Substitution of η^2-Dihydrogen by Toluene and Alkanes in $IrXH_2(H_2)(PPr^i_3)_2$ Complexes

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The energetics of the reversible dissociation of coordinated dihydrogen have been explored in several recent studies.[1−3] The equilibrium position between the dihydrogen complexes, $IrXH_2(H_2)(PR_3)_2$ (X = halide) and the resulting five-coordinate, $IrXH_2(PR_3)_2$ complexes has been found to be sensitive to the steric[4] and electronic[2,3] environment at the metal center. It has been suggested that σ-donor strength of the halide (electronegativity of the halogen) perturbs the electronic environment at the metal center thus effecting the stabilization of the dihydrogen ligand and the equilibrium position.[2] Alternatively, it has been proposed that the equilibrium position is dictated by the amount of halide π-donation stabilization of the five-coordinate complexes.[3] However, the influence of solvent interaction with the five-coordinate complexes has not been considered.

We have found that the equilibrium position is highly solvent dependent. It has also been observed that hydrogen is liberated with vigorous effervescence when solid samples of $IrXH_2(H_2)(PPr^i_3)_2$, X = Cl (**1**), Br (**2**), I (**3**), are dissolved in hydrocarbons. These observations suggest that the five-coordinate complexes establish a rapid equilibrium with solvent coordinated complexes in conjunction with the relatively slow equilibrium with the dihydrogen complex as seen in Scheme 1. In order to explore this possibility, we have carried out variable temperature ^1H NMR spectroscopic studies of equilibrated solutions of **1**, **2**, and **3** and the corresponding five-coordinate complexes, $IrXH_2(PPr^i_3)_2$, X = Cl (**4**), Br (**5**), I (**6**), in toluene-d_8, methylcyclohexane-d_{14}, and *n*-hexane-d_{14}.

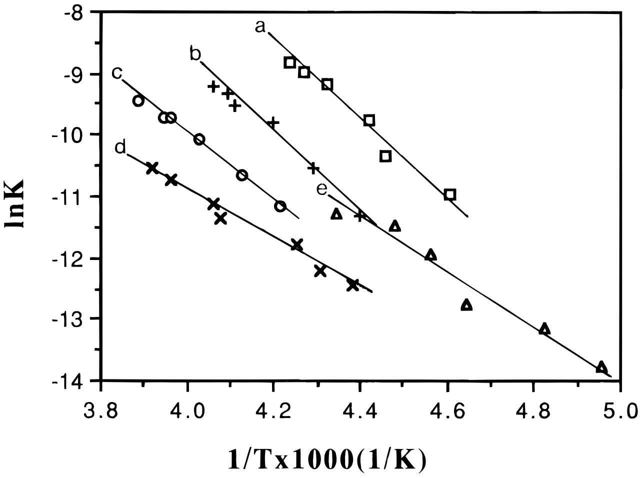

Figure 1. Plots of ln *K* vs 1/*T* for the reversible loss of H_2 from $IrXH_2(H_2)(PPr^i_3)_2$. (a) X = Cl in methylcyclohexane-d_{14}, (b) X = Br in methylcyclohexane-d_{14}, (c) X = I in methylcyclohexane-d_{14}, (d) X = Br in toluene-d_8, and (e) X = Cl in toluene-d_8.

Scheme 1

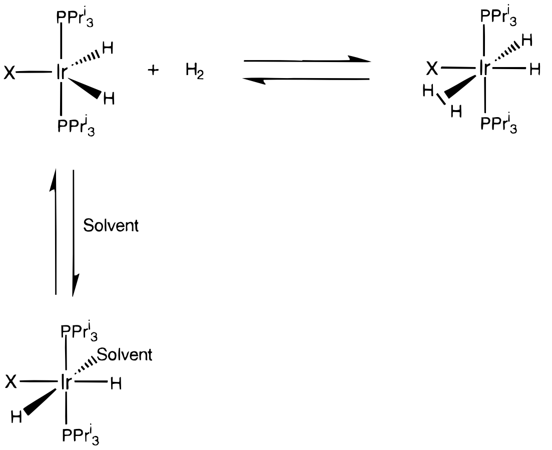

Table 1. Thermodynamic Data for the Loss of H_2 from $IrXH_2(H_2)(PPr^i_3)_2$ in Hydrocarbon Solvents

X	solvent	Δ*H* (kcal/mol)	Δ*S* (eu)
Cl	toluene-d_8	8.6(5)	15(2)
	methylcyclohexane-d_{14}	12.4(6)	35(3)
	n-hexane-d_{14}	12.3(3)	36(1)
Br	toluene-d_8	8.0(4)	10(2)
	methylcyclohexane-d_{14}	12.1(5)	31(2)
	n-hexane-d_{14}	12.0(2)	32(5)
I	toluene-d_8	a	a
	methylcyclohexane-d_{14}	10.5(4)	22(1)
	n-hexane-d_{14}	10.2(4)	22(2)

[a] Equilibrium shifted too far toward $IrIH_2(H_2)(PPr^i_3)_2$ for accurate determination of equilibrium constants.

As previously observed in toluene solution,[2−4] separate signals appear in the hydride region for the metal bound hydrogens of dihydrogen and five-coordinate complexes in the alkane solvents at temperatures below −30 °C. However, below −50 °C H_2 dissolves very slowly into solution. Solutions under 0.25 atm of H_2[5] require 12 h and periodic shaking to come to true equilibrium. The concentrations of the dihydrogen complexes, five-coordinate complexes, and dissolved hydrogen[6] were determined at various temperatures through ^1H NMR spectroscopy. The van't Hoff plots seen in Figure 1 of the equilibrium constants calculated from this data yield the values of Δ*H* and Δ*S* presented in Table 1. The values of Δ*H* and Δ*S* determined for the chloro and bromo complexes were significantly higher in the alkane solvents than in toluene.[7] These results suggest that while simple dissociation of H_2 occurs in alkane solution, solvent coordination to the resulting five-coordinate complex occurs in toluene solution which lowers Δ*H* by 3.7−4.1 kcal/mol and Δ*S* by 20−22 eu. Thus, the higher values found in alkane solutions reflect the energetics of the simple dissociation

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(5) Under constant hydrogen pressures as low as 0.5 atm the true equilibrium position in toluene is shifted to the point that the five-coordinate complex cannot be detected by ^1H NMR. Truly equilibrated solutions containing measurable amounts of both complexes are obtained at H_2 pressures ≤ 0.25 atm.

(6) As a result of exchange signal broadening and low solubility, free H_2 is not observed in the ^1H NMR spectra of equilibrated solutions of the dihydrogen and five-coordinate complexes.[2−4] Previous investigators have used literature data on hydrogen solubility to approximate hydrogen concentrations for equilibrium constant calculations.[3] However, literature data is unavailable for hydrogen solubilities at a pressure of 0.25 atm. Thus hydrogen solubility data was obtained from ^1H NMR spectra of samples of the solvent containing an internal standard amount of THF which were equilibrated under 0.25 atm of hydrogen for 12 h in a constant temperature bath.

(7) Significantly lower values of Δ*H* and Δ*S* were calculated for the dissociation of H_2 from $IrXH_2(H_2)(PBu^t_2Ph)_2$ (X = Cl, Br, I) using data obtained from toluene solutions which were presumed to be equilibrated upon standing for 5 h.[3]

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of H_2 from **1** and **2** with little or no complexation of solvent by **4** and **5**.

While very similar values of ΔH and ΔS were determined for the loss of H_2 from **1** and **2** in the alkane solvents, significantly lower values were determined for **3**. The 2 kcal/mol difference in the values of ΔH indicates that **6** establishes coordinative interactions with the alkane solvents and/or agostic interactions with the phosphine isopropyl groups. The coordinated alkane interpretation is favored by the finding of a 10 eu lower value of ΔS. Further evidence of alkane coordination by **6** is provided by the recent finding that **4**, **5**, and **6** act as alkane dehydrogenation catalysts.[8] Unfortunately, the barriers to the reversible loss of alkane from the $IrXH_2(PPr^i_3)_2$(alkane) complexes are too small to permit their detection as distinct species by NMR spectroscopy to the limit of solvent freezing. Such rapid dynamic behavior is expected since alkane complexes have been directly detected in solution only as transient species in laser flash photolysis experiments.[9] The Ir-H_2 interaction in **3** has been shown to be significantly stronger than in **1** and **2**.[2,10] This has been ascribed to increased electron density at the metal center and thus enhancement of the d-σ^*, metal−dihydrogen interaction resulting from the increased halide σ-donor strength (decreased halogen electronegativity).[2] Similarly, the finding of a significant interaction with alkanes only in the case of the iodo complex can be explained by the increased electron density at the metal center resulting in enhanced d-σ^*, metal-η^2−CH interactions.

Our studies demonstrate that the energetics of the reversible loss of H_2 from $IrXH_2(H_2)(PR_3)_2$ complexes are highly solvent dependent. Apparently toluene and, in the case of the iodo complex, alkanes can compete with H_2 for binding to the five-coordinate $IrXH_2(PR_3)_2$ complexes. The competitive interaction of hydrocarbon solvents has been overlooked in earlier analyses of the factors which influence the stabilization of dihydrogen $IrXH_2(H_2)(PR_3)_2$ complexes. This work illustrates that toluene and alkane complexes can be of major thermodynamic significance.

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Supporting Information Available: Plots of ln K vs $1/T$ for the reversible loss of H_2 from $IrXH_2(H_2)(PPr^i_3)_2$ (X = Cl, Br, I) in methylcyclohexane-d_{14}. Plots of H_2 solubility vs temperature in toluene-d_8, methylcyclohexane-d_{14}, and n-hexane-d_{14} under 0.25 atm H_2 pressure (3 pages). See any current masthead page for ordering and Internet access instructions.

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