Inorg. Chem. **1992**, *31*, 1827–1832

Contribution from the Department of Chemistry,
University of Hawaii, Honolulu, Hawaii 96822

Solid-State and Solution Dynamics of the Reversible Loss of Hydrogen from the Iridium Nonclassical Polyhydride Complexes $IrClH_2(PR_3)_2(H_2)$ (R = Pr^i, Cy, Bu^t)

Mario Mediati, Glen N. Tachibana, and Craig M. Jensen*

Received September 5, 1991

The complexes $IrClH_2(PR_3)_2(H_2)$ (R = Pr^i (**1a**), Cy (**1b**)) were generated through the reaction of the corresponding unsaturated dihydride complexes, $IrClH_2(PR_3)_2$ (R = Pr^i (**2a**), Cy (**2b**)), with H_2 in solution or the solid state. The complexes were also prepared through treatment of THF solutions of $IrCl_3{\cdot}3H_2O$ and 2 equiv of phosphine with 2 equiv of sodium naphthalide under an atmosphere of hydrogen. The molecular structure of **1a**$\cdot C_{10}H_8$ was determined by a single-crystal X-ray diffraction study. Crystallographic data for **1a**$\cdot C_{10}H_8$: triclinic $P\bar{1}$, $Z = 2$, $a = 8.069$ (3) Å, $b = 13.822$ (6) Å, $c = 14.519$ (5) Å, $\alpha = 82.56$ (3)°, $\beta = 82.34$ (3)°, $\gamma = 72.90$ (3)°, $V = 5170$ (5) Å^3; $\rho_{calcd} = 1.737$ g/cm^3. Under an atmosphere of argon, **1a** and **1b** eliminate H_2 and convert back to the unsaturated complexes. Variable-temperature ^1H NMR studies of **1a** and **1b** in toluene-d_8 solution under 0.5 atm of H_2 show that they establish rapid equilibria with **2a** and **2b**, respectively, which are sensitive to hydrogen pressure and temperature. Similar studies of the more sterically hindered $IrClH_2(PBu^t_3)_2$ (**2c**) under 0.5 atm of H_2 show only indirect evidence of a much slower equilibrium with **1c**, while low concentrations of **1c** can be directly observed under 1 atm of H_2. The presence of dihydrogen ligands in **1a** and **1b** are indicated by their extremely facile exchange with free H_2 and by the respective minimum T_1 values for the ^1H NMR resonance due to the exchanging metal-bound hydrogens at 300 MHz of 22 and 27 ms, respectively. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of **1a** dissolved in toluene-d_8 also demonstrate the interconversion of **1a** and **2a**. The metal bound hydrogens of **1a** and **1b** undergo D/H exchange in toluene-d_8, THF-d_8, and CD_2Cl_2 solutions. The reversible uptake of hydrogen by **2a** in the solid state was studied through monitoring of M–H absorptions by FTIR spectroscopy. Comparison of the relative intensities of the M–H infrared absorptions of **1a** and **2a** with those observed for **1b** and **2b** in equilibrated samples under 1 atm of H_2 indicates that the equilibrium position lies much more toward the dihydrogen complex in the case of the PPR^i_3 derivative. Similar studies of the reaction of **2a** with D_2 establish that the intramolecular exchange between the dihydrogen and hydride ligands of **1a** occurs in the solid state.

Introduction

Since Kubas' initial identification of a dihydrogen complex,[1] there has been a great deal of research activity[2-19] probing the possibility that polyhydride complexes contain both dihydrogen and hydride ligands. The presence of both types of metal-bound hydrogen has been established for a number of complexes by neutron[2,3] and X-ray[4-7] diffraction studies. Such "nonclassical" formulations have been strongly indicated by NMR spectroscopic studies[8-19] for many more polyhydride complexes. However, the nature and extent of the metal–hydrogen and hydrogen–hydrogen bonding interactions as well as the mechanisms of both intermolecular exchange between free and metal-bound hydrogen and the intramolecular exchange between hydride and dihydrogen ligands in these complexes remain a subject of continuing interest and controversy. The influence of the ligand environment and solvent interactions on the kinetics and thermodynamics of the exchange processes remains largely unexplored. An understanding of these influences should provide important information about the metal–hydrogen interactions.

In a preliminary communication,[14] we reported the synthesis and characterization of $IrH_2Cl(H_2)(PPr^i_3)_2$ (**1a**). A variable-temperature ^1H NMR study showed the complex to undergo intermolecular exchange between free and metal-bound hydrogen as well as the intramolecular exchange between hydride and dihydrogen ligands. We have now prepared a series of related complexes. The dynamic behavior of these complexes has been seen to be quite sensitive to their ligand environment and is dramatically different for **1a** in the solid state than in solution. We report here the results of our studies as well as our insights into the connections between the dynamic behavior and the ligand environment in our nonclassical polyhydride complexes.

Experimental Section

General Details. The following were purchased and used without further purification: PCy_3 (Aldrich Chemical Co.); $IrCl{\cdot}3H_2O$ and $[NH_4]_3[IrCl_6]$ (Johnson-Mathey); PBu^t_3 and PPr^i_3 (Strem Chemicals) and deuterium gas, 99.5+ atom % D (MSD Isotopes). The complexes $IrH_2Cl(PPr^i3)_2$[20] (**2a**) and $[IrCl(C_8H_{14})_2]_2$[21] were prepared by literature methods. $IrH_2Cl(PCy_3)_2$ (**2b**) was prepared by substitution of PCy_3 into the method used to prepare **2a**. Except where noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Mass spectral analyses were performed on a VG 70SE mass spectrometer. Elemental analyses were performed by Oneida Research Services Inc., Whitesboro, NY.

NMR Studies. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Nicolet NT300 spectrometer at 300.8 and 121.7 MHz. The ^2H NMR spectra were recorded on a GN Omega 500 spectrometer at 76.8 MHz. The ^1H NMR data are listed in ppm downfield from TMS at 0.00 ppm. The ^2H NMR data are listed in ppm relative to the methyl resonance of toluene-d_8 at 2.09 ppm. ^{31}P NMR chemical shifts were measured relative to the deuterium resonance of the solvent by using the internal frequency lock of the spectrometer so that the resonance from a capillary of 85% H_3PO_4, centered in a 5-mm NMR tube containing the deuterated solvent, appeared at 0.0 ppm at 20 °C. A preacquisition delay of 31 μs and a pulse delay of 1 s were used in the variable-temperature ^1H NMR studies

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Table I. Summary of Crystal Data for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$

formula	$IrClP_2C_{28}H_{54}$
fw	676.3
space group	$P\bar{1}$ (No. 2)
a, Å	8.069 (3)
b, Å	13.822 (6)
c, Å	14.519 (5)
α, deg	82.56 (3)
β, deg	82.34 (3)
γ, deg	72.90 (3)
V, Å^3	1527 (1)
Z	2
λ, Å (Mo Kα)	0.71073
ρ_{calc}, g/cm^3	1.471
T, K	295
μ, mm^{-1}	4.560
min, max transm coeff	0.4247, 0.9101
R,[a] %	3.46
R_w,[b] %	4.25
	1.16

[a] $R = \sum|F_o| - |F_c|/\sum F_o$. [b] $R_w = [w\sum(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

while a preacquisition delay of 31 μs and a pulse delay of 1 s were used in the variable-temperature ^{31}P NMR experiments.

Infrared Studies. KBr pellets were prepared in a glovebag, under argon. The sample holder, containing the pellet, was then placed into an IR gas cell and held centered by a plastic ring. The gas cell could then be evacuated on a vacuum line and other gases introduced (H_2 and D_2). The infrared spectra were recorded on a Nicolet 740 FT-IR spectrometer.

Preparation of $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$ (1a·$C_{10}H_8$). A solution of $IrCl_3\cdot 3H_2O$ (175 mg, 0.50 mmol) in 25 mL of dry THF was treated with PPr^i_3 (220 μL, 1.25 mmol) and the mixture allowed to stir for 1 h. The solvent was then frozen, and following removal of the nitrogen by vacuum, the reaction mixture was placed under 1 atm of hydrogen. Upon warming to room temperature, the mixture was treated with 1.0 mL of 1.0 M sodium naphthalide (1.0 mmol) and stirred for 1 h. The THF was removed by vacuum, producing an orange oil. Crystals of the product arose from the oil upon standing at room temperature for several days. The crystals were removed from the oily residue and washed with cold (−78 °C) pentane, giving purified **1a**·$C_{10}H_8$ in 32% yield. ^1H NMR (20 °C, toluene-d_8, under 0.5 atm of H_2), δ: 7.58 (d, J_{H-H} = 6 Hz), 7.24 (d, J_{H-H} = 6 Hz), $C_{10}H_8$; 2.25 (m), $CH(CH_3)_2$; 1.16 (m), $CH(CH_3)_2$; −19.1 (br s), Ir-*H*. $^{31}P\{^1H\}$ NMR (20 °C, toluene-d_8, under 0.5 atm of H_2), δ: 51 (br, s).

Preparation of $IrClH_2(PPr^i_3)_2(H_2)$ (1a). A solution of $[IrCl(C_8H_{14})_2]_2$ (200 mg, 0.22 mmol) in 20 mL of degassed pentane was stirred with PPr^i_3 (200 μL, 1.0 mmol) for 10 min. Hydrogen was then bubbled through the solution until the volume had been reduced to ca. 5 mL. Yellow powder precipitated, upon cooling in a dry ice–ethanol bath. The supernatant was removed via syringe under hydrogen. The crude product was recrystallized from pentane under hydrogen to give purified orange crystals in 74% yield. ^1H NMR (20 °C, toluene-d_8, under 0.5 atm of H_2), δ: 2.23 (m), $CH(CH_3)_2$; 1.15 (m), $CH(CH_3)_2$; −18.0 (br s), Ir-*H*. $^{31}P\{^1H\}$ NMR (20 °C, toluene-d_8, under 0.5 atm of H_2), δ: 51 (br, s). Anal. Calcd: C, 39.15; H, 8.40; Cl, 6.42. Found: C, 39.36; H, 8.09; Cl, 6.60.

Preparation of $IrClH_2(PCy_3)_2(H_2)$ (1b). The complex was prepared and isolated in 55% yield by substitution of PCy_3 into the preparation of **1a**. ^1H NMR (20 °C, toluene-d_8, under 0.5 atm of H_2), δ: 2.28 (m), 2.14 (m), 1.77 (m), 1.65 (m), 1.26 (m), $P(C_6H_{11})_3$; −19.3 (br s), Ir-*H*. Anal. Calcd: C, 54.56; H, 8.91. Found: C, 54.58; H, 8.42.

Preparation of $IrClH_2(PBu^t_3)_2$ (2c). The complex **2c** was obtained by substitution of PBu^t_3 into the preparation of **1a**. ^1H NMR (toluene-d_8), δ: 1.49 (br t, J_{P-H} = 6 Hz), $P[C(CH_3)_3$; −34.7 (t, J_{P-H} = 12 Hz), Ir-*H*.

Crystallographic Studies. Orange rhombohedral crystals of **1a**·$C_{10}H_8$ suitable for X-ray diffraction were obtained from a concentrated THF solution upon standing at room temperature. A crystal was mounted on a glass fiber with epoxy under a hydrogen atmosphere and centered on a Nicolet P3 automated diffractometer. The unit-cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections. Reflections with 2θ in the range 4 ≤ 2θ ≤ 55° (±*h*,±*k*,±*l*) were measured by using the ω-scan technique. A ψ-scan absorption correction was applied. Crystal and instrument stabilities were monitored with a set of three standard reflections measured every 97 reflections; no significant variations were found. Details of other crystal data and relevant information are summarized in Table I.

Scheme I

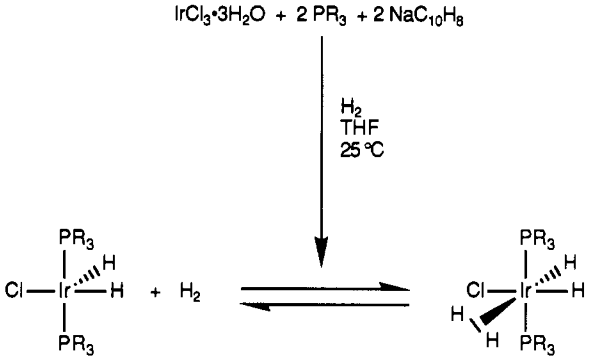

Table II. Bond Lengths (Å) and Angles (deg) for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$

Ir-Cl	2.427 (2)	Ir-P(1)	2.303 (2)
Ir-P(2)	2.306 (1)		
Cl-Ir-P(1)	93.6 (1)	Cl-Ir-P(2)	93.2 (1)
P(1)-Ir-P(2)	173.2 (1)		

Following data reduction and averaging of equivalent reflections, a unique set of 7041 reflections was obtained, of which 5362 reflections were observed ($F > 3.0\sigma(F)$). The structure was solved by Patterson and conventional Fourier techniques using SHELX PLUS computer programs (Nicolet Instrument Corp). Neutral-atom scattering factors were calculated by the standard procedures.[22] The positions and isotropic thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares procedures. During the refinement, a group of peaks not associated with the iridium complex became apparent in the difference Fourier maps. The peaks were refined isotropically as a naphthalene of crystallization. All non-hydrogen atoms were refined with anisotropic temperature coefficients. The hydrogen atoms were included by use of a riding model with C–H distances of 0.96 Å and isotropic thermal parameters fixed at 0.08 Å^2. In the final least-squares cycle, 344 parameters were refined. The largest peaks in the final difference Fourier map were 1.6 and 1.5 e/Å^3, located within 1.03 Å of the iridium atom.

Results and Discussion

Synthesis. The complexes $IrClH_2(PR_3)_2(H_2)$ (R = Pr^i (**1a**), Cy (**1b**)) were initially prepared through treatment of THF solutions of $IrCl_3\cdot 3H_2O$ and 2 equiv of phosphine with 2 equiv of sodium naphthalide under an atmosphere of hydrogen as seen in Scheme I. Filtration of the reaction mixtures, followed by removal of the THF solvent, produced oils from which orange crystals of the nonclassical polyhydride complexes arose upon standing under an atmosphere of H_2. These crystals were found to contain an equimolar amount of naphthalene. The complexes are stable in the solid state under an atmosphere of hydrogen. Under an atmosphere of argon, **1a** eliminates H_2 without a perceivable color change, giving the previously reported[20] complex, $IrClH_2(PPr^i_3)_2$ (**2a**), as seen in Scheme I. This process can be readily reversed by placing a sample of **2a** under an atmosphere of H_2. We have in fact found that complexes **1a** and **1b** can be prepared more conveniently through the reaction of the corresponding dihydride complexes, $IrClH_2(PR_3)_2$ (R = Pr^i (**2a**), Cy (**2b**)), prepared by the method of Werner[20] with H_2 either in solution or in the solid state as in Scheme I. Thus a pentane solution of **2a** placed under 1 atm of hydrogen and allowed to stand at room temperature gives rise to orange crystals of the less soluble **1a** in 70–80% yield.

Structure of 1a·$C_{10}H_8$. The molecular structure of **1a**·$C_{10}H_8$ was determined by a single-crystal X-ray diffraction study. An ORTEP projection with the atomic numbering scheme of the obtained molecular structure is seen in Figure 1. Selected bond angles and distances are listed in Table II; the final fractional coordinates are given in Table III. The Ir–Cl distance of 2.427 (2) Å reflects the pronounced influence of a trans hydride ligand, as it is appreciably longer than both the 2.35 Å sum of the atomic radii[23] and the 2.33–2.37 Å distances found[24] for trans terminal

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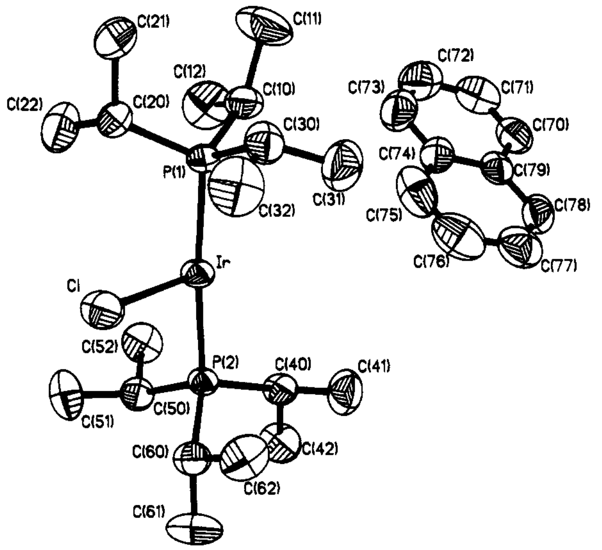

Figure 1. ORTEP projection of $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$ (**1a**$\cdot C_{10}H_8$). Thermal ellipsoids are at 50% probability, and the hydrogen atoms have been omitted for clarity.

Table III. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients[a] for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$

	x	*y*	*z*	*U*(eq), Å^2
Ir	0.1023 (1)	0.2412 (1)	0.2258 (1)	0.038 (1)
Cl	0.1944 (2)	0.0567 (1)	0.2440 (1)	0.062 (1)
P(1)	−0.0304 (2)	0.2534 (1)	0.3761 (1)	0.038 (1)
C(10)	−0.1887 (9)	0.3788 (5)	0.3909 (5)	0.056 (2)
C(11)	−0.261 (1)	0.4043 (8)	0.4890 (7)	0.099 (4)
C(12)	−0.333 (1)	0.4060 (7)	0.3277 (7)	0.084 (4)
C(20)	−0.1329 (8)	0.1519 (5)	0.4197 (4)	0.049 (2)
C(21)	−0.203 (2)	0.1475 (8)	0.5230 (6)	0.096 (5)
C(22)	−0.263 (1)	0.1441 (7)	0.3580 (6)	0.080 (4)
C(30)	0.1211 (9)	0.2452 (5)	0.4631 (4)	0.056 (3)
C(31)	0.207 (1)	0.3293 (8)	0.4441 (6)	0.083 (4)
C(32)	0.260 (1)	0.1421 (7)	0.4656 (7)	0.088 (4)
P(2)	0.2280 (2)	0.2498 (1)	0.0739 (1)	0.035 (1)
C(40)	0.2526 (8)	0.3782 (4)	0.0345 (4)	0.046 (2)
C(41)	0.383 (1)	0.4040 (6)	0.0848 (6)	0.070 (3)
C(42)	0.287 (1)	0.4039 (6)	−0.0704 (5)	0.073 (3)
C(50)	0.0940 (8)	0.2311 (5)	−0.0117 (4)	0.046 (2)
C(51)	0.068 (1)	0.1263 (5)	0.0032 (6)	0.068 (3)
C(52)	−0.0813 (9)	0.3108 (6)	−0.0104 (5)	0.064 (3)
C(60)	0.4374 (8)	0.1512 (5)	0.0530 (4)	0.048 (2)
C(61)	0.525 (1)	0.1519 (7)	−0.0455 (5)	0.076 (3)
C(62)	0.564 (1)	0.1494 (7)	0.1220 (6)	0.071 (3)
C(70)	−0.154 (1)	0.8869 (6)	0.2610 (5)	0.068 (3)
C(71)	−0.321 (1)	0.8961 (8)	0.2752 (6)	0.085 (4)
C(72)	−0.384 (1)	0.811 (1)	0.2926 (6)	0.089 (5)
C(73)	−0.269 (1)	0.7159 (8)	0.2933 (5)	0.080 (4)
C(74)	−0.0929 (9)	0.7047 (5)	0.2779 (4)	0.056 (3)
C(75)	0.035 (2)	0.6071 (6)	0.2759 (6)	0.085 (4)
C(76)	0.205 (2)	0.6004 (8)	0.2618 (6)	0.094 (5)
C(77)	0.262 (1)	0.6855 (8)	0.2477 (6)	0.081 (4)
C(78)	0.150 (1)	0.7782 (7)	0.2462 (5)	0.068 (3)
C(79)	−0.0309 (9)	0.7899 (5)	0.2611 (4)	0.051 (2)

[a] Equivalent isotropic *U* is one-third the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

chloride ligands on neutral iridium(III) complexes. The closest approach of a phosphine carbon to the iridium center is 3.44 Å, demonstrating the lack of agostic C–H–Ir interactions. Similarly, the closest approach of the naphthalene of crystallization to the iridium center of 5.06 Å clearly indicates the lack of a coordinative interaction. The hydride ligands could not be reliably located.[25]

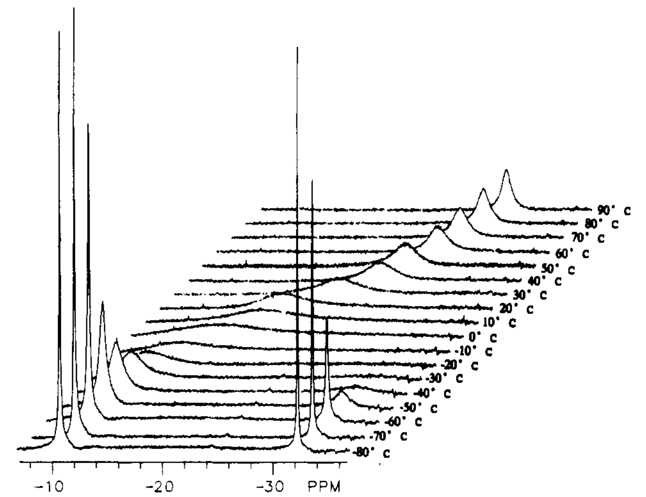

Figure 2. Variable-temperature ^1H NMR spectra (300 MHz) of the hydride region of $IrClH_2(PPr^i_3)_2(H_2)$ (**1a**) dissolved in toluene-d_8 under 0.5 atm of H_2 (total pressure).

Solution Dynamics. The ^1H NMR spectrum of **1a** in CD_2Cl_2 solution at 22 °C under 1 atm of hydrogen exhibits a broad ($\omega_{1/2} \approx 700$ Hz) singlet at ca. −17 ppm. Reduction of the hydrogen pressure by partial evacuation results in the resonance sharpening and moving upfield toward a limiting value of −33.0 ppm, the chemical shift observed for the hydride resonance of **2a** under an atmosphere of argon at 22 °C. A sample of **1a** that was dissolved in CD_2Cl_2 freeze/pump/thaw degassed, and allowed to stand under an atmosphere of argon for 0.5 h was seen to produce a hydride signal identical to that observed for **2a** (δ −33.0 ppm, $J_{P-H} = 13$ Hz). Conversely, spectra identical to those of **1a** under hydrogen pressure are obtained from samples of **2a** under hydrogen pressure. These observations cleary demonstrate that the metal-bound hydrogens of **1a** are in rapid exchange with free H_2. The rapid, reversible loss of H_2 from these complexes indicates they contain a dihydrogen ligand, as rapid exchange with free H_2 is a common characteristic of many dihydrogen complexes.[12,13,16,19,26-30] The facility with which **1a** undergoes this process is unusual, as dihydrogen complexes have generally been found to exchange metal-bound hydrogens with free H_2 too slowly for observation on the NMR time scale, reflecting a significantly lower kinetic barrier to the loss of H_2 from **1a**. ^1H NMR studies[17] of the highly related complex $IrHCl_2(PR_3)_2(H_2)$ (R = Pr^i, Cy) indicates the occurrence of similar rapid exchange with free H_2. A similar equilibrium has also been suggested as part of the more complex solution behavior of the Ir(IV) species $IrH_2Cl_2(PPr^i_3)_2$.[31]

The hydride regions of variable-temperature ^1H NMR spectra of a sample of **1a** dissolved in toluene-d_8 under 0.5 atm of H_2 are shown in Figure 2. Between −20 and −80 °C, the width of the −10.7 ppm resonance decreases with decreasing temperature, but

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(25) In an attempt to locate the metal-bound hydrogens, a second X-ray analysis was performed at −100 °C. After all atoms except the hydride ligands were located and refined, a difference Fourier synthesis yielded four peaks with intensities of approximately 1 e/Å^3. The peaks were located 1.3–1.5 Å from the iridium center, and two peaks were within 0.7 Å of each other. If the two close "hydrides" are viewed as a coordination dihydrogen, an approximately octahedral geometry about the iridium center can be recognized. The peaks could not be refined.

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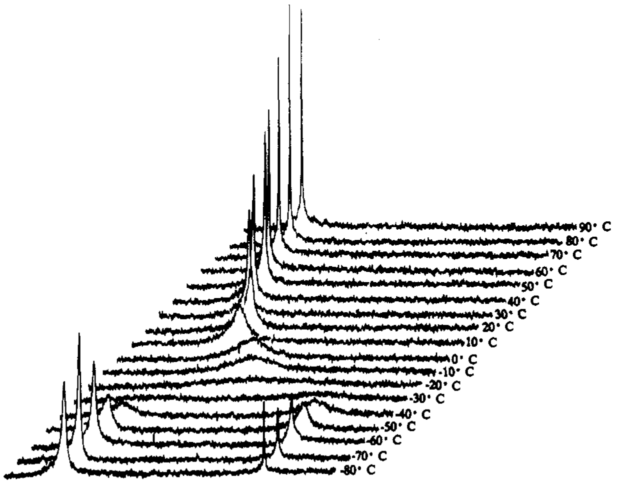

Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra (121.7 MHz) of $IrClH_2(PPr^i_3)_2(H_2)$ (**1a**) dissolved in CD_2Cl_2 under 0.5 atm of H_2 (total pressure).

at -80 °C it remains too broad ($\omega_{1/2} \approx 32$ Hz) for resolution of P–H coupling. Below -40 °C, separate resonances are clearly observed for the hydrides of **2a** and the metal-bound hydrogens of **1a** at -32.1 and -10.7 ppm, respectively. The variable-temperature spectra were obtained at this reduced H_2 pressure in this experiment to provide a direct evidence for the **1a**/**2a** equilibrium. The pronounced temperature-dependent changes in the **1a**/**2a** equilibrium position are more closely related to the temperature-dependent[32] concentration of free H_2 than to the energies of the reversible loss of H_2 from **1a**. In a similar study of a sample of **1a** dissolved in toluene-d_8 and sealed under 1 atm of H_2, **1a** was seen to be highly predominant at all temperatures below -20 °C and only a very minor amounts of **2a** were detected.

The minimum T_1 value of 22 ms found for the -10.7 ppm resonance at -60 °C and 300 MHz is consistent[10,33,34] with the presence of rapidly exchanging hydride and dihydrogen ligands in **1a**.[35] The T_1 minimum of 212 ms observed for the hydride resonance of a toluene-d_8 solution of **2a** under at atm of argon at -60 °C establishes that a classical hydride ligand in a similar coordination environment does not have a similarly short value of T_1 due to heteroatom–hydrogen dipole–dipole interactions.[36,37]

We have investigated the interconversion of **1a** and **2a** by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy. Spectra of a sample of **1a**, under 0.5 atm of H_2 in toluene-d_8, are displayed in Figure 3. These spectra show the same pronounced temperature-dependent trends in the **1a**/**2a** equilibrium position as were observed in the ^1H NMR studies. At room temperature, a broad ($\omega_{1/2} = 30$ Hz) resonance is observed at 51 ppm. As the temperature is lowered, the resonance is seen to broaden due to the slowing of the exchange process until the coalescence temperature of -25 °C is reached. Below -25 °C, a resonance is observed at the 53 ppm chemical shift previously reported[20] for **2a** along with a second resonance at 37 ppm for **1a**. The **1a** resonance continues to sharpen with decreasing temperature, while the resonance for **2a** is seen to sharpen only to -70 °C and then begins to broaden again. We are currently probing the cause of this second broadening, which may be related to the unexplained variable-temperature NMR spectra that have been reported for solutions of $IrHCl_2(PPr^i_3)_2$ under 1 atm of argon.[17]

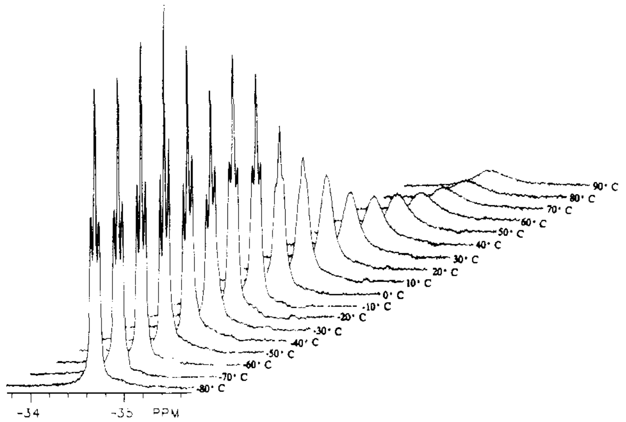

Figure 4. Variable-temperature ^1H NMR spectra (300 MHz) of the hydride region of $IrClH_2(PBu^t_3)_2(H_2)$ (**2c**) dissolved in toluene-d_8 under 0.5 atm of H_2 (total pressure).

Variable-temperature ^1H NMR spectra of the hydride region of a sample of the PCy_3 derivative, **1b**, dissolved in toluene-d_8 under 0.5 atm of H_2, are quite similar to those of the PPr^i_3 derivative. The signals for the metal-bound hydrogen of the dihydride, **2b**, and dihydrogen dihydride complex, **1b**, observed at -32.6 and -12.2 ppm, respectively, coalesce at about 0 °C. A minimum T_1 value of 27 ms (300 MHz) was observed for the **1b** resonance at -50 °C, indicating[10,33,34] the presence of a dihydrogen ligand. Quite different results were obtained for the PBu^t_3 derivative, **2c**. The variable-temperature ^1H NMR spectra of a sample of **2c**, dissolved in toluene-d_8 under 0.5 atm of H_2, are seen in Figure 4. The spectra at all recorded temperatures are seen to contain a resonance for the dihydride, **2c**, at -34.7 ppm but no signal for the metal-bound hydrogens of **1c**. Below -10 °C, the rate of the reversible uptake of H_2 by **2c** is sufficiently slow that P–H coupling ($J = 12$ Hz) can be observed for the hydride resonance along with a resonance at 4.57 ppm for free H_2. Although the hydride resonance is seen to broaden with rising temperature, it has not broadened into coalescence at 90 °C. In order to verify that the observed broadening is due to a **1c**/**2c** equilibrium, samples of **2c** were dissolved in toluene-d_8 both under argon and under 1.0 atm of H_2. The hydride signal in the ^1H NMR spectrum of the sample sealed under argon remained a sharp triplet at -34.7 ppm in the -80 to +80 °C temperature range, clearly demonstrating that the broadening of the signal for the metal-bound hydrogens in the sample sealed under 0.5 atm of H_2 is due to an interaction with hydrogen. The occurrence of a **1c**/**2c** equilibrium process is verified by the ^1H NMR spectrum of the sample of **2c** sealed under 1 atm of H_2 which, below -60 °C, contains a second upfield resonance for the metal-bound hydrogens of **1c** at -13.0 ppm along with the resonance for **2c** at -34.7 ppm. These results show that while the kinetics and thermodynamics of the reversible loss of H_2 from the iridium center are virtually unaffected by the increasing steric constraints between the PPr^i_3 (cone angle 162°) and the PCy_3 (cone angle 170°) complexes, the energetics of this process are sharply affected by the steric bulk of the PBu^t_3 ligands (cone angle 182°).

The interaction of solvents with the unsaturated iridium species seems to have increased steric requirements. Within 24 h of standing at 25 °C, the intensity of the ^1H NMR signals of the metal-bound hydrogens of toluene-d_8, methylene-d_2 chloride, and THF-d_8 solutions **1a** are significantly diminished and signals at the corresponding chemical shift are observed in the ^2H NMR spectra. The same degree of D/H exchange is seen for solutions of **1b** and **1c** only after standing for several weeks at 25 °C.

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(32) The concentrations of free H_2 could not be directly determined from the variable-temperature spectra due to exchange broadening of the signal for free H_2. The temperature dependence of the concentration of H_2 in a sample of toluene-d_8 sealed under 0.5 atm of H_2 was determined by comparison to a TMS internal standard. Since the tube was sealed at a fixed pressure of H_2, lowering the temperature of the tube decreases the H_2 pressure above the solution in accordance with the ideal gas law. As a consequence of this reduced pressure, the concentration of H_2 was found to decrease with decreasing temperature.

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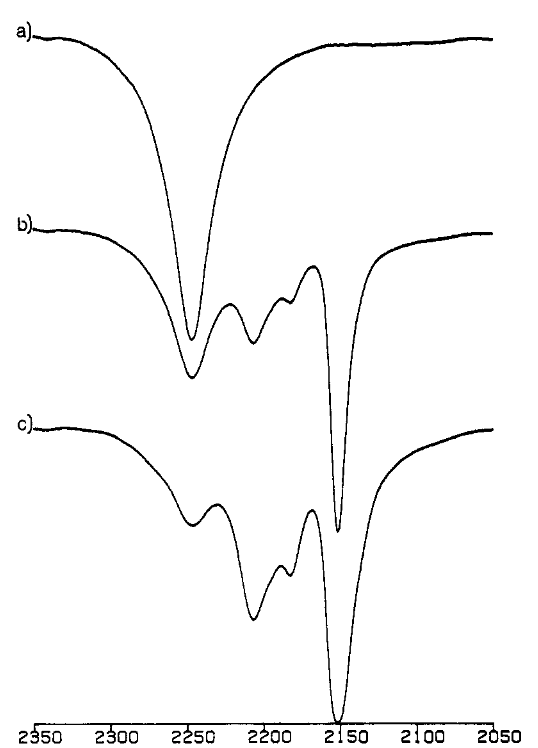

Figure 5. Infrared spectra: (a) $IrClH_2(PPr^i_3)_2$ (**2a**) under 1 atm of argon; (b) $IrClH_2(PPr^i_3)_2$ (**2a**) under 1 atm of H_2 for 1 h; (c) $IrClH_2(PPr^i_3)_2(H_2)$ (**1a**) under 1 atm of H_2.

The closely related pentahydride $IrH_5(PPr^i_3)_2$ is a classical metal hydride complex with highly stabilized metal–hydrogen interactions[38] and no character of a tautomeric complex containing a dihydrogen ligand. Thus, the stabilization of a dihydrogen ligand in our complexes appears to be highly influenced by the presence of the chloride ligand. Conversely, toluene solutions of the dichloro complex $IrHCl_2(PPr^i_3)_2$ have been found[17] to establish an equilibrium with the H_2 adduct $IrHCl_2(PPr^i_3)_2(H_2)$. A variable-temperature NMR study of this equilibrium process indicates a lower stabilization of H_2 in the dichloro vs the monochloro derivative. Clearly, the stabilization of the metal-bound hydrogen decreases with increasing chloride substitution. However, this trend cannot be accounted for simply in terms of the decreasing electron density at the iridium center resulting from substitution of hydride with chloride, since several cationic iridium nonclassical polyhydride complexes have been reported.[26,29] Furthermore, the dihydrogen ligands of the cationic iridium complexes are apparently more stabilized than those of our neutral derivative, as they do not exchange with free H_2 on the NMR time scale. We conclude that the chloride destabilization of the metal–hydrogen interaction is due either to steric constraints or to more subtle electronic interactions.

Solid-State Behavior. The reversible uptake of hydrogen by **2a** in the solid state was studied by Fourier transform infrared spectroscopy. The spectra obtained for **2a** seen in Figure 5 are representative of these studies. A KBr pellet of **2a** was prepared and placed into a gas IR cell under argon. Following evacuation of the cell, an atmosphere of hydrogen was introduced. The absorptions for **1a** at 2207 (w), 2183 (vw), and 2152 (m) cm^{-1} arise while the M–H stretch of **2a** at 2249 cm^{-1} greatly diminishes, as seen in Figure 5b. The rate of this process decreases with time, as diffusion of H_2 into the interior of the KBr pellet is quite slow; however, on prolonged standing, the spectrum becomes nearly identical with that obtained from a KBr pellet of **1a** prepared and maintained under 1 atm of H_2, seen in Figure 5c. This spectrum indicates that the room-temperature **1a**/**2a** equilibrium greatly favors **1a** in the solid state, as only a minor absorption for **2a** at 2249 cm^{-1} is observed. The vigorous release of H_2 which occurs when **1a** is dissolved under 1 atm of H_2 also demonstrates the large shift toward **2a** in solution. The difference between the solution and the solid-state equilibrium position is suggestive of the stabilization of **2a** through solvent interactions.

Figure 6. Infrared spectra of $IrClH_2(PPr^i_3)_2$ (**2a**) under (a) 1 atm of argon and (b) 1 atm of D_2. × = absorption due to $IrClH_5(PPr^i_3)_2$ impurity.

The reaction of **2a** with D_2 was also examined by this method, and isotopically shifted absorptions were seen to arise at 1617, 1585, 1566, and 1545 cm^{-1}, as seen in Figure 6. The appearance of the isotopically shifted M–D stretch for **2a**-d_2 at 1617 cm^{-1} in this experiment clearly establishes that both the reversible binding of hydrogen by **2a** and exchange between the dihydrogen and hydride ligands of **1a** occur in the solid state. This experiment also establishes that the three absorptions which appear in the conversion of **2a** to **1a** are hydrogen-associated. However, only two M–H stretches are predicted by symmetry for **1a**. The possibility that one of the observed absorptions is due to either a H–H or a M–H_2 stretching mode was discarded, as the corresponding absorption for a D–H or M–HD stretching mode for the HD produced in this reaction[39] does not appear in the expected 1840–1750-cm^{-1} range. This result was confirmed in an analogous experiment in which **2a** was reacted with HD; again, no absorption appeared in this region. We believe the additional metal hydride absorption may reflect alternative modes of coordination of the H_2 ligand to the iridium center, i.e., alignment of H_2 both parallel and perpendicular to the P–Ir–P axis or both symmetric η^2 and asymmetric H_2 bonding modes.

The infrared spectrum obtained from a KBr pellet of **1b** prepared and maintained under 1 atm of H_2 was seen to contain absorptions due to the M–H stretches of **1b** at 2180 (w), 2173 (sh, vw), and 2141 (m) cm^{-1} in addition to the M–H absorption of **2b** at 2232 cm^{-1}. Comparison of the relative intensities of the M–H absorptions of **1a** and **2a** with those observed for **1b** and **2b** in equilibrated samples under 1 atm of H_2 indicates that the equilibrium position lies much more toward the dihydrogen complex in the case of the PPr^i_3 derivative. The absence of observed absorptions in the expected[40] 2700–2350-cm^{-1} region in

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the spectra of both **2a** and **2b** eliminates the possibility that the equilibrium position is influenced by agostic C–H–M interactions. The absorptions due to **1b** disappear upon removal of the hydrogen atmosphere by vacuum followed by introduction of an argon atmosphere.

The infrared spectrum of a KBr pellet of **2c** under 1 atm of H_2 was seen to contain only the M–H absorptions of **2c** at 2334 and 2324 cm^{-1}, even upon prolonged standing. The infrared spectrum of a KBr pellet containing the material produced from a sample of **2c** which was dissolved in THF and recrystallized under 1 atm of H_2 was obtained under 1 atm of H_2. Similarly, the spectrum was seen to contain only the M–H absorptions of **2c**. Thus, we obtained no evidence for coordination of H_2 by **2c** in the solid state. As was the case with **2a** and **2b**, no absorptions assignable to agostic C–H stretches were observed, and we conclude that H_2 is excluded from the iridium center due to the steric shielding rather than competitive agostic interactions of the Bu^t groups.

Conclusion

Our solution NMR spectroscopic studies establish there is a threshold to the sensitivity of the kinetics and thermodynamics of the reversible loss of H_2 from our dihydrogen complexes to the steric environment at the iridium center. These studies indicate that the steric constraints are insignificant for the PPr^i_3 and PCy_3 (cone angles 152 and 170°, respectively) derivatives, **1a** and **1b**, but are dominant for the PBu^t (cone angle 182°) derivative, **1c**. The interaction of solvents with the unsaturated iridium species seems to have increased steric requirements, as both **2b** and **2c** appear to have much higher kinetic barriers to this process than **2a**. Reversible solvent coordination may stabilize **2a** in solution, thus accounting for the marked equilibrium shift toward **1a** in the solid state. Our results also demonstrate the pronounced destabilizing influence the chloride ligands have on the iridium–hydrogen interactions in saturated iridium polyhydride complexes.

The elimination of H_2 from our complexes is far more facile than has been generally observed for dihydrogen complexes and thus suggests a much weaker metal–dihydrogen bonding interaction. However, the rate of intramolecular exchange between the dihydrogen and hydride ligands in **1a** is similar to those that have been found for other iridium complexes containing dihydrogen and hydride ligands.[26,29] Thus our studies demonstrate that the strength of the iridium–dihydrogen interaction does not necessarily reflect the degree of activation of dihydrogen ligands in iridium polyhydride complexes.

Acknowledgment. The support of this research by the Solar Energy Research Institute is gratefully acknowledged.

Supplementary Material Available: A figure of variable-temperature ^1H NMR spectra for $IrClH_2(PCy_3)_2(H_2)$ and tables of crystal data, anisotropic thermal parameters, bond distances, bond angles, and hydrogen atom coordinates for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$ (7 pages); a listing of structure factors for $IrClH_2(PPr^i_3)_2(H_2)\cdot C_{10}H_8$ (26 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Biochemistry, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Kinetics and Mechanism of Metal Ion Substitution on a Cobalt(III) Complex Containing a Pendant Phenanthroline

Michael D. Johnson and Robert J. Balahura*

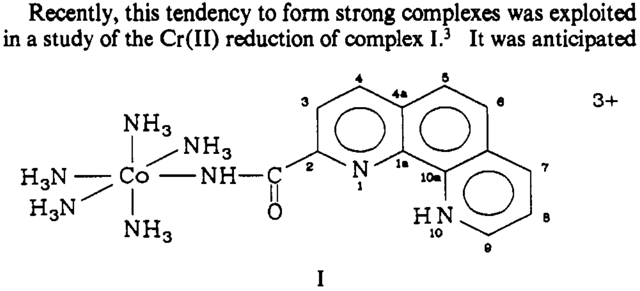
Received August 19, 1991

The kinetics for the substitution of the aqua ions of Fe(II), Co(II), and Ni(II) onto (phenanthroline-2-carboxamide)pentaamminecobalt(III) are reported in this study. For each metal studied, initial coordination occurs at *one* phenanthroline nitrogen and the adjacent carbonyl oxygen. For Co(II) and Ni(II), $k_{obsd} = k_1[M^{2+}] + k_{-1}$ where $k_1 = 980 \pm 70$ and 55 ± 4 M^{-1} s^{-1} and $k_{-1} = 5.8 \pm 0.3$ and 0.23 ± 0.01 s^{-1}, respectively, at 25 °C and $I = 1.0$ M ($LiClO_4$). For Fe(II), $k_{obsd} = k_1[Fe^{2+}] + k_r[H^+]$ where $k_1 = 480 \pm 30$ M^{-1} s^{-1} and $k_r = 525 \pm 40$ M^{-1} s^{-1} at 25 °C and $I = 1.0$ M ($LiClO_4$). Possible mechanisms for these reactions are discussed.

Introduction

During the last 25 years, 1,10-phenanthroline and its derivatives have played an important role in the understanding of both substitution and electron-transfer reactions of metal ion complexes.(1,2) One of the most important aspects of this ligand is the "inertness" it provides to otherwise labile metal ions, such as Cr(II) and Co(II), by binding strongly to these metals. This has allowed for a more complete study of their redox reactions.

Recently, this tendency to form strong complexes was exploited in a study of the Cr(II) reduction of complex I.(3) It was anticipated that the reductant would be strongly bound by the ligand and that the substitution and redox steps could be separated. Although saturation behavior was exhibited in this reaction, no hydrogen ion dependence was found as would be expected if Cr(II) were bound by *both* phenanthroline nitrogens before electron transfer. The authors were forced to conclude that the Cr(II) transferred its electron while bound to the carbonyl oxygen and one phenanthroline nitrogen. The subsequent Cr(III) complex then rearranged to give the final Cr(III) phenanthroline product with both nitrogens coordinated. This unexpected coordination behavior requires that protonation on the phenanthroline ligand be at the remote nitrogen as shown in I.



I

In order to explore the generality of this unusual binding step involving one phenanthroline nitrogen and the adjacent carbonyl oxygen, the substitution reactions of several redox-inert metals with complex I were studied. The results with the aqua ions of iron(II), cobalt(II), and nickel(II) are reported here.

Experimental Section

The cobalt(III) phenanthrolinecarboxamide complex(3) (I) and cobalt(III) pyridinecarboxamide,(4) $[(NH_3)_5CoNHCOpyH](ClO_4)_3$, com-

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