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Activation of Hydrogen on Iridium(I) Centers in Water: Solvent Effects, pH Effects, and Iridium−Hydride Exchange with D_2O

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The water-soluble iridium complexes *trans*-$Ir(CO)L_2X$ (X = Cl, OH; L = $PPh_2(m\text{-}C_6H_4SO_3K)$ (TPPMS), $P(m\text{-}C_6H_4SO_3Na)_3$ (TPPTS)) have been used to extend the range of solvent effect for H_2 activation at an iridium(I) center and to examine the effect of pH changes on the rate of H_2 addition to an organometallic center. Hydrogen adds to the square-planar iridium(I) complexes in H_2O and DMSO to give products analogous to those for *trans*-$Ir(CO)(Cl)(PPh_3)_2$ in organic solvents. The kinetic deuterium isotope effect, $k_H/k_D = 1.1$ (L = TPPMS) and 1.2 (L = TPPTS), for addition of H_2 to *trans*-$Ir(CO)(Cl)L_2$ in water is the same as that observed for *trans*-$Ir(CO)(Cl)(PPh_3)_2$ in toluene and indicates a common mechanism. More polar solvents accelerate the rate of H_2 addition to *trans*-$Ir(CO)(Cl)L_2$, indicating polarity in the transition state. Increasing the pH causes a decrease in the rate of H_2 addition for *trans*-$Ir(CO)(Cl)(TPPMS)_2$ and *trans*-$Ir(CO)(Cl)(TPPTS)_2$ in water. This pH effect, coupled with a shift of ν_{CO} to higher frequency in water, is ascribed to protonation/hydrogen bonding to the iridium center. The hydride ligands undergo H/D exchange with D_2O in a process that is quite dependent on the *trans* ligand.

Activation of hydrogen on transition metals is of importance to many catalytic reactions. From the early studies of activation of H_2 by metal ions[1] to the recent interest in molecular hydrogen complexes,[2] much effort has been devoted to understanding the interaction of hydrogen with metal complexes. The earlier studies on activation of H_2 by coordination complexes or ions in aqueous solution indicated a heterolytic cleavage mechanism.[1] Detailed studies on complexes such as *trans*-$Ir(CO)(Cl)(PPh_3)_2$ in organic solvents indicated a side-bound H_2 with very little H−H bond weakening in the transition state.[3−6] Molecular hydrogen complexes may provide a model for such transition states.[2] Different mechanisms for H_2 activation in water and in organic solvents remain as dogma.

The stereochemistry of H_2 oxidative addition has been carefully studied. The hydrides are always *cis* (prior to isomerization). For *trans*-$Ir(CO)(X)L_2$ complexes Crabtree coined the term "parallel" for addition in the X−Ir−CO plane and "perpendicular" for addition in the L-Ir-L plane.[7] Theoretical studies indicate that weak-donors (X = Cl) favor parallel addition while strong donors (X = Me, Ph) favor perpendicular addition.[8]

Despite the many studies of H_2 activation on metal complexes, fundamental questions remain unanswered, especially regarding the new research on catalysis by organometallic complexes in water.[9] Examples are as follows. (1) What effect does wide variation in solvent have on hydrogen activation? (2) What is the effect of pH on H_2 activation by organometallic complexes? (3) What are the rates for metal hydride exchange with D_2O? Investigations of general solvent effects have been limited by the lack of solubility of coordination complexes in nonaqueous solvents and of organometallic complexes in polar solvents.[1,3] We recently communicated the use of *trans*-$Ir(CO)(Cl)(PPh_3)_2$ in organic solvents and *trans*-$Ir(CO)(Cl)(TPPMS)_2$ (TPPMS = $PPh_2(m\text{-}C_6H_4SO_3K)$) in DMSO and H_2O to generalize the solvent effect.[10] We now expand the study of H_2 activation on iridium to include *trans*-$Ir(CO)(Cl)(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$), the effect of pH changes, and examples of Ir−H exchange with D_2O.

Experimental Section

Materials. $IrCl_3\cdot 3H_2O$ was purchased or borrowed from Johnson Matthey. Triphenylphosphine, fuming sulfuric acid (20% and 30% SO_3), *n*-octylamine, benzyltriethylammonium chloride, and trifluoroacetic acid were purchased from Aldrich Chemical Co. Deuterated solvents were purchased from

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Cambridge Isotope Labs, Aldrich Chemical Co., or MSD Labs. Gases (CO, H_2) were purchased from Matheson. All of these materials were used as received without further purification unless otherwise noted. The compounds *trans*-Ir(CO)(Cl)-$(PPh_3)_2$,[11] *trans*-Ir(CO)(OH)$(PPh_3)_2$,[12] *trans*-Ir(CO)(Cl)-$(TPPMS)_2$,[13] and *trans*-Ir(CO)(OH)$(TPPMS)_2$[13] were prepared as previously described. Solvents used outside of the glovebox were used as received without further drying or purification unless otherwise noted. The water used was triply distilled and deionized. Solvents used within the glovebox were dried by standard techniques.

Instrumental Measurements. ^{1}H and ^{31}P NMR spectra were recorded using a Varian VXR-400 NMR spectrometer. ^{1}H NMR spectra were referenced to residual solvent peaks. All ^{1}H NMR spectra contained resonances corresponding to aromatic protons; however, these resonances were not assigned. ^{31}P NMR spectra were referenced to an external sample of 85% H_3PO_4 in D_2O (reference was set to 0.0 ppm) and were proton-decoupled. Spectra recorded in H_2O used a sealed capillary with D_2O for the lock. All chemical shifts (δ) are reported in ppm, and all coupling constants (J) are reported in Hz.

Infrared spectra were obtained using a Mattson Polaris Fourier transform or a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Solution spectra were recorded using a 0.5 mm NaCl or 0.1 mm CaF_2 (used for spectra obtained in DMSO, 2-methoxyethanol, and water) solution cells. Solid-state spectra were recorded as KBr disks. All spectral data are reported in wavenumbers (cm^{-1}).

All pH measurements were made with a Fischer Scientific Accumet pH meter utilizing a glass pH electrode with a silver/silver chloride reference electrode. The pH meter was referenced to three buffers (pH 4, 7, 10) before all measurements.

Synthesis. *trans*-Ir(CO)(Cl)$(TPPTS)_2$. In the glovebox, a 100 mL Schlenk flask equipped with a stirbar was loaded with 0.100 g (0.149 mmol) of $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) and 0.371 g (0.595 mmol) of TPPTS. The Schlenk flask was sealed and removed from the glovebox.

On the Schlenk line 40 mL of deareated methanol was added to the flask. The resulting deep red solution was stirred overnight under a $N_2(g)$ atmosphere. The flask was then flushed with CO(g) for 15 min. The solution turned colorless. The CO atmosphere was removed by flushing the flask with N_2 for 15 min. The flask was sealed under a N_2 atmosphere and stirred overnight. Overnight a yellow precipitate formed. The flask was taken into the glovebox.

The yellow precipitate was collected on a medium-porosity sintered-glass frit, giving 0.315 g of material corresponding to a 70% yield based on the starting iridium complex. An infrared spectrum obtained as a KBr pellet showed a single absorbance in the carbonyl stretching region at 1962 cm^{-1}. The infrared spectrum of a H_2O solution of the product contained an absorbance at 1982 cm^{-1}, which was assigned as the carbonyl stretching frequency. A ^{31}P NMR spectrum obtained using d_6-DMSO as the solvent contained a single resonance at δ 27.5 (s) ppm. The D_2O spectrum contained a single resonance at δ 27 (br, s) ppm.

Elemental analysis was performed using the unpurified product and the observed mass percentages follow. Anal. Found (calcd) for Ir(CO)Cl$(TPPTS\text{-}Na_3{\cdot}3H_2O)_2$: C, 29.94 (29.62); H, 2.42 (2.21); P, 4.36 (4.13); Cl, 2.36 (2.50).

Kinetic Studies. Stock solutions of the following complexes were prepared in 25.00 mL volumetric flasks: 1.35×10^{-3} M *trans*-Ir(Cl)(CO)$(PPh_3)_2$ in toluene, 3.79×10^{-4} M *trans*-Ir(Cl)(CO)$(PPh_3)_2$ in DMSO, 2.76×10^{-4} M *trans*-Ir(Cl)(CO)-$(TPPMS)_2$ in DMSO, 3.09×10^{-4} M *trans*-Ir(Cl)(CO)$(TPPMS)_2$ in water, and 2.7×10^{-4} M *trans*-Ir(Cl)(CO)$(TPPTS)_2$ in water. The stock metal solutions were transferred into separate 50 mL Schlenk flasks, which were sealed. When the H_2-saturated solutions were prepared, a 5 mL Hamilton syringe was used to deliver a 3.8 mL aliquot into a quartz cuvette containing a nitrogen atmosphere. The H_2-saturated solution was then mixed with a 200 μL aliquot of the stock metal solution with a 250 μL Hamilton syringe. The cuvette was immediately sealed, and changes in the absorption of the strongest charge-transfer band (388 nm for PPh_3 in toluene, 386 nm for PPh_3 in DMSO, 386 nm for TPPMS in DMSO, 378 nm for TPPMS in H_2O, and 378 nm for TPPTS in H_2O) were monitored as a function of time for at least 5 half-lives. Since oxidative addition of H_2 to these metal complexes was a second-order process, pseudo-first-order conditions were employed. The initial concentration of dissolved H_2 was varied while maintaining at least a 10-fold excess in $[H_2]$.[14−17] The H_2 solutions were prepared under reduced H_2 pressures via high-vacuum techniques. This technique employed, first, a 10 min pump-down to degas the solvent. Hydrogen was then introduced through the Schlenk inlet valve. After three back-filling cycles, the inlet valve was sealed with a rubber septum and the H_2 pressure was adjusted. The solvent was then stirred vigorously for 20 min with a magnetic stirbar to allow the system to equilibrate. Next, the height of the mercury was recorded and a 3.8 mL aliquot of the H_2 solution was removed through the sealed inlet valve via a 5 mL Hamilton syringe. The aliquot was quickly delivered into the quartz cuvette and mixed with 200 μL of stock metal solution, and the appropriate charge transfer band's absorption changes were monitored as a function of time for at least 5 half-lives.

Table 1. Characterization Data for Ir(CO)(Cl)$(H)_2L_2$ (L = PPh_3, TPPMS, TPPTS)

technique	PPh_3	TPPMS	TPPTS
ν_{CO}, cm^{-1}	1978[a]	1990[b]	2014[c]
ν_{Ir-H}, cm^{-1}	2103 (s), 2191 (w)[a]	2093 (s), 2204 (w)[b]	2095[c]
^{1}H NMR, ppm	−7.3 (td), −18.6 (td)[d]	−8.3 (td), −20.4 (td)[e]	−7.8 (td), −19.4 (td)[c]
^{31}P NMR, ppm	7.6[d]	11.6[e]	14.3[f]

[a] Toluene. [b] DMSO. [c] H_2O. [d] For P(p-tolyl)$_3$ analogue in CD_2Cl_2. [e] d_6-DMSO. [f] D_2O.

Similar techniques were used to examine the rates with D_2, in the presence of KCl and in the presence of excess ligand.

The effect of pH on the rates was examined by using appropriate amounts of 0.1 M phosphate solutions (H_3PO_4, NaH_2PO_4, and Na_2HPO_4) to achieve the desired pH. The buffer solutions of known pH were then saturated with H_2 (740 mm at 21 °C). The procedure described above was accomplished for solutions of pH from 3.5 to 9.0.

Results and Discussion

Reaction of H_2 with iridium(I) complexes in organic solvents has been carefully investigated in terms of stereochemistry, rate law, and steric and electronic effects.[3−8] Reaction of H_2 with *trans*-Ir(CO)(Cl)$(PPh_3)_2$ leads to hydrides *trans* to CO and Cl (parallel)[7] in the product Ir(CO)(Cl)$(H)_2(PPh_3)_2$. Reaction of H_2 with the TPPMS or TPPTS analogues *trans*-Ir(CO)(Cl)L_2 in DMSO produces the analogous dihydride; the characterization data are shown in Table 1. In H_2O the reactions are not as clean; the reaction of *trans*-Ir(CO)-

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[14] The $[H_2]$ in each solvent is calculated from the mole fraction solubility, assuming that Henry's law applies for pressures <1 atm. The solubilities in H_2O,[15] DMSO,[16] and toluene[17] are literature values. In H_2O at 1 atm of H_2 the solubility is $\sim 7 \times 10^{-4}$ M.

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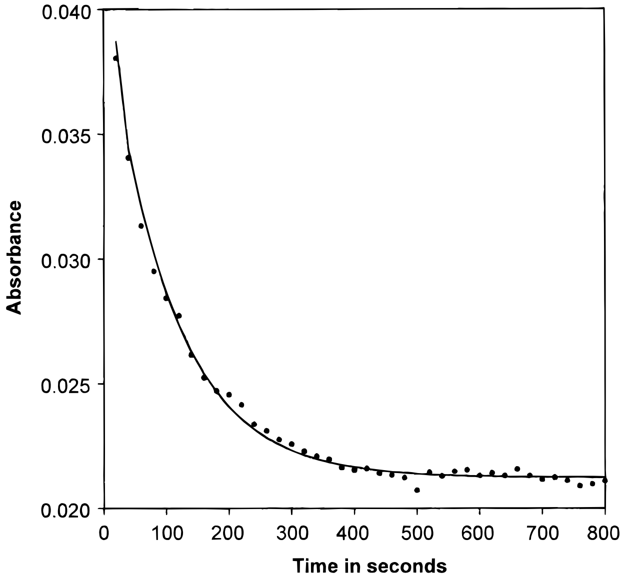

Figure 1. Decrease in absorbance at 374 nm for reaction of 1.3×10^{-5} M *trans*-Ir(CO)(Cl)(TPPMS)$_2$ with H_2 (7.4×10^{-4} M) in H_2O at 21°C.

(Cl)(TPPTS) with H_2 is shown below:

$$trans\text{-Ir(CO)(Cl)L}_2 \xrightarrow[H_2O]{H_2} \text{Ir(CO)(Cl)(H)}_2\text{L}_2 + \text{Ir(CO)(H}_2\text{O)(H)}_2\text{L}_2^{+} + \text{Cl}^- + \text{Ir(CO)(H)}_3\text{L}_2 \text{ (trace)}$$

$$L = \text{TPPTS}$$

In the presence of a large (100×) excess of Cl^- the formation of aquo complex is prevented, and only Ir(CO)(Cl)(H)$_2$L$_2$ is observed. In the absence of added Cl^-, Ir(CO)(H)$_3$L$_2$ and Ir(CO)(H)$_2$L$_3^+$ are observed at longer times.

Kinetic Studies. Kinetics of H_2 addition to *trans*-Ir(CO)(X)L$_2$ are well understood.[3-5] The rate law

$$\text{rate} = k[trans\text{-Ir(CO)(X)L}_2][\text{H}_2]$$

shows a dependence on [Ir(I)] and on [H_2]. Small changes in the phosphine ligand, i.e. PPh$_3$, P(*p*-tolyl)$_3$, and P(*p*-C$_6$H$_4$OMe)$_3$, result in small changes in the second-order rate constant, while change to PCy$_3$ causes dramatic slowing in the rate.[3] The complexes *trans*-Ir(CO)(Cl)(TPPMS)$_2$ and *trans*-Ir(CO)(Cl)(TPPTS)$_2$ show well-behaved kinetics for reaction with H_2. A sample of the absorbance decrease is shown in Figure 1. Plots of the pseudo-first-order rate constant versus [H_2] are shown in Figure 2. The second-order-rate constant is obtained as the slope of these plots. Table 2 gives the rate constants determined in this study. For DMSO where *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ and *trans*-Ir(CO)(Cl)(TPPMS)$_2$ can both be examined, the rate constants are nearly identical (1.2 ± 0.2 and 1.3 ± 0.2 s^{-1} M^{-1}, respectively), indicating the sulfonation has very little effect on the rate of reaction with H_2. Similarly, the rate for the TPPMS complex is very similar to that for the TPPTS complex in H_2O, 12 ± 2 and 14 ± 1 s^{-1} M^{-1}, respectively. Both comparisons indicate that the amount of sulfonation of the phenyl ring does not significantly affect the rate of reaction of *trans*-Ir(CO)(Cl)L$_2$ with H_2.

The kinetic deuterium isotope effect evaluated for *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ in toluene is 1.1.[5] For *trans*-Ir(CO)(Cl)(TPPMS)$_2$ in H_2O the value is also 1.1, and for *trans*-Ir(CO)(Cl)(TPPTS)$_2$ the value is 1.2; the rate constants are shown in Table 2. The similarity in kinetic deuterium isotope effects indicates a common mechanism. A value near 1 is frequently interpreted as an early transition state.[3] Theoretical studies indicate a transition state that has about 5% H−H bond lengthening with H−H distances of 0.777, 0.766, and 0.759 Å for the chloro, bromo, and iodo complexes and kinetic isotope effect (KIE) values of 1.19, 1.28, and 1.32, respectively.[6] The value for the H−H distance in molecular hydrogen complexes is about 0.8 Å;[2] thus, molecular hydrogen complexes provide a good model for the transition state in H_2 oxidative addition on Ir(I).

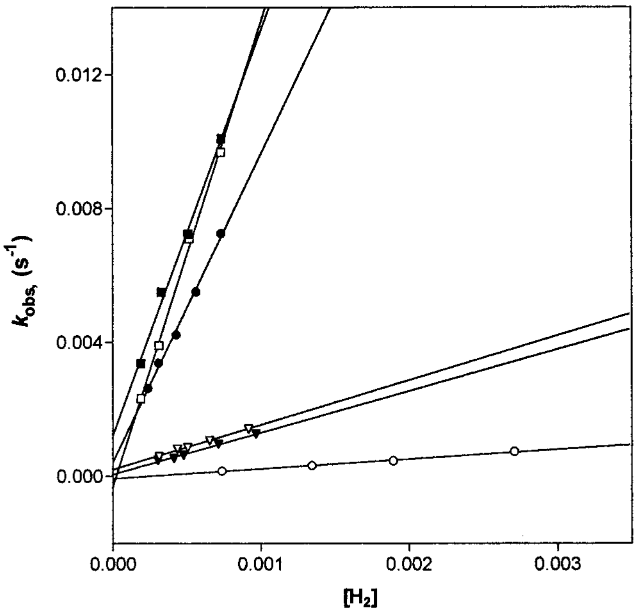

Figure 2. Plots of k_{obs} versus [H_2] for reactions of iridium(I) complexes at 21°C: (■), *trans*-Ir(CO)(Cl)(TPPMS)$_2$ in H_2O; (□), *trans*-Ir(CO)(Cl)(TPPTS)$_2$ in H_2O; (●), [*trans*-Ir(CO)(H_2O)(TPPTS)$_2$]$^+$ in H_2O; (▽), *trans*-Ir(CO)(Cl)(TPPMS)$_2$ in DMSO; (▼), *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ in DMSO; (○), *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ in toluene.

Table 2. Second-Order Rate Constants for Reaction of *trans*-Ir(CO)(Cl)L$_2$ with H_2

L	solvent	k (s^{-1} M^{-1})
PPh$_3$	toluene	0.29 ± 0.07
PPh$_3$	DMSO	1.2 ± 0.2
TPPMS	DMSO	1.3 ± 0.2
TPPMS	water	12 ± 2
TPPMS[a]	water	11 ± 2
TPPMS[b]	water	fast
TPPTS	water	14 ± 1
TPPTS[a]	water	12 ± 1
TPPTS[c]	water	9.2 ± 1

[a] Reaction with D_2. [b] For [Ir(CO)(TPPMS)$_3$]$^+$. [c] For [*trans*-Ir(CO)(H_2O)(L)$_2$]$^+$.

Previous rate studies on *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ indicated an increase in rate with increasing solvent polarity[3] but were limited by the solubility of *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$. The similarity in rate for *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ and for *trans*-Ir(CO)(Cl)(TPPMS)$_2$ in DMSO offers the possibility of extending the solvent effect on hydrogenation to more polar solvents, including H_2O. Hydrogen is considerably less soluble in H_2O than in organic solvents,[17] and this is accommodated in the plots shown in Figure 2, where the actual [H_2] in molarity is used. A number of parameters have been developed to

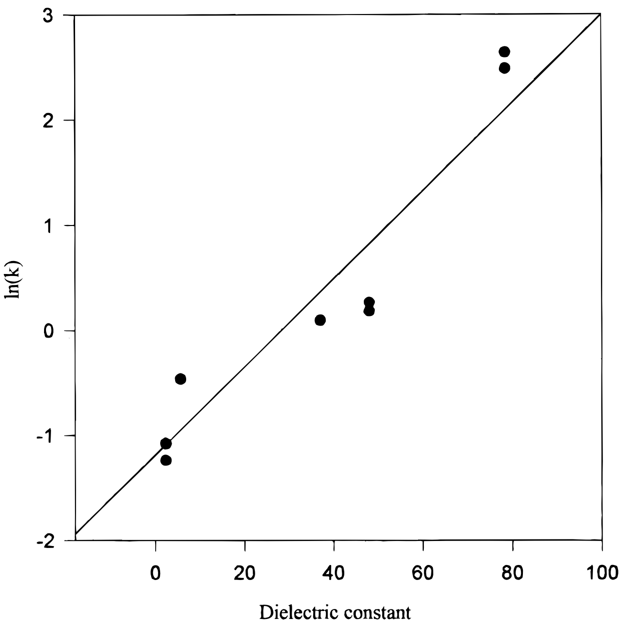

Figure 3. Plot of ln *k* for reaction of iridium(I) complexes with H_2 in various solvents versus dielectric constant.

Table 3. Rate Constants for *trans*-Ir(CO)(Cl)L_2 Reacting with H_2 versus Solvent Parameters

L	solvent	k (s^{-1} M^{-1})	ϵ	E_T
PPh_3[a]	toluene	0.34	2.4	33.9
PPh_3	toluene	0.29	2.4	33.9
PPh_3[a]	C_6H_5Cl	0.63	5.7	37.5
PPh_3[a]	DMF	1.1	37	43.8
PPh_3	DMSO	1.2	48	45
TPPMS	DMSO	1.3	48	45
TPPMS	H_2O	12.0	78.5	63.1
TPPTS	H_2O	14.0	78.5	63.1

[a] Reference 3.

measure solvation abilities.[18] The most commonly used is dielectric constant; a plot of ln *k* versus dielectric constant is shown in Figure 3. The plot shows an increase in rate with increasing dielectric constant. A much more linear plot is obtained by using E_T values, which measure the transition energy for the charge transfer band of pyridinium *N*-phenolbetaine, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinato)phenolate. The values for rate constants, dielectric constants, and E_T values are shown in Table 3, and a plot of ln *k* versus E_T is shown in Figure 4. The linear plots of ln *k* versus solvent parameter suggest a common mechanism unchanged by the nature of the solvent. The earlier study suggested that the six-coordinate dihydride was more polar than the square-planar starting complex.[3] If the transition state is very early with only about 5% H−H bond lengthening, the six-coordinate dihydride is a very poor model of the transition state.

Acceleration of hydrogenation rates in polar solvents has been observed in systems as disparate as Cu(II) salts,[19] $Co(CN)_5H^{3-}$,[20] and $Rh(Cl)(PPh_3)_3$.[21] While the range of solvents examined in these studies is not as wide as that reported in this paper, the rate enhancements with more polar solvents are comparable in

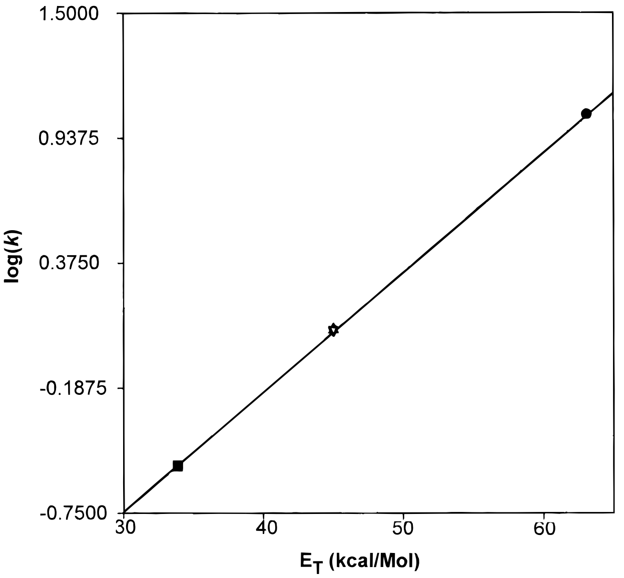

Figure 4. Plot of ln *k* for reaction of iridium(I) complexes with H_2 in various solvents versus E_T:[15] (■), *trans*-Ir(CO)(Cl)$(PPh_3)_2$ in toluene; (▽), *trans*-Ir(CO)(Cl)$(TPPMS)_2$ in DMSO; (▲), *trans*-Ir(CO)(Cl)$(PPh_3)_2$ in DMSO; (●), *trans*-Ir(CO)(Cl)$(TPPMS)_2$ in H_2O.

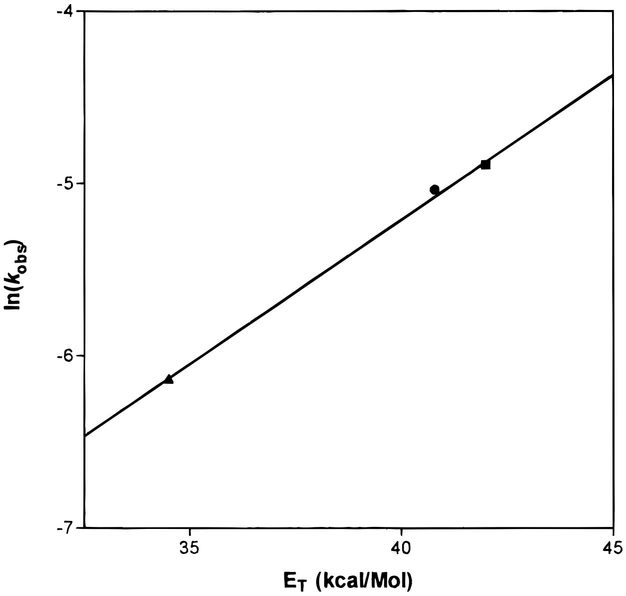

Figure 5. Plot of ln *k* for hydrogenation of 1-methylcyclohexene:[18b] (▲) in benzene; (●) in cyclohexanone; (■) in nitrobenzene.

magnitude. Excluding chlorinated solvents which are reported to react with the dihydride, the rate constants for hydrogenation with $Rh(Cl)(PPh_3)_3$ correlate well with the E_T values for three different solvents (Figure 5). Very different rationales have been offered for the increasing hydrogenation with solvent polarity in the different systems;[19−21] however, the similarities in magnitude and order may indicate a common explanation. For the Cu(II) salts a heterolytic cleavage of H_2 was suggested;[19] this would not be consistent with the small isotope effect[5] and calculations that indicate a side-bound H_2 with little H−H bond breaking for addition of H_2 to Ir(I).[6,8] If a common explanation exists for the solvent effect observed for Cu(II), $Co(CN)_5H^{3-}$, $Rh(Cl)(PPh_3)_3$, and *trans*-Ir(CO)(Cl)L_2, it must arise

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from an increase in polarity in a molecular-hydrogen-like transition state. The initial interaction is from donation of the H−H σ bond density to the metal.[2] This could create positive charge on the hydrogen atoms before donation from the metal to the hydrogen atoms gives more hydridic character and weakens, or breaks, the hydrogen−hydrogen bond. Stabilization of the initial positive charge on the hydrogen molecule could account for the solvent effect.

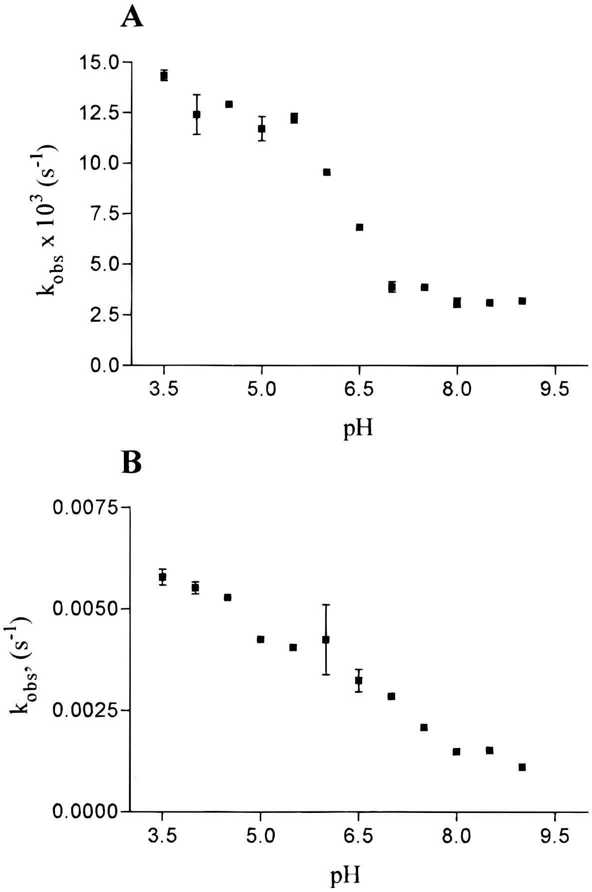

Figure 6. Effect of pH on rate constants for reaction of H_2 (1 atm) with *trans*-Ir(CO)(Cl)(TPPMS)$_2$ in H_2O: (A) reaction of 1.29×10^{-5} M *trans*-Ir(CO)(Cl)(TPPMS)$_2$ over 736 mm of H_2 pressure. (B) reaction of 1.23×10^{-5} M *trans*-Ir(CO)(Cl)(TPPTS)$_2$ over 744 mm of H_2 pressure. Note: the pH error limit was ±0.02.

Figure 6 shows the effect of pH on the rate constant for addition of H_2 to *trans*-Ir(CO)(Cl)(TPPMS)$_2$. A relatively small effect is observed as pH is increased until pH 6, where a decrease (a factor of ~3) occurs. Similar pH dependences have been observed for copper complexes such as $Cu(en)_2^{2+}$ [22] (en = ethylenediamine), where the effect was attributed to protonation of en. The pH dependence shown in Figure 6 indicates activation of the iridium center by protonation. There are three sites on the iridium where protonation could occur. Protonation of the sulfonate would be quite likely, but occurs at much lower pH's. Also, given the unchanged reactivity between *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$, *trans*-Ir(CO)(Cl)(TPPMS)$_2$, and *trans*-Ir(CO)(Cl)(TPPTS)$_2$ toward H_2 in a common solvent, protonation of the sulfonate would be unlikely to affect reaction with H_2. The chloride and the iridium offer the other two sites for protonation. Reaction of *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ with Lewis acids such as BF_3 and Ag^+ show the pair of electrons on the *z* axis of iridium to be more susceptible to attack.[23,24] Such adducts have ν_{CO} above 2050 cm^{-1}. The effect of pH on the ν_{CO} of Ir(CO)(Cl)(TPPTS)$_2$ is shown in Figure 7. At pH 4 only a small absorption is present at 2060 cm^{-1}; however, at pH 1 the protonated form is present in nearly equal amounts to *trans*-Ir(CO)(Cl)(TPPTS)$_2$. By removal of some electron density from the iridium (shown by the increase for ν_{CO}) the electron donation from H_2 to the iridium center may be facilitated, lowering the transition state energy. Regardless of the explanation, the ability to enhance hydrogenation by a factor of 3 by reducing the pH from 7 to 4 may be important in catalytic reactions that occur in water.

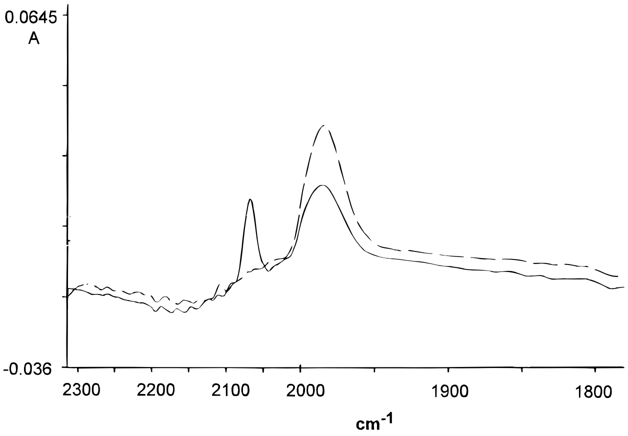

Figure 7. Infrared spectra (ν_{CO}) of *trans*-Ir(Cl)(CO)(TPPTS)$_2$ at pH 1 (solid line) and pH 4 (dashed line).

A phenomenon that may be related is the change in infrared stretching frequency for the CO ligand of square-planar iridium complexes in water compared to aprotic solvents. The ν_{CO} values for *trans*-Ir(CO)(X)L$_2$ in organic solvents (L = PPh$_3$), DMSO (L = TPPMS, TPPTS), and KBr (L = PPh$_3$, TPPMS, TPPTS) are nearly identical. For example for X = Cl all are 1962 ± 2 cm^{-1}. However, in water the ν_{CO} values are 1983 and 1985 cm^{-1} for L = TPPMS and TPPTS, respectively. This ~20 cm^{-1} blue shift is only observed for square-planar complexes—for Ir(CO)(H)L$_3$ ν_{CO} is 1928 ± 4 cm^{-1} for all three ligands in organic solution, aqueous solution, and the solid state. Further, the magnitude of shift is not strongly affected by the nature of X in *trans*-Ir(CO)L$_2$X. For X = Cl and OH the blue shift is 20 cm^{-1} in water. The probable source of this blue shift is hydrogen bonding to the pair of electrons in the *z* axis in the square-planar complex. The BF_3 adduct of *trans*-Ir(CO)(Cl)(PPh$_3$)$_2$ and the nucleophilic character of the square-planar iridium center in many reactions indicate the accessibility of the electron density on the *z* axis. Such hydrogen bonding would decrease the electron density at the iridium center and blue-shift the ν_{CO}. The BF_3 adduct has ν_{CO} 2063 cm^{-1}.[23] Thus, both the increase in rate for H_2 addition at lower pH and the blue shift of ν_{CO} for square-planar iridium complexes could arise from a protonation/hydrogen bonding interaction with the square-planar iridium center. Hydrogen-bonding interactions with square-planar platinum(II)

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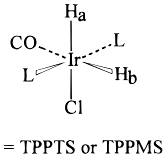

L = TPPTS or TPPMS

Figure 8. Geometry of Ir(CO)(Cl)(H)$_2$(TPPTS)$_2$.

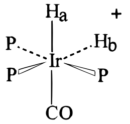

Figure 9. Geometry of Ir(CO)(H)$_2$P$_3^+$ (P = TPPMS, TPPTS).

complexes were previously demonstrated, including a neutron diffraction study.[25]

Deuterium/Hydrogen Exchange. The dihydrides formed by reaction of H_2 with *trans*-Ir(CO)(Cl)L$_2$ (L = TPPMS, TPPTS) have inequivalent hydrides and provide an excellent opportunity to examine exchange between Ir−H and D_2O. Both complexes behave similarly; the TPPTS complex can serve as an example. The geometry of the dihydride is shown in Figure 8. H_a is *trans* to chloride, and its ^{1}H NMR resonance is observed at −18 ppm; H_b is *trans* to CO and is observed at −7 ppm. When Ir(CO)(Cl)(H)$_2$(TPPTS)$_2$ is dissolved in D_2O under N_2, both hydrides slowly exchange with D_2O, H_a with a half-life of 20 h and H_b with a half-life of 40 h. It is interesting that the hydride with the more shielded chemical shift would undergo more rapid exchange with D_2O, a process that must occur as a proton. Similar behavior is seen for Ir(CO)(H)$_2$L$_3^+$ (L = TPPMS, TPPTS), whose geometry is shown in Figure 9. H_b (*trans* to phosphine ligand) exchanges very rapidly, while H_a (*trans* to CO) exchanges slowly. At this point insufficient data exist to interpret these Ir−H, D_2O exchanges, but considerable insight into metal hydrides may be obtained from further study.

Mechanism. The studies reported in this paper provide a clear description of the mechanism for H_2 activation by *trans*-Ir(CO)(Cl)L$_2$ (L = TPPTS, TPPMS). The shift of ν_{CO} to higher frequencies for *trans*-Ir(CO)(Cl)L$_2$ in water and the pH effect on hydrogenation rate indicate that *trans*-Ir(CO)(Cl)L$_2$ exists as a protonated/hydrogen-bonded species, probably to the iridium center. By removal of some electron density from the iridium, the interaction with H_2 is enhanced. The transition state involves very little H−H bond breaking but is polar through positive charge created on H_2 by donation of the H_2 σ-electron density to the iridium center. There is no effect on the rate from adding Cl$^-$ or L; further, *trans*-Ir(CO)(H$_2$O)L$_2^+$ adds H_2 more slowly. Thus, there appears to be no ligand dissociation from iridium prior to the H_2 addition.

The molecular-hydrogen-like transition state rearranges to *cis,trans*-Ir(CO)(Cl)(H)$_2$L$_2$, shown in Figure 8. In the dihydride Cl$^-$ dissociation occurs very readily, producing Ir(CO)(H$_2$O)(H)$_2$L$_2^+$ in an approximate 1:1 ratio with Ir(CO)(Cl)(H)$_2$L$_2$. In the presence of excess Cl$^-$ no further reaction occurs and Ir(CO)(Cl)(H)$_2$L$_2$ is stable. The aquo complex slowly undergoes further reaction with H_2 to Ir(CO)(H)$_3$L$_2$[26] and a proton or with L to form Ir(CO)(H)$_2$L$_3^+$. The reaction sequence is

$$\textit{trans}\text{-Ir(CO)(Cl)L}_2 + \text{H}_2 \rightarrow \text{Ir(CO)(Cl)(H)}_2\text{L}_2 \xrightarrow[+\text{H}_2\text{O}]{-\text{Cl}} \text{Ir(CO)(H}_2\text{O)(H)}_2\text{L}_2^{\;+}$$

$$\text{Ir(CO)(H}_2\text{O)(H)}_2\text{L}_2^{\;+} \xrightarrow[-\text{H}^+]{\text{H}_2} \text{Ir(CO)(H)}_3\text{L}_2 \xrightarrow{\text{L}} \text{Ir(CO)(H)}_2\text{L}_3^{\;+}$$

The HCl elimination producing Ir(CO)(H)$_3$L$_2$ is not a typical reductive elimination but is Cl$^-$ dissociation with subsequent deprotonation of the iridium.

Conclusion

A combination of spectroscopic and kinetic studies have shown H_2 additions to iridium(I) centers to have a common mechanism in solvents ranging from toluene to water. This mechanism is characterized by an early transition state, for which molecular hydrogen complexes are good models. In water Ir−H/D_2O exchange is observed, with the rate varying significantly with the *trans* ligand. Cl$^-$ dissociation is also facilitated by water. The solvent effect for H_2 activation on Ir(CO)(Cl)L$_2$ is characterized for a broader range of solvents but is in an order commonly observed.

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