$ (Eq 10). A solution was prepared of 22 mg of P^tBu_3 (0.11 mmol) and 17.3 mg of $O(CH_2CH_2)_2NH_2BF_4$ (0.10 mmol) in 1.0 mL of CD_3CN. The ^1H NMR spectrum was recorded after 2.5 h. The averaged chemical shift of the *tert*-butyl group methyls of 1.46 ppm indicated that 43% P^tBu_3 (methyl at 1.28 ppm) and 57% $HP^tBu_3^+$ (methyl at 1.59 ppm) were present. The methylene resonances of $O(CH_2CH_2)_2NH$ are observed at averaged positions of 3.66 and 2.92 ppm. The interpretation of these chemical shifts is complicated by the fact that $O(CH_2CH_2)_2NH$ is present not only in protonated form (methylene multiplets at 3.83 and 3.22 ppm in a pure sample) and in nonprotonated form (methylene multiplets at 3.52 and 2.71 ppm) but also in the self-associated $O(CH_2CH_2)_2NH{\cdot}NH_2(CH_2CH_2)_2O^+$ form. Norton and co-workers[59] have described how to treat this problem by use of the self-association constant, K_f, of 10 M^{-1} for $O(CH_2CH_2)_2NH$.[58] The concentration of P^tBu_3, the K_f, and the total starting concentration of $O(CH_2CH_2)_2NH$ (B) derivatives (0.100 M) are used to determine $[BHB^+] = 0.017$ M. The concentrations of B and HB^+ are then 0.049 and 0.034 M, respectively. The weighted averages of chemical shifts for the $O(CH_2CH_2)_2NH$ methylenes are calculated to be 3.65 and 2.93 ppm, in good agreement with the observed average chemical shifts; this assumes that the BHB^+ methylene multiplets would be observed at 3.68 and 2.92 ppm. Therefore, the equilibrium constant for this reaction is 2.1. A separate ^{31}P NMR experiment with starting concentrations of 0.10 M gave an averaged ^{31}P resonance at equilibrium of 58.2 ppm compared with 61.5 ppm for $HP^tBu_3^+$ and 55.7 ppm for P^tBu_3. From these data, an equilibrium constant of 2.5 is calculated, in reasonable agreement with the ^1H experiment. From the pK_a^{MeCN} of $O(CH_2CH_2)_2NH_2^+$ (16.6),[58] the pK_a^{MeCN} of $HP^tBu_3^+$ is then determined to be 17.0 ± 0.1.

X-ray Diffraction Structure Determination of $[Re(H)_2(PMe_3)_5]BPh_4$. Crystals suitable for X-ray diffraction were obtained by layering a THF solution of the salt with diethyl ether. Data were collected on a Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The CCD data were integrated and scaled using the DENZO-SMN software package, and the structure was solved and

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[58] Coetzee, J. F.; Padmanabhan, G. R. *J. Am. Chem. Soc.* **1965**, *87*, 5005−5010.

[59] Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257−2263.

Table 3. Thermodynamic Data for Acid/Base Equilibria at 20 °C[a]

acid	base	time to reach equilibrium	K	error	p*K*	ΔpK_d[b]	ΔpK_α[b]
$IrH_5(P^iPr_3)_2$	$Q[CPh_3]$[c]	<1 day	>100		<−2	+1	<−3
$IrH_5(P^iPr_3)_2$	$Q[\textit{cis}\text{-}IrH_4(PCy_3)_2]$	<1 day	0.57	10	0.24	0.0	0.2
$ReH_7(PCy_3)_2$	$Q[\textit{cis}\text{-}IrH_4(P^iPr_3)_2]$	<1 day	>100		<−2	0.0	<−2
$ReH_7(PCy_3)_2$	$Z[Ph_2N]$[c]	<1 day	0.68	20	0.17	0.0	0.2
$[HPCy_2Ph]BPh_4/Q[RuH_3(CO)(P^iPr_3)_2]$[e]	$Q[RuH_5(P^iPr_3)_2]$	<1 day	1.50[d]	20	−0.18[d]	0.5	−0.7
$OsH_4(CO)(P^iPr_3)_2$[e]	$Q[RuH_5(P^iPr_3)_2]$	<1 day	428	5	−2.6	−0.5	−2.1
$ReH_7(PCy_3)_2$[e]	*mer*-$Z[RuH_3(CO)(P^iPr_3)_2]$	<2.5 h	0.0030	20	2.5	0.0	2.5
$ReH_7(PCy_3)_2$[e]	*mer*- $Z[RuH_3(CO)(P^iPr_3)_2]$	<2.5 h	0.004	30	2.4	0.0	2.4
$OsH_4(CO)(P^iPr_3)_2$[e]	$Q[\textit{mer}\text{-}RuH_3(CO)(P^iPr_3)_2]$	<4 days	230	20	−2.4	0.0	−2.4
$OsH_4(CO)(P^iPr_3)_2$[e]	$Q[\textit{mer}\text{-}ReH_3(NO)(P^iPr_3)_2]$	<1 day	74	20	−1.9	0.0	−1.9
$OsH_6(P^iPr_3)_2$[e]	$Z[\textit{mer}\text{-}OsH_3(CO)(P^iPr_3)_2]$	<1 h	16	20	−1.2	0.0	−1.2
$OsH_4(CO)(P^iPr_3)_2$[e]	$Q[OsH_5(P^iPr_3)_2]$	<1 day	0.073	40	1.1	0.5	0.6
$OsH_6(P^iPr_3)_2$[e]	$Q[\textit{fac}\text{-}RuH_3(PPh_3)_3]$	<12 h	8.5	30	−0.9	0.0	−0.9
$HPPh_2$	$Q[OsH_5(P^iPr_3)_2]$	12−24 h	0.0136	20	1.9	−1.4	3.3
$P(O)(OEt)_2PhNH$	$Q[OsH_5(P^iPr_3)_2]$	<1 h	684	20	−2.8	0.0	−2.8
$OsH_6(P^iPr_3)_2$[e]	$Q[ReH_6(PPh_3)_2]$	<3 h	0.000025	100	4.6	0.0	4.6
$Fe(C_5Me_5)(CO)_2H$	$Q[ReH_6(PPh_3)_2]$	<1 h	0.1	30	1	0.0	1
$ReH_7(PPh_3)_2$	$Q[ReH_6(Ph_2PC_6H_4F)_2]$	<1 h	0.0031	50	2.5	0.0	2.5
$ReH_7(Ph_2PC_6H_4F)_2$	$Q[ReH_6(P(C_6H_4F)_3)_2]$	1−4 h	0.028	20	1.5	0.0	1.5
$ReH_7(Ph_2PC_6H_4F)_2$[f]	$ReH(PMe_3)_5$	6−12 h	$2.3\ M^{-1}$[g]	30	−0.37	−4[h]	4
$[ReH_2(PMe_3)_5]BPh_4$	$Q[ReH_6(Ph_2PC_6H_4F)_2]$	6−12 h	0.39 M	20	0.41	4	−4
$[ReH_2(PMe_3)_5]BPh_4$	$ReH_3(PMe_3)_4$	<6 days	.078	20	1.1	−0.2	1.3
$[ReH_4(PMe_2Ph)_4]BPh_4$	$ReH_3(PMe_3)_4$	<3 days	769	50	−2.9	0.0	−2.9
$[ReH_4(PMe_2Ph)_4]BPh_4$	$Z[CH(CN)_2]$	<2 days	0.04 M	50	1.4	5	−4
$CH_2(CN)_2$	$ReH_3(PMe_2Ph)_4$	<2 days	$13\ M^{-1}$	40	−1.1	−5	4
$[OsH_3(PEt_3)_4]BPh_4$	$ReH_3(PMe_2Ph)_4$	2−6 days	24	20	−1.4	−0.1	−1.3
$[OsH_3(PMe_3)_4]BPh_4$	$Z[Ph_2N]/[OsH_3(PEt_3)_4]BPh_4$	24 h	49[i]	20	−1.7[j]	0.2	−1.9
$[OsH_3(PMe_2Ph)_4]BPh_4$	$ReH_3(PMePh_2)_4$	<24 h	5.9	10	−0.8	0.2	−1.0
$[OsH_3(PMe_3)_4]BPh_4$	$OsH_2(PMe_2Ph)_4$	<24 h	0.0093	30	2.0	0.0	2.0
$[OsH_3(PMe_2Ph)_4]BPh_4$	NEt_3	<24 h	0.01	30	2.0	−0.4	2.4
$Mo(C_5H_5)(CO)_3H$	$OsH_2(PMePh_2)_4$	<1 h	$2.0\ M^{-1}$	30	−0.3	−5	5
$[OsH_3(PMePh_2)_4]BPh_4$	$RuH(C_5Me_5)(PMePh_2)_2$	12−24 h	3.2	10	−0.51	−0.6	0.1
$[OsH_3(PMePh_2)_4]BAr'_4$	$RuH(C_5Me_5)(PMePh_2)_2$	12−24 h	2.5	10	−0.40	−0.5	0.1
$[OsH_3(PMePh_2)_4]BPh_4$	NEt_3	<24 h	5.0	30	−0.70	−0.6	−0.1
$[OsH_3(PMePh_2)_4]BPh_4$	P^tBu_3	<24 h	0.056	20	1.25	−0.6	1.8
$[HP^tBu_3]BAr'_4$	PCy_3	<1 h	0.086	20	1.07	0.0	1.1
$[P^tBu_3]BPh_4$	PCy_3	<1 h	0.14	20	0.85	0.0	0.85
$[HP^iPr_3]BAr'_4$	PCy_3	<1 h	4.60	20	−0.66	0.0	−0.7
$[HP^tBu_3]BAr'_4$	P^tBu_2Me	<1 h	0.074	20	1.13	0.0	1.1
$[HP^tBu_3]BAr'_4$	P^tBu_2Me	<1 h	0.069	20	1.16	0.0	1.2
$[HP^nBu_3]BAr'_4$	P^iPr_3	<1 h	3.1	20	−0.49	0.0	−0.5
$[HP^iPr_3]BAr'_4$	PMe_3	<1 h	0.42	20	0.38	0.0	0.4
$[HP^{i}Pr_3]BAr'_4$	PEt_3	<1 h	0.30	20	0.52	0.0	0.5
$[HPCy_3]BAr'_4$	P^nBu_3	<1 h	0.063	20	1.2	0.0	1.2
$[HPCy_3]BPh_4$	P^nBu_3	<1 h	0.15	20	0.82[j]	0.0	0.8
$[HP^iPr_3]BAr'_4$	P^iPr_2Me	<1 h	0.27	20	0.57	0.0	0.6
$[HP^tBu_2Ph]BPh_4$	$RuH(C_5H_5)(dppm)$[k]	<1 h	0.18	20	0.74	0.0	0.7
$[HP^nBu_3]BPh_4$	$RuH(C_5H_5)(dppm)$	<1 h	0.032	20	1.5	0.0	1.5
$[HP^nBu_3]BPh_4$	P^tBu_2Ph	<1 h	0.14	20	0.85	0.0	0.9
$[HP^nBu_3]BPh_4$	P^tBu_2Ph	<1 h	0.12	20	0.92	0.0	0.9
$[HPCy_2Ph]BPh_4$	P^tBu_2Ph	<1 h	35	20	−1.5	0.0	−1.5
$[HP^tBu_2Ph]BPh_4$	PCy_2Ph	<1 h	0.023	20	1.6	0.0	1.6
$[Ru(H_2)(C_5H_5)(dppm)]BPh_4$[e]	PCy_2Ph	<1 h	0.18	20	0.74	0.0	0.7
$[Ru(H_2)(C_5H_5)(dppm)]BPh_4$[e]	PCy_2Ph	<1 h	0.19	20	0.72	0.0	0.7
$[HP^nBu_3]BPh_4$	$RuH(C_5H_5)(dppe)$	<1 h	0.030[l]	20	1.5[l]	0.0	1.5
$[HP^nBu_3]BPh_4$	$RuH(C_5H_5)(dppe)$	<1 h	0.013[m]	20	1.9[m]	0.0	1.9
$[HNMe_2Ph]BPh_4$	PCy_2Ph	<1 h	1.0	30	0.0	0.4	−0.4
$[HPCy_2Ph]BPh_4$	P^nBu_2Ph	<1 h	1.44	30	−0.16	0.0	−0.2
$[HP^nBu_2Ph]BPh_4$	PCy_2Ph	<1 h	0.71	30	0.15	0.0	0.1
$[HPEt_2Ph]BPh_4$	PCy_2Ph	<1 h	1.2	30	−0.08	0.0	−0.1
$[HPCy_2Ph]BPh_4$	PEt_2Ph	<1 h	1.2	30	−0.08	0.0	−0.1
$[HP^nBu_2Ph]BPh_4$	PEt_2Ph	<1 h	1.8	30	−0.26	0.0	−0.3
$[HPMePh_2]BPh_4$	PEt_2Ph	<1 h	1.3	30	−0.11	0.0	−0.1
$[HPEt_2Ph]BPh_4$	$PMePh_2$	<1 h	0.75	30	0.12	0.0	0.1
$[HPCy_2Ph]BPh_4$	$PMePh_2$	<1 h	0.95	30	0.02	0.0	0.0
$[HPEt_2Ph]BPh_4$	$PEtPh_2$	<1 h	0.07	30	1.15	0.0	1.2
$[HPMePh_2]BPh_4$	$PEtPh_2$	<1 h	0.09	30	1.0	0.0	1.0

[a] Samples in THF in the concentration range 0.02−0.07 M were sealed under Ar unless otherwise specified. [b] See the Appendix for the definition of ΔpK_d and ΔpK_α. [c] Q = $[K(18\text{-crown-}6)]^+$. Z = $[K(2,2,2\text{-crypt})]^+$ salt. [d] Calculated for protonation of $[K(18\text{-crown-}6)][RuH_5(P^iPr_3)_2]$ by $Ru(H_2)(H_2)(CO)(P^iPr_3)_2$ under H_2 (1 atm). [e] Sealed under H_2. [f] Plus 18 mM $QBPh_4$. [g] $QBPh_4$ = 0.018 M in eq 13. [h] See eq 14. [i] Calculated for protonation of $OsH_2(PEt_3)_4$ by $[OsH_3(PMe_3)_4]BPh_4$. ΔpK_a of 1.7 was previously reported.[47] [j] Reference 47. [k] Abbreviations in ref 45. [l] Data for the equilibrium involving $[Ru(H)_2(C_5H_5)(dppe)]^+$. [m] Data for the equilibrium involving $[(C_5H_5)Ru(H_2)(dppe)]^+$.

Table 4. Estimates of Ionic Radii To Be Used in the Fuoss Equation[a]

cation	ion-pair radius, Å	anion	ion-pair radius, Å
PHR_3^+	3.0	BPh_4^-	4.4[b]
NHR_3^+	2.2	$ReH_6L_2^-$	3.0
$M(C_5R'_5)H_2L_2^+$	3.0	$MH_5L_2^-$	3.0
$MH_x(PMePh_2)_4^+$	4.7	$RuH_3(PPh_3)_3^-$	3.0
$MH_x(PMe_2Ph)_4^+$	4.2	$MH_3(CO)(P^iPr_3)_2^-$	3.5,[c] 3.3[d]
$MH_x(PMe_3)_4^+$	4.0	PPh_2^-	2.0
$K(18\text{-crown-}6)^+$	2.0	NPh_2^-	2.0
$K(2,2,2\text{-crypt})^+$	5.0	CPh_3^-	2.1[e]
		$CF_3SO_3^-$	2.5[b]
		BF_4^-	2.5[b]

[a] See Table 3 for the specific compounds; values not found in the literature were estimated from related crystal structures; R = alkyl or aryl; L_2 = (phosphine)$_2$ or (diphosphine); M = Ru or Os or Re; $x = 2$ or 3. [b] Reference 23. [c] In ion-pair with K(crown)$^+$ because K^+ interacts with the carbonyl. [d] In ion-pair with K(crypt)$^+$. [e] Reference 17.

Table 5. Crystallographic Data for $[Re(H)_2(PMe_3)_5]BPh_4$

a, Å	26.6894(4)	formula	$C_{39}H_{67}BP_5Re$
b, Å	16.0571(3)	formula weight	887.79
c, Å	9.9528(1)	space group	*Pnma*
α, deg	90	T, K	150
β, deg	90	λ, Å	0.71073
γ, deg	90	ρ_{calc}, mg/m^3	1.383
V, Å^3	4265.3(1)	R_1 (all data)	0.042
Z	4	wR_2	0.087

Table 6. Selected Bond Distances and Angles for $[Re(H)_2(PMe_3)_5]BPh_4$

Distances, Å			
Re(1)−H(1RE)	1.53(4)	Re(1)−H(2RE)	1.64(6)
Re(1)−P(2)	2.368(1)	Re(1)−P(1 or 1A)	2.388(1)
Re(1)−P(3)	2.441(1)	Re(1)−P(4)	2.433(1)
Angles, deg			
H(1RE)−Re(1)−H(2RE)	138(3)	H(1RE)−Re(1)−P(2)	70(2)
H(2RE)−Re(1)−P(2)	68(2)	H(1RE)−Re(1)−P(1 or 1A)	90.49(3)
H(2RE)−Re(1)−P(1 or 1A)	89.88(3)	P(2)−Re(1)−P(1 or 1A)	90.49(2)
P(1)−Re(1)−P(1A)	178.80(5)	H(1RE)−Re(1)−P(4)	157(2)
H(2RE)−Re(1)−P(4)	66(2)	P(2)−Re(1)−P(4)	133.12(5)
P(1 or 1A)−Re(1)−P(4)	89.41(2)	H(1RE)−Re(1)−P(3)	58(2)
H(2RE)−Re(1)−P(3)	165(2)	P(2)−Re(1)−P(3)	127.9(1)
P(1 or 1A)−Re(1)−P(3)	89.96(2)	P(3)−Re(1)−P(4)	98.98(5)

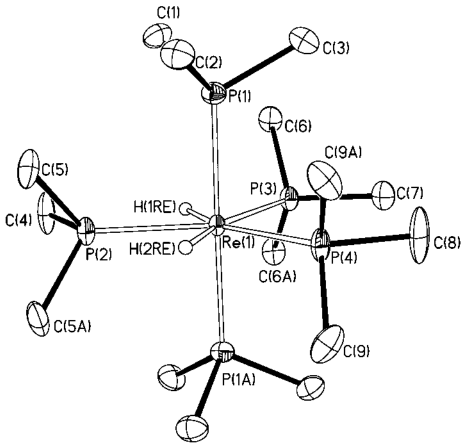

Figure 1. Molecular structure of the cation of $[Re(H)_2(PMe_3)_5]BPh_4$.

refined using SHELXTL V5.0. The crystallographic data are listed in Table 5 and selected bond distances and angles in Table 6. The hydrides were located and refined with isotropic thermal parameters (Figure 1).

Results

Preparation of the Acids and Bases. New routes were developed to several of the transition metal hydride complexes used in this work. The few steps now needed for their syntheses and the high yields in most cases makes their use as practical acids and bases more feasible. For example, $ReH_3(PR_3)_4$, PR_3 = $PMePh_2$ and PMe_2Ph, were prepared in two steps starting from the commercially available phosphine and rhenium powder. The cationic complex $[ReH_4(PMe_2Ph)_4]BPh_4$ was conveniently obtained as a byproduct in the synthesis $ReH_3(PMe_2Ph)_4$. A useful source of hydride in these preparations and also those of $ReH_7(PCy_3)_2$ is $[N^nBu_4]BH_4$. The complexes $OsH_2(PR_3)_4$ were obtained from OsO_4 efficiently by way of $K_2[OsO_2(OMe)_4]$ and its direct reaction with phosphine in ethanol. The preparation of the anionic hydrides by use of KH/18-crown-6 or KH/2,2,2-crypt in THF has been described elsewhere.[31,32,40,60,61]

Structures of the Acids and Bases. The structures of most of the hydride complexes have been determined elsewhere in the literature (see Figure 2). The coordination numbers of the complexes are listed in Tables 7 and 8 in the column labeled Δ; Δ is the change in coordination number from the acid to the base form. The dihydrogen complex acids of this study are identified by a Δ of 6/6 because they are all six-coordinate and, when they are deprotonated, the base hydride form is also six-coordinate (cyclopentadienyl ligands are considered to occupy three coordination sites). One interesting exception to this rule is the acid/base pair $RuH_2(H_2)_2(P^iPr_3)_2/[RuH_5(P^iPr_3)_2]^-$ (Table 8), where the acid is a six-coordinate bis-dihydrogen complex[61] while the base is a seven-coordinate pentagonal bipyramid.[40] When the polyhydride dihydrogen complexes are deprotonated, the base forms are too electron rich to retain H−H bonds.

The classical polyhydride acid complexes have coordination numbers ranging from nine- to six-coordinate (Tables 7 and 8). The acidity of $Ir(H)_2(C_5Me_5)(PMe_3)$ (Table 10) was recently reported by Bergman and co-workers.[62] The complex $ReH_7(PPh_2C_6H_4F)_2$ may contain an elongated dihydrogen ligand or, perhaps more suitably, a compressed dihydride moiety, on the basis of a study of $ReH_7(P(C_6H_4F)_3)_2$ by Crabtree and co-workers.[63,64] The structure of the cation of $[Re(H)_2(PMe_3)_5]BPh_4$ was determined by single-crystal X-ray diffraction to be a pentagonal bipyramid (Figure 1). The bond lengths (Table 6) are similar to those observed for the related dihydride $ReH_2(hq)(PMe_3)(PPh_3)_2$ (hq = 2 hydroxyquinoline monoanion).[65]

Determination of the Equilibrium Constants. As in previous studies, we have determined the equilibrium constants for cationic acid−neutral base reactions (eq 11) or neutral acid−anionic base reactions (eq 12) in THF or THF-d_8 by use of quantitative $^{31}P\{gated\ ^1H\}$ and ^1H NMR.

$$MHL_n + \{HB^+,Y^-\} \rightleftharpoons \{MH_2L_n^{\ +},Y^-\} + B \qquad (11)$$

$$B = \text{phosphine, amine, metal hydride;}$$

$$Y^- = BF_4^{\ -}, BPh_4^{\ -}, BAr'_4{}^-$$

$$MHL_n + \{Q^+,A^-\} \rightleftharpoons \{Q^+,ML_n^{\ -}\} + AH \qquad (12)$$

$$A^- = \text{organic or organometallic anion;}$$

$$Q^+ = [K(18\text{-crown-}6)]^+ (Z^+ = [K(2,2,2\text{-crypt})]^+ \text{ also used})$$

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(60) Landau, S. E.; Morris, R. H.; Lough, A. J. **1999**, in preparation.

(61) Abdur-Rashid, K.; Gusev, D.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652−1660.

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

(63) Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.* **1991**, *29*, S89−93.

(64) Michos, D.; Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 3914−3916.

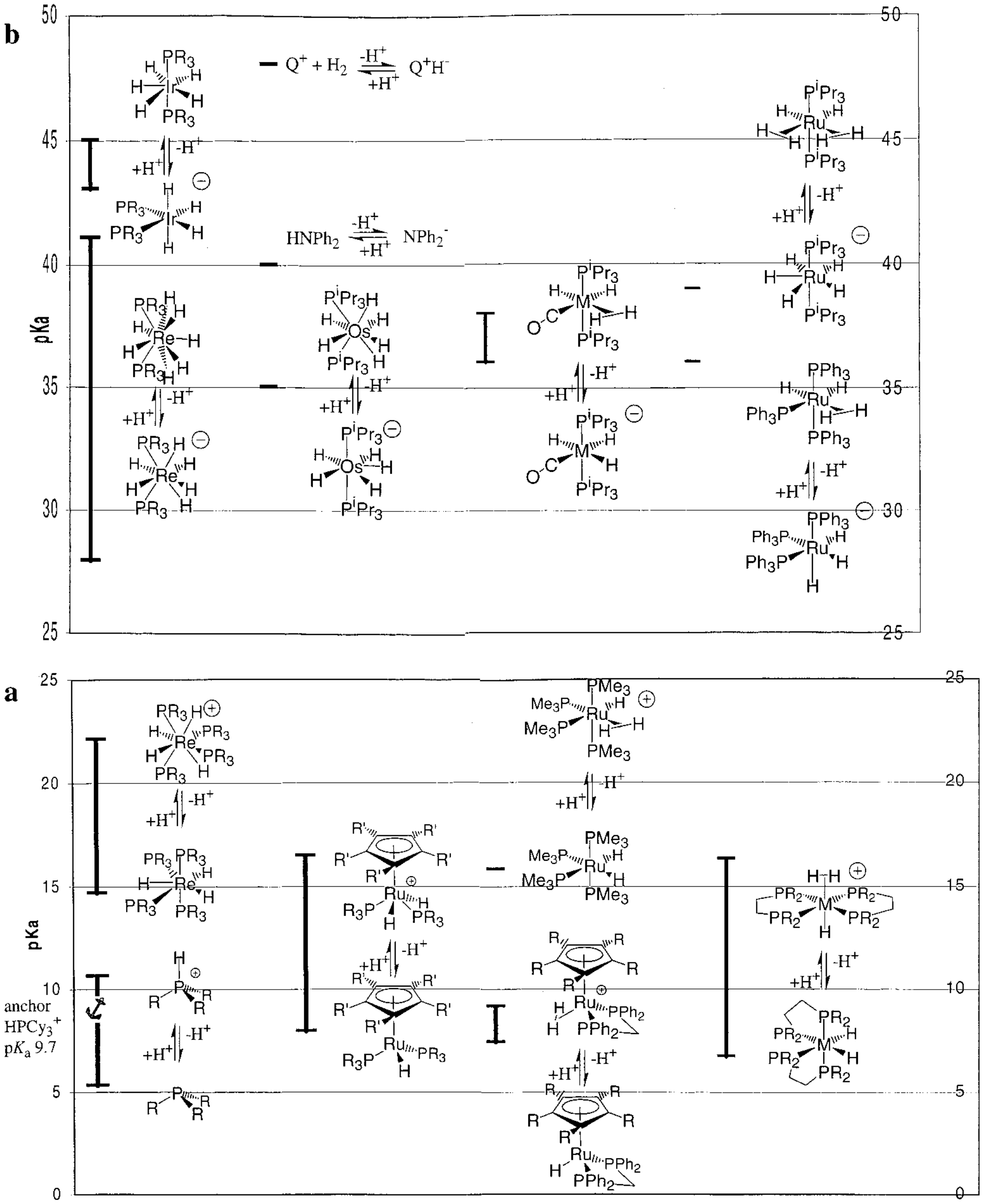

Figure 2. Ladder of pK_{α}^{THF} ranges: (a) 0−25 and (b) 25−50. Selected classical hydride acids are on the left side, while dihydrogen acids are on the right of each diagram.

Typically constants in the range 10^3−10^{-3} can be measured with a 10−30% error. An advantage of this NMR method is that reactions that proceed with the formation of unexpected NMR-active side products can be easily detected and rejected. Methods based on electronic spectroscopy rely on the presence of isosbestic points to prove that the equilibrium is "clean". An advantage of NMR over the UV/vis method is that no extinction coefficients need be determined since NMR is inherently quantitative.

Equilibrium data could be reliably determined in THF even for quite unstable compounds such as the dihydrogen complexes $RuH_2(H_2)(CO)(P^iPr_3)_2$ and $RuH_2(H_2)_2(P^iPr_3)_2$ by preparing their equilibrium mixtures in situ (in sealed NMR tubes) from the isolable $[RuH_3(CO)(P^iPr_3)_2]^-$ and $[RuH_5(P^iPr_3)_2]^-$ anions under H_2. The use of expensive THF-d_8 is not always required since, in the case of hydride complexes containing phosphine ligands, the phosphorus signals are easily integrated and the hydride signals are sufficiently negative of 0 ppm in the ^1H NMR spectrum to be detectable in nondeuterated THF.

Equilibrium constants determined in this work are listed in Table 3 along with ΔpK_{α} calculated according to eqs 5 and 6 by use of ion-pair radii of Table 4 (see the Appendix for more details). The calculated pK_{α}^{THF} values are listed in Tables 7 ($pK_{\alpha}(HB^+)$) and 8 ($pK_{\alpha}(HA)$). When more than one isomer (tautomer) of a complex is present in solution, the stereochemistry of the isomer, of which the concentration was used for the calculation of pK_{α}, is indicated.

Tricyclohexylphosphonium tetraphenylborate, $[HPCy_3]BPh_4$, with $pK_{\alpha}^{THF} = pK_a^{aq} = 9.7$, was chosen as the anchor for our scale. Although somewhat arbitrarily chosen, this anchor fortuitously leads to a ladder of pK_{α}^{THF} values that approximate the true pK_a in THF, as we will demonstrate below.

Overlapping equilibria were examined to more and to less acidic compounds to create a continuous ladder of values (Tables 7 and 8, Figure 2). For example, clean reactions of PCy_3 with $[HP^tBu_3]BPh_4$ and separately with $[HP^nBu_3]BPh_4$ in THF allow

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(65) McKinney, T. M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1999**, *38*, 1548−1554.

Table 7. Ladder of $pK_{\alpha}^{THF}(HB^+)$ Values for Cationic Acids with Different Anions[a]

acid	base	Δ	BF_4^-	BPh_4^-	$BAr'_4{}^-$
$[ReH_2(PMe_3)_5]^+$	$ReH(PMe_3)_5$	7/6		24.2	
$[ReH_4(PMe_3)_4]^+$	$ReH_3(PMe_3)_4$	8/7		22.9	
$[ReH_4(PMe_2Ph)_4]^+$	$ReH_3(PMe_2Ph)_4$	8/7		20.0	
$[OsH_3(PEt_3)_4]^+$	$OsH_2(PEt_3)_4$	7/6		18.7	
$[Ru(H)_2(C_5Me_5)(PMe_3)_2]^+$	$RuH(C_5Me_5)(PMe_3)_2$	7/6		16.5	
trans-$[Ru(H_2)H(dape)_2]^+$	*cis*-$RuH_2(dape)_2$	6/6		17.4	
$[OsH_3(PMe_3)_4]^+$	$OsH_2(PMe_3)_4$	7/6		16.9	
cis-$[Ru(H_2)H(PMe_3)_4]^+$	$RuH_2(PMe_3)_4$	6/6		16.6	
$[RuH_3(PEt_3)_4]^+$	$RuH_2(PEt_3)_4$	7/6		16.5	
$[FeH_3(PMe_3)_4]^+$	$FeH_2(PMe_3)_4$	7/6 + 6/6		15.9	
$[ReH_4(PMePh_2)_4]^+$	$ReH_3(PMePh_2)_4$	8/7		15.8	
$[Ru(H)_2(C_5Me_5)(PMe_2Ph)_2]^+$	$RuH(C_5Me_5)(PMe_2Ph)_2$	7/6		14.4	
$[OsH_3(PMe_2Ph)_4]^+$	$OsH_2(PMe_2Ph)_4$	7/6		14.9	
trans-$[Ru(H_2)H(dppe)_2]^+$	*cis*-$RuH_2(dppe)_2$	6/6		14.7	
trans-$[Os(H_2)H(dppe)_2]^+$	*cis*-$OsH_2(dppe)_2$	6/6		13.3	
$[HNEt_3]^+$	NEt_3	4/3		12.5	
$[OsH_3(PMePh_2)_4]^+$	*cis*-$OsH_2(PMePh_2)_4$	7/6		12.4	12.4
$[Ru(H)_2(C_5Me_5)(PMePh)_2]^+$	$RuH(C_5Me_5)(PMePh_2)_2$	7/6		12.3	12.3
trans-$[Fe(H_2)H(dppe)_2]^+$	*cis*-$FeH_2(dppe)_2$	6/6		13	
$[Ru(H)_2(C_5Me_5)(PPh_3)_2]^+$	$RuH(C_5Me_5)(PPh_3)_2$	7/6		10.9	
$[HP^tBu_3]^+$	P^tBu_3	4/3		10.6	10.8
$[HPCy_3]^+$	PCy_3	4/3	9.7	9.7	9.7
$[HP^tBu_2Me]^+$	P^tBu_2Me	4/3			9.4
$[Ru(H_2)(C_5Me_5)(dppm)]^+$	$RuH(C_5Me_5)(dppm)$	6/6	9.2	9.2	
$[HP^iPr_3]^+$	P^iPr_3	4/3			9.0
$[Ru(H)_2(C_5Me_5)(dppm)]^+$	$RuH(C_5Me_5)(dppm)$	7/6	8.7	8.9	
$[HPMe_3]^+$	PMe_3	4/3			8.7
$[HPEt_3]^+$	PEt_3	4/3			8.5
$[HP^nBu_3]^+$	P^nBu_3	4/3		8.9	8.5
$[Ru(H)_2(C_5H_5)(dppp)]^+$	$RuH(C_5H_5)(dppp)$	7/6	8.7		
$[HP^iPr_2Me]^+$	P^iPr_2Me	4/3			8.5
$[HP^tBu_2Ph]^+$	P^tBu_2Ph	4/3		8.0	
$[Ru(H)_2(C_5H_5)(PPh_3)_2]^+$	$RuH(C_5H_5)(PPh_3)_2$	7/6	8.0		
trans-$[Ru(H_2)H(dtfpe)_2]^+$	*cis*-$RuH_2(dtfpe)_2$	6/6	8.0		
trans-$[Os(H_2)H(dtfpe)_2]^+$	*cis*-$OsH_2(dtfpe)_2$	6/6	7.3		
trans-$[Fe(H_2)H(dtfpe)_2]^+$	*cis*-$FeH_2(dtfpe)_2$	6/6	6.7		
$[Ru(H_2)(C_5H_5)(dppm)]^+$	$RuH(C_5H_5)(dppm)$	6/6	7.4	7.2	
$[Ru(H)_2(C_5H_5)(dppe)]^+$	$RuH(C_5H_5)(dppe)$	7/6	7.4	7.4	
$[Ru(H_2)(C_5H_5)(dppe)]^+$	$RuH(C_5H_5)(dppe)$	6/6	7.2	7.0	
$[HP^nBu_2Ph]^+$	P^nBu_2Ph	4/3		6.6	
$[HPEt_2Ph]^+$	PEt_2Ph	4/3		6.5	
$[HPCy_2Ph]^+$	PCy_2Ph	4/3		6.4	
$[HPMePh_2]^+$	$PMePh_2$	4/3		6.4	
$[HNMe_2Ph]^+$	NMe_2Ph	4/3		6.0	
$[HPEtPh_2]^+$	$PEtPh_2$	4/3		5.3	

[a] Abbreviations in ref 45; Δ = change in coordination number.

equilibrium constants of 0.14 and 1/0.15 = 6.7, respectively, to be determined by quantitative ^{31}P NMR. There is no 1:1 ion-pair correction ΔK_d for these equilibria because the inter-ion-pair distance should be the same for all HPR_3BPh_4 salts. In these ion-pairs the tetraphenylborate ion ($r^- = 4.4$ Å) is assumed to be situated near the open hemisphere of the phosphonium ion containing the P−H bond ($r^+ = 3.0$ Å). The phosphonium salts of these compounds with $pK_{\alpha} = 10.6$ and 8.9, respectively (Table 7), then provide secondary standards to proceed up and down the ladder of hydride- and phosphorus-containing cationic and neutral acid/base pairs. In earlier work, the tetrafluoroborate salt, $[HPCy_3]BF_4$, was used as a reference at 9.7, and a smaller continuous scale was developed. These values are included in Table 7 for comparison. Also included are values determined in previous work but now corrected for 1:1 ion-pairing for the complexes *cis*-$[Fe(H_2)H(PMe_3)_4]BPh_4$,[47] $[Ru(H)_2(C_5Me_5)(PR_3)_2]BPh_4$,[8] and *trans*-$[M(H_2)(H)(diphosphine)_2]BPh_4$[10] in THF.

For a few phosphonium salts, the BPh_4^- anion did not provide a sufficiently soluble compound for use by this method. In these cases, the CF_3-substituted tetraarylborate anion, $BAr'_4{}^-$, was found to be useful. A limited ladder of pK_{α} values referenced to $[HPCy_3]BAr'_4$ at 9.7 was also determined (Table 7).

The reaction between $[ReH_2(PMe_3)_5]^+$ and $[ReH_6(PPh_2C_6H_4F)_2]^-$ provides a link to the neutral/anionic hydride pairs of Table 8 (eq 13, $K = 0.39$ M). So far, this is the only clean equilibrium discovered to make this link. Even still, there is a small amount of decomposition of $ReH_7(PPh_2C_6H_4F)_2$ to $Re_2H_8(PPh_2C_6H_4F)_4$, a reaction that is much slower than reaction 13. Fortunately, when 1 equiv of $[K(crown)]BPh_4$ is added with $ReH(PMe_3)_5$ and $ReH_7(PPh_2C_6H_4F)_2$ under H_2, an equilibrium is established starting from the right-hand side of eq 13. The pK_{α}^{THF} for $ReH_7(PPh_2C_6H_4F)_2$ is then determined to be 28 ± 3 by use of eq 5 with $K = 0.39$ M, $pK_{\alpha}^{THF}([ReH_2(PMe_3)_5]^+) = 24.2 \pm 1.0$, and $\Delta pK_d = -4 \pm 2$ from eq 14 instead of eq 6, where the 1:1 ion-pair dissociation constants are estimated by use of eq 4 and the ionic radii from Table 4.

$$\{ReH_2(PMe_3)_5{}^+,BPh_4{}^-\} + \{K(18\text{-}crown\text{-}6)^+,ReH_6(PPh_2C_6H_4F)_2{}^-\} \rightleftharpoons ReH(PMe_3)_5 + ReH_7(PPh_2C_6H_4F)_2 + \{K(18\text{-}crown\text{-}6)^+,BPh_4{}^-\} \quad (13)$$

$$\Delta pK_d = -\log[K_d{}^{QReH6L2}K_d{}^{ReH2L'5BPh4}/K_d{}^{QBPh4}] \quad (14)$$

Table 8. Ladder of $pK_\alpha^{THF}(HA)$[a] of Neutral Acids

acid	base	Δ	pK_α^{THF}	pK_{fi}^{THF}	pK_a^{DMSO}
$CHPh_3$	$[CPh_3]^-$		≥46	30.8[b]	30.6[b]
$IrH_5(P^iPr_3)_2$	[*cis*-$IrH_4(P^iPr_3)_2]^-$	7/6	≥43		
$IrH_5(PCy_3)_2$	[*cis*-$IrH_4(PCy_3)_2]^-$	7/6	≥43		
$ReH_7(PCy_3)_2$	$[ReH_6(PCy_3)_2]^-$	9/8	41 ± 4		
Ph_2NH	$[Ph_2N]^-$	3/2	41 ± 4	24.2[c]	25[d]
$RuH_2(H_2)_2(P^iPr_3)_2$	$[RuH_5(P^iPr_3)_2]^-$	6/7	39 ± 4		
$RuH_2(H_2)(CO)(P^iPr_3)_2$	$[RuH_3(CO)(P^iPr_3)_2]^-$	6/6	38 ± 4		
$Re(H)_4(NO)(P^iPr_3)_2$	$[ReH_3(NO)(P^iPr_3)_2]^-$	7/6	38 ± 4		
$HPPh_2$	$[PPh_2]^-$	3/2	38 ± 4	23.8[e]	23.1[e]
$Os(H_2)(H)_2(CO)(P^iPr_3)_2$	$[OsH_3(CO)(P^iPr_3)_2]^-$	6/6	36 ± 4		
$RuH_2(H_2)(PPh_3)_3$	$[RuH_3(PPh_3)_3]^-$	6/6	36 ± 4		
$OsH_6(P^iPr_3)_2$	$[OsH_5(P^iPr_3)_2]^-$	8/7	35 ± 4		
$P(O)(OEt)_2PhNH$	$[P(O)(OEt)_2PhN]^-$	2/1	32 ± 4		18.3[d]
$Fe(C_5Me_5)(CO)_2H$	$[Fe(C_5Me_5)(CO)_2]^-$	6/5	31 ± 4		
$ReH_7(PPh_3)_2$	$[ReH_6(PPh_3)_2]^-$	9/8	30 ± 3		
$ReH_7(PPh_2C_6H_4F)_2$	$[ReH_6(PPh_2C_6H_4F)_2]^-$	9/8	28 ± 3		
$CH_2(CN)_2$	$[CH(CN)_2]^-$	4/3	24 ± 2	12.0[b]	11.1[b]
$MoH(C_5H_5)(CO)_3$	$[Mo(C_5H_5)(CO)_3]^-$	7/6	17 ± 1		
2,4,6-$C_6H_2(NO_2)_3OH$	[2,4,6-$C_6H_2(NO_2)_3O]^-$	2/1	10 ± 2	(11.6)[f]	0[d]

[a] $pK_\alpha^{THF}(HA)$ is corrected for ion-pairing and should be approximately independent of the cation. See Table 3 for the nature of the cation used. [b] Reference 18. [c] Reference 16. [d] Reference 1. [e] Reference 19. [f] pK_a^{THF} determined potentiometrically by Coetzee et al.[20]

Table 9. Acidity Constants Determined for THF Solutions of Cations and for Other Solvents

acid	pK_α^{THF}	$pK_a^{H_2O}$ or pK_a^{MeOH}	pK_a^{DMSO}	pK_a^{MeCN}	-Δ*H* in $CClH_2CClH_2$[a]
$(P(NMe_2)_3N)_2P(NMe_2)NH^tBu^+$	31[b]		26.2[c]	38.6[c]	
$[P(NMe_2)_3NP(NMe_2)_2NH^tBu]^+$	26[b]		21.5[c]	33.5[c]	
$[ReH_4(PMe_2Ph)_4]^+$	20.0			25.4[d]	
$[OsH_3(PMe_3)_4]^+$	16.9	11.5[e]			
$[RuH_3(PMe_3)_4]^+$	16.6	11.3[e]			
$[OsH_3(PMe_2Ph)_4]^+$	14.9				43.3
$[HNEt_3]^+$	12.5	10.7[f,g]	9[h]	18.5[g]	39.3
$[OsH_3(PMePh_2)_4]^+$	12.4				38.8
$[HP^tBu_3]^+$	10.7	11.4[i,j]		17.0	36.6
$[HPCy_3]^+$	9.7	9.7[i,k]			33.2
$[HP^nBu_3]^+$	8.7	8.43[i,k]			
$[HPMe_3]^+$	8.7	8.65[l]			
$[Ru(H)_2(C_5H_5)(PPh_3)_2]^+$	8.0[m]				29.7
$[Ru(H_2)(C_5H_5)(dppm)]^+$	7.2				28.9
$[Ru(H)_2(C_5H_5)(dppe)]^+$	7.4				29
$[Ru(H_2)(C_5H_5)(dppe)]^+$	7.0				29
$[HPEt_2Ph]^+$	6.5	6.15[f,k]			
$[HPMePh_2]^+$	6.4	4.57[i,k]		9.6	24.7
$[HNMe_2Ph]^+$	6.0	5.18[f]	2.45[h]		28.4
$[HPEtPh_2]^+$	5.3	4.90[i,k]			

[a] OTf^- salts.[14,56] [b] These are our estimates based on the reported equilibria in THF referenced to 9-phenylfluorene ($pK_\alpha^{THF} \approx 30$) in THF.[6] [c] Reference 66. [d] Reference 5. [e] In MeOH relative to $pK_a^{aq}(MeOH) = 16.7$.[47] [f] Determined in H_2O. [g] Reference 68. [h] Reference 1. [i] Determined in CH_3NO_2 and then correlated to the water scale. [j] Reference 82. [k] Reference 67. [l] Determined in H_2O by NMR.[83] [m] BF_4^- salt.[11]

Table 10. Estimated pK_α^{THF} Values of Selected Acids

acid	base	estimated pK_α^{THF}	pK_a other	-Δ*H* in $CClH_2CClH_2$[a]
$Ir(H)_2(C_5Me_5)(PMe_3)$	$IrH(C_5Me_5)(PMe_3)Li$	>51	38−41[a]	
H_2	QH	49	35.3[b]	
$HCPh_3$	CPh_3^-	44	31.0[c]	
cyclo-$C_6H_{11}OH$	cyclo-$C_6H_{11}O^-$	38[d]	32[e]	
$HPPh_2$	PPh_2^-	35	23.8[f]	
$WH(C_5H_5)(PMe_3)(CO)_2$	$W(C_5H_5)(PMe_3)(CO)_2^-$	32	26.6[g]	
9-phenylfluorene	9-phenylfluorenide⁻	30	17.9[e]	
$[PtH(dmpe)_2]PF_6$	$Pt(dmpe)_2$	21	28.5[h]	
$[NiH(dmpe)_2]PF_6$	$Ni(dmpe)_2$	18	24.3[h]	
$[PtH(dppe)_2]PF_6$	$Pt(dppe)_2$	16	22[h]	
[TMGH]OTf	tetramethylguanidine	15	13.6,[i] 23.3[j]	43.2[k]
$[Os(H)_2(C_5H_5)(PPh_3)_2]BF_4$	$OsH(C_5H_5)(PPh_3)_2$	12	13.4[l]	37.3[k]
$[OsH(C_5Me_5)_2]OTf$	$Os(C_5Me_5)_2$	6	9.9[m]	26.6[k]
$[ReH_2(C_5H_5)_2]^+$	$ReH(C_5H_5)$	6	5.5[n]	
$[HPPh_3]BPh_4$	PPh_3	3	2.7[i] 8.0[o]	21.2[j]

[a] On the basis of the reaction of the anion with H_2 or DMSO but lack of reaction with toluene.[62] [b] In THF, see text.[84] [c] pK_a^{DMSO}.[18] [d] Based on the equilibrium with $RuH_4(PPh_3)_4$.[85] [e] pK_a^{DMSO}.[1] [f] pK_{fi}^{THF}.[19] [g] pK_a^{MeCN}.[2] [h] pK_a^{MeCN}.[69] [i] pK_a^{aq}. [j] pK_a^{MeCN}.[15] [k] Reference 14. [l] In CH_2Cl_2.[28] [m] pK_a^{MeCN}.[86] [n] 60% dioxane/water mixture.[87] [o] pK_a^{MeCN} (this work).

A continuously linked set of neutral acids with pK_α^{THF} between 28 and 41 ($ReH_7(PCy_3)_2$) was then established by use of the equilibrium method represented by eq 12. In one case, the cation $[K(2,2,2\text{-crypt})]^+$ (Z^+) was used as well as Q^+ to demonstrate that the calculation of pK_α^{THF} values is independent of the cation.

$IrH_5(P^iPr_3)_2$ was not sufficiently acidic to establish equilibrium with $ReH_7(PCy_3)_2$, and so its pK_α^{THF} is estimated to be greater than 43. Similarly, triphenylmethane is not acidic enough to protonate $[IrH_4(P^iPr_3)_2]^-$. This is a thermodynamic effect instead of a kinetic effect because [K(crown)]CPh_3 completely deprotonates $IrH_5(P^iPr_3)_2$. If the pK_α^{THF} of $HCPh_3$ is about 44 (estimated from pK_a^{DMSO}, Table 10), then the pK_α^{THF} of $IrH_5(P^iPr_3)_2$ and also $IrH_5(PCy_3)_2$ (Table 8) must be about 43.

A useful equilibrium is established between $[ReH_4(PMe_2Ph)_4]^+$ ($pK_\alpha^{THF} = 20.0$) and $CH_2(CN)_2$ (eq 15, Table 3, $K = 13$ M^{-1}). Here, pK_α^{THF} of $CH_2(CN)_2$ is determined to be 24 ± 2 on the basis of the estimated K_d of the ion-pair of 5×10^{-6} M ($a = 6$ Å in eq 4).

$$CH_2(CN)_2 + ReH_3(PMe_2Ph)_4 \rightleftharpoons \{ReH_4(PMe_2Ph)_4{}^+, CH(CN)_2{}^-\} \quad (15)$$

The reverse equation between $\{Kcrypt^+, CH(CN)_2{}^-\}$ and $\{ReH_4(PMe_2Ph)_4{}^+, BPh_4{}^-\}$ also established the pK_α^{THF} of $CH_2(CN)_2$ to be 24 ± 2.

We find that picric acid completely protonates PBu_2Ph ($pK_\alpha^{THF} = 6.6$) and then oxidizes it to a variety of products (under Ar). It is not as acidic as $HPPh_3{}^+$ ($pK_\alpha^{THF} \approx 3$, Table 10), although the slow oxidation of the PPh_3 complicates the experiment. We estimate the pK_α^{THF} for picric acid to be 10 ± 2, which is in agreement with the Coetzee value ($pK_a^{THF} = 11.6$)[20] and indicates that our pK_α^{THF} values are close to absolute ones.

$MoH(C_5H_5)(CO)_3$ forms a clean equilibrium upon reaction with $OsH_2(PMePh_2)_4$ in THF-d_8 to give the 1:1 ion-pair $\{OsH_3(PMePh_2)_4, Mo(C_5H_5)(CO)_3\}$. Therefore, the pK_α^{THF} of $MoH(C_5H_5)(CO)_3$ is 17, with K_d estimated as 10^{-5} M. $Fe(C_5Me_5)(CO)_2H$ reacts with $Q[ReH_6(PPh_3)_2]$ to give an equilibrium with $[K(crown)][Fe(C_5Me_5)(CO)_2]$ and $ReH_7(PPh_3)_2$ and another unidentified species in lower concentration with a ^{31}P chemical shift at 50 ppm. Assuming that ion-pair dissociation constants are comparable, the pK_α^{THF} of the iron complex is approximately 31. The pK_a^{MeCN} values for these Mo and Fe hydrides are also known to be 13.9 and 26.3, respectively.[59]

Error in pK_α^{THF} Values of Cationic Acids. The error in the equilibrium constant determination depends on the magnitude of the constant, the signal-to-noise of each species in the spectrum of the equilibrium mixture, and whether signals for all of the species are resolvable. The estimated errors for the equilibrium constants are listed in Table 3. The ladder approach provides pK_α^{THF} values that have errors that accumulate as they become farther removed from the reference value of 9.7 due to the equilibrium constant errors plus errors in the estimate of ΔpK_d which are on the order of ±0.1 for the cationic acids. The absolute values of ΔpK_d range from 0.0 to ±0.6, with the largest ΔpK_d for the equilibria between the smaller pairs $\{NHEt_3{}^+, BPh_4{}^-\}$ and the larger ion-pairs $\{OsH_3L_4{}^+, BPh_4{}^-\}$, L = PMe_2Ph and $PMePh_2$. However, in these cases and in other cases, the cumulative errors tend to cancel since the ΔpK_d values tend to alternatively add and subtract as one goes up the ladder according to the reactions of Table 3. The estimated cumulative error for a pK_α^{THF} value of the cationic acids is given by eq 16.

$$\text{cumulative error in } pK_\alpha^{THF} = \pm 0.08|pK_\alpha^{THF} - 9.7| \quad (16)$$

Therefore, the pK_α^{THF} of the weakest cationic acid, $[ReH_2(PMe_3)_5]^+$, is 24 ± 1 relative to $HPCy_3{}^+$ at 9.7. The uncertainty in the pK_α^{THF} values will be reduced as more measurements are made in the future.

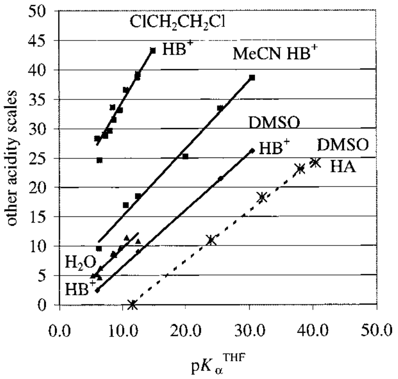

Figure 3. Correlation between other acid scales and the pK_α^{THF} scale. The points are from Tables 8 and 9.

Error in pK_α^{THF} Values of Neutral Weak Acids. The errors in these pK_α^{THF} values are indicated in Table 8. They are larger than the cationic acids because of the error in the estimate of the K_d values in the linking of the cationic and neutral scales (±2), plus an accumulation of errors in the measurement of K and in the estimate of individual ΔpK_d.

Equations Linking Other Acidity Scales. Table 9 compares the pK_α^{THF} values for some of the cationic compounds determined in this work with those determined in other solvents, often with other anions. Also included are two phosphazene acids of which the ion-pair pK value has been determined in THF and pK_a^{DMSO} and pK_a^{MeCN} have also been measured or estimated.[6,66] We estimate the pK_α^{THF} of $[P(NMe_2)_3NP(NMe_2)_2NH^tBu]^+$ to be 26 (Table 9) on the basis of its reported equilibrium in THF with 9-phenylfluorene[66] ($pK_\alpha^{THF} = 31$) and an estimated K_d of 10^{-5} M; the other phosphazenium acid is reported to be 5 pK units less acidic in THF.[66]

A significant observation is that there are separate $pK_a^{DMSO}/pK_\alpha^{THF}$ correlations for cationic (HB^+) and neutral (HA) acids (Figure 3). The data for the two cationic ammonium ions and the two protonated phosphazene compounds of Table 9 provide an approximate conversion equation for the line (Figure 3) relating $pK_\alpha^{THF}(HB^+)$ and Bordwell's pK_a^{DMSO} scales (eq 17, $R^2 = 0.99$).

$$pK_a^{DMSO} = 0.95pK_\alpha^{THF}(HB^+) - 3.0 \quad (17)$$

The data for the neutral acids picric acid, $CH_2(CN)_2$, $P(O)(OEt)_2PhNH$, PPh_2H, and NPh_2H (Table 8) are plotted in Figure 3. The least-squares regression provides eq 18 ($R^2 = 0.99$).

$$pK_a^{DMSO} = 0.85pK_\alpha^{THF}(HA) - 9.6 \quad (18)$$

Since the Streitwieser pK_{fi}^{THF} scale of neutral acids was anchored to the pK_a^{DMSO} of fluorene and found to be equivalent to the pK_a^{DMSO} values for a variety of hydrocarbon acids with delocalized anions,[17] eq 18 also applies to the many pK_{fi}^{THF} values reported by Streitwieser and co-workers and Antipin and co-workers.[18] Therefore, the slope of eq 18 should be 1.0. Errors in our estimates of pK_α^{THF} probably account for this deviation.

A least-squares fit line through eight points (Figure 3) relating the aqueous scale (pK_a^{aq}) of the cationic compounds listed in Table 9 to the pK_α^{THF} scale gives eq 19 ($R^2 = 0.89$). The small correlation coefficient shows, as expected, that water and THF

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(66) Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji, G. Z.; Peters, E. M.; Peters, K.; vonSchnering, H. G.; Walz, L. *Liebigs Ann.* **1996**, 1055−1081.

$$\mathrm{p}K_\mathrm{a}^{\mathrm{aq}} = 1.0\mathrm{p}K_\alpha^{\mathrm{THF}}(\mathrm{HB}^+) - 0.7 \tag{19}$$

are very different in their solvating properties. This may also reflect the fact that the pK_a values of some of the protonated phosphines were actually determined by potentiometric titration in CH_3NO_2 and then correlated to the water scale.[67] The compounds $[HPMePh_2]^+$, $[HP^tBu_3]^+$, and $[HNEt_3]^+$ show the largest deviations from the correlation. Neutral acids would be expected to have greater pK_α^{THF} values than those predicted by the use of eq 19. For example, 2,6-dinitrophenol has a p$K_\mathrm{a}^{\mathrm{aq}}$ of 3.6 but has a pK_α^{THF}(HA) estimated to be 18 on the basis of its p$K_\mathrm{a}^{\mathrm{DMSO}}$ (4.9) and p$K_\mathrm{a}^{\mathrm{MeCN}}$ (16.5) values.[68]

Utilizing MeCN as a solvent and similar NMR detection, PPh_3 was found to be in equilibrium with CF_3-4-$C_6H_4NH_3^+BF_4^+$, $PMePh_2$ with $C_6H_5NH_3^+BF_4^-$, and P^tBu_3 with protonated morpholine tetrafluoroborate; these provide the p$K_\mathrm{a}^{\mathrm{MeCN}}$ values of 8.0, 9.6, and 17.0, respectively. The last two are useful links to the THF scale (Table 9, Figure 3). When combined with the values for $[HNEt_3]^+$,[59] $[Re(H)_4(PMe_2Ph)_4]BPh_4$,[5] and the two phosphazenium acids[66] of Table 9, a linear fit provides the relationship of eq 20 ($R^2 = 0.99$ for six points). This allows

$$\mathrm{p}K_\mathrm{a}^{\mathrm{MeCN}} = 1.13\mathrm{p}K_\alpha^{\mathrm{THF}}(\mathrm{HB}^+) + 3.7 \tag{20}$$

the approximate placement on our scale of eight cationic nickel group hydrides $[MH(\text{diphosphine})_2]^+$ determined by DuBois and co-workers (see examples in Table 10).[69] Triphenylphosphonium tetraphenylborate is insoluble in THF but soluble in MeCN and CH_2Cl_2, and so eq 20 can be used to estimate its pK_α^{THF} to be 3 (Table 10).

Two metal hydrides, $Mo(C_5H_5)(CO)_3H$ and $Fe(C_5Me_5)(CO)_2H$, with p$K_\mathrm{a}^{\mathrm{MeCN}}$ values of 13.9 and 26.3, respectively, were found to have approximate pK_α^{THF} values of 17 and 31, respectively. These two points plus the point (pK_α^{THF}(HA), p$K_\mathrm{a}^{\mathrm{MeCN}}$) = (11.6, 11) for picric acid[68] provide correlation eq 21 ($R^2 = 0.99$). Equation 21 then provides a link to relate the

$$\mathrm{p}K_\mathrm{a}^{\mathrm{MeCN}} = 0.81\mathrm{p}K_\alpha^{\mathrm{THF}}(\mathrm{HA}) + 1.0 \tag{21}$$

p$K_\mathrm{a}^{\mathrm{MeCN}}$ values of the 20 neutral carbonyl hydride complexes studied by Norton and co-workers to the THF scale.[2,5] The very basic anionic hydride $[RuH_5(P^iPr_3)_2]^-$ (pK_α^{THF} of the acid form is 39) reacts immediately with MeCN, presumably via an initial proton-transfer reaction.

The heats of protonation by trifluoromethylsulfonic acid (HOTf) of the compounds in CH_2ClCH_2Cl where available from the literature[15,56] are also included in Table 9. The conversion equation is eq 22 ($R^2 = 0.94$ for 10 points neglecting $HPMePh_2^+$). It is interesting that both amines and phosphines

$$-\Delta H_{\mathrm{HM}}^{\mathrm{CH_2ClCH_2Cl}}(\mathrm{HB^+OTf^{--}}) = 1.8\mathrm{p}K_\alpha^{\mathrm{THF}}(\mathrm{HB^+BPh_4^-}) + 16.3 \tag{22}$$

fall approximately on the same line. If pseudoaqueous pK_a values are used instead, then distinct lines are obtained for amines and phosphines (Figure 1 of ref 15). Therefore, solvation effects are similar in dichloroethane and THF but different in water. Only the last solvent can act as a hydrogen bond donor. The $-\Delta H_{\mathrm{HM}}$ values were measured for cations with $CF_3SO_3^-$ counterions, while the pK_α^{THF} values were determined with BPh_4^- counterions. The differences in ion-pairing and hydrogen-bonding may account for the deviation of the slope of eq 22 (1.8) from that predicted by thermodynamics, $RT \ln(10) = 1.35$.

Correlation with Metal Hydride Vibrational Modes. Metal hydride vibrational data for selected complexes are listed in Table 11. There is a general trend that, for related complexes, the metal hydride stretch in both the acid and base forms drops to lower wavenumber as the complex becomes more basic. Thus, for the series of Re^V/Re^{III} acid/base pairs of Table 11, a change in pK_a from 7 to 20 is reflected in a change in ν(Re−H) from 2061 to 1933 cm^{-1} for the acid and from 2019 to 1782 cm^{-1} for the base (Figure 4). The base form always has lower ν(M−H) than the acid form. The metal hydride modes for the base form move to very low frequency for the neutral/anionic hydrides (Figure 5).

Electrochemical Measurements. Reversible electrochemical potentials corresponding to the oxidation of the conjugate base of a hydride or dihydrogen complex along with the pK_a of the acid are needed to calculate a metal hydride bond dissociation energy.[10,14,70] Unfortunately, the anionic hydrides $[MH_3(\text{CO or NO})L'_2]^-$ (M = Re, Os, Ru; L′ = P^iPr_3) in THF/$N^nBu_4PF_6$ display irreversible oxidations in the range from −0.06 to −0.42 V vs $Fe(C_5H_5)_2^+/Fe(C_5H_5)_2$ (Table 12).

Discussion

The Anchor for the Scale. Protonated tricyclohexylphosphine with pK_a = 9.7 was chosen as the anchor for our scale for a variety of reasons. Equilibrium constants are conveniently determined by ^{31}P NMR; several have already been determined. The base is bulky and rarely substitutes for other ligands in metal complexes. The phosphonium tetraphenylborate salt is easily prepared and has a high enough pK_a to place it toward the middle of the scale. Protonated triethylamine with pK_α^{THF} = 12.5 is a useful secondary standard. Its p$K_\mathrm{a}^{\mathrm{MeCN}}$ and p$K_\mathrm{a}^{\mathrm{DMSO}}$ values have also been reported (Table 9). The enthalpies of protonation of PCy_3 and NEt_3 in $CHCl_2CHCl_2$ have been determined. Therefore, our scale can be related to the other important acidity scales. In addition, NEt_3 is often used as a base in organometallic reactions.

Picric acid is another possible choice for an anchor for the THF scale. Its p$K_\mathrm{a}^{\mathrm{THF}}$(HA) was determined by potentiometric measurements to be 11.6, while its p$K_\mathrm{a}^{\mathrm{DMSO}}$ value is about 0.[20] As noted above, these values are consistent with eq 18, and this suggests that our pK_α^{THF} values are close to absolute p$K_\mathrm{a}^{\mathrm{THF}}$ values. As mentioned, the Streitwieser p$K_{\mathrm{fi}}^{\mathrm{THF}}$(HA) scale arbitrarily uses the p$K_\mathrm{a}^{\mathrm{DMSO}}$ value of fluorene for its anchor. This explains the large discrepancy in p$K_{\mathrm{fi}}^{\mathrm{THF}}$(HA) and p$K_\alpha^{\mathrm{THF}}$(HA) values for $HPPh_2$ and $HNPh_2$ (Table 8).

Comparison with Other Scales. A significant observation is that there are separate p$K_\mathrm{a}^{\mathrm{DMSO}}$/p$K_\alpha^{\mathrm{THF}}$ correlations for cationic (HB^+) acids (eq 17) and the neutral (HA) acids (eq 18). The reason is that the dissociation of HA results in a net increase in the population of ions (eqs 23 and 24), compared to that of HB^+ (eq 25), that will be opposed by a lowering of the dielectric constant from DMSO to THF. There will also be two separate correlations for HB^+ and HA in MeCN (eqs 20 and 21) and in H_2O (eq 19, equation for HA not determined).

The pK_α^{THF} values for phosphonium salts (Table 7) correlate with literature values (Figure 3; eqs 19 and 20) with a few exceptions. The pK_α^{THF} value of $[HP^tBu_3]BPh_4$ is 10.6 (Table 7), while that of $HNEt_3^+$ is 12.5. This is a different ordering than the p$K_\mathrm{a}^{\mathrm{aq}}$ values of 11.4 and 10.7, respectively. Note also that the heat of protonation of NEt_3 with HOTf in CH_2ClCH_2-

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(68) Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23−28.

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Table 11. pK_α^{THF} Values of Acids and Infrared Wavenumbers of Metal Hydride Modes of the Acid and Conjugate Base Complexes in Nujol

pK_α	acid	ν(M−H)	base	ν(M−H)
6[a]	$[Re^{V}H_2(C_5H_5)_2]^{+\,b}$	2061	$Re^{III}H(C_5H_5)_2$	2019
15.8	$[Re^{V}H_4(PMePh_2)_4]BPh_4$	2023, 1938	$Re^{III}H_3(PMePh_2)_4$	1956, 1851
20.0	$[Re^{V}H_4(PMe_2Ph)_4]BPh_4$	1933	$Re^{III}H_3(PMe_2Ph)_4$	1782
24.2	$[Re^{III}H_2(PMe_3)_5]BPh_4$	1852	$Re^{I}H(PMe_3)_5$	1757
6[a]	$[Os^{IV}H(C_5Me_5)_2]^+$	2194	$Os^{II}(C_5Me_5)_2$	
		2164[c]		
12[a]	$[Os^{IV}H_2(C_5H_5)(PPh_3)_2]BPh_4$	2163, 2130[d]	$Os^{II}H(C_5H_5)(PPh_3)_2$	2060[d]
16.9	$[Os^{IV}H_3(PMe_3)_4]PF_6$	2043[e]	$Os^{II}H_2(PMe_3)_4$	1985[e]
30	$Re^{VII}H_7(PPh_3)_2$	1984, 1961	$Q[Re^{V}H_6(PPh_3)_2]$	1884, 1853
41	$Re^{VII}H_7(PCy_3)_2$	1970 w	$Q[Re^{V}H_6(PCy_3)_2]$	1935 sh, 1884 m
		1935 sh		1823 m
		1915 s		1717 s
35	$Os^{VI}H_6(P^iPr_3)_2$	1980, 1910	$Q[Os^{IV}H_5(P^iPr_3)_2]$	1836
				1858,[f] 1843[f]
∼43	$Ir^{V}H_5(P^iPr_3)_2$	1950	$Q[cis\text{-}Ir^{III}H_4(P^iPr_3)_2]$	1965, 1688[g]
∼43	$Ir^{V}H_5(PCy_3)_2$	1945	$Q[cis\text{-}Ir^{III}H_4(PCy_3)_2]$	1960, 1680[g]

[a] See Table 10. [b] Reference 88; anion was not specified. [c] Reference 89. [d] Reference 90. [e] Reference 91. [f] In THF. [g] Reference 60.

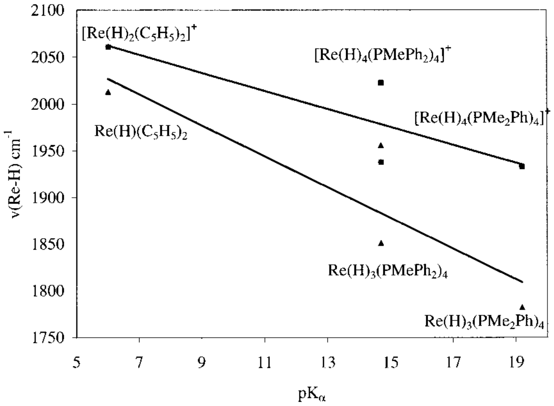

Figure 4. Plot of ν(Re−H) versus pK_α^{THF} for the series of Re^{V}/Re^{III} acid/base pairs of Table 11.

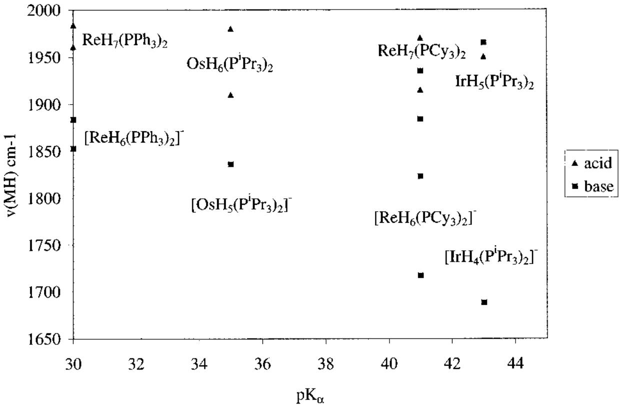

Figure 5. Plot of ν(M−H) versus pK_α^{THF} for the anionic hydrides of Table 11.

$$HA + xTHF \overset{K_{23}}{\rightleftharpoons} \{H(THF)_x{}^+,A^-\} \overset{K_{d23}}{\rightleftharpoons} H(THF)_x{}^+ + A^- \quad (23)$$

$$K_\alpha{}^{THF}(HA) = K_{23}K_{d23} \quad (24)$$

$$\{HB^+,Y^-\} + xTHF \overset{K_{d25}}{\rightleftharpoons} HB^+ + Y^- + xTHF$$
$$\overset{K_\alpha{}^{THF(HB^+)}}{\rightleftharpoons} B + H(THF)_x{}^+ + Y^- \quad (25)$$

Table 12. Peak Potentials from Cyclic Voltammetry for Anionic Hydrides with L′ = P^iPr_3[a]

complex	E_p (V)	E_{calc}[b]
$Q[ReH_3(CO)L'_2]$	−0.42	−0.6
$Q[OsH_3(CO)L'_2]$	−0.32	−0.6
$Z[OsH_3(CO)L'_2]$	−0.29	−0.6
$Q[RuH_3(CO)L'_2]$	−0.29	−0.2
$Q[RuH_5L'_2]$	−0.06	

[a] Versus $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$ in 0.2 M $N^nBu_4PF_6$ in THF; scan rates 0.25 V/s. [b] d^5/d^6 reduction potentials predicted by use of Lever's method.[26,92]

Cl is 2.7 kcal/mol greater than that of P^tBu_3 (Table 9), also in keeping with the greater basicity of NEt_3 in these aprotic solvents.

The pK_α^{THF} values for the complexes $[MH_3(PMe_3)_4]BPh_4$, M = Ru (16.6, Table 9), Os (16.9), are quite different from those reported for MeOH solutions of $[MH_3(PMe_3)_4]OMe$ (11.3, 11.5) created by dissolving $MH_2(PMe_3)_4$ in MeOH.[47] The differences in anions and solvent character make comparisons difficult, but the MeOH values are probably closer to true aqueous pK_a values than the THF ones.

The pK_a^{MeCN} values of some 20 neutral carbonyl hydride complexes, mainly of the types $MH(CO)_x(L)$ and $MH(C_5R_5)(CO)_xL$ (M = Cr, Mo, W, Mn, Re, Fe, Ru, Os; L = CO, phosphine) have been determined to fall in the range from 8 to 26.8.[2] By use of eq 21 their pK_α^{THF} values can be estimated to fall in the range from 8 to 32.

The pK_α^{THF} values of more than 38 cationic hydrides, mainly of the types $[MH(CO)_xL_y](OTf)$ and $[MH(C_5R_5)XL_x](OTf)$ (X = halide or hydride), can be estimated by use of eq 22 from their $-\Delta H_{HM}$ values determined in $CHCl_2CHCl_2$.[15] These fall in the range from 0 to 14. For example, $[Os(C_5H_5)(H)_2(PPh_3)_2]OTf$ is predicted to have a pK_α^{THF} of 12 on the basis of its $-\Delta H_{HM}$ value of 37.3 (Table 10). The pK_a (not corrected for ion-pair effects) of the $BF_4{}^-$ salt of this complex in CH_2Cl_2 was reported to be 13.4 relative to $HPCy_3{}^+$ at 9.7.[28] Most basic hydrides with conjugate acids with pK_α^{THF} > 15 are expected to react with these chlorinated solvents.

pK_a of Dihydrogen. The correlation of pK_α^{THF}(HA) with pK_a^{DMSO} allows an estimate of the pK_α^{THF} of H_2/Q^+H^- (not corrected for ion-pairing) as about 49 on the basis of the work by Buncel and Menon in 1977.[71] Their determination of the pK_a of H_2 at 35.3 (also not corrected for ion-pairing) was based on the reaction of H_2 with $Q[CH(C_6H_2\text{-}2,4\text{-}Me_2)_2]$ in THF and anchored to 9-phenylfluorene, estimated to have a pK_a of 18.5. The pK_α^{THF} of CH_2Ph_2 is estimated to be 48 on the basis of its pK_a^{DMSO} of 32.3.[18] Therefore, the pK_α^{THF} of $CH_2(C_6H_2\text{-}2,4\text{-}Me_2)_2$ is about 50, and therefore, the ion-pair pK_α^{THF} of $H_2/$

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(70) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.
(71) Buncel, E.; Menon, B. *J. Am. Chem. Soc.* **1977**, *99*, 4457−4461.

Q^+H^- is about 49 according to data from Buncel et al.[71] Our value of 49 (Table 10) still remains an estimate until direct links are found to fill in the gap between the top of our scale, 41 for $ReH_7(PCy_3)_2$, and the pK_α^{THF} of H_2(g). The pK_a of $Ir(C_5Me_5)(H)_2(PMe_3)/Ir(C_5Me_5)(H)(Li)(PMe_3)$ has been reported to be in the range 38−41 because the lithium salt deprotonates H_2(g) and DMSO but not toluene in THF;[62] this translates into a $pK_\alpha^{THF} > 51$ (Table 10). A low ν(Ir−H) would be expected for this lithium salt on the basis of the IR trends reported in Table 11, but no IR spectrum was reported in the work.

Equation 26 is useful in relating the bond dissociation of an element−hydrogen bond $BDE\{EH/(E^\bullet + H^\bullet)\}$ in kilocalories per mole with its $pK_a\{EH/(E^- + H^+)\}$ on the MeCN scale and the reduction potential $E_{1/2}\{(E^\bullet + e^-)/E^-\}$ versus $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$.[69,70,72,73] Since $BDE\{H_2(g)/(2H^\bullet)\} = 103.25$ kcal/mol

$$\mathrm{BDE}\{\mathrm{EH}/(\mathrm{E}^\bullet + \mathrm{H}^\bullet)\} = 1.37\mathrm{p}K_a\{\mathrm{EH}/(\mathrm{E}^- + \mathrm{H}^+)\} + 23.1E_{1/2}\{(\mathrm{E}^\bullet + \mathrm{e}^-)/\mathrm{E}^-\} + 59.5 \quad (26)$$

for dihydrogen and $E_{1/2}\{(H^\bullet + e^-)/H^-\}$ is assigned to be −1.1 V vs $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$ in MeCN,[74] the $pK_a^{MeCN}\{H_2(g)/(H^- + H^+)\}$ is calculated by use of eq 26 to be 50 on the CH_3CN scale. Conversion eq 21 provides an extrapolated pK_α^{THF} value of 60. This value, when compared to the ion-pair $pK_\alpha^{THF}(H_2/Q^+H^-) = 49$, would suggest that $K_d(Q^+H^- \rightarrow Q^+ + H^-)$ is very small (approximately 10^{-11} M).

Effect of the Substituents and the Metal on pK_a. The expected substituent effect of increasing acidity of the phosphonium with the substitution of Ph for Et or Cy is observed. Thus, there are the pK_α orderings $HPEt_3{}^+ > HPEt_2Ph^+ > HPEtPh_2{}^+$ and $HPCy_3{}^+ > HPCy_2Ph^+$ (Table 7). Replacing Me for Ph in the complexes $[Re(H)_4(PR_3)_4]^+$ causes a decrease in pK_α: PMe_3 (22.9) > PMe_2Ph (20.0) > $PMePh_2$ (15.8) (Table 7). A similar result is observed for $[Os(H)_3(PR_3)_4]^+$: PMe_3 (16.9) > PMe_2Ph (14.9) > $PMePh_2$ (12.4) (Table 7).

An unusual observation is that methyl substituents make phosphines more basic than do ethyl or butyl substituents, while the effect is the opposite for the Os complexes $[OsH_3(PR_3)_4]^+$. Compare, for example, the pK_α of $HPMePh_2{}^+BPh_4{}^-$ (6.4) versus that of $HPEtPh_2{}^+BPh_4{}^-$ (5.3), and the pK_α of $HPMe_3{}^+BAr'_4{}^-$ (8.7) versus that of $HPEt_3{}^+BAr'_4{}^-$ (8.5). In the gas phase, bases with Me substituents are known to be more basic than those with Et or Bu. However, this effect is not observed for heats of protonation in CH_2ClCH_2Cl where $HPMe_3{}^+OTf^-$ ($-\Delta H = 31.6$) is more acidic than $HPEt_3{}^+OTf^-$ ($-\Delta H = 33.7$). In addition, $[Os(H)_3(PMe_3)_4]^+$ is more acidic than $[Os(H)_3(PEt_3)_4]^+$. Therefore, solvation effects make the prediction of substituent effects somewhat difficult.

Osmium and rhenium hydrides of the types $[OsH_3(PR_3)_4]^+$, $[ReH_4(PR_3)_4]^+$, and $[ReH_2(PMe_3)_5]^+$ were found to be the least acidic cationic compounds of the scale, with the rhenium complexes being 4−6 units less acidic than the osmium ones with the same ligand set (e.g., $[ReH_4(PMe_2Ph)_4]^+$ with 20.0 versus $[OsH_3(PMe_2Ph)_4]^+$ with 14.9, Table 7). On a per-proton basis the Os complexes are even more acidic, considering that they have three deprotonation sites while the Re complexes have four. This probably reflects the greater stabilization on going from seven-coordinate $Os^{IV}(d^4)$ to six-coordinate $Os^{II}(d^6)$ compared with going from eight-coordinate $Re^V(d^2)$ to seven-coordinate $Re^{III}(d^4)$.

The acidity of the complexes $ReH_7(PR_3)_2$ (Table 8) is surprisingly sensitive to substituent effects. Changing from $PPh_2C_6H_4F$ to PPh_3 results in a 2 pK unit change, while changing from PPh_3 to PCy_3 results in an 11 pK unit change! While the IR spectra of the neutral acids ReH_7L_2 are comparable (Table 11, Figure 5), there are much lower ν(Re−H) modes for the anionic PCy_3 complex (a strong mode at 1717 cm^{-1}) compared to those of the PPh_3 complex (1884, 1853 cm^{-1}). This indicates that the destabilization of rhenium−ligand bonding in the anions is a strong determinant of the acidity of the acid form. The effect of replacing L = PPh_3 by L = PCy_3 on the acidity of some iridium complexes $[Ir(C_5H_5)(CO)(L)(H)]OTf$ is much smaller than that observed for our rhenium system. In the case of iridium, the $-\Delta H_{HM}$ changed from 30 to 32.7 kcal/mol;[14] this represents a pK change of 1.3 units according to eq 22. The replacement of two L = PPh_3 by two L = PMe_3 in $[Ru(C_5Me_5)L_2(H)_2]^+$ results in a ΔpK of 5.6 (Table 7), again much smaller than the observed change for ReH_7L_2.

A lower metal hydride stretching frequency might be expected to be indicative of weaker metal hydride bonding. The cationic polyhydrides of Table 11 show a decrease in ν(MH) with increasing pK_α. The neutral polyhydride weak acids of Table 11 (ReH_7L_2, OsH_6L_2, and IrH_5L_2) all have metal hydride modes at about 1950 cm^{-1}. An increase in the wavenumbers of M−H modes with increase in pK_α of the hydrides might have been expected on the basis of the report of an increase in M−H bond dissociation energy with a decrease in acidity of related cationic hydride complexes[14] and on the basis of eq 26. But this is not observed.[75] It is significant that the conjugate base hydrides have lower metal hydride modes that drop with increasing pK_a down to 1680 cm^{-1} for $[IrH_4L_2]^-$. It appears from these data that the weak acidity of these polyhydrides is due in part to the destabilization of bonding in the conjugate base hydride, with the assumption that there is some direct relationship between ν(MH) and M−H bond strength. The very low metal hydride mode for the iridium anions is due to the high trans influence of the mutually trans hydride ligands. However, caution is needed in interpreting the IR data of anions because the cation can greatly affect the metal hydride vibrational modes. The spectacular example of this is the series of complexes $M_2[OsH_6]$, where ν(Os−H) is 1500 cm^{-1} for M = Ba and 1850 cm^{-1} for M = Mg.[76] In our case, the crown cation remains the same, although its interaction with the hydrides on the anion probably varies. In cases where Nujol mull and THF samples have been compared, the wavenumbers of modes are quite similar.

Dihydrogen Complexes. Previous determinations of constants for equilibria between metal hydrides and phosphonium salts can be used to place a variety of hydride and dihydrogen species on the pK_α^{THF} scale (Table 7). The tetrafluoroborate salts of the dihydrogen complexes $[Ru(H_2)(C_5H_5)(L)]BF_4$ (L = dppm,[77] dppe) and the dihydride tautomer $[Ru(H)_2(C_5H_5)(dppe)]BF_4$[8] were previously determined to be 2.2, 2.5, and 2.2 units more acidic, respectively, than $HPCy_3{}^+BF_4{}^-$ ($pK_a^{aq} = 9.7$) in THF, although these numbers were not corrected for ion-pair dissociation.[11] The present work with the $BPh_4{}^-$ salts give similar numbers and produces pK_α^{THF} values of 7.2, 7.0, and

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(75) A reviewer noted that the metal hydride IR wavenumber and the bond dissociation energy may not be related since the former emphasizes an ionic component to the bonding (on the way to heterolytic splitting) while the latter is a homolytic splitting process.

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7.4, respectively (Table 7). Similarly, the pK_a of the complexes $[Ru(H)_2(C_5H_5)(PPh_3)_2]BF_4$ and *trans*-$[M(H_2)(H)(dtfpe)_2]BF_4$ (dtfpe = $(CF_3\text{-}4\text{-}C_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}CF_3)_2$),[10] were previously estimated in THF and anchored to $HPCy_3^+$. As reported previously, the pK_a of the dtfpe dihydrogen complexes increases in the aperiodic order Fe < Os < Ru. A similar order exists for the series *trans*-$[M(H_2)(H)(dppe)_2]BPh_4$/*cis*-$MH_2(dppe)_2$ (Table 7). The pK_a order Os < Ru also applies to the neutral dihydrogen complexes $M(H_2)(H)_2(CO)(P^iPr_3)_2$ (Table 8). The Os complex has a "slow-spinning" dihydrogen ligand with an H−H distance of 1.14 Å according to the minimum T_1 (17 ms, 300 MHz) and J_{HD} (16 Hz) data.[78] The Ru complex has a fast-spinning dihydrogen with an H−H distance of 0.88 Å according to similar data (T_1^{min} = 8 ms at 200 MHz, J_{HD} = 32.4 Hz). The ruthenium dihydrogen complexes are thought to be less acidic than corresponding osmium ones because of the stronger (shorter) H−H bond.[10] This would also explain why the dihydrogen complex $Ru(H_2)_2(H)_2(P^iPr_3)_2$ is less acidic than the classical hexahydride $OsH_6(P^iPr_3)_2$ (Table 8). The usual rule is that the 5d metal hydride is less acidic than the 4d metal hydride.[2] For example, on the basis of $-\Delta H_{HM}$, the osmium complex is more basic by 7.6 kcal mol^{-1} (approximately 4 pK_a units) than the ruthenium one for both $M(C_5H_5)H(PPh_3)_2$ and $M(C_5H_5)_2$, where classical hydrides are formed on protonation with HOTf.[14] Similarly, $Os(H)_2(CO)_4$ is less acidic than $Ru(H)_2(CO)_4$ in CH_3CN by 2.1 pK units.[4]

It is interesting to note that the complexes $Re(H)_4(NO)(P^iPr_3)_2$ and $Os(H_2)(H)_2(CO)(P^iPr_3)_2$ have close pK_α^{THF} values (Table 8); therefore, replacement of Re(NO) by Os(CO) gives somewhat comparable properties, although the osmium complex is a dihydrogen complex, while the rhenium complex is classical.[79] The peak potentials for oxidation of the conjugate base anions are also similar (Table 12). The dihydrogen complexes $Ru(H_2)_2(H)_2(P^iPr_3)_2$ and $Ru(H_2)(CO)(H)_2(P^iPr_3)_2$ have similar pK_α^{THF} values; these structures are related by replacing a π-acid H_2 ligand with a π-acid CO ligand.

Kinetics of Proton Transfer. Dramatic differences in the rates of proton transfer were noted. The equilibria between complexes with several large ligands and high pK_α values (e.g., $[Re(H)_4L_4]^+$, $[Os(H)_3L_4]^+$, and $[Ru(C_5Me_5)(H)_2(PMePh)_2]^+$) were very slow (12 h to 3 days, Table 3). The most dramatic effect was observed for $[Re(H)_4(PEt_3)_4]^+$, which continued to react with $Re(H)_3(PMe_3)_4$ for months without reaching equilibrium. The exact pK_α^{THF} for the PEt_3 complex has not yet been determined for this reason. By contrast, the acidic phosphonium salts apparently reached equilibrium in seconds.

Steric effects are very important in such reactions. This was clearly demonstrated in an earlier study by Hanckel and Darensbourg, where proton transfer from sterically congested $[MoH(CO)_2(dppe)_2]^+$ to F^- was fast (1 h) but that to NEt_2H was slow (10 days) and that to $Mo(^{13}CO)_2(dppe)_2$ was extremely slow.[80]

Use of pK_α^{THF} Correlations. The correlation between acid scales will prove useful in predicting new reactions and explaining reported ones. For example, it appeared puzzling why the reaction of $RuH(C_5H_5)(dppm)$ with HBr (pK_a^{DMSO} 0.9) did not produce $\{Ru(H_2)(C_5H_5)(dppm)^+,Br^-\}$ in THF[81] while reaction with $\{HOEt_2,BF_4\}$ did produce $\{Ru(H_2)(C_5H_5)(dppm),BF_4\}$.[11] The present work shows that the dihydrogen complex has pK_α^{THF} = 7.4, while HBr has pK_α^{THF} ≈ 12 on the basis of eq 18, and so it will not react.

Conclusions

A continuous ladder of acid/base equilibria determined by NMR has now been constructed for THF solutions of phosphorus-containing species that spans the pK_α^{THF} range from 5 to 41. Convenient syntheses of acids and bases that cover this pK range are reported. The ladder includes 14 phosphonium salts/phosphine couples, 14 dihydrogen/hydride couples, 17 cationic hydride/neutral hydride couples, and 9 neutral hydride/anionic hydride couples. This is just the starting point. As more rungs of the ladder are interlinked, the pK_α^{THF} values will become more accurate and converge on absolute pK_a^{THF}. The effects of concentration on ion-pairing, ion aggregation, and pK_α^{THF} values need to be examined more closely. However, the concentrations used here are practical for NMR experiments.

Correlations with other scales allow an estimate of the pK_α^{THF} values of more than 1000 organic acids, 20 carbonyl hydrides, and of 46 cationic hydrides on the basis of work by the groups of Bordwell, Streitwieser, Antipin, Norton, Angelici, and DuBois. Therefore, the various acidity scales have been approximately united, and new acid−base reactions can be predicted. Correlations with ν(M−H) noted here for the first time suggest that destabilization of M−H bonding in the conjugate base hydride is an important contributor to the pK_a. It appears that Re−H bonding in the anions $[ReH_6(PR_3)_2]^-$ is greatly weakened by small increases in basicity of PR_3, resulting in a large increase in pK_a of the conjugate acid $ReH_7(PR_3)_2$. Work is still needed to link H_2(g) to our scale. It is estimated on our scale to have an ion-pair pK_α^{THF} of 49 on the basis of earlier work by Menon and Buncel.

We and others are developing a similar scale in CH_2Cl_2 for very acidic dihydrogen complexes.[13,38] Here, THF cannot be used as a solvent because some of these complexes protonate THF.

Appendix

The definition of ΔpK_α of Table 3 for reactions like eq 12 is

$$\Delta pK_\alpha = pK_\alpha(HA_1) - pK_\alpha(HA_2) = pK - \Delta pK_d$$

as in eqs 5 and 6.

For reactions like eq 11, the definition of ΔpK_α is

$$\Delta pK_\alpha = pK_\alpha(HB,Y) - pK_\alpha(MH_2L_n,Y) = pK - \Delta pK_d$$

where the inter-ion distance a for {HB,Y} is used in place of a_{MA_2} in eq 6 for the calculation of ΔpK_d and the a for $\{MH_2L_n,Y\}$ is used in place of a_{MA_1}.

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Supporting Information Available: Crystallographic data for $[Re(H)_2(PMe_3)_5]BPh_4$ (CIF, PDF) and a table of elemental analyses of representative salts (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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