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Large Effects of Ion Pairing and Protonic–Hydridic Bonding on the Stereochemistry and Basicity of Crown-, Azacrown-, and Cryptand-222-potassium Salts of Anionic Tetrahydride Complexes of Iridium(III)

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The compounds $[K(Q)][IrH_4(PR_3)_2]$ (Q = 18-crown-6, R = Ph, ^{i}Pr, Cy; Q = aza-18-crown-6, R = ^{i}Pr; Q = 1,10-diaza-18-crown-6, R = Ph, ^{i}Pr, Cy; Q = cryptand-222, R = ^{i}Pr, Cy) were formed in the reactions of $IrH_5(PR_3)_2$ with KH and Q. In solution, the stereochemistry of the salts of $[IrH_4(PR_3)_2]^-$ is surprisingly sensitive to the countercation: either *trans* as the potassium cryptand-222 salts (R = Cy, ^{i}Pr) or exclusively *cis* (R = Cy, Ph) as the crown- and azacrown-potassium salts or a mixture of *cis* and *trans* (R = ^{i}Pr). There is IR evidence for protonic–hydridic bonding between the NH of the aza salts and the iridium hydride in solution. In single crystals of [K(18-crown-6)][*cis*-$IrH_4(PR_3)_2$] (R = Ph, ^{i}Pr) and [K(aza-18-crown-6)][*cis*-$IrH_4(P^{i}Pr_3)_2$], the potassium bonds to three hydrides on a face of the iridium octahedron according to X-ray diffraction studies. Significantly, [K(1,10-diaza-18-crown-6)][*trans*-$IrH_4(P^{i}Pr_3)_2$] crystallizes in a chain structure held together by protonic–hydridic bonds. In [K(1,10-diaza-18-crown-6)][*cis*-$IrH_4(PPh_3)_2$], the potassium bonds to two hydrides so that one NH can form an intra-ion-pair protonic–hydridic hydrogen bond while the other forms an inter-ion-pair NH$\cdots$HIr hydrogen bond to form chains through the lattice. Thus, there is a competition between the potassium and NH groups in forming bonds with the hydrides on iridium. The more basic $P^{i}R_3$ complex has the lower N–H stretch in the IR spectrum because of stronger N–H$\cdots$HIr hydrogen bonding. The *trans* complexes have very low Ir–H wavenumbers (1670–1680) due to the *trans* hydride ligands. The $[K(cryptand)]^+$ salt of [*trans*-$IrH_4(P^{i}Pr_3)_2]^-$ reacts with $WH_6(PMe_2Ph)_3$ (pK_α^{THF} 42) to give an equilibrium ($K_{eq} = 1.6$) with $IrH_5(P^{i}Pr_3)_2$ and $[WH_5(PMe_2Ph)_3]^-$ while the same reaction of $WH_6(PMe_2Ph)_3$ with the $[K(18\text{-crown-}6)]^+$ salt of [*cis*-$IrH_4(P^{i}Pr_3)_2]^-$ has a much larger equilibrium constant ($K_{eq} = 150$) to give $IrH_5(P^{i}Pr_3)_2$ and $[WH_5(PMe_2Ph)_3]^-$; therefore, the tetrahydride anion displays an unprecedented increase (about 100-fold) in basicity with a change from $[K(crypt)]^+$ to $[K(crown)]^+$ countercation and a change from *trans* to *cis* stereochemistry. The acidity of the pentahydrides decrease in THF as $IrH_5(P^{i}Pr_3)_2$/[K(crypt)][*trans*-$IrH_4(P^{i}Pr_3)_2$] ($pK_\alpha^{THF} = 42$) > $IrH_5(PCy_3)_2$/[K(crypt)][*trans*-$IrH_4(PCy_3)_2$] ($pK_\alpha^{THF} = 43$) > $IrH_5(P^{i}Pr_3)_2$/[K(crown)][*cis*-$IrH_4(P^{i}Pr_3)_2$] ($pK_\alpha^{THF} = 44$) > $IrH_5(PCy_3)_2$/[K(crown)][*cis*-$IrH_4(PCy_3)_2$]. The loss of PCy_3 from $IrH_5(PCy_3)_2$ can result in mixed ligand complexes and H/D exchange with deuterated solvents. Reductive cleavage of P–Ph bonds is observed in some preparations of the PPh_3 complexes.

Introduction

Hydride ligands are known to form hydrogen bonds with proton donors in solution and in the solid state.[1−13] These have been called dihydrogen, proton−hydride, or protonic−hydridic bonds.[9b] The strength of this bond is influenced by the donor acidity and the basicity of the hydride ligand. Most reports thus far involve neutral or cationic hydride complexes

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that serve as proton acceptors, and these are not very basic or hydridic.

Most of the known polyhydride complexes of iridium are neutral with coordination numbers varying from five to seven.[14] However, some anionic hydride complexes of iridium have been reported including $[IrH_6]^{3-}$,[15,16] $[IrH_6]^{4-}$,[17] and $[IrH_5]$.$^{4-}$[18] The present study involves the preparation and characterization of the new and basic anionic hydride complexes $[IrH_4(PR_3)_2]^-$ (R = Ph, ^{i}Pr, Cy). The series of phosphine ligands PPh_3, P^iPr_3, and PCy_3 provides increasingly more basic and more crowded metal complexes that can be tested as hydrogen bond acceptors toward the cations [K(1,10-diaza-18-crown-6)]$^+$ and [K(aza-18-crown-6)]$^+$ as some of us have also done for anionic rhenium polyhydrides.[19] These complexes, regardless of their configuration about the iridium atom, possess mutually *trans* hydride ligands that are potentially good hydrogen-bond acceptors. In some cases, the resulting interactions were found to direct the formation of networks in the solid state.

In preliminary work, [K(1,10-diaza-18-crown-6)][*trans*-$IrH_4(P^iPr_3)_2$] was found to form a chain structure held together by 1.85 Å NH···HIr bonds as shown schematically in Figure 1.[4] The X-ray diffraction data set was exceptionally good and allowed the hydride positions to be clearly located as evidenced by the electron density contour map for the plane containing the iridium atom and hydride ligands (Figure 2). The Ir(1)−H(1IR) bond lengths are 1.54(3) Å, and the Ir(1)−H(2IR) bond lengths are 1.68(3) Å. The observed H(1N)−H(2IR) separation was 2.07 Å which is indicative of protonic−hydridic bonding. This observed separation is probably greater than the true separation because the observed N(1)−H(1N) bond length of 0.77(3) Å is likely less than the true value as would be determined in a neutron diffraction study because this bond is highly polarized with the electrons being associated more with N than with H. By increasing the length of the N(1)−H(1N) bond to a more typical length of 1.00 Å, an H(1N)−H(2IR) separation of 1.85 Å is obtained. This corrected separation is within the typical range observed for protonic−hydridic bonds (between 1.7 and 2.1 Å). On the other hand, [K(18-crown-6)][*cis*-$IrH_4(P^iPr_3)_2$] exists in the crystalline state as ion pairs with potassium−hydride interactions.[4]

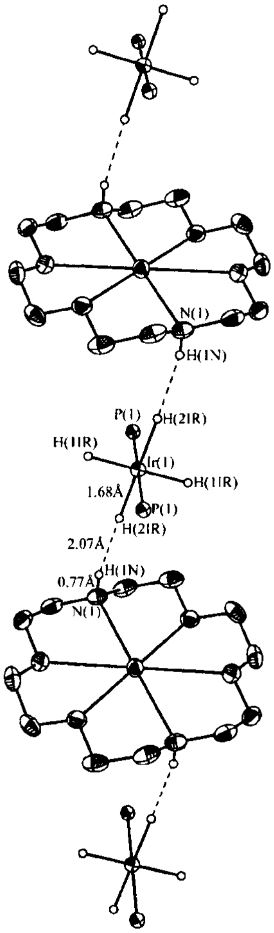

Figure 1. Chain structure of [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$]. P^iPr_3 carbon and hydrogen atoms and nonessential crown hydrogen atoms have been omitted for clarity. The distances given are observed distances.

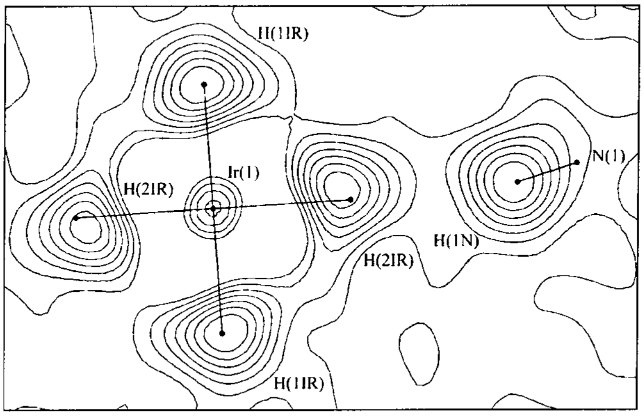

Figure 2. [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$] electron contour map. Gradient = 0.1 e/Å^3.

This study explores the dependence of structure and reactivity of these ion pairs with potassium−hydride or protonic−hydridic bonds as a function of the phosphine ligands present.

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Experimental Section

General Procedures. Unless otherwise stated, all manipulations and reactions were carried out under an atmosphere of prepurified argon or nitrogen using standard Schlenk and glovebox techniques. All solvents were thoroughly dried over the appropriate drying agents and made free of oxygen and nitrogen by distillation under argon. THF, Et_2O, toluene, and hexanes were refluxed over sodium wire with benzophenone indicator. CH_2Cl_2 was refluxed over CaH_2. ^iPrOH and EtOH were refluxed over iodine-activated magnesium turnings. Acetone was refluxed over anhydrous $CaSO_4$. THF-d_8, C_6D_6, CD_2Cl_2, and $CDCl_3$ were obtained from Cambridge Isotopes Laboratories. These deuterated solvents were degassed by freeze−pump−thaw (3 cycles) and dried over molecular sieves.

All ^1H and ^{31}P NMR spectra were acquired on a Varian Gemini 300 MHz spectrometer running at 300 MHz for ^1H and 121 MHz for ^{31}P. These instruments were used to acquire both ^1H and ^{31}P NMR spectra in deuterated and nondeuterated solvents. For the acquisition of ^1H NMR spectra of samples in nondeuterated solvents, the following criteria were essential: deactivation of deuterium locking, minimization of pulse width, and minimization of gain. For good quality spectra, a double precision Fourier transform and a high sample concentration were desirable. The acquisition of ^{31}P NMR spectra for samples in nondeuterated solvents required only the deactivation of deuterium locking. ^1H NMR spectra were indirectly referenced to TMS via solvent peaks, and ^{31}P spectra were referenced to external 85% H_3PO_4.

CAUTION must be exercised when heating samples sealed in NMR tubes as excessively high pressures may result in explosion of tubes. The solution component should be only partially immersed in an oil bath maintained at a temperature slightly above the normal boiling point of the solvent. In most cases, immersing only 1 cm of the tube is sufficient to heat the contents to reflux and adequately mix the contents by convection.

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

$IrH_5(PCy_3)_2$,[20] $IrH_3(PPh_3)_3$,[21] and $ReH_7(PCy_3)_2$[22] were prepared by literature methods. $IrCl_3$ was obtained in various hydrated forms from Johnson Matthey Chemicals (approximately $IrCl_3{\cdot}3H_2O$), Strem Chemicals, and Pressure Chemicals. 18-Crown-6, 1,10-diaza-18-crown-6, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (cryptand-222, also known as Kryptofix-222), and KH were purchased from Aldrich Chemical Co. The KH obtained was in the form of a suspension in mineral oil; the salt was isolated by filtration and washing with hexanes under a nitrogen atmosphere. PPh_3 was obtained from BDH. PCy_3 and $HPPh_2$ were obtained from Organometallics. P^iPr_3 was obtained from Strem. High purity N_2 gas, Ar gas, and H_2 gas were obtained from BOC Gases Canada.

Preparation of $IrHCl_2(P^iPr_3)_2$ (1). A literature method[23] was improved slightly. A 7 mL portion of ^iPrOH was added to a flask containing $IrCl_3{\cdot}3H_2O$ (1.108 g, 3.71 mmol) and P^iPr_3 (1.779 g, 11.12 mmol). The resulting mixture was refluxed under Ar for 24 h over which time the color changed from yellow to brown to red. The mixture was allowed to return to room temperature, and the purple solids were collected by filtration. The product was washed with 3 × 3 mL of ^iPrOH and dried under vacuum. Yield 85%. ^1H NMR ($CDCl_3$), δ: 3.10 (m, 6H, CH), 1.34 (m, 36H, CH_3), −49.31 (t, ^2J(HP) = 11.4, 1H, IrH).[24,25] $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 32.9 (s).[24,25] IR (Nujol), cm^{-1}: 2228 (IrH).

Preparation of $IrHCl_2(PPh_3)_3$ (2). A 20 mL portion of ^iPrOH was added to a flask containing $IrCl_3{\cdot}3H_2O$ (0.746 g, 2.50 mmol) and PPh_3 (3.981 g, 15.18 mmol). The resulting mixture was refluxed for 1.5−3 days. After 1.5 days, mainly or exclusively *cis,mer*-**2** can be isolated. After 3 days, a mixture of *cis,mer*-**2** and *trans,mer*-**2** is isolated. During the first 48 h, the mixture changed from green-brown to yellow. The mixture was allowed to return to room temperature and extracted with Et_2O (3 × 20 mL; each extract was carefully decanted off, filtered to recover any product, and finally discarded). The yellow product was collected by filtration, washed with 3 × 5 mL of Et_2O, and dried under vacuum. Yield 95%. *cis,mer*-**2**. ^1H NMR (CD_2Cl_2), δ: 7.6−6.8 (m, 45H, phenyl H), −19.13 (d of t, $^2J(HP_A)$ = 12.4 Hz, $^2J(HP_B)$ = 17.5 Hz, IrH). ^{31}P-$\{^1H\}$ NMR (CD_2Cl_2), δ: −2.1 (d, ^2J(PP) = 16.1 Hz, 2P, P_A), −8.3 (t, ^2J(PP) = 16.1 Hz, 1P, P_B). *trans,mer*-**2**. ^1H NMR (CD_2Cl_2), δ: −14.00 (d of t, $^2J(HP_{trans})$ = 160.1 Hz, $^2J(HP_{cis})$ = 16.4 Hz, IrH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ: −7.5 (d, ^2J(PP) = 13.4 Hz, 2P, P_{cis}), −29.7 (t, ^2J(PP) = 13.4 Hz, 1P, P_{trans}). IR (Nujol), cm^{-1}: 2200 (IrH). Anal. Calcd for $C_{54}H_{46}Cl_2IrP_3$: C, 61.71; H, 4.42%. Found: C, 61.90; H, 4.54%.

Preparation of $IrH_5(P^iPr_3)_2$ (3). THF (30 mL) was added to a mixture of $IrHCl_2(P^iPr_3)_2$ (0.370 g, 0.633 mmol) and NaOH (2.7 g, 67.5 mmol) under 1 atm H_2. The resulting mixture was stirred for 3 h over which time it gradually changed from purple to colorless. All volatiles were removed under vacuum, and the white residue was collected and washed on a frit with 5 × 5 mL of distilled, degassed H_2O. The white product was finally dried under vacuum for several hours. Yield 84%. ^1H NMR (THF-d_8), δ: 1.80 (m, 6H, CH), 1.12 (m, 36H, CH_3), −11.29 (t, ^2J(HP) = 12.3 Hz, 5H, IrH). ^1H NMR (C_6D_6), δ: 1.70 (m, 6H, CH), 1.12 (m, 36H, CH_3), −10.85 (t, ^2J(HP) = 12.2 Hz, 5H, IrH). $^{31}P\{^1H\}$ NMR (THF-d_8), δ: 46.2 (s). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 45.6 (s).[26] IR (Nujol), cm^{-1}: 1950 (IrH). Anal. Calcd for $C_{18}H_{47}IrP_3$: C, 41.75; H, 9.17%. Found: C, 41.42; H, 9.33%.

Preparation of $IrH_5(PPh_3)_2$ (4). A mixture of THF (40 mL), $IrHCl_2(PPh_3)_3$ (2.110 g, mixture of *cis,mer* and *trans,mer* isomers, 2.008 mmol), and KH (0.815 g, 20.3 mmol) was maintained at a temperature of 100 °C under 75 atm H_2 with stirring for 3 days in an autoclave. The mixture was returned to room temperature, and all solids were removed by filtration and washed with THF (3 × 3 mL). The red filtrate and washings were combined and evaporated to dryness under reduced pressure. The residue was collected and washed on a frit with 3 × 10 mL of distilled, degassed H_2O which resulted in a color change from orange to white. The solids were finally washed with THF (3 × 5 mL) and dried under vacuum. Yield 60%. IR (Nujol), cm^{-1}: 1950 (IrH).

Preparation of [K(18-crown-6)][PPh_2]. A mixture of KH (0.050 g, 1.2 mmol), 18-crown-6 (0.316 g, 1.20 mmol), $HPPh_2$ (0.224 g, 1.20 mmol), and THF (5 mL) was stirred for 5 h. The solids were removed by filtration, and 20 mL of hexanes was added to the orange filtrate to precipitate the orange product. The product was collected by filtration, washed with 3 × 3 mL of hexanes, and dried under vacuum. Yield 90%. ^{31}P NMR (THF), δ: −0.707 (s).

Observation of [K(18-crown-6)][*fac*-$IrH_3(PPh_3)_2(PPh_2)$]. An NMR tube was charged with $IrH_3(PPh_3)_3$ (0.014 g, 0.014 mmol),

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[K(18-crown-6)][PPh$_2$] (0.007 g, 0.014 mmol), and C_6D_6 (0.65 mL). The tube was flame-sealed, and the contents were gently refluxed for 12 h. ^{1}H NMR (C_6D_6), δ: −11.89 (2nd order, 2H, $H_{AA'}$ pattern), −14.09 (d of t of t, $^2J(H_{AA'}H_B) = 5.1$ Hz, $^2J(H_BP_Y) = 54.4$ Hz, $^2J(H_BP_{XX'}) = 14.7$ Hz, 1H, H_B pattern). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 10.1 (d, $^2J(P_{XX'}P_Y) = 14.9$ Hz, 2P, $P_{XX'}$ pattern), −9.5 (t, $^2J(P_{XX'}P_Y) = 14.9$ Hz, 1P, P_Y pattern, PPh_2).

Observation of K[IrH$_4$(P^{i}Pr$_3$)$_2$] (K6). A mixture of THF (0.65 mL) or C_6D_6 (0.65 mL), KH (0.010 g, 0.25 mmol), and $IrH_5(P^iPr_3)_2$ (0.015 g, 0.026 mmol) was sealed in an NMR tube under 1 atm N_2. The mixture was gently refluxed for 12 h and then examined by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy. ^{1}H NMR (THF), δ: −14.95 (t of t, $^2J(HH) = 4.9$ Hz, $^2J(HP) = 13.4$ Hz, 2H, *cis*-**6**), −15.51 (2nd order, 2H, $H_{AA'}$ of *cis*-**6**), −15.74 (t, $^2J(HP) = 17.2$ Hz, 4H, *trans*-**6**). ^{1}H NMR (C_6D_6), δ: 1.89 (m, CH, [*cis*-$IrD_4(P^iPr_3)_2]^-$), 1.28 (m, CH_3, [*cis*-$IrD_4(P^iPr_3)_2]^-$). $^{31}P\{^1H\}$ NMR (THF), δ: 60.2 (s, *trans*-**6**), 39.9 (s, *cis*-**6**). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 40.4 (s, *cis*-**6**). No *trans* isomer was observed for the reaction done in C_6D_6, and H/D exchange between the solvent and hydride ligands of the complex did not permit the determination of upfield ^{1}H NMR chemical shifts.

Preparation of [K(18-crown-6)][IrH$_4$(P^{i}Pr$_3$)$_2$] ([K(*crown*)]6). THF (5 mL), $IrH_5(P^iPr_3)_2$ (0.296 g, 0.572 mmol), KH (0.105 g, 2.62 mmol), and 18-crown-6 (0.160 g, 0.604 mmol) were combined in a flask, and the resulting mixture was stirred for 3 h. The solids were then removed by filtration, and hexanes (25 mL) were slowly added with stirring to precipitate the white product. In some cases, where the product did not precipitate immediately from solution, cooling overnight at −30 °C resulted in the formation of colorless crystals. The product was collected by filtration, washed with hexanes (2 × 3 mL), and dried under vacuum. Yield 70%. ^{1}H NMR (C_6D_6), δ: 3.25 (m, 24H, crown H), 2.17 (m, 6H, CH), 1.57 (m, 36H, CH_3), −14.23 (t of t, $^2J(H_AH_B) = 4.9$ Hz, $^2J(HP) = 13.4$ Hz, 2H, H_A of $A_2BB'XX'$ pattern of *cis*-**6**), −15.04 (t, $^2J(HP) = 16.7$ Hz, 4H, IrH, *trans*-**6**), −15.12 (BB, 2H, *cis*-**6**). ^{1}H NMR (THF), δ: −14.79 (t of t, $^2J(HH) = 4.9$ Hz, $^2J(HP) = 13.4$ Hz, 2H, H_A of *cis*-**6**), −15.45 (BB′, $^2J(H_BH_{B'}) = \pm 3.5$ Hz, $^2J(H_BP_{X'}) = {}^2J(H_{B'}P_X) = \pm 121.5$ Hz, $^2J(H_BP_X) = {}^2J(H_{B'}P_{X'}) = \pm 24.8$ Hz, the signs of the coupling constants may all be reversed, 2H, *cis*-**6**), −15.62 (t, $^2J(HP) = 17.4$ Hz, 4H, IrH, *trans*-**6**). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 60.1 (s, *trans*-**6**), 42.1 (s, *cis* -**6**). $^{31}P\{^1H\}$ NMR (THF), δ: 65.7 (s, *trans*-**6**), 42.6 (s, *cis*-**6**). IR (Nujol), cm^{-1}: 1922 (IrH), 1698 (IrH). IR (THF), cm^{-1}: 1965 (IrH), 1688 (IrH). Anal. Calcd for $C_{30}H_{70}IrKO_6P_2$: C, 43.93; H, 8.62%. Found: C, 43.81; H, 8.91%.

For the X-ray structure determination of [K(18-crown-6)][$IrH_4(P^iPr_3)_2$], a crystal was grown by layering of hexanes above a THF solution of the salt. A well-formed, colorless crystal was obtained in one week.

Preparation of [K(aza-18-crown-6)][*cis*-IrH$_4$(P^{i}Pr$_3$)$_2$] ([K(*aza*)]6). THF (3 mL) was added to a mixture of $IrH_5(P^iPr_3)_2$ (0.157 g, 0.303 mmol), KH (0.043 g, 1.07 mmol), and aza-18-crown-6 (0.092 g, 0.349 mmol), and the resulting mixture was stirred under N_2 for 4 h. The solids were removed by filtration, and the filtrate was concentrated to 1.5 mL under reduced pressure. A 20 mL portion of hexanes was slowly added to the brown filtrate with stirring to precipitate the white product. The product was collected by filtration, washed with hexanes (2 × 1 mL), and dried under vacuum. Yield 89%. ^{1}H NMR (C_6D_6), δ: 4.2−2.8 (br, crown H), 3.08 (br s, crown H), 3.02 (br s, crown H), 2.59 (br s, crown H), 2.15 (m, 6H, CH), 1.56 (m, 36H, CH_3), −14.10 (t of t, $^2J(HH) = 5.1$ Hz, $^2J(HP) = 13.3$ Hz, 2H, H_A of $A_2BB'XX'$ pattern), −15.27 (BB′, 2H). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 40.8 (s). IR (Nujol), cm^{-1}: 3252 (NH), 1926 (IrH), 1707 (IrH). IR (THF), cm^{-1}: 3232 (NH), 1975 (IrH), 1693 (IrH).

A single crystal was grown by diffusion of hexanes into a solution of the salt in THF. The colorless crystal was analyzed by single-crystal X-ray diffraction.

Preparation of [K(1,10-diaza-18-crown-6)][IrH$_4$(P^{i}Pr$_3$)$_2$] ([K(*di-aza*)]6). A mixture of KH (0.127 g, 3.17 mmol), $IrH_5(P^iPr_3)_2$ (0.152 g, 0.294 mmol), and THF (1.5 mL) was stirred for 12 h. The solids were removed by filtration, and the filtrate was slowly added with stirring to a solution of 1,10-diaza-18-crown-6 (0.092 g, 0.35 mmol) in THF (5 mL). The resulting solution was stored at −30 °C, and the colorless, crystalline product was collected after 2 days. The product was washed with hexanes (3 × 1.5 mL) and then dried under vacuum. Yield 54%. ^{1}H NMR (THF-d_8), δ: 3.58 (m, 16H, CH_2), 2.75 (m, 8H, CH_2 α to N), 2.14 (qi, $^3J(HH) = 7.3$ Hz, 2H, NH), 1.80 (m, 6H, CH), 1.18 (m, 36H, CH_3), −14.63 (t of t, $^2J(HH) = 4.9$ Hz, $^2J(HP) = 13.4$ Hz, 2H, H_A of $A_2BB'XX'$ pattern of *cis*-**6**), −15.56 (BB′, 2H, *cis*-**6**), −15.60 (t, $^2J(HP) = 17.2$ Hz, IrH, *trans*-**6**). ^{1}H NMR (C_6D_6), δ: 3.57−2.0 (extremely broad resonances, 26H, crown H), −14.09 (t of t, $^2J(HH) = 5.1$ Hz, $^2J(HP) = 13.3$ Hz, 2H, H_A of *cis*-**6**), −15.27 (BB′, 2H, *cis*-**6**). $^{31}P\{^1H\}$ NMR (THF-d_8), δ: 65.7 (s, *trans*-**6**), 42.6 (s, *cis*-**6**). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 40.7 (s, *cis*-**6**). IR (Nujol), cm^{-1}: 3148 (NH), 1680 (IrH). IR (THF), cm^{-1}: 3300 (NH), 3227 (NH), 1970 (IrH), 1694 (IrH).

A colorless crystal suitable for structural determination by single-crystal X-ray diffraction was grown by a small-scale preparation. $IrH_5(P^iPr_3)_2$ (0.023 g, 0.044 mmol), KH (0.010 g, 0.25 mmol), diaza-18-crown-6 (0.017 g, 0.065 mmol), and 0.6 mL THF were combined in an NMR tube, and the mixture was shaken vigorously for 5 min. The solid contents were allowed to settle, and over 24 h, crystals grew from the solution component of the reaction mixture.

Preparation of [K(cryptand-222)][IrH$_4$(P^{i}Pr$_3$)$_2$] ([K(*crypt*)]6). THF (5 mL), $IrH_5(P^iPr_3)_2$ (252 mg, 0.49 mmol), KH (98 mg, 2.45 mmol), and cryptand-222 (190 mg, 0.5 mmol) were combined in a flask, and the resulting mixture was stirred for 3 h. The solids were then removed by filtration, and hexanes (25 mL) were slowly added with stirring to precipitate the white product. The product was collected by filtration, washed with hexanes (2 × 3 mL), and dried under vacuum. Yield 33%. ^{1}H NMR (C_6D_6), δ: 3.32 (m, 12H, crypt H), 3.23 (m, 12H, crypt H), 2.28 (m, 6H, CH), 2.19 (m, 12H, crypt H), 1.45 (m, 36H, CH_3), −15.02 (t, $^2J(HP) = 17.5$ Hz, 4H, IrH). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 66.5 (s). IR (Nujol), cm^{-1}: 1953 w (IrH of IrH_5L_2 impurity), 1673 s (IrH).

Observation of [K(18-crown-6)][*cis*-IrH$_4$(PCy$_3$)$_2$] ([K(*crown*)]-7). A mixture of THF (3 mL), KH (0.028 g, 0.70 mmol), $IrH_5(PCy_3)_2$ (0.058 g, 0.076 mmol), and 18-crown-6 (0.035 g, 0.13 mmol) was stirred under an atmosphere of N_2 for 24 h. The reaction mixture in THF was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy (δ): 28.5 (s). The reaction mixture was filtered and the filtrate characterized by IR spectroscopy: 1960 cm^{-1} (IrH), 1680 cm^{-1} (IrH). The reaction mixture was evaporated to dryness under reduced pressure, and the gray residue was analyzed by IR spectroscopy (Nujol): 1986 cm^{-1} (IrH), 1697 cm^{-1} (IrH). The residue was also extracted with C_6D_6 for ^{1}H and $^{31}P\{^1H\}$ NMR analysis. ^{1}H NMR (C_6D_6), δ: 3.3 (s, 24H, crown H), 1.0−2.5 (m, 66H, PCy_3), −14.04 (t of t, $^2J(HH) = 4.5$, $^2J(HP) = 13.5$, 2H, H_A), −15.43 (BB′, 2H, IrH). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 28.3 (s).

Preparation of [K(cryptand-222)][IrH$_4$(PCy$_3$)$_2$] ([K(*crypt*)]7). THF (5 mL), $IrH_5(PCy_3)_2$ (300 mg, 0.40 mmol), KH (80 mg, 2.0 mmol), and cryptand-222 (151 mg, 0.41 mmol) were combined in a flask, and the resulting mixture was stirred for 3 h. The solids were then removed by filtration, and hexanes (25 mL) were slowly added with stirring to precipitate the white product. The product was collected by filtration, washed with hexanes (2 × 3 mL), and dried under vacuum. Yield 33%. ^{1}H NMR (C_6D_6), δ: 3.23 (m, 12H, crypt H), 2.82 (m, 12H, crypt H), 2.63−2.06 (m, 66H, CH), 1.83 (m, 12H, crypt H), −14.71 (t, ^2J(HP) = 17.5 Hz, 4H, IrH). ^{31}P{^{1}H} NMR (C_6D_6), δ: 51.76 (s). IR (Nujol), cm^{-1}: 1953, 1935 w (IrH of IrH_5L_2 impurity), 1680 s (IrH).

Observation of [K(1,10-diaza-18-crown-6)][*cis*-$IrH_4(PCy_3)_2$] ([K(*diaza*)]7). A mixture of THF (3 mL), KH (0.028 g, 0.70 mmol), $IrH_5(PCy_3)_2$ (0.065 g, 0.086 mmol), and diaza-18-crown-6 (0.029 g, 0.11 mmol) was stirred under an atmosphere of N_2 for 24 h. The reaction mixture in THF was analyzed by ^{31}P{^{1}H} NMR spectroscopy (δ): 28.5 (s, $P_{XX'}$ pattern). For IR characterization of the THF solution, the reaction mixture was filtered, and the gray to brown filtrate was analyzed: 3300 cm^{-1} (NH), 3228 cm^{-1} (NH), 1965 cm^{-1} (IrH), 1685 cm^{-1} (IrH). For the solid-state IR characterization, the filtrate was evaporated to dryness under reduced pressure, and the residue was ground with Nujol: 3289 cm^{-1} (NH), 3222 cm^{-1} (NH), 1957 cm^{-1} (IrH), 1668 cm^{-1} (IrH).

Observation of [K(18-crown-6)][*cis*-$IrHD_3(PCy_3)_2$]. A solution of [K(18-crown-6)][$IrH_4(PCy_3)_2$] (0.012 g, mmol) dissolved in C_6D_6 (0.65 mL) was gently refluxed in a flame-sealed NMR tube for 12 h and then examined by ^{1}H NMR spectroscopy. ^{1}H NMR (C_6D_6), δ: −13.95 (t, ^2J(HP) = 13.5 Hz, 1H, H *trans* to D), −15.40 (d of d, $^2J(HP_{trans})$ = 120 Hz, $^2J(HP_{cis})$ = 26 Hz, 1H, H *trans* to P). The sample was contaminated with approximately 20% $IrH_5(PCy_3)_2$ as evidenced by ^{1}H NMR spectroscopy. The same reaction carried out in the presence of excess KH resulted in little or no H/D exchange over the same time period.

Preparation of [K(18-crown-6)][$IrH_4(PPh_3)_2$] ([K(*crown*)]5). A mixture of $IrH_5(PPh_3)_2$ (0.119 g, 0.165 mmol), THF (1.5 mL), KH (0.027 g, 0.67 mmol), and 18-crown-6 (0.065 g, 0.25 mmol) was stirred for 12 h under an atmosphere of N_2. The resulting mixture was pale orange indicating the presence of PPh_2^-. However, its ^{31}P{^{1}H} NMR spectrum consisted of just a single resonance (26.3 ppm) corresponding to the desired product. All solids were removed by filtration, and the colorless to pale yellow product was crystallized from the filtrate by vapor diffusion of Et_2O. ^{1}H NMR (C_6D_6), δ: 7.97 (m, 12H, phenyl H), 6.98 (m, 18H, phenyl H), 3.28 (s, 24H, crown H), −11.88 (t of t, ^2J(HH) = 5.1 Hz, ^2J(HP) = 13.2 Hz, 2H, H_A of $A_2BB'XX'$ pattern), −12.30 (BB′, 2H). ^{31}P{^{1}H} NMR (C_6D_6), δ: 26.1 (s). ^{31}P{^{1}H} NMR (THF), δ: 26.3 (s). IR (Nujol), cm^{-1}: 2010 (IrH), 1716 (IrH). IR (THF), cm^{-1}: 2005 (IrH), 1713 (IrH). Anal. Calcd for $C_{48}H_{58}IrKO_6P_2$: C, 56.28; H, 5.72%. Found: C, 56.0; H, 5.71%.

For X-ray structural characterization, a colorless crystal was grown by vapor diffusion of Et_2O into a THF solution of the salt.

Preparation of [K(1,10-diaza-18-crown-6)][$IrH_4(PPh_3)_2$] ([K(*diaza*)]5). The preparation of [K(18-crown-6)][$IrH_4(PPh_3)_2$] was followed substituting diaza-18-crown-6 (0.048 g, 0.18 mmol) for 18-crown-6. The quantities of other reagents used were as follows: THF (1.5 mL), KH (0.025 g, 0.62 mmol). As was the case for the preparation of [K(18-crown-6)][$IrH_4(PPh_3)_2$], the ^{31}P{^{1}H} NMR spectrum for the orange reaction mixture consisted of a single resonance at 25.6 ppm. Yield 68%. ^{1}H NMR (C_6D_6), δ: 7.95 (m, phenyl H), 7.00 (s, phenyl H), 6.98 (s, phenyl H), 3.30 (br s, crown H), 3.15 (br s, crown H), 2.29 (br s, crown H), −11.79 (t of t, ^2J(HH) = 5.0 Hz, ^2J(HP) = 13.2 Hz, 2H, H_A of $A_2BB'XX'$ pattern), −12.41 (BB′). ^{31}P{^{1}H} NMR (C_6D_6), δ: 25.6 (s). ^{31}P{^{1}H} NMR (THF), δ: 25.6 (s). IR (Nujol), cm^{-1}: 3198 (NH), 1974 (IrH), 1712 (IrH). IR (THF), cm^{-1}: 3299 (NH), 3205 (NH), 1999 (IrH), 1714 (IrH).

A crystal suitable for structural determination by single-crystal X-ray diffraction was grown by vapor diffusion of Et_2O into a THF solution of the salt.

Reaction of ([K(*crown*)]6) with $ReH_7(PCy_3)_2$. An NMR tube was charged with $ReH_7(PCy_3)_2$[27] (0.016 g, 0.021 mmol), [K(18-crown-6)][$IrH_4(P^iPr_3)_2$] (0.016 g, 0.020 mmol), and THF (0.65 mL). The tube was flame sealed, and the solution was analyzed by NMR after 1 h. ^{1}H NMR (THF), δ: −7.09 (t, ^2J(HP) = 18.8 Hz, $ReH_7(PCy_3)_2$), −9.69 (t, ^2J(HP) = 16.4 Hz, $[ReH_6(PCy_3)_2]^-$ [19,27]), −11.34 (t, ^2J(HP) = 12.3 Hz, $IrH_5(P^iPr_3)_2$). ^{31}P{^{1}H} NMR (THF), δ: 57.9 (s, $[ReH_6(PCy_3)_2]^-$), 48.4 (s, $ReH_7(PCy_3)_2$), 46.3 (s, $IrH_5(P^iPr_3)_2$).

Reaction between ([K(*crown*)]6) and $WH_6(PMe_2Ph)_3$. An NMR tube was charged with $WH_6(PMe_2Ph)_3$ (14.7 mg, 0.024 mmol), [K(18-crown-6)][$IrH_4(P^iPr_3)_2$] (20 mg, 0.024 mmol), and THF-d_8 (0.65 mL). The tube was sealed, and the solution was analyzed by ^{1}H NMR after 1 h. ^{1}H NMR (THF-d_8), δ: −2.4 (q, ^2J(HP) = 36.0 Hz, $WH_6(PMe_2Ph)_3$, 6H, I = 67.6), −4.6 (m, $[WH_5(PMe_2Ph)_3]^-$, 5H, I = 65.9), −11.3 (t, ^2J(HP) = 12.3 Hz, $IrH_5(P^iPr_3)_2$, 5H, I = 100), −14.7 (tt, [*cis*-$IrH_4(P^iPr_3)_2]^-$, 2H, I = 0.3), −15.5 (m, [*cis*-$IrH_4(P^iPr_3)_2]^-$, 2H, I = 0.3), −15.6 (t, [*trans*-$IrH_4(P^iPr_3)_2]^-$, 4H, I = 0.3). A small amount of *mer*-$IrH_3(P^iPr_3)_2(PMe_2Ph)$ was also produced: −13.1 (d qrt, 2H), −15.6 (dtd, 1H).

Reaction between ([K(*crypt*)]6) and $WH_6(PMe_2Ph)_3$. An NMR tube was charged with $WH_6(PMe_2Ph)_3$ (13 mg, 0.02 mmol), [K(*crypt*)][*trans*-$IrH_4(P^iPr_3)_2$] (20 mg, 0.02 mmol), and THF (0.65 mL). The tube was sealed, and the solution was analyzed by quantitative ^{31}P NMR after 1 and 24 h. The reaction was complete in less than 1 h. ^{31}P NMR (THF), δ: 66.77 (s, [*trans*-$IrH_4(P^iPr_3)_2]^-$, I = 15.62), 46.0 (s, $IrH_5(P^iPr_3)_2$, I = 22.22), 0.0 (t, ^1J(WP) = 84.5 Hz, $[WH_5(PMe_2Ph)_3]^-$, I = 31.29), −3.151 (t, ^1J(WP) = 37.3, $WH_6(PMe_2Ph)_3$, I = 30.87).

Determination of the Δp*K* Value between $IrH_5(P^iPr_3)_2$ and $IrH_5(PCy_3)_2$. (a) An NMR tube was charged with $IrH_5(PCy_3)_2$ (0.016 g, 0.020 mmol), [K(18-crown-6)][$IrH_4(P^iPr_3)_2$] (0.016 g, 0.020 mmol), and THF (0.65 mL). The tube was flame-sealed and warmed (50 °C) for 4 h while the contents were occasionally shaken to dissolve suspended complex. The solution was cooled to room temperature, and the ^{31}P{^{1}H, inverse-gated decoupled} NMR spectrum was recorded (THF), δ: 65.5 (s, [*trans*-$IrH_4(P^iPr_3)_2]^-$, I = 140), 46.0 (s, $IrH_5(P^iPr_3)_2$, I = 195), 42.2 (s, [*cis*-$IrH_4(P^iPr_3)_2]^-$, I = 361), 32.5 (s, $IrH_5(PCy_3)_2$, I = 75), 28.5 (s, [*cis*-$IrH_4(PCy_3)_2]^-$, I = 243). The equilibrium constant was determined to be 0.6. (b) A solution of [K(crypt)][*trans*-$IrH_4(PCy_3)_2$] (20 mg, 0.02 mmol) and $IrH_5(P^iPr_3)_2$ (9 mg, 0.02 mmol) in THF-d_8 was prepared in a similar fashion at room temperature. The tube was sealed, and the solution was analyzed quantitatively by ^{31}P NMR after 3 and 24 h. There were negligible differences in the two spectra. ^{31}P NMR (THF-d_8) δ: 63.42 (s, [*trans*-$IrH_4(P^iPr_3)_2]^-$, I = 62.15), 48.36 (s, [*trans*-$IrH_4(PCy_3)_2]^-$, I = 4.96), 43.52 (s, $IrH_5(P^iPr_3)_2$, I =19.88), 43.52 (s, $IrH_5(PCy_3)_2$, I =13.01). The equilibrium constant was determined to be 8.2.

Observation of $IrH_5(PCy_3)(P^iPr_3)$ and K[$IrH_4(PCy_3)(P^iPr_3)$]. A mixture of $IrH_5(PCy_3)_2$ (0.015 g, 0.018 mmol), K[$IrH_4(P^iPr_3)_2$] (0.015 g, 0.027 mmol), and THF (0.65 mL) was sealed in an NMR tube under an atmosphere of N_2. The mixture was gently refluxed for 2 days and then analyzed by ^{31}P{^{1}H} NMR spectroscopy. The complexes were not isolated from solution. ^{31}P{^{1}H} NMR (THF), δ: 59.9 (s, [*trans*-**6** 46.2 (d, ^2J(PP) = 319 Hz, P^iPr_3 resonance of *trans*-$IrH_5(P^iPr_3)(PCy_3)$), 46.0 (s, **3**), 40.6 (d, ^2J(PP) = 12 Hz, P^i-

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Pr_3 resonance of [*cis*-$IrH_4(P^iPr_3)(PCy_3)]^-$), 39.8 (s, *cis*-**6**), 32.6 (s, $IrH_5(PCy_3)_2$), 32.4 (d, $^2J(PP) = 319$ Hz, PCy_3 resonance of *trans*-$IrH_5(P^iPr_3)(PCy_3)$), 27.6 (s, **7**), 25.7 (d, $^2J(PP) = 11$ Hz, PCy_3 resonance of [*cis*-$IrH_4(P^iPr_3)(PCy_3)]^-$).

Reaction of $IrH_5(P^iPr_3)_2$ with $IrH_5(PCy_3)_2$. A solution of $IrH_5(P^iPr_3)_2$ (0.009 g, 0.017 mmol) and $IrH_5(PCy_3)_2$ (0.009 g, 0.012 mmol) in 0.65 mL of THF was sealed in an NMR tube under 1 atm of N_2. The mixture was gently refluxed for 24 h and then analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. The complexes were not isolated from the reaction mixture. $^{31}P\{^1H\}$ NMR (THF), δ: 46.3 (d, $^2J(PP) = 319$ Hz, P^iPr_3 of *trans*-$IrH_5(P^iPr_3)(PCy_3)$), 46.1 (s, **3**), 32.7 (s, $IrH_5(PCy_3)_2$), 32.5 (d, $^2J(PP) = 319$ Hz, PCy_3 of *trans*-$IrH_5(P^iPr_3)(PCy_3)$).

Reaction of $IrH_5(PCy_3)_2$ with P^iPr_3. A mixture of $IrH_5(PCy_3)_2$ (0.020 g, 0.026 mmol), P^iPr_3 (0.010 g, 0.062 mmol), and THF (0.65 mL) was sealed in an NMR tube under an atmosphere of N_2. The mixture was gently refluxed for 48 h and then analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The complexes were not isolated from the reaction mixture. ^1H NMR (THF), δ: -11.22 (t, $^2J(HP) = 12$ Hz, $IrH_5(PCy_3)_2$), -11.28 (t, $^2J(HP) = 12.3$ Hz, **3**), -11.35 (t, $^2J(HP) = 12.1$ Hz, $IrH_5(P^iPr_3)(PCy_3)$). $^{31}P\{^1H\}$ NMR (THF), δ: 46.3 (d, $^2J(PP) = 319$ Hz, P^iPr_3 of *trans*-$IrH_5(P^iPr_3)(PCy_3)$), 46.2 (s, **3**), 32.7 (s, $IrH_5(PCy_3)_2$), 32.5 (d, $^2J(PP) = 319$ Hz, PCy_3 of *trans*-$IrH_5(P^iPr_3)(PCy_3)$), 20.2 (s, P^iPr_3), 10.5 (s, PCy_3).

Preparation of *trans,mer*-$IrH_3(PCy_3)_2(PPh_3)$. A mixture of $IrH_5(PCy_3)_2$ (0.302 g, 0.398 mmol), PPh_3 (0.127 g, 0.484 mmol), and THF (10 mL) was refluxed for 24 h under Ar. The resulting brown mixture was filtered through Celite, and the yellow filtrate was evaporated to dryness under reduced pressure. The residue was stirred with 5 mL of Et_2O, and the white solids were collected by filtration. The white product was washed with Et_2O (2 × 3 mL) and dried under vacuum. Yield 56%. ^1H NMR (C_6D_6), δ: 8.30 (t, phenyl H), 7.18 (m, phenyl H), 7.05 (m, phenyl H), 2.03−1.03 (m, PCy_3), -11.96 (m, $^2J(HH)$ not resolved, $^2J(HP_X) = 15.1$ Hz, $^2J(HP_Y) = 15.2$ Hz, 2H, H *trans* to H), -14.99 (d of t, $^2J(HH)$ not resolved, $^2J(HP_X) = 23$ Hz, $^2J(HP_Y) = 116.2$ Hz, H *trans* to P). $^{31}P\{^1H\}$ NMR (C_6D_6), δ: 24.1 (d, $^2J(PP) = 14.6$ Hz, $2PCy_3$, P_X *trans* to P_X), 19.7 (t, $^2J(PP) = 14.6$ Hz, $1PPh_3$, P_Y). $^{31}P\{^1H\}$ NMR (THF), δ: 24.4 (d, $^2J(PP) = 14.6$ Hz, 2P, P_X), 19.7 (t, $^2J(PP) = 14.7$ Hz, 1P, P_Y). IR (THF), cm^{-1}: 2090 (IrH), 1757 (IrH).

Variable-Temperature ^1H NMR Study of [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$]. A ^1H NMR spectrum of a solution of [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$] in THF-d_8 was obtained at several temperatures. The chemical shifts of the NH resonances for some of these spectra are as follows: 2.14 (298 K, qi), 2.22 (273 K, qi), 2.29 (248 K, qi), 2.35 (223 K, br s), 2.43 (198 K, br s). The chemical shift was found to vary linearly with temperature: $\delta/\text{ppm} = -0.0028\ T/K + 2.99$.

X-ray Structural Determinations. All single-crystal X-ray diffraction data were collected with a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° φ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package. The structures were solved and refined using the SHELXTL[\]PC V5.1 package.[28] Refinement was by full-matrix least-squares on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions, except for the hydride atoms which were refined with isotropic thermal parameters. The structure data acquisition and solution details are listed in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3, respectively. For [K(*crown*)][$IrH_4(PPh_3)_2$], only data for subunit A are given.

Table 1. Crystal Structure Data Acquisition and Solution Details

	[K(*crown*)]**5**	[K(*diaza*)]**5**·Et_2O·$THF_{0.5}$	[K(*aza*)]**6**
formula	$C_{48}H_{58}IrKO_6P_2$	$C_{54}H_{74}IrKN_2O_{5.5}P_2$	$C_{30}H_{71}IrKNO_5P_2$
fw	1024.18	1132.39	819.12
cryst syst	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	10.3032(2)	36.056(7)	9.0778(3)
b/Å	21.5110(4)	14.394(3)	11.1705(2)
c/Å	23.1192(5)	23.799(5)	20.1852(5)
α/deg	64.927(1)	90	76.836(2)
β/deg	80.982(1)	121.11(3)	81.083(2)
γ/deg	84.862(1)	90	71.597(1)
V/Å^3	4582.2(2)	10575(4)	1883.47(8)
Z	4	8	2
d_{calc}/Mg m^{-3}	1.485	1.422	1.444
μ(Mo Kα)/mm^{-1}	3.121	2.712	3.774
T/K	110(1)	150(1)	101(1)
rflns	34034	14307	34296
indep rflns	17311	3889	9328
R_{merge}	0.051	0.059	0.081
R1^a [$I > 2\sigma(I)$]	0.0356	0.0289	0.0346
wR2^a (all data)	0.0997	0.0777	0.0626
GOF	1.09	1.03	0.93

^{a} $R1=\Sigma(F_o - F_c)/\Sigma(F_o)$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Lengths

	Bond length/Å		
	[K(*crown*)]**5**	[K(*diaza*)]**5**·Et_2O·$THF_{0.5}$	[K(*aza*)]**6**
Ir(1)−P(1)	2.259(1)	2.259(1)	2.2964(9)
Ir(1)−P(2)	2.265(1)	2.2837(9)	2.2923(9)
Ir(1)−H(1IR)	1.53(4)	1.64(5)	1.66(4)
Ir(1)−H(2IR)	1.53(4)	1.66(4)	1.64(4)
Ir(1)−H(3IR)	1.55(4)	1.54(4)	1.56(4)
Ir(1)−H(4IR)	1.68(4)	1.51(3)	1.63(3)

Table 3. Selected Bond Angles

	Bond angle/deg		
	[K(*crown*)]**5**	[K(*diaza*)]**5**·Et_2O·$THF_{0.5}$	[K(*aza*)]**6**
H(1IR)−Ir(1)−H(2IR)	175(2)	171(2)	173(2)
H(1IR)−Ir(1)−H(3IR)	85(2)	87(2)	90(2)
H(2IR)−Ir(1)−H(3IR)	91(2)	87(2)	85(2)
H(1IR)−Ir(1)−H(4IR)	95(2)	86(2)	84(2)
H(2IR)−Ir(1)−H(4IR)	82(2)	87(2)	91(2)
H(3IR)−Ir(1)−H(4IR)	87(2)	78(2)	82(2)
H(1IR)−Ir(1)−P(1)	86(2)	92(2)	93(1)
H(2IR)−Ir(1)−P(1)	97(2)	94(1)	91(1)
H(3IR)−Ir(1)−P(1)	85(2)	88(2)	84(1)
H(4IR)−Ir(1)−P(1)	172(2)	165(1)	165(1)
H(1IR)−Ir(1)−P(2)	98(2)	95(2)	93(1)
H(2IR)−Ir(1)−P(2)	86(2)	90(1)	91(1)
H(3IR)−Ir(1)−P(2)	171(2)	168(2)	166(1)
H(4IR)−Ir(1)−P(2)	84(2)	91(1)	85(1)
P(1)−Ir(1)−P(2)	103.89(5)	103.91(4)	109.34(3)

Results and Discussion

Preparation and Properties of $IrHCl_2(P^iPr_3)_2$ and $IrHCl_2(PPh_3)_3$. $IrHCl_2(P^iPr_3)_2$ (**1**) was prepared in 85% yield by refluxing a mixture of $IrCl_3$ and P^iPr_3 in ^iPrOH. Compound **1** is a dark purple solid soluble in CH_2Cl_2, $CHCl_3$, and THF. Other synthetic routes to **1** reported in the literature require more steps and give yields of 64% or less. Compound **1** is reported to have a square pyramidal geometry with mutually *trans* P^iPr_3 ligands and a hydride ligand occupying the apical position.[25]

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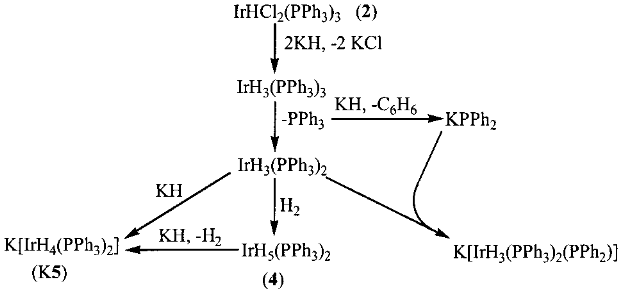
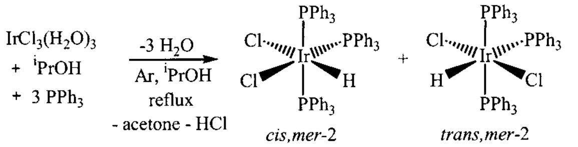
(28) Sheldrick, G. M. *SHELXTL[\]PC V5.1*; Bruker Analytical X-ray Systems: Madison, WI, 1997.

Scheme 1. Preparation of Some Triphenylphosphine Iridium Hydride Complexes



$IrHCl_2(PPh_3)_3$ (**2**) is a pale yellow, air-stable solid which is quite soluble in CH_2Cl_2 and $CHCl_3$ and less soluble in THF and toluene. This compound has been reported several times and has been obtained by various routes, but no NMR data have been reported.[29,30] These literature preparations yield a product which is in some cases a mixture of *cis*,*mer* and *trans*,*mer* isomers and in some cases a pure isomer.[31] Reported here is the preparation of **2** in 95% yield (eq 1). Depending on reflux time, the isolated product may be a mixture of isomers or a pure isomer. Shorter reflux times (1.5 days) yield a product which is enriched in or is exclusively the *cis*,*mer* isomer. Another preparation with a reflux time of 3 days afforded a product that was roughly a 1:1 mixture of the two isomers. On the basis of these observations, one may conclude that the *cis*,*mer* isomer is the kinetic product and the *trans*,*mer* isomer results by way of slow isomerization.



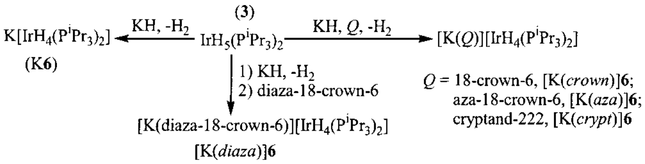
(1)

Preparation and Properties of $IrH_5(P^iPr_3)_2$ and $IrH_5(PPh_3)_2$. Pentagonal bipyramidal $IrH_5(P^iPr_3)_2$ (**3**)[26] was prepared in 84% by the method outlined in eq 2. Pentahydride **3** is a pale-yellow to colorless solid that is soluble in most solvents with the exception of some alcohols and water. Compound **3** is relatively air-stable in the solid state; however, its solutions decompose readily when exposed to air.

$$IrHCl_2(P^iPr_3)_2 + 3H_2 + 2NaOH \xrightarrow[\text{THF/H}_2]{} IrH_5(P^iPr_3)_2 + 2NaCl + 2H_2O \quad (2)$$

$IrH_5(PPh_3)_2$ (**4**) was prepared by the route outlined in Scheme 1. Treatment of **2** with excess KH under 75 atm H_2 pressure at 100 °C results in the generation of $K[IrH_4(PPh_3)_2]$ (K**5**). This transformation proceeds via $IrH_3(PPh_3)_3$[21] which has been observed as an intermediate in some small scale NMR tube preparations. In the proposed mechanism, dissociation of 1 equiv of PPh_3 from $IrH_3(PPh_3)_3$ is followed by coordination and oxidative addition of H_2. In the presence of KH, **4** thus produced is deprotonated to give $K[IrH_4(PPh_3)_2]$. The 16-electron transient species $IrH_3(PPh_3)_2$ (not observed) may also react directly with KH to yield K**5**.

Scheme 2. Preparation of the Triisopropylphosphine Complexes



The free PPh_3 generated under these reaction conditions may react with excess KH to produce $KPPh_2$. A high H_2 pressure is essential in order to minimize the side reaction of the postulated $IrH_3(PPh_3)_2$ intermediate with $KPPh_2$ which generates $K[IrH_3(PPh_3)(PPh_2)]$ (this reaction has been verified independently). The formation of $[IrH_3(PPh_3)(PPh_2)]^-$ by a reaction of KH with $IrH_3(PPh_3)_3$ has not been ruled out. The K**5** salt is not easily isolated from the dark red $KPPh_2$ byproduct because these salts have similar solubilities. Instead, the crude K**5** is protonated with H_2O, and the highly insoluble $IrH_5(PPh_3)_2$ produced is washed with copious amounts of water and THF to remove all traces of KOH and $HPPh_2$. The IR IrH stretch (Nujol, 1950 cm^{-1}) of the isolated white $IrH_5(PPh_3)_2$ agrees with previously reported literature values for this complex. The complex is too insoluble, even at 100 °C in toluene, to be characterized by solution NMR spectroscopy.

Preparation and Properties of $[IrH_4(P^iPr_3)_2]^-$ Salts. Treatment of **3** with KH in THF, benzene, or toluene results in the generation of the new salt $K[IrH_4(P^iPr_3)_2]$ (K**6**; Scheme 2). The reaction is fastest in THF and in all cases may be aided by gentle heating. K**6** produced in this way was characterized in the reaction mixture by ^1H and ^{31}P NMR spectroscopy and used in further preparations but was not isolated from solution. [K(*crown*)]**6**, [K(*aza*)]**6**, and [K(*crypt*)]**6** (*crown* = 18-crown-6, *aza* = aza-18-crown-6, *crypt* = cryptand-222) were prepared by the treatment of **3** with KH in THF in the presence of a slight excess of the appropriate crown ether or cryptand (Scheme 2). [K(*diaza*)]**6** (*diaza* = 1,10-diaza-18-crown-6), because of its poor solubility in THF, was prepared by addition of a THF solution of *diaza* to a freshly prepared THF solution of K**6** which resulted in the crystallization of the product (Scheme 2). Salts of **6** are colorless and extremely water- and oxygen-sensitive. The K^+, $[K(crown)]^+$, $[K(aza)]^+$, and $[K(crypt)]^+$ salts are soluble in THF, benzene, and toluene. The $[K(diaza)]^+$ salt is only sparingly soluble in THF and even less soluble in benzene and toluene. The X-ray crystal structures of [K(*crown*)]**6** and [K(*diaza*)]**6** have been described briefly recently.[4] The structure of [K(*aza*)]**6** will be described later.

These salts were also prepared by the corresponding reactions with $IrHCl_2(P^iPr_3)_2$ in place of $IrH_5(P^iPr_3)_2$ under an atmosphere of H_2. However, the spectra indicate that the isolated products are contaminated with a complex suspected to be a salt of $[IrH_6(P^iPr_3)]^-$. The presence of the latter in C_6D_6 is signaled in the ^1H NMR spectrum by a doublet at −12.2 ppm (J(HP) = 15.3 Hz). However, there were several

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(29) Vaska, L. *J. Am. Chem. Soc.* **1961**, *83*, 756.
(30) Vaska, L.; DiLuzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4989−4990.
(31) Mynott, R. J.; Trogu, E. F.; Venanzi, L. M. *Inorg. Chim. Acta* **1974**, *8*, 201−207.

unassigned resonances in the corresponding $^{31}P\{^1H\}$ NMR spectra, and the concentration of this species was always too low to identify its $^{31}P\{^1H\}$ resonance(s). Precedents for such a structure are $[IrH_6(PCy_3)]^-$ (see later) and $[ReH_8(PPh_3)]^-$.[32] $IrHCl_2(P^iPr_3)_2$ is not a practical starting material for the preparation of [K(*diaza*)]**6** because this salt is not easily extracted from the KCl and KH salts of the reaction mixture.

Preparation and Properties of Salts of $[IrH_4(PCy_3)_2]^-$ (7). Treatment of $IrH_5(PCy_3)_2$ with KH and *Q* (*Q* = 18-crown-6, diaza-18-crown-6 or cryptand-222) in THF generates the new and very basic salts $[K(Q)][IrH_4(PCy_3)_2]$ (eq 3, R = Cy). However, only the crypt salt could be isolated without contamination from $IrH_5(PCy_3)_2$, and all attempts to produce single crystals for structural determination resulted in the formation of a white, amorphous precipitate. The salts of **7** are extremely water- and oxygen-sensitive and are soluble in THF, benzene and toluene, with the crypt salt being the least soluble. The $^{31}P\{^1H\}$ NMR spectra for gray to brown reaction mixtures of the crown and aza-crown salts $[K(Q)][IrH_4(PCy_3)_2]$ exhibit only a single resonance which is attributed to $[cis\text{-}IrH_4(PCy_3)_2]^-$ while a colorless solution of the crypt salt exhibits a single resonance due to $[trans\text{-}IrH_4(PCy_3)_2]^-$.

$$IrH_5(PR_3)_2 \xrightarrow[\text{THF}]{\text{KH, }Q,\ -H_2} [K(Q)][IrH_4(PR_3)_2] \qquad (3)$$

$$Q = \text{18-crown-6, diaza-18-crown-6, cryptand-222;} \quad R = Cy,\ ^iPr,\ Ph$$

These salts were also generated by the treatment of $IrHCl_2(PCy_3)_2$ with KH and *Q* in THF under an atmosphere of H_2. As was similarly observed for the preparation of the $[IrH_4(P^iPr_3)_2]^-$ salts, this reaction generates substantial amounts of the new hydride salts $[K(Q)][IrH_6(PCy_3)]$ in a competing reaction (^1H hydride (C_6D_6) at −12.16 ppm (d, $^2J(HP) = 15.5$), ^{31}P at 35.4 ppm (m with coupling to 6 H)). The $^{31}P\{^1H\}$ NMR spectra of the reaction mixtures revealed the presence of free PCy_3.

Observation of $[K(18\text{-crown-6})][IrHD_3(PCy_3)_2]$. $IrH_5(PCy_3)_2$ is known to undergo H atom exchange with aromatic solvents such as benzene and toluene.[14] To assess whether this reactivity is also displayed by **7**, a solution of [K(*crown*)]-**7** in C_6D_6 was refluxed for 12 h and then examined by ^1H NMR spectroscopy. The reaction mixture exhibited first-order patterns for the two hydride positions in $[cis\text{-}IrHD_3(PCy_3)_2]^-$ as well as for $IrHD_4(PCy_3)_2$.

The same reaction carried out in the presence of an excess of KH resulted in a severe decrease in the rate of H/D scrambling. The presence of KH in the reaction mixture served to deprotonate any acidic species in solution including $IrH_5(PCy_3)_2$. The reduced H/D scrambling rate indicates that complex **7** and its isotopomers are not as reactive as $IrH_5(PCy_3)_2$ and/or the process is mediated by $IrH_5(PCy_3)_2$.

Preparation and Properties of $[IrH_4(PPh_3)_2]^-$ Salts. Pure [K(*crown*)]**5** and [K(*diaza*)]**5** were prepared by the treatment of **4** with KH in the presence of a slight excess of the appropriate crown ether (eq 3, R = Ph). These colorless, water- and oxygen-sensitive salts are quite soluble in THF. The $[K(crown)]^+$ salt is also soluble in benzene; however, the $[K(diaza)]^+$ salt is less soluble in benzene but is more soluble than the P^iPr_3 analogue.

Acidity of $IrH_5(P^iPr_3)_2$ and $IrH_5(PCy_3)_2$. An attempt to establish an acid−base equilibrium between $ReH_7(PCy_3)_2$ and [K(*crown*)]**6** resulted in the complete protonation of **6**. From this experiment, it is concluded that the pK_α^{THF} of $IrH_5(P^iPr_3)_2/[K(crown)][cis\text{-}IrH_4(P^iPr_3)_2]$ is at least 2 units greater than that of $ReH_7(PCy_3)_2/[K(crown)][ReH_6(PCy_3)_2]$ ($pK_\alpha^{THF} = 41$).[27] The hydride $WH_6(PMe_2Ph)_3$ ($pK_\alpha^{THF}(WH_6(PMe_2Ph)_3/[K(crypt)][WH_5(PMe_2Ph)_3]) = 42$)[33] is almost completely deprotonated by the 2:1 mixture of $[K(crown)][cis\text{-}IrH_4(P^iPr_3)_2]$ (eq 4) and $[K(crown)][trans\text{-}IrH_4(P^iPr_3)_2]$ to produce an equilibrium with a constant of 150.

$$WH_6(PMe_2Ph)_3 + [K(crown)][cis\text{-}IrH_4(P^iPr_3)_2] \rightleftharpoons [K(crown)][WH_5(PMe_2Ph)_3] + IrH_5(P^iPr_3)_2 \quad (4)$$

This gives the $pK_\alpha^{THF}(IrH_5(P^iPr_3)_2/[K(crown)][cis\text{-}IrH_4(P^iPr_3)_2])$ as 44 with the assumption that ion pair interactions between the crown and tungsten hydrides are similar to that for the iridium hydride. Surprisingly, the $[K(crypt)]^+$ salt of $[trans\text{-}IrH_4(P^iPr_3)_2]^-$ reacts with $WH_6(PMe_2Ph)_3$ to give an equilibrium with a constant of about 1.6 (eq 5). Ion pair dissociation constants of the tungsten and iridium salts are expected to be similar so that the $pK_\alpha^{THF}(IrH_5(P^iPr_3)_2/[K(crypt)][trans\text{-}IrH_4(P^iPr_3)_2])$ is determined to be 42. This ratio of about 10^2 in acid dissociation constant of the two salts is an effect of ion pairing that is unprecedented as far as we are aware. There is no spectroscopic evidence that the stereochemistry and hence basicity of the reference tungsten complexes are affected by the change in countercation.

$$WH_6(PMe_2Ph)_3 + [K(crypt)][IrH_4(P^iPr_3)_2] \rightleftharpoons [K(crypt)][WH_5(PMe_2Ph)_3] + IrH_5(P^iPr_3)_2 \quad (5)$$

A question raised by these results is how can there also be $[K(crown)][trans\text{-}IrH_4(P^iPr_3)_2]$ present in equilibrium 4 (not shown) when the $pK_\alpha^{THF}(IrH_5(P^iPr_3)_2/[trans\text{-}IrH_4(P^iPr_3)_2]^-)$ is so much smaller than that of the *cis* isomer? This might be explained by the fact that there is a difference between the structure of the countercations of the *cis* and *trans* isomers. A solvation of the $[K(crown)]^+$ countercations in THF that do not interact with the hydrides of the *trans* isomer would produce ion pairs of the type $[K(crown)(THF)_2][trans\text{-}IrH_4(P^iPr_3)_2]$. The $[K(crown)(THF)_2]^+$ cation has been observed in many crystal structures.[33] Therefore, the analogous reaction to eq 4 involving the *trans* isomer would result in the favorable release of two THF molecules assuming that the entropy gain and the formation of K−H−W interactions more than overcomes the loss of the small K−THF bond energies. In contrast, the *cis* isomer interacts via three

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[32] Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133.

[33] Hinman, J. G.; Lough, A. J.; Morris, R. H. To be submitted.

hydrides with its nonsolvated [K(*crown*)] countercation on the basis of the geometry of its crystal structure.[4]

A mixture of [K(*crown*)]**6** and $IrH_5(PCy_3)_2$ was warmed to 50 °C and allowed to reach acid−base equilibrium and then was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy at room temperature. Making use of the equilibrium constant (0.6), it is estimated that the two complexes $IrH_5(P^iPr_3)_2$/[K(*crown*)]**6** and $IrH_5(PCy_3)_2$/[K(*crown*)]**7** have similar pK_α^{THF} values of about 44 with the PCy_3 system being slightly less acidic. Note that $ReH_7(PCy_3)_2$/[K(*crown*)][$ReH_6(PCy_3)_2$] is 2 units more basic than $ReH_7(P^iPr_3)_2$/[K(*crown*)][$ReH_6(P^iPr_3)_2$].[19] From the equilibrium constant of 8.2 for the reaction of $IrH_5(P^iPr_3)_2$ and [K(crypt)]**7**, it is concluded that $IrH_5(PCy_3)_2$/[K(crypt)]**7** has a pK_α^{THF} of about 43.

It was unexpected that the approximate pK_a values for the acid pentahydrides converting to the conjugate base *cis*-tetrahydrides are about 2 units higher (44 vs 42) than those for converting to the conjugate base *trans*-tetrahydrides. The stabilization of the conjugate base *cis*-isomer from Ir−H···K interactions and reduced *trans*-H−Ir−H destabilization must be overcome by interligand destabilizing interactions in the *cis* form relative to the *trans* form.

Formation of Mixed Ligand Complexes. A mixture of K**6** and $IrH_5(PCy_3)_2$ in refluxing THF was observed to undergo a phosphine-exchange reaction to give some [*cis*-$IrH_4(PCy_3)(P^iPr_3)$]$^-$. Refluxing THF solutions of $IrH_5(PCy_3)_2$ and $IrH_5(P^iPr_3)_2$ (1:1) afforded a mixture containing $IrH_5(P^iPr_3)(PCy_3)$. There is no resonance for uncoordinated phosphine in these reactions. However, it is likely that these reactions proceed via phosphine dissociation. The reaction of $IrH_5(PCy_3)_2$ with P^iPr_3 yields $IrH_5(PCy_3)(P^iPr_3)$ but no $IrH_3(PCy_3)_2(P^iPr_3)$. The related reaction of $IrH_5(PCy_3)_2$ with PPh_3 results in the formation of $IrH_3(PCy_3)_2(PPh_3)$. The dissociation of PCy_3 from $IrH_5(PCy_3)_2$ would explain its property of exchanging hydride hydrogen with C_6D_6 deuterium; the reactive 16-electron intermediate $IrH_5(PCy_3)$ is likely to insert into a C−D bond to cause this reaction.

Solution Structure and NMR Properties of $[IrH_4(PR_3)_2]^-$ (R = ^{i}Pr, Cy, Ph). The complexes $[IrH_4(PCy_3)_2]^-$ and $[IrH_4(PPh_3)_2]^-$ as crown- and azacrown-potassium salts exist in solution with an exclusive *cis* configuration about the iridium atom while the complex $[IrH_4(P^iPr_3)_2]^-$ exists in solution as an equilibrium mixture of *cis* and *trans* isomers. Surprisingly, the cryptand-potassium salts of $[IrH_4(PCy_3)_2]^-$ and $[IrH_4(P^iPr_3)_2]^-$ exist exclusively in the *trans* form as indicated by a binomial triplet resonance in the ^1H NMR spectrum.

The second-order $H_{BB'}$ resonances for the three [*cis*-$IrH_4(PR_3)_2$]$^-$ complexes are similar in appearance. This pattern for [K(*crown*)]**6** in THF was simulated, and the results are illustrated in Figure 3. The $^2J(HP_{trans})$ value of 121.5 Hz determined by simulation is comparable to the corresponding value of 120 Hz observed for [K(*crown*)][*cis*-$IrHD_3(PCy_3)_2$] and simulated for $IrH_3(PPh_3)_3$.[21] The simulated second-order $|^2J(HP_{cis})|$ of 24.8 Hz is similar to the value of 26 Hz observed for [K(*crown*)][$IrHD_3(PCy_3)_2$] but significantly greater than the value of 18 Hz simulated for $IrH_3(PPh_3)_3$. The second-order patterns for [*cis*-$IrH_4(PPh_3)_2$]$^-$ and [*cis*-$IrH_4(PCy_3)_2$]$^-$ have magnitudes and therefore coupling constants similar to those for [*cis*-$IrH_4(P^iPr_3)_2$]$^-$.

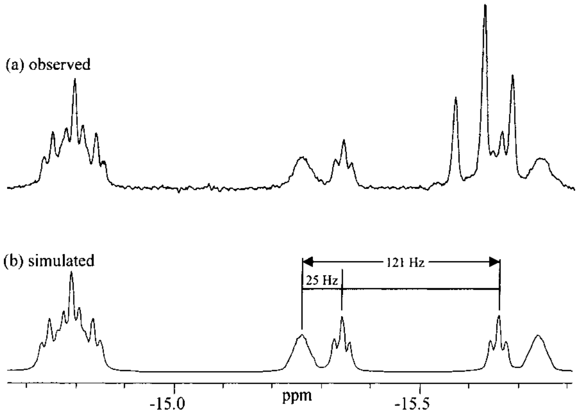

Figure 3. (a) Observed and (b) simulated upfield 300 MHz ^1H NMR spectra of [K(18-crown-6)][*cis*-$IrH_4(P^iPr_3)_2$] in THF. The large triplet at −15.6 ppm in (a) is due to *trans*-$[IrH_4(P^iPr_3)_2]^-$.

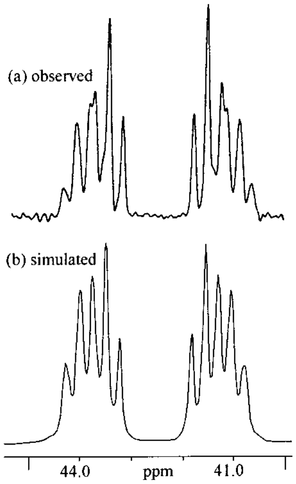

Figure 4. (a) Observed and (b) simulated hydride-coupled 121 MHz ^{31}P NMR spectra of [K(18-crown-6)][*cis*-$IrH_4(P^iPr_3)_2$] in THF.

To check the validity of this simulation, the hydride-coupled ^{31}P NMR **6** resonance for the same sample of [K(*crown*)]**6** was also simulated with the same parameters (Figure 4). There is reasonable agreement between the observed and simulated spectra of the *cis* isomer.

For $[IrH_4(P^iPr_3)_2]^-$, the [*cis*]/[*trans*] ratio is highly sensitive to the nature of the solvent and the crown- or azacrown-potassium cation. The [*cis*]/[*trans*] ratio in THF increases from 2:1 to 8:1 on changing the cation from [K(*crown*)]$^+$ to [K(*diaza*)]$^+$. This indicates that a combination of protonic−hydridic bonding and increased potassium−hydride interactions causes a stabilization of the *cis* isomer in an ion pair structure that is similar to the one observed in the solid state for [K(*aza*)][$IrH_4(P^iPr_3)_2$]. On changing the cation to K^+, the [*cis*]/[*trans*] ratio increases to 15:1, and this increase is attributed to a strong interaction between the small and electrophilic K^+ cation and three facial hydride ligands. The largest [*cis*]/[*trans*] ratios are observed for the [K(*aza*)]$^+$ and [K(*diaza*)]$^+$ salts in toluene and benzene for which no *trans* isomer is observed. Complex **6** exists exclusively as the *cis* isomer with stronger ion pairing in this environment because of the lower dielectric constant of toluene compared to THF.

Table 4. IR Data (cm^{-1}) for [K(Q)][$IrH_4(PR_3)_2$] in THF^a

	Q = 18-crown-6		Q = diaza-18-crown-6			
R	ν(H−IrP)	ν(H−IrH)	ν(NH)	$\Delta\nu^b$	ν(H−IrP)	ν(H−IrH)
Ph	2005	1713	3299, 3205	1, 95	2001	1716
^{i}Pr	1965	1688	3300, 3227	0, 73	1970	1695
Cy	1960	1680	3300, 3228	0, 72	1965	1685

^{a} The frequencies of the H−IrP absorptions in THF solution are imprecise, and this is in most part due to the presence of a strong solvent absorption at approximately 2000 cm^{-1}. ^{b} Decrease in ν(NH) from ν(NH) = 3300 cm^{-1} for [K(1,10-diaza-18-crown-6)]BPh_4.

At 298 K, both NH protons of [K(*diaza*)]**6** in THF-d_8 resonate at 2.14 ppm while they result in two vibrational modes in the infrared spectrum (Table 4). One may infer that the observed ^{1}H NMR chemical shift for the NH protons of [K(*diaza*)]**6** is in fact that for an averaged environment. With this in mind, an attempt was made to observe inequivalent NH protons at low temperature by ^{1}H NMR spectroscopy. The chemical shift of the NH resonance for a solution of [K(*diaza*)]**6** in THF-d_8 was found to vary linearly with temperature, but no decoalescence was observed down to 167 K. This precluded the effective use of nOe and T_1 measurements for the detection of close proton−hydride contacts.

X-ray Structures of [K(18-crown-6)][$IrH_4(P^iPr_3)_2$] and [K(18-crown-6)][$IrH_4(PPh_3)_2$]. In solution, [$IrH_4(P^iPr_3)_2$]$^-$ exists as an equilibrium mixture of *cis* and *trans* isomers where in all cases the *cis* isomer predominates. A single-crystal X-ray structural determination for [K(*crown*)]**6** revealed that this salt crystallizes from THF solution with the anion in the *cis* configuration. The structure was described briefly.[4] The hydride ligands were located and refined and had Ir−H bond lengths ranging from 1.52(7) to 2.0(1) Å. A typical iridium(III)−hydride distance is 1.60(2) Å.[34] The observed Ir−P bond lengths of 2.290(1) and 2.295(1) Å are typical for P^iPr_3 complexes of iridium. The K atom completes a distorted tetrahedron with three hydride ligands arranged facially about the iridium atom. This arrangement is recurring and will be subsequently referred to as the tripod arrangement.

In terms of the spatial relationship between anion and cation, the solid-state structure of [K(*crown*)]**5** is essentially the same as that of its P^iPr_3 counterpart. However, in this case, there are two similar formula units, with only one illustrated in Figure 5.

The Ir−H bond lengths range from 1.53(4) to 1.68(4) Å. The Ir−P bond lengths of approximately 2.26 Å are shorter than the bond lengths of 2.36(5) Å typically observed for 6-coordinate PPh_3 complexes of iridium. The short Ir−P bond lengths for this salt seem even more peculiar when one realizes that the phosphine ligands are *trans* to hydride ligands. However, the steric requirements of the hydride ligands are quite small, and this allows for a close approach of the phosphine ligands to the metal as the P−Ir−P angle (104°) deviates from ideal octahedral geometry. The H−Ir−P angles (H *trans* to P) are substantially less than 180° which may reduce the *trans* influence and result in shorter-than-expected Ir−P bond lengths.

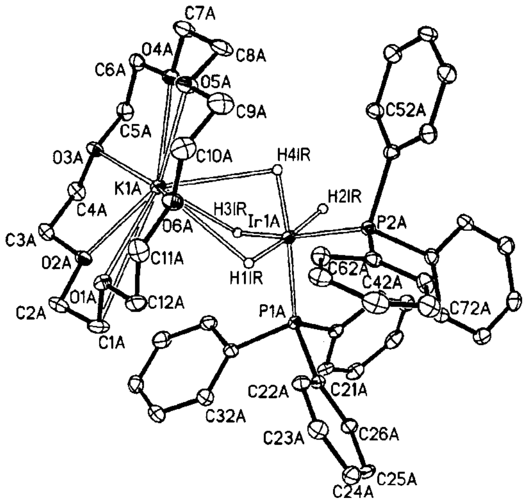

Figure 5. X-ray structure of [K(18-crown-6)][$IrH_4(PPh_3)_2$] (subunit A).

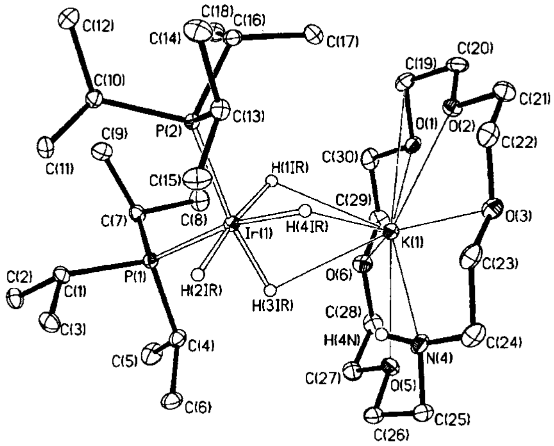

Figure 6. X-ray structure of [K(aza-18-crown-6)][$IrH_4(P^iPr_3)_2$].

X-ray Structure of [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$]. Unlike [K(*crown*)]**6**, the related salt [K(*diaza*)]**6** crystallizes with the anion in the *trans* configuration, Figure 1.[4] It is clear that when the *trans* isomer with [K(*diaza*)]$^+$ as the cation forms a chain of protonic−hydridic bonds in the crystalline state, it is less soluble than the *cis* isomer because the *trans* isomer is in lower concentration than the *cis* one in THF solution ([*trans*]/[*cis*] ratio is 1:8).

X-ray Structure of [K(aza-18-crown-6)][$IrH_4(P^iPr_3)_2$]. The X-ray structure of [K(*aza*)]**6** revealed a *cis* configuration for the anion of this salt (Figure 6). This structure possesses the tripod K$^+$/hydride arrangement observed also for [K(*crown*)]**6**. The X-ray data do not directly indicate the presence of any NH···HIr hydrogen bonds for [K(*aza*)]**6** because the smallest observed NH···HIr separation is 2.47(5) Å. The crown NH proton lies in the H(3IR)−Ir(1)−H(4IR) plane and also very nearly bisects the H(3IR)−Ir(1)−H(4IR) angle. This is similar to the bifurcated interaction arrangement observed for the $ReH_5(PPh_3)_2$•indole system,[35]

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(34) Typical bond lengths for comparison are obtained from the following review: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(35) Wessel, J.; Lee, J. C.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507−2509.

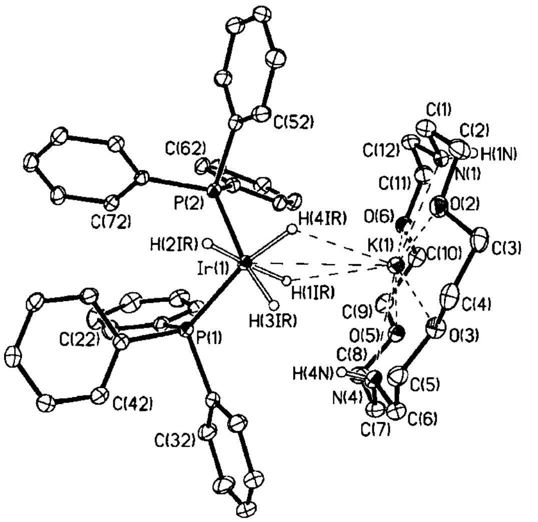


Figure 7. X-ray structure of [K(1,10-diaza-18-crown-6)][$IrH_4(PPh_3)_2$].

but the H···H distances are much longer in the iridium salt. However, if the N−H bond length is increased to 1.00 Å and the Ir−H distances are increased to 1.65 Å, the corrected H(4N)−H(2IR) and H(4N)−H(3IR) bond lengths are 2.3 and 2.6 Å, respectively. The 2.3 Å distance is indicative of an NH···HIr hydrogen bond and is consistent with the lowered NH stretch of the IR spectrum.

Another interesting feature of the [K(*aza*)]**6** structure is the very short H(4A)−H(27A) separation of 2.1 Å (between an isopropyl methine hydrogen and an *aza* methylene hydrogen). This close contact likely impedes a closer approach of the NH group to the hydride ligands.

X-ray Structure of [K(1,10-diaza-18-crown-6)][*cis*-IrH_4-$(PPh_3)_2$]. As in solution, the anion of [K(*diaza*)]**5** adopts a *cis* configuration about the iridium atom in the solid state (Figure 7). The anions and cations form a chain by way of alternating protonic−hydridic bonds and (K^+)···(H^-) interactions as illustrated in Figure 8. For this structure, the Ir−H bond lengths range from 1.51(3) to 1.66(4) Å. The observed H(4N)-H(3IR) separation is 2.50(6) Å if the observed N−H bond length of 0.79(4) Å is considered. If the N(4)−H(4N) bond is elongated to a more reasonable length of 1.00 Å, one obtains a corrected H(4N)−H(3IR) distance of 2.33 Å which is marginally indicative of protonic−hydridic bonding within the ion pair. The importance of this interaction is illustrated by the fact that the potassium atom of the cation is displaced from the tripod arrangement observed for [K(*crown*)][*cis*-$IrH_4(PR_3)_2$] (R = Ph, ^{i}Pr) and [K(*aza*)][*cis*-$IrH_4(P^iPr_3)_2$] to accommodate the NH···HIr interaction. The inter-ion-pair NH···HIr interaction in [K(*diaza*)][*cis*-IrH_4-$(PPh_3)_2$] is characterized by an observed H(1N)−H(2IR) separation of 2.08(6) Å. By increasing the N(1)−H(1N) bond length from the observed value of 0.81(5) Å to a more reasonable value of 1.00 Å, the corrected H(1N)−H(2IR) separation is 1.91 Å. This separation is very similar to that of 1.85 Å observed for [K(*diaza*)][*trans*-$IrH_4(P^iPr_3)_2$]. The complex [K(*diaza*)][$ReH_6(PPh_3)_2$] forms similar intra- and inter-ion-pair protonic−hydridic bonds but instead of forming a chain of ion pairs, it forms a ring of four linked ion pairs.[19]

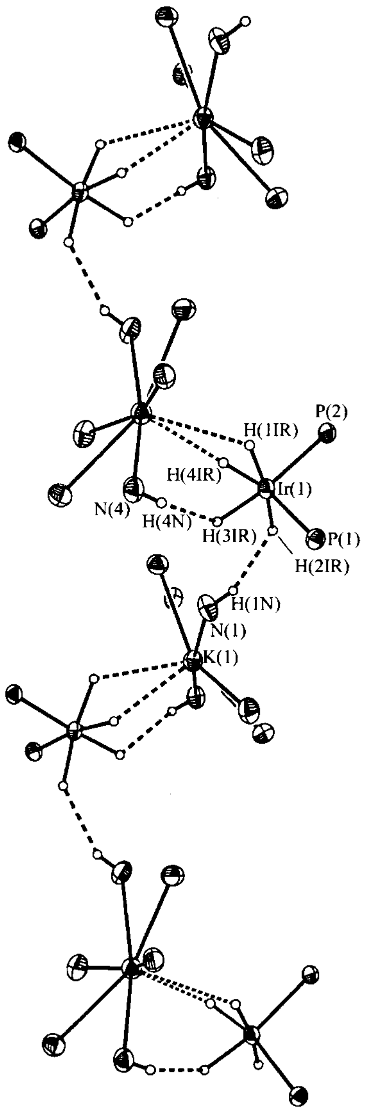


Figure 8. Chain structure of [K(1,10-diaza-18-crown-6)][$IrH_4(PPh_3)_2$]. Carbon and nonessential hydrogen atoms have been omitted for clarity.

IR Studies of Anionic Hydride Salts. In solution, the configuration about the iridium atom for all of the $[IrH_4(PR_3)_2]^-$ salts studied is exclusively *cis* (R = Ph, Cy) or primarily *cis* (R = ^{i}Pr) except for the cryptate salt. In each case, the *cis* arrangement results in two intense IrH stretching absorptions. Typically, one of these has a frequency of approximately 2000 cm^{-1} while the second may be found at or near 1700 cm^{-1}. Although these modes are probably coupled, the higher mode can be associated with hydride *trans* to phosphine, while the lower, to hydride *trans* to hydride. This is consistent with the fact that the *trans* tetrahydride salts in Nujol display only one intense H−IrH mode in the region of 1670−1680 cm^{-1}. [K(*diaza*)][*trans*-$IrH_4(P^iPr_3)_2$] exhibits an H−IrH mode at 1680 cm^{-1} but no H−IrP absorption. Similarly, the [K(*crypt*)][*trans*-IrH_4-$(P^iPr_3)_2$] and [K(*crypt*)][*trans*-$IrH_4(PCy_3)_2$] salts in Nujol have strong H−IrH modes at 1673 and 1680 cm^{-1}, respectively. These complexes also give weak absorptions between 1960 and 1930 cm^{-1} that are very similar to those of the neutral pentahydride species; these are probably produced during

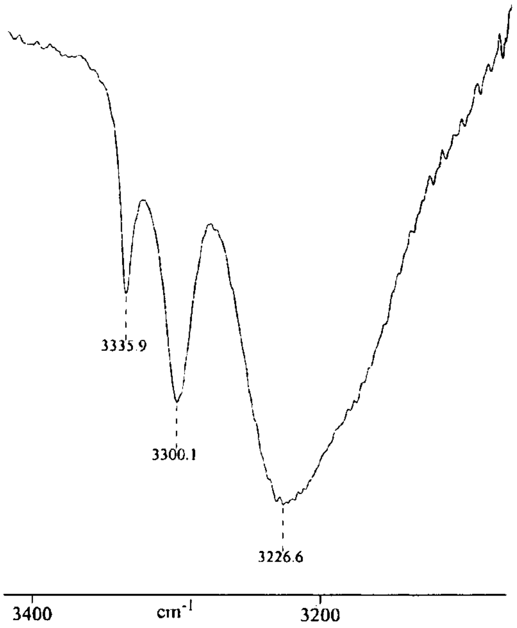


Figure 9. Solution IR spectrum of [K(1,10-diaza-18-crown-6)][IrH_4-($P^iPr_3)_2$] (NH region). The absorption at 3336 cm^{-1} is attributed to the presence of diaza-18-crown-6 or [K(*diaza*)$(THF)_2]^+$.[33]

sample preparation by protonation of the anions with adventitious water.

The solution IR spectroscopic properties of the [K(*crown*)]$^+$ and [K(*diaza*)]$^+$ salts of the three anionic hydride complexes are given in Table 4. From these data, it is apparent that an increase in phosphine basicity results in a reduction in the frequency of both IrH absorptions. The presence of a hydrogen-bond donor does not appear to significantly affect the IrH stretching frequencies in solution, and so, any IrH stretches for hydrogen-bonded hydride ligands were not resolved from the non-hydrogen-bonded absorptions.

The position, intensity, and breadth of the NH absorptions are quite sensitive to the nature of the anionic hydride complexes (Table 4). For comparison, diaza-18-crown-6 has an NH stretching frequency of approximately 3335 cm^{-1} while [K(*diaza*)][BPh_4] in THF has an NH stretching frequency of 3300 cm^{-1}. All three of the iridium complex [K(*diaza*)]$^+$ salts in THF exhibit two or three IR NH absorptions, one of which is in good agreement with that observed for [K(*diaza*)][BPh_4] and is thus attributed to an NH group which is not interacting with any hydride ligands (cf. Figure 9). In all cases, there is a second [K(*diaza*)]$^+$ NH stretch that is shifted to lower frequency, broadened, and considerably more intense than the absorption at 3300 cm^{-1}. These features are typical of protonic−hydridic hydrogen-bonded systems. The reduction in NH wavenumber attributed to this interaction ($\Delta\nu$ in Table 4) increases as $PCy_3 = P^iPr_3 < PPh_3$. This is opposite to the trend expected on the basis of the anion basicity: $PPh_3 < P^iPr_3 < PCy_3$ and opposite to the order observed for some rhenium anions $[ReH_6L_2]^-$ where $\Delta\nu$ and anion basicity both increased as $PPh_3 < P^iPr_3 < PCy_3$.[19] The interaction of the potassium with the hydride tripod on iridium and the associated interligand interactions appear to complicate the nature of the hydrogen-bonding interactions present in the case of iridium.

Table 5. Solid-State (cm^{-1}) IR Data for [K(*Q*)][$IrH_4(PR_3)_2$] in Nujol

	Q = 18-crown-6		*Q* = diaza-18-crown-6			
R	ν(H−IrP)	ν(H−IrH)	ν(NH)	$\Delta\nu^a$	ν(H−IrP)	ν(H−IrH)
Ph	2010	1716	3198	82	1974	1712
^{i}Pr	1922	1698	3148	132	-	1680
Cy	1986	1697	3289, 3222	−9, 58	1957	1668

[a] Decrease in ν(NH) from ν(NH) = 3280 cm^{-1} for [K(1,10-diaza-18-crown-6)]BPh_4.

Some solid-state IR data for the salts [K(*Q*)][$IrH_4(PR_3)_2$] are given in Table 5. [K(*diaza*)][BPh_4] exhibits a single NH stretching absorption at 3287 cm^{-1}. The IR spectra of samples in Nujol are quite distinct from the corresponding ones for THF solutions. In Nujol, the [K(*diaza*)]$^+$ salts of both $[IrH_4(P^iPr_3)_2]^-$ and $[IrH_4(PPh_3)_2]^-$ exhibit NH vibrations perturbed by protonic−hydridic bonding. [K(*diaza*)][*trans*-$IrH_4(P^iPr_3)_2$] exhibits only one NH absorption which is consistent with its X-ray structure. The NH absorption of [K(*diaza*)][*cis*-$IrH_4(PPh_3)_2$] in Nujol is asymmetric and appears to consist of two overlapping absorptions. This is consistent with the X-ray-determined structure that has two types of NH groups interacting with the hydride ligands of the anions. The NH region for [K(*diaza*)][*cis*-$IrH_4(PCy_3)_2$] exhibits an absorption at 3289 cm^{-1} and a second absorption of roughly equal intensity at 3222 cm^{-1}. The first of these is attributed to a cation NH group which is not interacting with the anion, and the second is attributed to the second cation NH group which is weakly interacting with the anion. The salt [K(*diaza*)][*trans*-$IrH_4(P^iPr_3)_2$] causes the largest reduction in the NH vibration ($\Delta\nu = 132$) in keeping with the high basicity of this anion and the strong hydrogen bonds (see Figure 1).

Conclusions

$IrHCl_2(P^iPr_3)_2$ and $IrHCl_2(PPh_3)_3$ were prepared by refluxing mixtures of $IrCl_3$ and phosphine in ^{i}PrOH. $IrHCl_2(PPh_3)_3$ may be a mixture of *cis,mer* and *trans,mer* isomers or it may be exclusively *cis,mer* depending on reaction time.

$IrHCl_2(PR_3)_2$ (R = ^{i}Pr, Cy) and $IrHCl_2(PPh_3)_3$ have been treated with KH and *Q* under H_2 atmosphere to yield the basic anionic hydride salts [K(*Q*)][$IrH_4(PR_3)_2$] (*Q* = 18-crown-6, R = Ph, ^{i}Pr, Cy; *Q* = aza-18-crown-6, R = ^{i}Pr; *Q* = diaza-18-crown-6, R = Ph, ^{i}Pr, Cy). When R = ^{i}Pr and Cy, the isolated products are usually contaminated with the new salts [K(*Q*)][$IrH_6(PR_3)$]. When R = Ph, the isolated products are usually contaminated with [K(*Q*)][PPh_2] and the new salts [K(*Q*)][*trans,mer*-$IrH_3(PPh_3)(PPh_2)$]. Alternatively, the treatment of $IrH_5(PR_3)_2$ (R = Ph, ^{i}Pr, Cy) with KH and *Q* under a non-hydrogen atmosphere cleanly yields [K(*Q*)][$IrH_4(PR_3)_2$] although the crown and diaza-crown $[IrH_4(PCy_3)_2]^-$ salts could not be crystallized or isolated free of $IrH_5(PCy_3)_2$. The $IrH_5(PR_3)_2$ (R = ^{i}Pr, Cy) precursors were prepared by the treatment of $IrHCl_2(PR_3)_2$ with NaOH under H_2 atmosphere. The $IrH_5(PPh_3)_2$ precursor was prepared in two steps: first, the preparation of crude K[$IrH_4(PPh_3)_2$] from

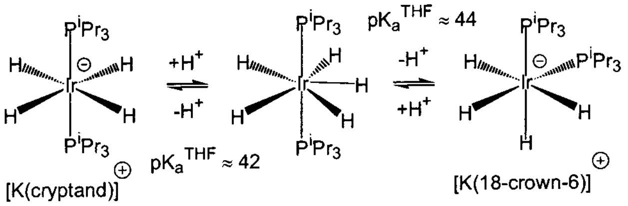
$IrHCl_2(PPh_3)_3$ and then its reaction with H_2O. This route to $IrH_5(PPh_3)_2$ is far more efficient than previously reported methods.

The salts [K(18-crown-6)][$IrH_4(PR_3)_2$] (R = Ph, ^iPr) crystallize with the anion in a *cis* configuration. In these salts, the potassium atom and three *facially*-arranged hydride ligands form a tetrahedron. [K(aza-18-crown-6)][$IrH_4(P^iPr_3)_2$] also crystallizes with a *cis* configuration about the iridium atom and exhibits the potassium/hydride arrangement observed for the [K(18-crown-6)]$^+$ salts. There is IR and structural evidence of significant protonic−hydridic interactions in [K(aza-18-crown-6)][$IrH_4(P^iPr_3)_2$] although the observed (X-ray) proton−hydride distance is greater than 2.4 Å.

The salt [K(1,10-diaza-18-crown-6)][$IrH_4(PPh_3)_2$] crystallizes with the anion in a *cis* configuration while the anion in [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$] is *trans*. In the solid state, both of these salts form extended chains with protonic−hydridic hydrogen-bond links. The protonic−hydridic bonds in [K(1,10-diaza-18-crown-6)][$IrH_4(P^iPr_3)_2$] are key to the crystallization of this salt from THF with the anion in the *trans* configuration because the [*cis*]/[*trans*] ratio is 8:1 for this salt in THF. Thus, there is a competition between the potassium and NH groups in forming bonds with the hydrides on iridium.

There are at least four factors that are thought to influence the stereochemistry of these tetrahydride complexes in THF solution. The first and most important is the potassium−hydride interactions in the ion pairs that favor the *cis* isomer for [K(*Q*)]**5**, [K(*Q*)]**7**, K**6**, [K(*crown*)]**6**, [K(*aza*)]**6**, and [K(*diaza*)]**6**. The cryptate salts that cannot make potassium−hydride bonds are *trans*. On the basis of the [*cis*]/[*trans*] ratios for the salts of **6**, the Lewis acidity of the potassium cation decreases as $K^+ >$ [K(*diaza*)]$^+ >$ [K(*aza*)]$^+ >$ [K(*crown*)]$^+ \gg$ [K(*crypt*)]$^+$. A second factor is protonic−hydridic bonding that would also contribute to a strengthening of the cation−anion interaction, an effect that would also decrease as [K(*diaza*)]$^+ >$ [K(*aza*)]$^+ >$ [K(*crown*)]$^+$. A third factor is interligand repulsions in the anion, expected to increase with the Tolman cone angle of the phosphine ligand: PPh_3 (145°) < P^iPr_3 (160°) < PCy_3 (170°). This explains why [K(*crypt*)]**6** and [K(*crypt*)]**7** are *trans* in the absence of potassium−hydride interactions. However, a fourth factor is the destabilization of isomers that have *trans* hydride ligands in octahedral structures. This would disfavor the formation of *trans* tetrahydride isomers (with two sets of *trans* hydrides) over *cis* isomers (with one set). The fact that the [K(*crown*)][$IrH_4(PCy_3)_2$] and [K(*diaza*)][$IrH_4(PCy_3)_2$] salts are exclusively *cis*, when *trans* might be expected on the basis of interligand repulsions, indicates that the *fac*-hydrides in this particularly electron-rich *cis* complex are excellent donors to potassium and in addition that the *trans*-tetrahydride geometry is avoided.

Scheme 3



The nature of the cation and hence the stereochemistry of the anions [$IrH_4(PR_3)_2$]$^-$ has a large influence on the basicity with respect to the acid $WH_6(PMe_2Ph)_3$ and hence the pK_α^{THF} value of the conjugate acids. The acidity decreases in THF as $IrH_5(P^iPr_3)_2$/[K(crypt)][*trans*-$IrH_4(P^iPr_3)_2$] ($pK_\alpha^{THF} = 42$) > $IrH_5(PCy_3)_2$/[K(crypt)][*trans*-$IrH_4(PCy_3)_2$] ($pK_\alpha^{THF} = 43$) > $IrH_5(P^iPr_3)_2$/[K(crown)][*cis*-$IrH_4(P^iPr_3)_2$] ($pK_\alpha^{THF} = 44$) > $IrH_5(PCy_3)_2$/[K(crown)][*cis*-$IrH_4(PCy_3)_2$]. This is the first example that we are aware of such a large counterion effect on stereochemistry and acidity as summarized in Scheme 3.

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Supporting Information Available: Crystallographic CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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