

Properties of the Polyhydride Anions $[\text{WH}_5(\text{PMe}_2\text{Ph})_3]^-$ and $[\text{ReH}_4(\text{PMePh}_2)_3]^-$ and Periodic Trends in the Acidity of Polyhydride Complexes

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The new anionic complexes $[\text{K}(18\text{-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$, $[\text{K}(1,10\text{-diazia-18-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$, $[\text{K}(2,2,2\text{-crypt})][\text{ReH}_4(\text{PMePh}_2)_3]$, and $[\text{K}(1,10\text{-diazia-18-crown-6})][\text{ReH}_4(\text{PMePh}_2)_3]$ were prepared by reaction of KH/crown or KH/crypt with the appropriate neutral polyhydride $\text{WH}_6(\text{PMe}_2\text{Ph})_3$ or $\text{ReH}_5(\text{PMePh}_2)_3$. The rate of deprotonation of the rhenium hydride in THF is much greater for the reaction involving crypt compared with that of crown. The structure of $[\text{ReH}_4(\text{PMePh}_2)_3]^-$ is distorted pentagonal bipyramidal as determined by an X-ray diffraction study of the crypt salt. No hydridic–protonic $\text{M}-\text{H}\cdots\text{HN}$ bonding is detected between the hydrides of the anionic hydrides and the amino hydrogens of the cations $[\text{K}(1,10\text{-diazia-18-crown-6})]^+$ suggesting that stronger $\text{M}-\text{H}\cdots\text{K}$ interactions are present. Acid dissociation constants K_a of polyhydride complexes in THF, approximately corrected for ion pairing, are determined by NMR in order to better understand the periodic trends of metal hydrides. The $\text{p}K_a^{\text{THF}}$ of $(\text{WH}_6(\text{PMe}_2\text{Ph})_3)/[\text{WH}_5(\text{PMe}_2\text{Ph})_3]^-$ is 42 ± 4 according to the equilibrium set up by reacting $\text{WH}_6(\text{PMe}_2\text{Ph})_3$ with $[\text{K}(2,2,2\text{-crypt})][\text{ReH}_6(\text{PCy}_3)_2]$. The $\text{p}K_a^{\text{THF}}$ for $\text{ReH}_5(\text{PMePh}_2)_3$ can be estimated as greater than the $\text{p}K_a^{\text{THF}}$ of 38 for HNPh_2 and less than the $\text{p}K_a^{\text{THF}}$ of 41 for $\text{ReH}_7(\text{PCy}_3)_2$. Reaction of the phosphazene base $\text{P}_4\text{-}^t\text{Bu}$ with $\text{ReH}_7(\text{PCy}_3)_2$ gave an equilibrium with $[\text{HP}_4\text{-}^t\text{Bu}]^+[\text{ReH}_6(\text{PCy}_3)_2]^-$ whereas reaction with $\text{WH}_6(\text{PMe}_2\text{Ph})_3$ gave an equilibrium with $[\text{HP}_4\text{-}^t\text{Bu}]^+[\text{WH}_5(\text{PMe}_2\text{Ph})_3]^-$. From these and a related equilibrium, the $\text{p}K_a^{\text{THF}}$ of $[\text{HP}_4\text{-}^t\text{Bu}]^+$ is found to be 40 ± 4 . In general, neutral complexes $\text{MH}_x(\text{PR}_3)_n$ ($\text{M} = \text{W}, \text{Re}, \text{Ru}, \text{Os}, \text{Ir}; n = 3, 2$) studied to date have $\text{p}K_a^{\text{THF}}$ values from 30 to 44 on going from phenyl-substituted to alkyl-substituted phosphine ligands whereas $\text{MH}_x(\text{PR}_3)_n^+$ ($\text{M} = \text{Re}, \text{Fe}, \text{Ru}, \text{Os}, \text{Co}, \text{Rh}, \text{Ni}, \text{Pd}, \text{Pt}; n = 4, 3$), including diphosphine ligands ($(\text{PR}_3)_2 = \text{PR}_2\text{-PR}_2$), have values from 12 to 23. From the equilibrium established from the reaction of $[\text{HP}_2\text{-}^t\text{Bu}][\text{BPh}_4]$ and $[\text{K}(2,2,2\text{-crypt})][\text{OP}(\text{OEt})_2\text{NPh}]$, $[\text{HP}_2\text{-}^t\text{Bu}]^+$ was calculated to have a $\text{p}K_a^{\text{THF}}$ of 30 ± 4 . The equilibrium constant for the similar deprotonation reaction with $[\text{K}(18\text{-crown-6})][\{\text{ReH}_2(\text{PMePh}_2)_2\}_2(\mu\text{-H})_3]$ confirmed this value.

Introduction

A characteristic property of transition metal hydride complexes is their reactivity as acids as well as bases. The determination of acid dissociation constants helps to systematize and understand this reactivity. Some trends are emerging for the acidity of hydride complexes on going down groups of transition metals.¹ However, little is known about

trends across periods. The practical applications of this knowledge include the rational design of electrocatalysts for dihydrogen evolution² and the design of catalysts for polar bond hydrogenation^{3–7} and dehydrogenation.⁸

Tetrahydrofuran (THF) is an excellent solvent for studying the widest range of transition metal hydride complexes.^{9–11} The $\text{p}K_a^{\text{THF}}$ values can range from 0 for protonated THF to over 50 for deprotonated THF. The acidity of a wide range

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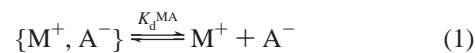
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of C–H,^{12–16} Si–H,¹⁷ N–H,^{18–21} P–H,^{9,22} and O–H^{23–25} acids in THF has been evaluated.

However, there are difficulties in accounting for referencing and for ion-pairing effects. For example the pK_a^{THF} value of $\text{CH}_2(\text{CN})_2$ has been reported as 12 ($pK_{\text{ip}}^{\text{THF}}$)²⁶ and 23 (pK_a^{THF}).⁹ Streitwieser and co-workers,^{27,28} Antipin and co-workers,^{29,30} Leito and co-workers,¹⁸ and our lab⁹ have accounted for ion-pairing by the use of dissociation constants for cation–anion ion pairing in THF (eqs 1 and 2). The use of acetonitrile (MeCN) as a solvent would avoid most ion-pairing problems in acid–base studies.^{1,31–42} However it is not useful for acids with values of $pK_a^{\text{MeCN}} > 34$ that have

conjugate bases strong enough to be completely protonated by acetonitrile, such as the anionic hydrides of our study.⁹



$$K_d^{\text{MA}} = \frac{[\text{M}^+][\text{A}^-]}{[\{\text{M}^+, \text{A}^-\}]} \quad (2)$$

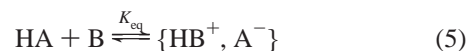
The 1:1 ion-pair dissociation constants, K_d (eq 2), are determined by conductivity measurements or are estimated theoretically by use of the Fuoss model of ion-pairs⁴³ or other methods. Recently, the Fuoss model has been shown to be quite inaccurate when applied to certain ion-pairing in THF.²²

Our lab introduced a pK_a^{THF} expression as an approximation of the free ion pK_a^{THF} acidity and reported a ladder scale of over 70 cationic and neutral acids, with acidities ranging from pK_a^{THF} of $([\text{HPeEtPh}_2]^+/\text{PEtPh}_2) = 5.3$ to pK_a^{THF} of $(\text{IrH}_5\text{-(PiPr}_3)_2/[\text{cis-IrH}_4(\text{PiPr}_3)_2]^-) = 44$.^{9,44} The scale is based on linked acid–base equilibria constants that are determined by ¹H and ³¹P NMR measurements and is anchored to $pK_a^{\text{THF}} = pK_a^{\text{aq}} = 9.7$ for $[\text{HPCy}_3][\text{BPh}_4]/\text{PCy}_3$ and 12 for picric acid/picrate.^{9,18–20} The pK_a^{THF} of an unknown acid can be determined from reaction of the acid or conjugate base with a known reference base or acid to give K_{eq} (eq 3), and eq 4 can be used to solve for $K_a^{\text{THF}}(\text{HA}_1/\text{A}_1^-)$ or $K_a^{\text{THF}}(\text{HA}_2/\text{A}_2^-)$. In the case of unknown K_d values, this approach provides the least uncertainty, especially when ions have similar properties on each side of eq 3.



$$K_{\text{eq}} = \frac{K_d^{\text{MA}_2} K_a^{\text{THF}}(\text{HA}_1/\text{A}_1^-)}{K_d^{\text{MA}_1} K_a^{\text{THF}}(\text{HA}_2/\text{A}_2^-)} \quad (4)$$

In the case where the reaction of a neutral acid and a neutral base is being used to provide an equilibrium constant K_{eq} (eq 5), the K_a^{THF} for either $(\text{HB})^+$ or (HA) can be calculated from eq 6 by using either $K_a^{\text{THF}}(\text{HB}^+/\text{B})$ or $K_a^{\text{THF}}(\text{HA}/\text{A}^-)$ as a reference. When K_d has to be estimated, this approach gives a larger uncertainty.²²



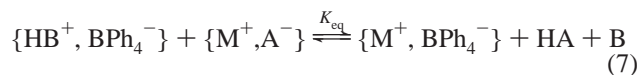
$$K_{\text{eq}} = \frac{K_a^{\text{THF}}(\text{HA}/\text{A}^-)}{K_d^{\text{HBA}} K_a^{\text{THF}}(\text{HB}^+/\text{B})} \quad (6)$$

In the case where a cationic acid reacts with an anionic base to give an equilibrium (eq 7), eq 8 can be used to calculate $K_a^{\text{THF}}(\text{HB}^+/\text{B})$ when $K_a^{\text{THF}}(\text{HA}/\text{A}^-)$ is used as a

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reference and vice versa.



$$K_{\text{eq}} = \frac{K_{\alpha}^{\text{THF}} (\text{HB}^+/\text{B}) K_{\text{d}}^{\text{HBBPh}_4} K_{\text{d}}^{\text{MA}}}{K_{\text{d}}^{\text{MBPh}_4} K_{\alpha}^{\text{THF}} (\text{HA}/\text{A}^-)} \quad (8)$$

Some strengths of the NMR method for the construction of acidity scales are that it is easy to implement and provides an accurate equilibrium constant from the species present when they have characteristic ^1H and ^{31}P resonances. It also provides a means of detecting side reactions; if they occur, that may not be detected by methods like UV-vis spectroscopy. Some weaknesses include the higher sample concentrations needed compared with UV-vis spectroscopy and the difficulty in accounting for ion pairing, solvation, and hydrogen bonding in this low dielectric constant solvent. Thus the values of $\text{p}K_{\alpha}^{\text{THF}}$ reported here are not thermodynamically accurate $\text{p}K_{\text{a}}$ values but are nevertheless useful in estimating the relative acidity of compounds in THF.

An objective of the current work is to study the basicity of anionic polyhydrides and the acidity of their conjugate acid form $\text{MH}_{x+1}(\text{PR}_3)_n$ in order to discover periodic trends in their acid-base properties and to probe the interesting phenomenon of hydridic-protonic $\text{MH}\cdots\text{HN}$ bonding.⁴⁵ The polyhydride anions $[\text{MH}_x(\text{PR}_3)_n]^-$ have hydrogen-accepting hydrides pointed in opposite directions and so the introduction of cations such as $[\text{K}(1,10\text{-diazia-18-crown-6})]^+$ ($[\text{K}(\text{HNQN})]^+$) with divergent hydrogen bond donor N-H groups should encourage the self-assembly of chain structures. Indeed this is the case for $[\text{K}(\text{HNQN})]^+[\text{IrH}_4(\text{P}^i\text{Pr}_3)_2]^-$,⁴⁴ $[\text{K}(\text{HNQN})]^+[\text{MH}_5(\text{P}^i\text{Pr}_3)_2]^-$, $\text{M} = \text{Ru}, \text{Os}$,⁴⁶ $[\text{K}(\text{HNQN})]^+[\text{ReH}_6(\text{PR}_3)_2]^-$, $\text{R} = \text{Me}, ^i\text{Pr}$,⁴⁷ and $[\text{K}(\text{HNQN})]^+[\{\text{ReH}_2(\text{PMePh}_2)_2\}_2(\mu\text{-H})_3]^-$.⁴⁸ Here, we examine whether such structures can form with polyhydrides that have three phosphine ligands per metal.

Experimental Section

Unless otherwise stated, all manipulations and reactions were carried out under ultrahigh purity argon or prepurified nitrogen using Schlenk and glovebox techniques. All solvents were distilled under argon over appropriate drying agents. THF, toluene, diethyl ether, and hexanes were dried and distilled from sodium metal and benzophenone indicator. CH_2Cl_2 was refluxed and distilled over calcium hydride, and ethanol and methanol were refluxed and distilled over iodine-activated magnesium turnings. CDCl_3 , CD_2Cl_2 , C_6D_6 , and THF- d_8 were obtained from Cambridge Isotope Laboratories and dried by storing over molecular sieves (3-Å beads, 8–12 mesh, Aldrich Chemical Co.).

^1H NMR spectra were acquired on Varian Gemini 200 MHz, Varian Gemini 300 MHz, Varian Mercury 300 MHz, or Varian

Unity 400 MHz spectrometers. ^{31}P NMR spectra were acquired on a Varian Gemini 300 MHz or a Varian Mercury 300 MHz spectrometer operating at 121 MHz for ^{31}P . ^1H NMR spectra were referenced indirectly to TMS via solvent peaks; ^{31}P NMR spectra were referenced to external 85% H_3PO_4 or to internal $\text{P}(\text{OMe})_3/\text{C}_6\text{D}_6$. Equilibrium constants were determined by gated ^1H decoupled ^{31}P NMR in nondeuterated THF, employing 90° pulses and a recycling time (D1 + AT) of 46 s.

Infrared spectra were acquired on a Nicolet Magna-IR spectrometer 550 or a Perkin-Elmer Paragon 500 FT-IR spectrometer.

Elemental analyses were performed by Guelph Chemical Laboratories, Guelph Canada, except for the analysis of $[\text{K}(1,10\text{-diazia-18-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$, which was performed by Oneida Research Services, Inc., Whitesboro, NY.

Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The CCD data were integrated and scaled using the Denzo-SMN package. The structures were solved and refined using SHELXTL V5.1. Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). Hydride atoms were located and refined with isotropic thermal parameters.

The following compounds were prepared by literature methods: $\text{ReOCl}_3(\text{PPh}_3)_2$,⁴⁹ $\text{WCl}_4(\text{PMe}_2\text{Ph})_3$,⁵⁰ $\text{WH}_6(\text{PMe}_2\text{Ph})_3$,⁵¹ $[\text{HNEt}_3][\text{BPh}_4]$,⁹ $[\text{K}(2,2,2\text{-crypt})][\text{OP}(\text{OEt})_2\text{NPh}]$,⁹ $\text{ReH}_7(\text{PCy}_3)_2$,⁹ $[\text{K}(2,2,2\text{-crypt})][\text{ReH}_6(\text{PCy}_3)_2]$,^{9,47} $\text{ReH}_3(\text{PMe}_2\text{Ph})_4$,⁹ $[\text{ReH}_4(\text{PMe}_2\text{Ph})_4][\text{BPh}_4]$,⁹ $\text{ReCl}_3(\text{PMePh}_2)_3$,⁵² $\text{ReH}_5(\text{PMePh}_2)_3$,⁵³ and $[\text{K}(18\text{-crown-6})][\{\text{ReH}_2(\text{PMePh}_2)_2\}_2(\mu\text{-H})_3]$.⁴⁸ The compounds 18-crown-6, 1,10-diazia-18-crown-6, KH, LiAlH_4 , 2,2,2-crypt, and Re metal powder were purchased from the Aldrich Chemical Co. KH was obtained as a suspension in mineral oil; the salt was filtered and washed with hexanes under a nitrogen atmosphere prior to use. Strem Chemical Company supplied PMePh_2 , PMe_2Ph , PCy_3 , and WCl_6 , Fluka Laboratory Chemicals supplied $\text{P}_2\text{-}^t\text{Bu}$ (2 M in THF) and $[\text{HP}_4\text{-}^t\text{Bu}][\text{BF}_4]$, and Chem. Service, Inc., provided $\text{OP}(\text{OEt})_2\text{NHP}$. Nitrogen (prepurified grade) and argon gases (ultrahigh purity grade) were obtained from Matheson Gases Canada. Hydrogen gas (grade 4.0) was obtained from BOC Gases Canada and used without further purification.

$[\text{K}(18\text{-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$. THF (5 mL) was added to $\text{WH}_6(\text{PMe}_2\text{Ph})_3$ (353 mg, 0.584 mmol), KH (65 mg, 1.62 mmol), and 18-crown-6 (153 mg, 0.584 mmol) under Ar. The solution turned deep red and was stirred for 3 h at ambient temperature. The excess potassium hydride was filtered from solution and washed with THF (3 mL). The solvent was removed from the combined filtrate by vacuum, yielding $[\text{K}(18\text{-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$ as a deep red-purple microcrystalline solid which was then washed with hexanes (2×5 mL) and dried in vacuo. Yield: 440 mg (83.3%). Anal. Calcd: C, 47.69; H, 6.89. Found: C, 48.04; H, 6.52. ^1H NMR (C_6D_6) δ : 8.21–7.00 (m, Ph, 15H), 3.17 (s, CH_2 , 24H), 2.04 (d, $^2J(^1\text{H}, ^{31}\text{P}) = 6$ Hz, PMe_2 , 18H), –4.22 (br, WH, 5H). $^{31}\text{P}\{^1\text{H}\}$ NMR(C_6D_6) δ : –3.23 (s; d $^1J(^{183}\text{W}, ^{31}\text{P}) = 171.2$ Hz).

$[\text{K}(1,10\text{-diazia-18-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$. A procedure similar to the preparation of $[\text{K}(18\text{-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$ was employed with the following quantities: THF (3 mL), $\text{WH}_6(\text{PMe}_2\text{Ph})_3$ (280 mg, 0.463 mmol), KH (30 mg, 0.75 mmol), and 1,10-diazia-18-crown-6 (122 mg, 0.465 mmol). Yield: 362 mg (86.5%). Anal. Calcd C, 47.79; H, 7.13; N, 3.10. Found: C, 47.81; H, 7.02; N, 3.34. ^1H NMR (C_6D_6) δ : 8.00–6.99 (m, Ph, 15H), 3.06 (br,

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CH₂, 8H), 3.00 (br, CH₂, 8H), 2.15 (br, CH₂, 8H), 1.83 (s, PMe₃, 18H), 0.64 (s, NH, 2H), -4.36 (m, WH, 5H). ³¹P{¹H} NMR(C₆D₆) δ: 0.03 (s; d ¹J(¹⁸³W, ³¹P) = 165.2 Hz). IR (Nujol): ν_{NH} 3283 cm⁻¹; ν_{WH} 1798, 1769, 1735 cm⁻¹.

pK_α^{THF} Determination of WH₆(PMe₂Ph)₃ Relative to ReH₇(PCy₃)₂. An NMR tube charged with WH₆(PMe₂Ph)₃ (10 mg, 0.016 mmol), [K(2,2,2-crypt)][ReH₆(PCy₃)₂] (20 mg, 0.017 mmol), and THF (0.65 mL) under Ar was periodically shaken over the course of 3 h. The NMR spectra were recorded. The solution immediately turned from colorless to red. The spectrum was checked by use of NMR again after 8 h, and no further changes were detected. ³¹P-{¹H gated} NMR δ: 64.7 (s, I = 29.4, [ReH₆(PCy₃)₂]⁻), 47.2 (s, I = 11.4, ReH₇(PCy₃)₂) - 0.9 (s, I = 7.9; d ¹J(¹⁸³W, ³¹P) = 165.1 Hz, [WH₅(PMe₂Ph)₃]⁻), -4.1 (s, I = 48.9; d, ¹J(¹⁸³W, ³¹P) = 75.0 Hz, WH₆(PMe₂Ph)₃).

[K(2,2,2-crypt)][ReH₄(PMePh₂)₃]. THF (5 mL) was added to ReH₅(PMePh₂)₃ (0.245 g, 0.309 mmol), 2,2,2-crypt (0.116 g, 0.308 mmol), and KH (0.040 g, 1.0 mmol). The solution turned deep red after 45 min and was stirred for an additional 4 h at room temperature. Excess KH salts were filtered from solution, and the solvent was removed from the filtrate by vacuum. The resulting orange residue was washed with hexanes (6 mL) and dried in vacuo to yield [K(2,2,2-crypt)][ReH₄(PMePh₂)₃]. Yield: 0.260 g (69.7%). Anal. Calcd: C, 56.74; H, 6.60; N, 2.32. Found: C, 56.10; H, 6.41; N, 2.36. ¹H NMR (C₆D₆) δ: 7.62–6.82 (m, 30 H, Ar–H), 3.48 (s, 12 H, CH₂), 3.44 (t, 12 H, CH₂), 2.44 (t, 12 H, CH₂), 1.68 (s, 9 H, PMe), -7.91 (qrt, ²J(³¹P, ¹H) = 17.4 Hz, 4H, ReH). ³¹P{¹H} NMR (C₆D₆) δ: 11.41 (s). IR (Nujol): ν_{ReH} 1949 (s), 1930 (s) cm⁻¹.

[K(1, 10-diaza-18-crown-6)][ReH₄(PMePh₂)₃]. THF (5 mL) was added to ReH₅(PMePh₂)₃ (155 mg, 0.196 mmol), 1,10-diaza-18-crown-6 (51 mg, 0.194 mmol), and KH (25 mg, 0.62 mmol). The solution was heated to 68 °C for 24 h, and the solution turned from colorless to red-orange. Excess KH was filtered from the solution, and the solvent was removed by vacuum from the filtrate. The red-orange residue was washed with diethyl ether (20 mL) and dried in vacuo to yield [K(1,10-diaza-18-crown-6)][ReH₄(PMePh₂)₃] as an orange powder. Yield: 50 mg (23%). ¹H NMR (THF-*d*₆) δ: 7.85–6.95 (m, 30 H, Ar–H), 3.65 (t, 8 H, CH₂), 3.60 (t, 8 H, CH₂), 2.40 (s, 8 H, CH₂), 1.85 (s, 9 H, PMe), 0.85 (s, 2H, NH), -7.77 (qrt, ²J(³¹P, ¹H) = 17.8 Hz, 4 H, ReH). IR (neat): ν_{Re–H} 1988 (s), 1924 (s), 1884(s); ν_{NH} 3291 (m) cm⁻¹.

Attempted Reaction of ReH₅(PMePh₂)₃ with [K(2,2,2-crypt)][NPh₂]. An NMR tube charged with ReH₅(PMePh₂)₃ (5 mg, 0.006 mmol), [K(2,2,2-crypt)][NPh₂] (6 mg, 0.01 mmol), and THF (0.65 mL) under N₂ was flame-sealed and heated to 45 °C for 72 h. The colorless solution analyzed by ³¹P NMR showed only ReH₅(PMePh₂)₃.

Attempted Reaction of [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] and ReH₇(PCy₃)₂. An NMR tube charged with ReH₇(PCy₃)₂ (12 mg, 0.016 mmol), [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] (23 mg, 0.019 mmol), and THF (0.65 mL) under N₂ was sealed and periodically shaken for 48 h at room temperature. The red solution analyzed by ³¹P NMR showed ReH₇(PCy₃)₂, [K(2,2,2-crypt)][ReH₄(PMePh₂)₃], and a trace amount of ReH₅(PMePh₂)₃ presumably due to trace amounts of H₂O present in the THF.

P₄-Bu. THF (6 mL) was added to [HP₄-Bu][BF₄] (1.30 g, 1.80 mmol), KH (0.35 g, 8.75 mmol), and 2,2,2-crypt (10 mg, 0.027 mmol). The suspension was heated to 60 °C for 6 h and then stirred at room temperature for 48 h. The solvent was removed by vacuum from the resulting white powder, and the neutral P₄ base was extracted with hexanes (3 × 10 mL). The solvent was removed by vacuum from the combined hexane extracts to yield P₄-Bu base

as a white powder. Yield: 1.12 g (97.8%). ¹H NMR (C₆D₆) δ: 2.72 (d, ³J(³¹P, ¹H) = 9.9 Hz, 54 H), 1.85 (d, ⁴J(³¹P, ¹H) = 0.9 Hz, 9 H). ³¹P {¹H} NMR (THF) δ: 3.85 (d, ²J(³¹P, ³¹P) = 18.1 Hz, 3 P), -26.19 (qrt, ²J(³¹P–³¹P) = 18.1 Hz, 1 P).

[HP₄-Bu][BPh₄]. THF (4 mL) was added to the P₄ base (175 mg, 0.276 mmol) and [HNEt₃][BPh₄] (114 mg, 0.270 mmol), and the solution was stirred for 12 h at ambient temperature. The solvent was removed by vacuum, and the resulting white residue was filtered and washed with diethyl ether (5 mL) to yield [HP₄-Bu][BPh₄] as a white powder. Yield: 220 mg (85%). Anal. Calcd: C, 57.92; H, 8.88; N, 19.09. Found: C, 57.87; H, 9.14; N, 18.60. ¹H NMR (CD₂Cl₂) δ: 7.5–6.9 (m, BPh₄, 20 H), 2.69 (m, NMe₂, 54 H), 2.13 (br d, ²J(³¹P, ¹H) 6 Hz, NH, 1H), 1.34 (s, ^tBu, 9H). ³¹P-{¹H} NMR (CD₂Cl₂) δ: 13.45 (d, ²J(³¹P, ³¹P) = 49.8 Hz, 3P), -22.73 (qrt, ²J(³¹P, ³¹P) = 49.8 Hz, 1 P).

A1. pK_α^{THF} Determination of [HP₄-Bu]⁺. Method 1. An NMR tube charged with P₄-Bu (9 mg, 0.014 mmol), ReH₇(PCy₃)₂ (11 mg, 0.015 mmol), and THF (0.65 mL) under Ar was periodically shaken over the course of 3 h, and the ³¹P NMR spectrum was recorded. Another spectrum was collected after 8 h, and no further changes were detected. ³¹P{¹H gated} NMR (THF) δ: 63.5 (s, I = 14.7, [ReH₆(PCy₃)₂]⁻), 45.7 (s, I = 3.8, ReH₇(PCy₃)₂), 10.7 (d, I = 52.7, ²J(³¹P, ³¹P) = 49.8 Hz, [HP₄-Bu]⁺), -25.7 (qrt, I = 20.43, ²J(³¹P, ³¹P) = 49.8 Hz, [HP₄-Bu]⁺), 3.0 (d, I = 5.22, ²J(³¹P, ³¹P) = 18.1 Hz, P₄).

A2. Method 2. An NMR tube charged with WH₆(PMe₂Ph)₃ (16 mg, 0.026 mmol), P₄-Bu (16 mg, 0.025 mmol), and THF (0.65 mL) under Ar was periodically shaken over the course of 3 h. The ³¹P NMR spectrum was recorded. Another spectrum was recorded after 8 h, and no further changes were detected. The solution was observed to immediately change from colorless to red. ³¹P{¹H gated} NMR δ: 8.2 (d, I = 29.89, ²J(³¹P, ³¹P) = 49.8 Hz, [HP₄-Bu]⁺), -28.2 (quartet, ²J(³¹P, ³¹P) = 49.8 Hz, [HP₄-Bu]⁺), 0.33 (d, I = 11.8, ²J(³¹P, ³¹P) = 18.1 Hz, P₄-Bu), -4.8 (s, I = 26.95; d ¹J(¹⁸³W, ³¹P) = 165.1 Hz, [WH₅(PMe₂Ph)₃]⁻), -8.1 (s, I = 20.72; d, ¹J(¹⁸³W, ³¹P) = 75.0 Hz, WH₆(PMe₂Ph)₃).

A3. Method 3. An NMR tube charged with [K(18-crown-6)][WH₅(PMe₂Ph)₃] (23 mg, 0.024 mmol), [HP₄-Bu][BPh₄] (23 mg, 0.024 mmol), and THF (0.65 mL) under Ar was periodically shaken over the course of 3 h, and the NMR spectra were recorded. The solution was checked again after 5 h, and no further changes were detected. ³¹P{¹H gated} NMR : 8.8 (d, I = 39.0, ²J(³¹P, ³¹P) = 49.8 Hz, [HP₄-Bu]⁺), -27.53 (qrt, ²J(³¹P, ³¹P) = 49.8 Hz, [HP₄-Bu]⁺), 1.2 (d, I = 1.52, ²J(³¹P, ³¹P) = 18.1 Hz, P₄-Bu), -4.6 (s, I = 42.9; d ¹J(¹⁸³W, ³¹P) = 165.1 Hz, [WH₅(PMe₂Ph)₃]⁻), -7.3 (s, I = 3.7; d, ¹J(¹⁸³W, ³¹P) = 75.0 Hz, WH₆(PMe₂Ph)₃).

Reaction of P₄-Bu and Triphenylmethane. An NMR tube charged with P₄-Bu (30 mg, 0.047 mmol), triphenylmethane (10 mg, 0.041 mmol), and THF (0.65 mL) under Ar was sealed and periodically shaken, and the solution remained colorless for several days. ³¹P NMR δ: 12.28 (br, I = 39.6), 4.82 (br, I = 39.4), -25.0 (br, I = 21.06).

Preparation of [HP₂-Bu][BPh₄]. A solution of P₂-Bu in THF (0.30 mL of 2.0 M, 0.60 mmol) was added to [HNEt₃][BPh₄] (250 mg, 0.593 mmol) in THF (4 mL). The solution was stirred at ambient temperature for 12 h, and the solvent was removed by vacuum. The resulting white powder was washed with diethyl ether/hexanes (3 mL:3 mL) and filtered. Yield: 346 mg (84%). Anal. Calcd: 66.37; H, 8.79; N, 14.26. Found: C, 66.82; H, 8.95; N, 14.13. ¹H NMR (CD₂Cl₂) δ: 7.40–6.80 (BPh₄, 20 H), 2.69 (d, ³J(³¹P, ¹H) = 11 Hz, 18 H, NMe₂), 2.67 (d, ³J(³¹P, ¹H) = 11 Hz, NMe₂, 12 H), 2.31 (br d, ²J(³¹P, ¹H) = 51 Hz, NH, 1 H), 1.33 (s,

Table 1. Crystal Data and Structure Refinement for [K(2,2,2-crypt)][ReH₄(PMePh₂)₃]

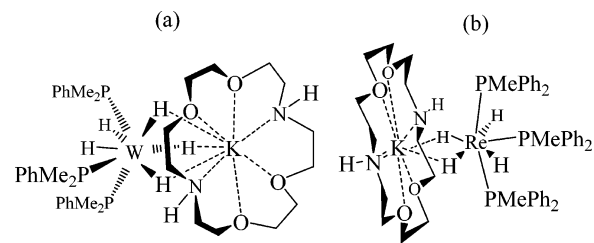
temp, K	150(1)
wavelength, Å	0.71073
cryst syst	monoclinic
space group	<i>P</i> 2(1)/ <i>n</i>
unit cell dimens	
<i>a</i> , Å	26.6572(3)
<i>b</i> , Å	13.7512(2)
<i>c</i> , Å	31.9934(4)
α , deg	90
β , deg	102.6630(10)
γ , deg	90
<i>V</i> , Å ³	11442.5(3)
<i>Z</i>	8
density (calcd), Mg/m ³	1.401
abs coeff, mm ⁻¹	2.329
<i>F</i> (000)	4976
cryst size, mm	0.34 × 0.26 × 0.16
θ range for data collection, deg	2.57 to 27.47
index ranges	0 ≤ <i>h</i> ≤ 34, 0 ≤ <i>k</i> ≤ 17, −41 ≤ <i>l</i> ≤ 40
reflens collected	74 078
indep reflens	26 070 [<i>R</i> (int) = 0.080]
completeness to $\theta = 27.47^\circ$, %	99.5
abs correction	multiscan
max and min transm	0.7069 and 0.5047
refinement method	full-matrix least-squares on <i>F</i> ²
data/restraints/param	26 070 / 0 / 1291
GOF on <i>F</i> ²	1.030
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0523, <i>wR</i> 2 = 0.0871
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0951, <i>wR</i> 2 = 0.0979
largest diff peak and hole, e Å ⁻³	1.176 and −1.061

^tBu, 9H). ³¹P {¹H} NMR (THF) δ : 17.35 (d, ²*J*(³¹P, ³¹P) = 67.8 Hz, 1 P), 9.69 (d, ²*J*(³¹P, ³¹P) = 67.8 Hz, 1 P).

³¹P NMR Spectra of [HP₂-^tBu][BPh₄]/P₂-^tBu mixtures. NMR tubes were charged with the amounts of P₂-^tBu, [HP₂-^tBu][BPh₄], and THF (0.65 mL) listed in the Supporting Information. Unlike mixtures of P₄-^tBu and [HP₄-^tBu]⁺, where distinct chemical shifts for both the acid and base forms are observed in solution, mixtures of P₂-^tBu and [HP₂-^tBu]⁺ in solution are in fast exchange on the NMR time scale and two averaged chemical shifts are observed. Linear calibration lines were determined between each of the phosphorus chemical shifts and the mole fraction of P₂-^tBu/[HP₂-^tBu]⁺ and between the ²*J*(³¹P, ³¹P) coupling and the mole fraction of P₂-^tBu/[HP₂-^tBu]⁺. The ²*J*(³¹P, ³¹P) coupling gave the best correlation, having a line of best fit with *R*² = 0.999, likely due to the fact that the coupling is independent of small referencing errors.

B1. p*K*_a^{THF} Determination of [HP₂-^tBu]⁺. Method 1. An NMR tube was charged with [HP₂-^tBu][BPh₄] (15 mg, 0.022 mmol), [K(2,2,2-crypt)][OP(OEt)₂NPh] (15 mg, 0.023 mmol), and THF (0.65 mL). The tube was sealed under Ar and periodically shaken over the course of 5 h, and the NMR spectrum was recorded. It was checked again after 8 h, and no further changes were noted. ³¹P{¹H gated} NMR δ : 15.80 (d, ²*J*(³¹P, ³¹P) = 56.4 Hz, *I* = 21.0, [HP₂-^tBu]⁺/P₂-^tBu), 6.12 (d, ²*J*(³¹P, ³¹P) = 56.4 Hz, *I* = 18.5, [HP₂-^tBu]⁺/P₂-^tBu), 4.07 (s, *I* = 22.8, OP(OEt)₂NPh/[OP(OEt)₂NPh][−]).

B2. Method 2. An NMR tube was charged with [HP₂-^tBu][BPh₄] (16 mg, 0.023 mmol), [K(18-crown-6)][{ReH₂(PMePh₂)₂(μ -H)₃}] (35 mg, 0.024 mmol), and THF (0.65 mL). The tube was sealed under Ar and periodically shaken, and after 8 h an NMR spectrum was recorded. The NMR spectrum was checked again after 20 h, and no further changes were detected. ³¹P NMR{¹H gated} δ : 12.36 (s, *I* = 17.2, {ReH₂(PMePh₂)₂(μ -H)₄}, 18.08 (s, *I* = 45.0, [{ReH₂-

**Figure 1.** Proposed ion pairing of (a) [K(1,10-diaza-18-crown-6)]-[WH₅(PMe₂Ph)₃] and (b) [K(1,10-diaza-18-crown-6)][ReH₄(PMePh₂)₃].

(PMePh₂)₂}(μ -H)₃][−], 16.36 (d, ²*J*(³¹P, ³¹P) = 64.1 Hz, *I* = 19.9), 8.40 (d, ²*J*(³¹P, ³¹P) = 64.1 Hz, *I* = 18.0).

X-ray Structural Analysis of [K(2,2,2-crypt)][ReH₄(PMePh₂)₃]. Crystals suitable for X-ray crystallography were grown by slow diffusion of hexanes into a THF solution of the salt. The crystal data are listed in Table 1. The hydride ligands were located and refined isotropically.

Results and Discussion

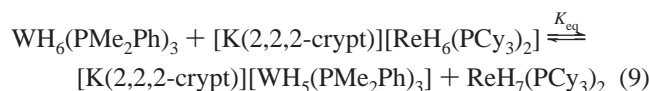
Synthesis of [K(Q)][WH₅(PMe₂Ph)₃] (Q = 18-crown-6 and 1,10-diaza-18-crown-6) and p*K*_a^{THF} Determination of WH₆(PMe₂Ph)₃. WH₆(PMe₂Ph)₃ was prepared by the reduction of the known WCl₄(PMe₂Ph)₃ complex using NaH₂Al(OCH₂CH₂OMe)₂ as described by Crabtree and Hlatky.⁵¹ Caulton and co-workers previously observed the pentahydride K[WH₅(PMe₂Ph)₃] in solution by NMR when treating WH₆(PMe₂Ph)₃ with KH in THF.⁵⁴ For our study, [K(Q)][WH₅(PMe₂Ph)₃] (Q = 18-crown-6 and 1,10-diaza-18-crown-6) were both prepared in high yield by treating WH₆(PMe₂Ph)₃ with KH in the presence of the respective crown-Q. Both the 18-crown-6 and 1,10-diaza-18-crown-6 salts were isolated as extremely air sensitive, microcrystalline red-purple solids, and both are soluble in THF and benzene. The synthetic routes to the salts [K(18-crown-6)][WH₅(PMe₂Ph)₃], [Na(15-crown-5)][WH₅(PMe₂Ph)₃], and [WH₅(PMe₂Ph)₃][−]Li⁺₄ are known, and their structures have been previously discussed.^{55–57} The broad multiplet detected in the hydride region of the room temperature ¹H NMR spectra for [K(Q)][WH₅(PMe₂Ph)₃] (Q = 1,10-diaza-18-crown-6 and 18-crown-6) is consistent with the ¹H NMR spectra of related [WH₅(PMe₂Ph)₃][−] and [WH₅(PMe₂Ph)₃][−] salts.^{54,55} The infrared NH stretching frequency of the [K(1,10-diaza-18-crown-6)]-[WH₅(PMe₂Ph)₃] at 3283 cm^{−1} is similar to that of [K(1,10-diaza-18-crown-6)][BPh₄] at 3287 cm^{−1}.⁴⁶ This suggests that there is no significant WH⋯HN hydridic–protonic interaction in the [K(1,10-diaza-18-crown-6)][WH₅(PMe₂Ph)₃] salt. The ¹H NMR chemical shift of the NH moiety at δ = 0.64 is low and would also suggest the absence of an WH⋯HN interaction in benzene-*d*₆ solution. The X-ray structure of the similar [K(18-crown-6)][WH₅(PMe₂Ph)₃] complex shows that the metal cation interacts with the hydrides and forms ion pairs with relatively short K–W distances of 3.660(1) Å.⁵⁵ This may suggest that the K⁺ is forming an ion pair with the tungsten hydride anion as shown in Figure 1 and cannot form significant WH⋯HN hydridic–protonic hydrogen bonds.

Attempts to obtain X-ray quality crystals of [K(1,10-diaza-18-crown-6)][WH₅(PMe₂Ph)₃] have been unsuccessful.

Table 2. Ion Pair Radii Used to Calculate K_d

formula	ion-pair radius, Å
[WH ₅ (PMe ₂ Ph) ₃] [−]	2.0
[ReH ₆ (PCy ₃) ₂] [−]	3.0
[OP(OEt) ₂ NPh] [−]	3.0
[{ReH ₂ (PMePh ₂) ₂] ₂ (μ-H) ₃] [−]	4.3
[BPh ₄] [−]	4.4
[HP ₄ -t-Bu] ⁺	4.7
[HP ₂ -t-Bu] ⁺	3.3
[ReH ₄ (PMe ₂ Ph) ₄] ⁺	4.2
[K(18-crown-6)] ⁺	2.0
[K(2,2,2-crypt)] ⁺	5.0

The equilibrium constant of eq 9, as calculated from ³¹P-{¹H, inverse gated decoupled} NMR data, was used in eq 4 to calculate the p*K*_α^{THF} value of 42 for WH₆(PMe₂Ph)₃. The ion pair radii used to estimate *K*_d from the Fuoss equation were based on the K⋯W distance determined for the related [K(18-crown-6)][WH₅(PMe₃)₃] complex (Table 2). The *K*_{eq} and *K*_d values used to calculate p*K*_α^{THF} are listed in Table 3.



The p*K*_α^{THF} of 42 for WH₆(PMe₂Ph)₃ makes this one of the least acidic phosphine-containing transition metal hydride complexes measured to date.

Preparation of ReH₅(PMePh₂)₃ and [K(Q)][ReH₄(PMePh₂)₃] (Q = 2,2,2-crypt or 1,10-diaza-18-crown-6) Complexes. The precursor ReCl₃(PMePh₂)₃ has been prepared by Cotton and Luck by treatment of ReCl₅ with PMePh₂.⁵⁸ In this study, ReCl₃(PMePh₂)₃ was prepared in quantitative yield by substitution and reduction of ReOCl₃-(PPh₃)₂ with PMePh₂, in a similar method to the one described by Chatt et al.⁵² ReH₅(PMePh₂)₃ was prepared by hydride addition to ReCl₃(PMePh₂)₃ using LiAlH₄ followed by ethanol addition, similar to the method used by Douglas and Shaw to prepare ReH₅(PMe₂Ph)₃.⁵³

The first report of the deprotonation of a ReH₅(PR₃)₃ (PR₃ = tertiary phosphine) by Caulton and co-workers in 1989⁵⁴ described the treatment of ReH₅(PMePh₂)₃ with KH in THF to produce the salt K[ReH₄(PMePh₂)₃] that was observed by ¹H NMR. It was also noted that deprotonation of ReH₅(PMe₂-Ph)₃ was particularly slow compared with other similar metal hydrides and the reaction required reflux for 24 h to go to completion.⁵⁴ We found that the addition of 2,2,2-crypt significantly increased the rate of deprotonation of ReH₅(PMePh₂)₃ in THF so that complete conversion occurred after

just a few hours. The analogous deprotonation reaction with KH in the presence of 1,10-diaza-18-crown-6 was found to require 24 h of reflux to go to completion. This demonstrates the catalytic enhancement of the rate of deprotonation by the addition of 2,2,2-crypt. The air sensitive, red-orange [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] salt was isolated in 70% yield and is soluble in THF but insoluble in toluene, diethyl ether, and hexanes.

The structure for [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] as determined by X-ray crystallography is shown in Figure 2. [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] crystallized with two very similar molecules in the unit cell. Selected bond lengths and angles are listed in Table 4. The geometry around rhenium is distorted pentagonal bipyramidal with a pair of axial phosphorus atoms P(2A) and P(3A). The angle of P(2A)–Re(A)–P(3A) is 163.58(4)°, bent toward the smaller hydride ligands. The ReH bond distances range from 1.52(4) to 1.70(4) Å and are typical of such bonds. The Re–P bond distances, ranging from 2.301(1) to 2.355(1) Å, are typical of Re–P bonds. The ¹H NMR spectrum of [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] shows a quartet in the hydride region at δ = −7.91, ²J(³¹P, ¹H) = 17.4 Hz, due to rapid exchange between the hydride ligands. The ³¹P{¹H} NMR spectrum shows a singlet at δ = 11.41, consistent with three equivalent phosphines.

When hydridic and protonic groups form a nonclassical hydrogen bond, the ¹H NMR chemical shift of the hydridic hydrogen is usually shifted slightly upfield and the protonic hydrogen is shifted slightly downfield. However, the hydride ¹H NMR signal of [K(1,10-diaza-18-crown-6)][ReH₄(PMePh₂)₃] is shifted slightly downfield with δ(ReH) = −7.71 from the analogous [K(2,2,2-crypt)]⁺ salt (δ(ReH) = −7.91), and the NH proton chemical shift of 0.85 ppm is comparable to that for the [K(1,10-diaza-18-crown-6)][BPh₄] salt (1.00 ppm), which contains no hydridic–protonic interactions. This suggests that there is negligible nonclassical hydrogen bonding between the NH of the 1,10-diaza-18-crown-6 and the [ReH₄(PMe₂Ph)₃][−] anion. Attempts to obtain X-ray quality crystals of the [K(1,10-diaza-18-crown-6)]⁺ salt have been unsuccessful.

The IR spectrum of [K(1,10-diaza-18-crown-6)][ReH₄(PMePh₂)₃] also suggests the absence of such an interaction; the NH stretch is observed at 3291 cm^{−1}, and this is consistent with the ν(NH) stretch data for [K(1,10-diaza-18-crown-6)][BPh₄]. Potassium–hydride–rhenium interactions are suspected to be stronger than hydridic–protonic interactions in this case as shown in Figure 1b, as previously discussed for [K(1,10-diaza-18-crown-6)][WH₅(PMe₂Ph)₃] and the Re, Os, and Ir complexes mentioned above. The bulkiness of the three PR₃ groups may prevent MH⋯HN bonding with the [K(1,10-diaza-18-crown-6)]⁺ cation.

The p*K*_α^{THF} for ReH₅(PMePh₂)₃ can be estimated as greater than the p*K*_α^{THF} of 38 for HNPh₂ and less than the p*K*_α^{THF} of 41 for ReH₇(PCy₃)₂. This is based on the evidence that [K(2,2,2-crypt)][NPh₂] was not basic enough to deprotonate ReH₅(PMePh₂)₃ and [K(2,2,2-crypt)][ReH₄(PMePh₂)₃] could not deprotonate ReH₇(PCy₃)₂.

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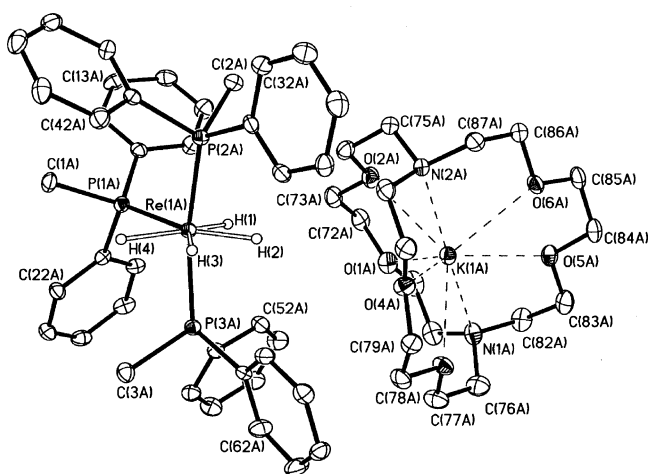
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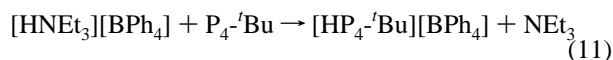
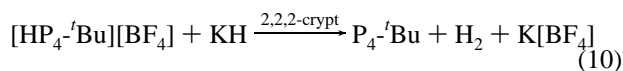
Table 3. The K_{eq} and K_d Values Used To Calculate pK_a^{THF}

acid	base	time to reach equilibrium	K_{eq}	$K_d/10^{-5}$
$WH_6(PMe_2Ph)_3$	$[K(Z)][ReH_6(PCy_3)_2]^a$	<3 h	0.26	5 $\{[K(Z)]^+, [ReH_7(PCy_3)_2]^- \}$ 2 $\{[K(Z)]^+, [WH_5(PMe_2Ph)_3]^- \}$
$ReH_7(PCy_3)_2^a$	P_4^tBu	<4h	2.0×10^3 (1/M)	4 $\{[HP_4^tBu]^+, [ReH_6(PCy_3)_2]^- \}$
$WH_6(PMe_2Ph)_3^b$	P_4^tBu	<4 h	1.3×10^2 (1/M)	1 $\{[HP_4^tBu]^+, [WH_5(PMe_2Ph)_3]^- \}$
$[HP_4^tBu][BPh_4]$	$[K(Q)][WH_5(PMe_2Ph)_3]^b$	<4 h	5×10^{-6} (M)	11 $\{[HP_4^tBu]^+, [BPh_4]^- \}$ 0.003 $\{[K(Q)]^+, [WH_5(PMe_2Ph)_3]^- \}$
$[HP_2^tBu][BPh_4]$	$[K(Z)][OP(OEt)_2NPh]^c$	<5 h	2.3×10^{-3} (M)	4 $\{[HP_2^tBu]^+, [BPh_4]^- \}$ 5 $\{[K(Z)]^+, [OP(OEt)_2NPh]^- \}$
$[HP_2^tBu][BPh_4]$	$[K(Q)]$ $\{[ReH_2(PMePh_2)_2]_2(\mu-H)_3\}^d$	<6 h	4.2×10^{-3} (M)	13 $\{[K(Z)]^+, [BPh_4]^- \}$ 4 $\{[HP_2^tBu]^+, [BPh_4]^- \}$ 1 $\{[K(Q)]^+, \{[ReH_2(PMePh_2)_2]_2(\mu-H)_3\}^- \}$ 1 $\{[K(Q)]^+, [BPh_4]^- \}$

^a $pK_a^{THF}(ReH_7(PCy_3)_2) = 41$, $Z = 2,2,2$ -crypt. ^b $pK_a^{THF}(WH_6(PMe_2Ph)_3) = 42$, $Q = 18$ -crown-6. ^c $pK_a^{THF}(OP(OEt)_2NPh) = 32$. ^d $pK_a^{THF}(\{[ReH_2(PMePh_2)_2]_2(\mu-H)_3\}) = 32$.

**Figure 2.** Structure of one of the molecules (A) of $[K(2,2,2\text{-crypt})][ReH_4(PMePh_2)_3]$ in the unit cell.

Basicities of P_4^tBu and P_2^tBu in THF. The phosphazene base chemistry has been well studied and previously discussed by Schwesinger.^{59–61} In the present study the neutral P_4^tBu base (Figure 3) was isolated as a white powder in quantitative yield by treatment of commercially available $[HP_4^tBu][BF_4]$ with KH and a catalytic amount of 2,2,2-crypt in THF (eq 10). Schwesinger previously reported that treatment of $[HP_4^tBu][BF_4]$ with NaH resulted in decomposition of the phosphazene base;⁵⁹ however, there was no evidence for any decomposition products in this reaction using KH. The neutral P_4^tBu base is extremely moisture sensitive, and this may have been the cause of the decomposition described previously.



It was necessary to prepare the acid $[HP_4^tBu]^+$ with the $[BPh_4]^-$ counterion for equilibrium studies in THF in order to minimize the effect of ion pairing. The white powder $[HP_4^tBu]$

Table 4. Select Bond Lengths (Å) and Angles (deg) for $[K(2,2,2\text{-crypt})][ReH_4(PMePh_2)_3]$

Re(1A)–H(1)	1.52(4)	Re(1B)–H(8)	1.62(4)
Re(1A)–H(2)	1.63(4)	Re(1B)–H(7)	1.68(4)
Re(1A)–H(3)	1.65(4)	Re(1B)–H(5)	1.69(4)
Re(1A)–H(4)	1.65(4)	Re(1B)–H(6)	1.70(4)
Re(1A)–P(2A)	2.301(1)	Re(1B)–P(3B)	2.310(1)
Re(1A)–P(3A)	2.326(1)	Re(1B)–P(2B)	2.311(1)
Re(1A)–P(1A)	2.353(1)	Re(1B)–P(1B)	2.355(1)
H(1)–Re(1A)–H(2)	70(2)	H(8)–Re(1B)–H(7)	68(2)
H(1)–Re(1A)–H(4)	153(2)	H(8)–Re(1B)–H(5)	153(2)
H(2)–Re(1A)–H(4)	136(2)	H(7)–Re(1B)–H(5)	138(2)
H(1)–Re(1A)–H(3)	139(2)	H(8)–Re(1B)–H(6)	135(2)
H(2)–Re(1A)–H(3)	69(2)	H(7)–Re(1B)–H(6)	67(2)
H(4)–Re(1A)–H(3)	67(2)	H(5)–Re(1B)–H(6)	72(2)
H(1)–Re(1A)–P(2A)	98(1)	H(8)–Re(1B)–P(3B)	91(1)
H(2)–Re(1A)–P(2A)	84(1)	H(7)–Re(1B)–P(3B)	83(1)
H(4)–Re(1A)–P(2A)	93(1)	H(5)–Re(1B)–P(3B)	92(1)
H(3)–Re(1A)–P(2A)	83(1)	H(6)–Re(1B)–P(3B)	86(1)
H(1)–Re(1A)–P(3A)	87(1)	H(8)–Re(1B)–P(2B)	90(1)
H(2)–Re(1A)–P(3A)	83(1)	H(7)–Re(1B)–P(2B)	79(1)
H(4)–Re(1A)–P(3A)	90(1)	H(5)–Re(1B)–P(2B)	96(1)
H(3)–Re(1A)–P(3A)	83(1)	H(6)–Re(1B)–P(2B)	79(1)
P(2A)–Re(1A)–P(3A)	163.58(4)	P(3B)–Re(1B)–P(2B)	159.60(4)
H(1)–Re(1A)–P(1A)	81(1)	H(8)–Re(1B)–P(1B)	80(1)
H(2)–Re(1A)–P(1A)	151(1)	H(7)–Re(1B)–P(1B)	148(1)
H(3)–Re(1A)–P(1A)	74(1)	H(5)–Re(1B)–P(1B)	73(1)
H(4)–Re(1A)–P(1A)	141(1)	H(6)–Re(1B)–P(1B)	145(1)
P(2A)–Re(1A)–P(1A)	95.07(4)	P(3B)–Re(1B)–P(1B)	96.28(4)
P(3A)–Re(1A)–P(1A)	101.22(4)	P(2B)–Re(1B)–P(1B)	104.03(4)

$[Bu][BPh_4]$ salt was prepared in quantitative yield by treating the P_4^tBu base with $[HNEt_3][BPh_4]$ in THF (eq 11). The 1H NMR spectrum for $[HP_4^tBu][BPh_4]$ was similar to that previously reported for $[HP_4^tBu][BF_4]$.⁶⁰ $^{31}P\{^1H\}$ NMR data for both $[HP_4^tBu]^+$ and the neutral P_4^tBu have not previously been reported. The neutral base shows two signals: a doublet for the three P_A at $\delta = 3.85$ ($^2J(^{31}P, ^{31}P) = 18.1$ Hz) and a quartet for P_B at $\delta = -26.19$ ($^2J(^{31}P, ^{31}P) = 18.1$ Hz).

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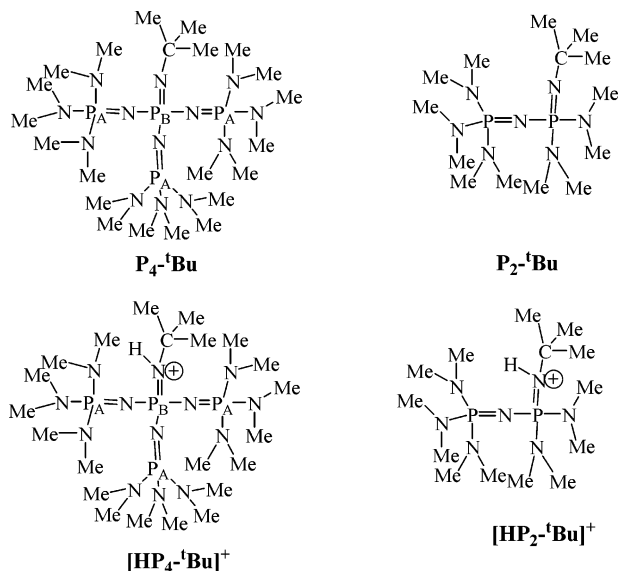
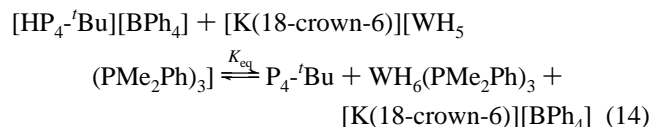
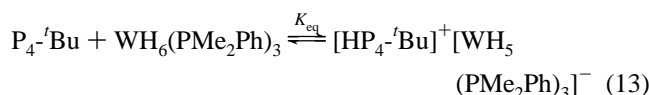
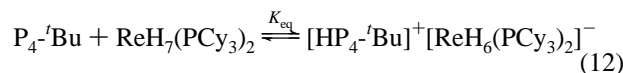


Figure 3. Structures of the phosphazene compounds P_4 -tBu, P_2 -tBu, $[HP_4$ -tBu] $^+$, and $[HP_2$ -tBu] $^+$.

The protonated cation also shows two signals: a doublet at $\delta = 13.45$ ($3P_A$, $^2J(^{31}P, ^{31}P) = 49.8$ Hz) and a quartet at $\delta = -22.73$ (P_B , $^2J(^{31}P, ^{31}P) = 49.8$ Hz).

The three following observed equilibria were used to calculate pK_a^{THF} values for $[HP_4$ -tBu] $^+$ (eq 12, eq 13, eq 14) (Table 2, Table 3).

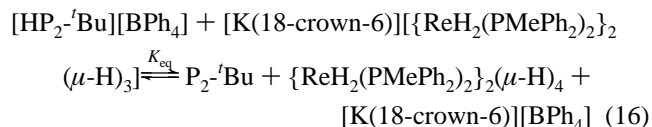
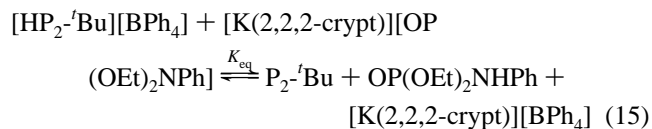


By use of the equilibrium established starting with neutral $\text{ReH}_7(\text{PCy}_3)_2$ and P_4 -tBu, $[HP_4$ -tBu] $^+$ was calculated to have a pK_a^{THF} of 39.9 by eq 6. In comparison, the equilibrium established starting with $\text{WH}_6(\text{PMe}_2\text{Ph})_3$ and P_4 -tBu (eq 13) gave a pK_a^{THF} of $[HP_4$ -tBu] $^+$ = 39.3. However, starting with $[HP_4$ -tBu] $^+$ and $[\text{K}(18\text{-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$ (eq 14), $[HP_4$ -tBu] $^+$ was determined to have a pK_a^{THF} value of 40.8 by the use of eq 8. Attempts to establish an equilibrium by deprotonating $[HP_4$ -tBu] $^+$ with $[\text{K}(2,2,2\text{-crypt})][\text{ReH}_6(\text{PCy}_3)_2]$ were unsuccessful as the neutral P_4 -tBu base was not detected and only a trace amount of $\text{ReH}_7(\text{PCy}_3)_2$ was observed, likely due to residual water in the solvent reacting with $[\text{ReH}_6(\text{PCy}_3)_2]^-$. The differences between the three pK_a^{THF} could be due to experimental error or due to errors in the ion pairing correction, but we can assign a pK_a^{THF} of $[HP_4$ -tBu] $^+$ = 40 ± 4 accounting for the cumulative error in estimating K_d values and making links to reference cationic acids.

Schwesinger reported that the P_4 -tBu was in equilibrium with triphenylmethane,⁵⁹ however, few experimental details were provided. In this study an attempt to establish an equilibrium between P_4 -tBu and HCPH_3 in THF indicates that the reaction of P_4 -tBu and HCPH_3 in THF results in a colorless solution and detection of three broad peaks in the ^{31}P NMR, assigned to equal amounts of $[HP_4$ -tBu] $^+$ and the neutral P_4 -tBu compound. However, the colorless solution indicates the absence of red trityl anion $[\text{CPh}_3]^-$, which has a λ_{max} of 502 nm.⁶² Because the pK_a^{THF} of (HCPH_3) is estimated to be equal to or greater than 45,⁹ an equilibrium between P_4 -tBu and HCPH_3 in THF seems unlikely.

$[HP_2$ -tBu] $^+$ $[\text{BPh}_4]^-$ was obtained as a white powder in 84% yield by treatment of the neutral P_2 -tBu with $[\text{HNEt}_3][\text{BPh}_4]$ (eq 11). The ^1H NMR data were similar to those previously reported for analogous ClO_4^- salts.⁶¹ The ^{31}P NMR spectrum for the neutral P_2 -tBu shows two doublets of equal intensity at $\delta = 12.95$ and $\delta = -8.87$ with $^2J(^{31}\text{P}, ^{31}\text{P}) = 35.1$ Hz. Similarly, the $[HP_2$ -tBu] $^+$ $[\text{BPh}_4]^-$ ^{31}P NMR spectrum shows two doublets at $\delta = 17.35$ and $\delta = 9.69$ with $^2J(^{31}\text{P}, ^{31}\text{P}) = 67.8$ Hz.

The pK_a^{THF} for $[HP_2$ -tBu] $^+$ was determined from the following equilibria as detected by ^{31}P NMR (eq 15 and eq 16).



From the K_{eq} of eq 15 and the data in Table 2 and Table 3, $[HP_2$ -tBu] $^+$ was calculated to have a pK_a^{THF} of 30 using eq 8. The similar deprotonation reaction with $[\text{K}(18\text{-crown-6})][\{\text{ReH}_2(\text{PMePh}_2)_2\}_2(\mu\text{-H})_3]$ (eq 16) confirmed the pK_a^{THF} to be 30.⁶³ However, in the reverse of eq 15, the neutral P_2 -tBu did not react with $\text{OP}(\text{OEt})_2\text{NPh}$ in THF as monitored by ^{31}P NMR. It remains unclear if this is due to a kinetic effect or an effect of ion pairing. However, $[\text{K}(18\text{-crown-6})][\text{ReH}_6(\text{PPh}_3)_2]$ ($pK_a^{\text{THF}}(\text{ReH}_7(\text{PPh}_3)_2) = 30$) was found to be too weak a base to deprotonate $[HP_2$ -tBu] $^+$ and give an equilibrium detectable by NMR.

Acidity and Periodic Trends. The pK_a^{THF} values of various neutral and cationic binary ligand complexes with hydrides and phosphines are organized in Table 5 according

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(63) The pK_a^{THF} of $[HP_2$ -tBu] $^+$ is expected to be 25 ± 1 on the basis of the value for $[\text{HP}_2\text{-Et}][\text{O}_3\text{SMe}]$,^{9,21,59} whereas that of $[HP_4$ -tBu] $^+$ is predicted to be about 36.^{21,59} The poor agreement between our determined values and the expected values could be caused by the use of different counteranions (BPh_4^- in our work vs SO_3Me^- in the literature), errors in the calculation of the ion pair dissociation constants by use of the Fuoss equation, and overestimates of the pK_a^{THF} values of our neutral acids with pK_a^{THF} greater than 28 caused by cumulative errors in making links to reference cationic acids. The cumulative error is estimated to be about ± 4 (see ref 9).

Table 5. Selected pK_a^{THF} Values for MH_xL_n , $[MH_xL_n]^+$, and $[PtH_2(L_2)_2]^{2+}$ Complexes

d^n/d^{n+2}	neutral hydride	pK_a^{THF}	ref	cationic hydride	pK_a^{THF}	ref
d^0/d^2	WH_6^- (PMe_2Ph) ₃	42	this work			
d^2/d^4	ReH_5^- ($PMePh_2$) ₃	~40	this work	$ReH_4(PR_3)_4^+$	16–23	9
	$RuH_6(P^iPr_3)_2^a$	38	9			
	$OsH_6(P^iPr_3)_2$	35	9			
d^4/d^6				$FeH_3(PMe_3)_4^+$	16	9,11
	$RuH_4(PPh_3)_3^a$	36	9	$RuH_3(PMe_3)_4^+^a$	17	9,11
	$IrH_3(PR_3)_2$	40–44	44	$OsH_3(PR_3)_4^+$	12–19	9,11
d^6/d^8				$CoH_2(dppe)_2^+$	16 ^b	39
				$RhH_2(depx)_2^+$	23 ^b	69
				$IrH_2(PMe_3)_4^+$	>20	70
				PtH_2^- ($EtXantphos$) ₂ ²⁺	1 ^{b,c}	64
d^8/d^{10}	$CoH(dppe)_2$	≥38 ^d	39	$NiH(depe)_2^+$	17 ^b	42
	$RhH(depx)_2$	51 ^d	69	$PdH(depe)_2^+$	16 ^b	71
				$PtH(depe)_2^+$	22 ^b	1

^a Dihydrogen complex. ^b Converted from pK_a^{MeCN} with the use of the correlation found in Fig. 2 of ref 21. ^c Note that this is for a dication. ^d Neutral acids in THF have similar or greater values than those in MeCN (see ref 9).

to the d electron count change upon deprotonation. One general observation is that the monocationic polyhydrides with four phosphorus donors, at least for $M = Re, Fe, Ru, Os, Co, Rh, Ni, Pd, Pt$, have pK_a^{THF} values in the approximate range of 12–23. The neutral polyhydrides with two or three phosphorus donors generally have pK_a^{THF} values in the range of 30–44 (Table 5). The high end of the ranges generally is associated with donating trialkylphosphines and the low end with phenyl-substituted phosphines as for the series of $ReH_7(PR_3)_2$, $[ReH_4(PR_3)_4]^+$, and $[OsH_3(PR_3)_4]^+$ type complexes.⁹ We tried to deprotonate $WH_4(PMePh_2)_4$ by refluxing with excess KH and 2,2,2-crypt under Ar for 24 h in THF but were unsuccessful in deprotonating the complex. Apparently some neutral polyhydrides with four phosphorus donors are even less acidic. Dubois and co-workers have calculated from a thermodynamic cycle that the rhodium(I) complex $RhH(depx)_2$ of Table 5 should have a pK_a^{MeCN} of 51.⁶⁹ However, there is a large contribution from the metal since $CoH(dppe)_2$ is calculated to be much more acidic with a pK_a^{MeCN} value of 38.³⁹

One general periodic trend for classical transition metal hydride complexes that has been noted is a decrease in acidity moving down the periodic table.³³ This trend has been demonstrated for the series of cationic hydrides $[MH_3L_4]^+$, where $M = Fe, Ru, \text{ and } Os$, and $L = PMe_3$ or PEt_3 (note that $[RuH(H_2)(PMe_3)_4]^+$ contains an η^2 -dihydrogen ligand and is an exception in that it is not a classical metal hydride).¹¹ In general, an η^2 -dihydrogen complex is somewhat less acidic than a comparable classical polyhydride complex. An example is the neutral η^2 -dihydrogen complex, $RuH_2(H_2)_2(P^iPr_3)_2$, which is less acidic than the classical hydride $OsH_6(P^iPr_3)_2$ (Table 5). The reduced acidity presumably is

due to the H–H bond strength of the η^2 -dihydrogen ligand. An exception to the decrease in acidity going down the group is the order $Pd \geq Ni \gg Pt$ for similar complexes of the type $[MH(\text{diphos})_2]^+$.⁶⁴

For the series of $MH_x(P^iPr_3)_2$ neutral third row transition metal complexes, the acidity increases across the periodic table from Re to Os and decreases across to Ir. The IrH_5L_2 complex is likely less acidic because the octahedral d^6 $[IrH_4L_2]^-$ conjugate base contains unfavorable *trans*-hydride ligands. Similarly, for the series of cationic $[MH_xL_4]^+$ third row metal hydride type complexes, the acidity increases from Re across to Os and decreases from Os to Ir. In this series it is likely that Os is the most acidic as the conjugate base of $[OsH_3L_4]^+$ is octahedral with the maximum ligand field stabilization energy. Likewise, the d^6 octahedral $[IrH_2L_4]^+$ complex is less acidic as it loses the favorable octahedral geometry to form the five coordinate neutral conjugate base. For MH_xL_3 neutral metal hydrides, the W and Re complexes appear to be weakly acidic with comparable pK_a^{THF} values; however, further trends remain unclear until the pK_a^{THF} for the Os and Ir complexes are determined. The complex $[K(\text{THF})(18\text{-crown-6})][OsH_3(PPh_3)_3]$ has recently been prepared by reacting $OsH_4(PPh_3)_3$ with KH/crown.⁶⁵ Other factors such as the sterics and stereochemistry of the acid/conjugate base also contribute to the acidity of transition metal complexes in ways that are still to be unraveled.⁶⁴

Conclusions

$[K(18\text{-crown-6})][WH_5(PMe_2Ph)_3]$ was prepared by treatment of the known $WH_6(PMePh_2)_3$ with KH in the presence of 18-crown-6. The analogous $[K(1,10\text{-diazia-18-crown-6})]^+$ salt was prepared similarly; however, from the IR and NMR data it appears unlikely that there is hydridic–protonic bonding in the ion pairs. $WH_6(PMe_2Ph)_3$ was determined to have a pK_a^{THF} of 42 ± 4 as determined from the equilibrium established from the reaction of $[K(2,2,2\text{-crypt})][ReH_6(PCy_3)_2]$ with $WH_6(PMe_2Ph)_2$.

$[K(2,2,2\text{-crypt})][ReH_4(PMePh_2)_3]$ was prepared and is the first example of a $[ReH_4(L)_3]^-$ anion to be characterized by X-ray crystallography. The analogous $[K(1,10\text{-diazia-18-crown-6})]^+$ salt was also prepared; IR and ¹H NMR studies suggest that there is little or no hydridic–protonic interaction between the ReH and the HN groups. It appears that anionic transition metal hydrides of the type $[MH_x(PR_3)_3]^-$ are not suited to form chain structures with the $[K(1,10\text{-diazia-18-crown-6})]^+$ NH donor. Such chains have been observed for $[MH_x(PR_3)_2(CO)]^-$ and $[MH_x(PR_3)_2]^-$ anions, but three PR_3 groups may prevent the close approach of the cation. The pK_a^{THF} of $(ReH_5(PMePh_2)_3)$ is estimated to be much less than the pK_a^{THF} of $(H_2/K(18\text{-crown-6})H)$. It is between the values of pK_a^{THF} ($NHPh_2$) = 38 and pK_a^{THF} ($ReH_7(PCy_3)_2$) = 41, assuming that the reactions are under thermodynamic and not kinetic control.

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The salts $[\text{HP}_4\text{-}^i\text{Bu}][\text{BPh}_4]$ and $[\text{HP}_2\text{-}^i\text{Bu}][\text{BPh}_4]$ have been prepared from the reaction of $[\text{HNEt}_3][\text{BPh}_4]$ with the respective neutral phosphazene base. A new route was developed to $\text{P}_4\text{-}^i\text{Bu}$ by the treatment of the commercially available $[\text{HP}_4\text{-}^i\text{Bu}][\text{BF}_4]$ salt with KH in the presence of a catalytic amount of 2,2,2-crypt. The $\text{p}K_{\alpha}^{\text{THF}}$ value of $([\text{HP}_4\text{-}^i\text{Bu}]^+) = 40 \pm 4$ was determined from the equilibrium established from the reaction of $\text{ReH}_7(\text{PCy}_3)_2$ or $\text{WH}_6(\text{PMe}_2\text{-Ph})_3$ with $\text{P}_4\text{-}^i\text{Bu}$. The equilibrium established from $[\text{K}(\text{18-crown-6})][\text{WH}_5(\text{PMe}_2\text{Ph})_3]$ and $[\text{HP}_4\text{-}^i\text{Bu}][\text{BPh}_4]$ confirmed the value. The $\text{p}K_{\alpha}^{\text{THF}}$ value of $([\text{HP}_2\text{-}^i\text{Bu}]^+) = 30 \pm 4$ was determined from the equilibrium established from the reaction of $[\text{HP}_2\text{-}^i\text{Bu}][\text{BPh}_4]$ with $[\text{K}(2,2,2\text{-crypt})][\text{PO}(\text{OEt})_2\text{NPh}]$ or $[\text{K}(\text{18-crown-6})][\{\text{ReH}_2(\text{PMePh}_2)_2\}_2(\mu\text{-H})_3]$. Certain mixtures did not produce the reactions expected on the basis of the $\text{p}K_{\alpha}^{\text{THF}}$ values. This may be due to ion-pair phenomena that have not been accounted for.

The $\text{p}K_{\alpha}^{\text{THF}}$ determinations of $[\text{HP}_4\text{-}^i\text{Bu}]^+$ and $[\text{HP}_2\text{-}^i\text{Bu}]^+$ allow for improved correlations between the $\text{p}K_{\alpha}^{\text{THF}}(\text{HB}^+)$ and $\text{p}K_{\text{a}}^{\text{DMSO}}(\text{HB}^+)$ and $\text{p}K_{\text{a}}^{\text{MeCN}}(\text{HB}^+)$ scales. The correlations allow for estimates of $\text{p}K_{\alpha}^{\text{THF}}$ values for the many cationic and neutral acids measured in DMSO and MeCN and allow for the prediction of many new acid–base reactions.

The $\text{P}_4\text{-}^i\text{Bu}$ base has been used in place of KO^iBu to dehydrochlorinate complexes such as $\text{RuCl}_2((S)\text{-binap})((S,S)\text{-dpen})$, $\text{binap} = 2,2'\text{-bis}(\text{diphenylphosphino})\text{-1,1'\text{-binaphthyl}}$, $\text{dpen} = 1,2\text{-diphenylethylenediamine}$,⁶⁶ $\text{RuHCl}((R)\text{-binap})\text{-}((R,R)\text{-dpen})$,⁶⁷ and $\text{RuHCl}(\text{PPh}_3)_2((R,R)\text{-dach})$, $\text{dach} = 1,2\text{-}$

diaminocyclohexane.⁶⁸ The high value of $\text{p}K_{\alpha}^{\text{THF}}$ ($[\text{HP}_4\text{-}^i\text{Bu}]^+/\text{P}_4\text{-}^i\text{Bu} = 40$) explains this reactivity.

Two important generalizations resulting from this work are that the cationic polyhydrides MH_xL_4^+ , at least for Re, Fe, Ru, Os, Co, Rh, Ni, Pd, and Pt, have $\text{p}K_{\alpha}^{\text{THF}}$ values in the range of 12–23 on going from phenyl-substituted to alkyl-substituted phosphine ligands L, whereas neutral polyhydrides MH_xL_n , at least for M = W, Re, Ru, Os, and Ir, with $n = 3$ or 2, have $\text{p}K_{\alpha}^{\text{THF}}$ values in the range of 30–44. The neutral complex $\text{WH}_4(\text{PMePh}_2)_4$ with $n = 4$ is less acidic.

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Supporting Information Available: Correlations between the mole fraction of $\text{P}_2\text{-}^i\text{Bu}$ base and protonated $\text{P}_2\text{-}^i\text{Bu}$ and their averaged NMR properties and the crystallographic CIF file for $[\text{K}(2,2,2\text{-crypt})][\text{ReH}_4(\text{PMePh}_2)_3]$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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