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Temperature- and Solvent-Dependent Binding of Dihydrogen in Iridium Pincer Complexes

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Abstract: Mixtures of deuterium labeled complexes (p-XPOCOP)Ir$H_{2-x}D_x$ (**1**−**6**-d_{0-2}) {POCOP = [C_6H_2-1,3-[OP(tBu)$_2$]$_2$]; X = MeO (**1**), Me (**2**), H (**3**), F (**4**), C_6F_5 (**5**), and Ar^F = 3,5-$(CF_3)_2$-C_6H_3 (**6**)} have been generated by reaction of (p-XPOCOP)IrH_2 complexes with HD gas in benzene followed by removal of the solvent under high vacuum. Spectroscopic analysis employing ^{1}H and ^{2}D NMR reveals significant temperature and solvent dependent isotopic shifts and HD coupling constants. Complexes **1**−**6**-d_1 in toluene and pentane between 296 and 213 K exhibit coupling constants J_{HD} of 3.8−9.0 Hz, suggesting the presence of an elongated H_2 ligand, which is confirmed by T_1(min) measurements of complexes **1**, **3**, and **6** in toluene-d_8. In contrast, complex **6**-d_1 exhibits J_{HD} = 0 Hz in CH_2Cl_2 or $CDCl_2F$ whereas isotopic shifts up to −4.05 ppm have been observed by lowering the temperature from 233 to 133 K in $CDCl_2F$. The large and temperature-dependent isotope effects are attributed to nonstatistical occupation of two different hydride environments. The experimental observations are interpreted in terms of a two component model involving rapid equilibration of solvated Ir(III) dihydride and Ir(I) dihydrogen structures.

Introduction

The study of dihydrogen interactions with transition metals has been an active field of research in recent years. Understanding the activation of H_2 at a metal center may provide insights useful in hydrogenation and dehydrogenation catalysis. Until 1984, the binding of H_2 to a transition metal was regarded to exclusively proceed via oxidative addition to form transition metal di- or polyhydrides. The pioneering work of Kubas *et al.* showed that in certain cases H_2 is capable of coordinating to a metal without the rupture of the H−H bond.[1] Subsequently, a large number of dihydrogen complexes have been described, with the vast majority having a d^6 metal configuration.[2]

The commonly accepted model for the interaction of H_2 with a metal moiety invokes electron donation from the bonding HH σ orbital into a metal orbital, and some degree of π-backdonation from a filled metal orbital into the nonbonding HH σ^* orbital. If the degree of π-backdonation from the metal is too high, oxidative addition to afford metal dihydride complexes occurs, denoted by L_nMH_2.[3]

Early examples of transition metal H_2 complexes, including those reported by Kubas, exhibited short H−H distances r_{HH}, usually between 0.8 and 1.0 Å, compared to 0.74 Å in free H_2.[2] Subsequently, a small number of so-called *elongated* hydrogen complexes have been reported.[4] On the basis of neutron diffraction data, these complexes exhibit 1.1 Å < r_{HH} < 1.5 Å. In cases where neutron diffraction is not feasible, structural information can be extracted by measurement of minimum relaxation times, T_1(min).[5] A correlation between J_{HD} in deuterium labeled compounds and r_{HH} derived from neutron diffraction has been developed, which allows r_{HH} to be readily derived from the measurement of J_{HD}.[6] In contrast to the r_{HH} obtained from neutron diffraction, interpretation of T_1(min) and J_{HD} data in terms of r_{HH} may be more complicated. These parameters may reflect a weighted average or dynamic r_{HH} in solution obtained by fast equilibration, for example of a metal dihydride MH_2 with a metal dihydrogen $M(H_2)$ geometry. Early examples of this phenomena are provided by the work of Morris and coworkers, who found temperature- and solvent-dependent relaxation times and J_{HD} in complexes such as *trans*-$[Os(H_2)Cl(dppe)_2]^{+}$[7] and *trans*-$[Os(H_2)(H)(dppe)_2]^{+}$[8]. Such observations

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Table 1. Temperature-Dependent Isotopic Shifts $\Delta\delta$ and J_{HD} Coupling Constants for Isotopically Labeled Complexes (*p*-XPOCOP)IrHD (**1**−**6**-d_1) in Pentane-h_{12} Solution

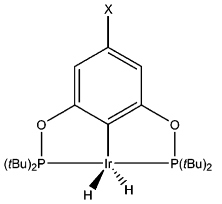
	1-$d_{0,1}$		**2**-$d_{0,1}$		**3**-$d_{0,1}$		**4**-$d_{0,1}$		**5**-$d_{0,1}$		**6**-$d_{0,1}$	
	X = MeO		X = Me		X = H		X = F		X = C_6F_5		X = Ar^F	
T(K)	$\Delta\delta^a$ [ppm]	J_{HD} [Hz]	$\Delta\delta^a$ [ppm]	J_{HD} [Hz]	$\Delta\delta^a$ [ppm]	J_{HD} [Hz]	$\Delta\delta^a$ [ppm]	J_{HD} [Hz]	$\Delta\delta^a$ [ppm]	J_{HD} [Hz]	$\Delta\delta^a$ [ppm]	J_{HD} [Hz]
296	+0.035	6.5	−0.024	7.7	−0.095	8.0	−0.018	7.7	−0.251	9.0	−0.207	9.0
253	+0.119	5.8	+0.075	7.4	+0.007	7.5	+0.075	7.3	−0.196	8.7	−0.127	9.0
233	+0.147	5.7	^{b}	^{b}	^{b}	^{b}	^{b}	^{b}	^{b}	^{b}	−0.086	9.0
213	+0.170	5.0	+0.156	7.0	+0.092	7.2	+0.165	6.9	−0.132	8.1	−0.042	9.0

[a] $\Delta\delta = \delta_{HH} - \delta_{HD}$. [b] Not determined.

were initially explained in terms of equilibria between energetically distinct minima, but this hypothesis was ultimately rejected in favor of a single minimum/soft potential model based on computational studies.[4,9]

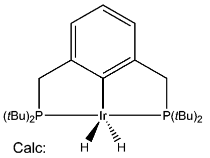
A further complication arises from the fact that r_{HH} obtained by T_1(min) relaxation times in an equilibrium situation is dominated by the short r_{HH} species due to the $T_1(\text{min}) \propto (r_{HH})^6$ dependence.[8] In contrast, the observed J_{HD} is the average of different J_{HD}'s weighted with the relative concentration of the respective species. Additionally, the analysis of T_1(min) data is complicated by the fact that the H_2 ligand may rotate much faster than, much slower than, or at a rate similar to the Larmor frequency. This situation has been summarized by Caulton and Gusev.[5b]

We recently reported that (*p*-XPOCOP)IrH_2 complexes [*p*-XPOCOP = 5-X−C_6H_2-1,3-[OP(*t*Bu)$_2$]$_2$ {X = MeO (**1**), Me (**2**), H (**3**), F (**4**), C_6F_5 (**5**), Ar^F = 3,5-bis(trifluoromethyl)phenyl] (**6**)} exhibit very high activity for the transfer dehydrogenation of (cyclo)alkanes.[10]

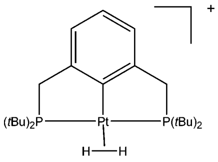


X = OMe (1); Me (2); H (3); F (4); C_6F_5 (5); 3,5 bis(CF_3)phenyl (6)

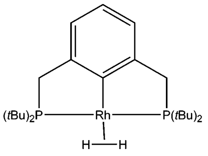
The related PCP complex {C_6H_3-2,6-[$CH_2P(tBu)_2$]$_2$}IrH_2 has been calculated to have a distorted trigonal bipyramidal structure (below).[11,12] In contrast, a rhodium PCP complex has been reported by Jensen, Goldman, and coworkers to be a dihydrogen complex based on HD coupling.[13] Similarly, a cationic platinum PCP complex has been reported by Bullock and coworkers to be a dihydrogen complex.[14]



Calc:
H-Ir-H = 62.7°
Ir-H = 1.595 Å
H-H = 1.660 Å



J_{HD}= 33.4 Hz



J_{HD}= 33 Hz

Because complexes **1**−**6** and related species are useful dehydrogenation catalysts, it is important to determine the structure of these molecules *in solution*, under catalytically relevant conditions. We anticiptated that complexes **1**−**6** might present a range of structures between the limits of dihydrogen and dihydride complexes. Here we report our NMR studies of partially deuterated derivatives of **1**−**6** and the structural complexity that is indicated by these observations. The experimental observations are interpreted in terms of a solvent- and temperature-dependent equilibrium between a four coordinate Ir(I) dihydrogen species and an Ir(III) dihydride which incorporates solvent coordination. This situation differs from previously reported cases of dihydrogen/dihydride equilibria in that the dihydrogen form is four coordinate and has a d^8 configuration, whereas the dihydride form incorporates a solvent molecule.

Results

Synthesis and Deuterium Labeling. Complexes **1**−**6** were prepared as previously described.[10] Deuterium incorporation was achieved by stirring benzene solutions under an atmosphere of HD gas.

Observations in Pentane. Partial deuterium labeling of the hydridic sites of **1**−**6** reveals substituent dependent J_{HD} = 6.5 Hz (**1**-d_1), 7.7 Hz (**2**-d_1), 8.0 Hz (**3**-d_1), 9.0 Hz (**5**-d_1), 9.0 Hz (**6**-d_1) in pentane at 296 K. Interestingly, the observed coupling constants, chemical shifts, and isotope effects on the chemical shifts exhibit a significant temperature dependence (see Table 1).

Observations in Freon or Methylene Chloride. When a mixture of **6**-d_{0-2} was dissolved in $CDCl_2F$ rather than pentane and examined by ^1H NMR spectroscopy at 233 K, no J_{HD} is detectable in the resonance due to **6**-d_1. Careful comparison of the ^1H chemical shift differences between **6** and **6**-d_1 reveals that $\Delta\delta = -1.841$ ppm ($\Delta\delta = \delta\ IrH_2 - \delta\ IrHD$). In the deuterium NMR spectrum, the respective $\Delta\delta = \delta\ IrD_2 - \delta\ IrHD$ was found to be ca. +1.90 ppm. Thus, the Ir(*H*D) resonance appears at −17.865 ppm in the ^1H NMR spectrum,

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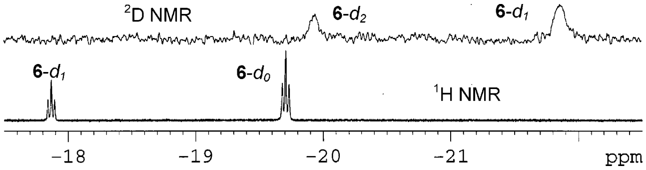


Figure 1. Partial NMR spectra (hydride region) of **6**-d_{0-2} in $CDCl_2F$ at 233 K. (Top) 61 MHz ^{2}D. (Bottom) 400 MHz ^{1}H.

whereas the Ir(H*D*) resonates at ca. −21.86 ppm in the ^{2}D NMR spectrum. A much smaller intrinsic isotopic shift, $\delta(IrH_2) - \delta(IrD_2)$ of ca. +0.21 ppm is observed (Figure 1).

Lowering the observation temperature to 133 K increases $\Delta\delta$ to a remarkable −4.053 ppm due to an upfield shift of $\delta(IrH_2)$ to −21.428 ppm and only moderate downfield shifting of δ-(Ir*H*D) to −17.375 ppm. Similar but smaller isotopic shift effects have been observed in 4:1 mixtures of $CDCl_2F$:toluene-d_8 or in neat CD_2Cl_2.

Observations in Toluene. Complexes **1**, **3**, **4**, and **6** were also studied by ^{1}H and ^{1}H{^{31}P} NMR spectroscopy in toluene-d_8, with results similar to those in pentane (see Table 3).

Relaxation Time Measurements. T_1 relaxation times for the hydridic resonances of complexes **1**, **3**, and **6** were measured in toluene-d_8 as a function of temperature at 400 MHz using standard inversion recovery methodology. The maximum rate of relaxation (T_1(min)) is 107 ms for **1** and 103 ms for **3**, both at 233 K. A T_1(min) value of 100 ms is found for **6** at 243 K.

Discussion

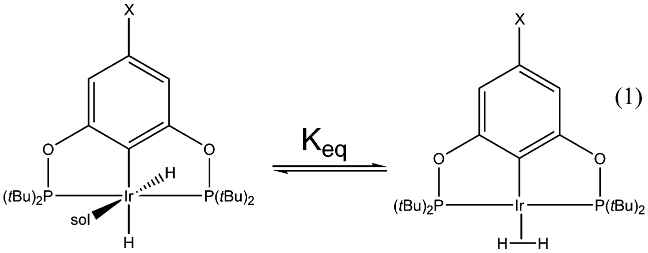
Observations in Pentane and Toluene. The measurement of J_{HD} in partially deuterated derivatives has proven to be the most straightforward method for determining the structures of dihydogen and dihydride complexes. For complexes **1**−**6**, the situation is complicated by temperature dependence of this crucial parameter in some solvents, which we believe reflects a rapid equilibration of two distinct structures. In pentane at ambient temperature, J_{HD} = 6.5 Hz (**1**-d_1), 7.7 Hz (**2**-d_1), 8.0 Hz (**3**-d_1), 7.7 Hz (**4**-d_1), 9.0 Hz (**5**-d_1), 9.0 Hz (**6**-d_1), which based on the most recent correlation,[6e] suggests r_{HH} = 1.54 Å for **1**, decreasing to 1.43 Å for **5** and **6.** These values are within the range of r_{HH} previously suggested for elongated H_2 complexes.[4] The observed correlation of J_{HD} with substituent X on the POCOP ligand backbone is in accordance with the ability of the (*p*-XPOCOP)Ir fragment to donate electron density into the σ*-orbital of the bound H_2-ligand and thus facilitate oxidative addition. In comparison, the calculated r_{HH} of the dihydride PCP Ir complex noted above is 1.660 Å,[11] which is also consistent with a more π-donating $\{C_6H_3\text{-}2,6\text{-}[CH_2(tBu)_2]_2\}$-Ir ligand when compared to the (*p*-XPOCOP)Ir ligands of complexes **1**−**6**. It is important to note that this calculation does not take into account the possible effect of solvation.

At lower observation temperatures in pentane, there is a significant temperature dependence of J_{HD} for complexes **1**−**5**, with a diminishing of the coupling at lower temperatures. For purposes of comparison to relaxation time data (*vide infra*), it is instructive to consider data collected at 213 K. At this temperature, the coupling constants are J_{HD} = 5.0 Hz (**1**-d_1), 7.0 Hz (**2**-d_1), 7.2 Hz (**3**-d_1), 6.9 Hz (**4**-d_1), 8.1 Hz (**5**-d_1), and 9.0 Hz (**6**-d_1). These couplings correspond to r_{HH} = 1.63 Å (**1**), 1.52 Å (**2**), 1.51 Å (**3**), 1.53 Å (**4**), 1.47 Å (**5**), and 1.43 Å (**6**).

In toluene solvent, similar trends are observed, with slightly lower coupling constants and the same trend of larger couplings (and shorter values of r_{HH}) for the less electron donating X groups. Thus, complex **1**-d_1 in toluene exhibits J_{HD} = 3.8 Hz at 233 K, whereas J_{HD} = 6.0 Hz for **3**-d_1 and J_{HD} = 6.7 Hz for **6**-d_1. This corresponds to r_{HH} = 1.70 Å (**1**), 1.57 Å (**3**), and 1.53 Å (**6**).

Additional structural information can be obtained for these complexes by study of the relaxation time T_1 as a function of temperature. If the maximum rate of dipole−dipole relaxation (corresponding to the minimum T_1) can be determined, then r_{HH} can in principle be estimated using the methodology developed by Halpern and co-workers.[5a] Thus, the T_1(min) value of 107 ms for complex **1** (233 K, 400 MHz) corresponds to r_{HH} = 1.48 Å. Similar analysis for **3** gives r_{HH} = 1.47 Å and r_{HH} = 1.46 Å for **6.** This analysis assumes the so-called slow rotation regime for the dihdyrogen ligand. The assumption of rapid rotation leads to unreasonably short values of r_{HH}. These values for r_{HH} are slightly shorter than the corresponding values derived from HD coupling data for these complexes at very similar temperatures in toluene. Because the relaxation rate will be averaged over all contributing structures and the relaxation rate is proportional to $(r_{HH})^{-6}$, structures with shorter HH distances will contribute disproportionately to the average value.

On the basis of these observations, we postulate that complexes **1**−**6** may possess two quite different structures in a rapid solvent-dependent equilibrium. We suggest that an Ir(I) elongated dihydrogen complex coexists with an Ir(III) dihydride, which achieves a six coordinate structure by a weak interaction with solvent (eq 1). The equilibrium constant varies with the nature of X, with the dihydride form predominant except for the very electron deficient complex **6**, which exhibits essentially no temperature dependence of the HD coupling constant in pentane. In toluene, the Ir(III) complexes solvate more strongly, leading to diminished values of J_{HD}.



(1)

Observations in Chlorinated Solvents. In contrast to hydrocarbon solvents, in methylene chloride and Freon solvents, partially deuterated samples of complex **6** exhibit no measurable HD coupling over a wide range of observation temperatures. In these solvents, unusually large and temperature-dependent isotope effects on the hydride chemical shifts are observed. For example, at 213 K in CD_2Cl_2, the chemical shift of the hydridic resonance in **6** is observed at −18.987 ppm, while the resonance due to **6**-d_1 is found at −17.456 ppm (Table 2). The isotope effect $\Delta\delta$ is −1.53 ppm or −1530 ppb. This is an unusually large value for this isotope effect, which is typically on the order of 100 ppb or less in dihydrogen and dihydride complexes. In Freon solvent and at lower temperatures, the isotope effect is even larger, with a truly extraordinary value of 4.05 ppm in $CDFCl_2$ at 133 K (Table 2).

Unusually large and temperature-dependent isotope effects in metal dihydrides have been previously interpreted in terms

Table 2. Temperature-Dependent Isotopic Shifts $\Delta\delta$ of Complex **6**-$d_{0,1}$ in Halogenated Solvents

	CD_2Cl_2			$CDCl_2F$:Tol-d_8 (4:1)			$CDCl_2F$		
T (K)	$\delta(IrH_2)$	$\delta(IrHD)$	$\Delta\delta$	$\delta(IrH_2)$	$\delta(IrHD)$	$\Delta\delta$	$\delta(IrH_2)$	$\delta(IrHD)$	$\Delta\delta$
273				−18.084	−17.148	−0.936			
253				−18.676	−17.458	−1.218	−18.921	−17.548	−1.373
233				−19.242	−17.682	−1.560	−19.706	−17.865	−1.841
213	−18.987	−17.456	−1.531	−19.788	−17.829	−1.959	−20.105	−17.908	−2.197
193	−19.517	−17.589	−1.928	−20.319	−17.880	−2.439	−20.643	−17.915	−2.728
173				−20.789	−17.821	−2.968	−21.025	−17.806	−3.219
153				−21.143	−17.640	−3.504	−21.331	−17.542	−3.789
133							−21.428	−17.375	−4.053

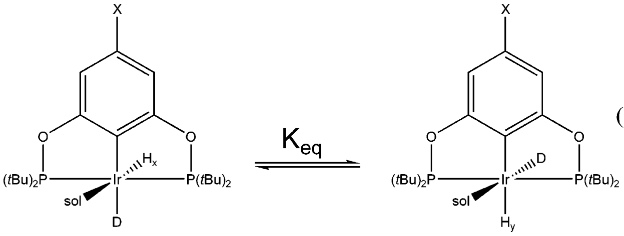
Table 3. Chemical Shifts, Isotopic Shifts, and J_{HD} of Complexes **1**,**3**,**4**,**6**-$d_{1,0}$ in Toluene-d_8

	1-$d_{1,0}$				**3**-$d_{1,0}$				**4**-$d_{1,0}$				**6**-$d_{1,0}$			
	X = MeO				X = H				X = F				X = Ar^F			
T(K)	$\delta(IrH_2)$ [ppm]	$\delta(IrHD)$ [ppm]	$\Delta\delta$ [ppm]	J_{HD} [Hz]	$\delta(IrH_2)$ [ppm]	$\delta(IrHD)$ [ppm]	$\Delta\delta$ [ppm]	J_{HD} [Hz]	$\delta(IrH_2)$ [ppm]	$\delta(IrHD)$ [ppm]	$\Delta\delta$ [ppm]	J_{HD} [Hz]	$\delta(IrH_2)$ [ppm]	$\delta(IrHD)$ [ppm]	$\Delta\delta$ [ppm]	J_{HD} [Hz]
353					−16.770	−16.517	−0.253	[c]								
333					−16.842	−16.597	−0.245	[c]								
313					−16.923	−16.690	−0.233	[c]								
296	−17.578	[a]	[a]	6.9	−16.993	−16.775	−0.218	7.9	−17.130	−17.038	−0.092	7.0	−16.032	−15.684	−0.348	8.0
273	−17.635	−17.663	0.028	6.2	−17.069	−16.871	−0.198	7.3	−17.221	−17.166	−0.055	[c]	−16.167	−15.821	−0.346	7.6
253	−17.693	−17.758	0.065	5.0	−17.142	−16.964	−0.178	6.5	−17.272	[a]	[a]	[c]	−16.304	−15.958	−0.346	6.9
233	−17.743	−17.849	0.106	3.8	−17.209	−17.059	−0.150	6.0	−17.320	[a]	[a]	[c]	−16.412	−16.066	−0.346	6.7
213	−17.787	−17.932	0.144	[b]	−17.273	−17.145	−0.128	[b]	−17.357	−17.419	0.062		−16.504	−16.153	−0.352	[b]
193									−17.389	−17.493	0.104		−16.655	−16.295	−0.360	
183									−17.405	−17.528	0.123		−16.709	−16.337	−0.372	

[a] Not resolvable due to overlap of the Ir(HD) and $Ir(H_2)$ resonances. [b] Not resolved. [c] Not determined.

of isotopic perturbation of equilibrium effects.[15] This situation requires a molecule with two hydride environments exchanging rapidly on the NMR time scale. An additional requirement is that there must be non-statistical occupation of the two sites by deuterium.

In the iridium complexes studied here, the lack of HD coupling suggests that in chlorinated solvents, the structure is predominantly the solvated Ir(III) dihydride. This structure has two quite different hydride environments; trans to the aryl carbon or trans to solvent (eq 2).



(2)

Although the dynamic process interchanging these two hydride environments cannot be frozen out, an estimate of the chemical shifts of the two hydride sites can be made by comparison to related complexes. In Scheme 1 below, the chemical shift of the hydride ligands in several closely related complexes are depicted. A general observation is that the chemical shift of hydride ligands trans to solvent are found at very high field, *ca*. −42 ppm, whereas hydride ligands trans to C or H are found at *ca*. −10 ppm. Thus, we anticipate a *very* large chemical shift difference between a hydride trans to the aryl carbon versus trans to the weakly bound solvent of about 32 ppm.

Although quantitative analysis remains elusive, qualitative conclusions can be reached based on the data of Tables 2 and 3 and spectra such as those depicted in Figure 1. The observed isotopic perturbation effects could arise from perturbation of the equilibria depicted in eq 1 above *or* eq 2. In the latter case, the chemical shift perturbations result from non statistical occupation by D of chemically inequivalent hydride sites in a single dihydride complex. The other possibility, represented by eq 1, is that two *different* molecules are involved, and that D concentrates preferentially in one of them. As pointed out by Hartwig and De Gala, in a two site system these possibilities can be distinguished by careful comparison of the chemical shifts of the HH, HD, and DD isotopomers.[16] The data for complexes **1**−**6**, typified by that shown in Figure 1 for complex **6**, establishes that the equilibrium depicted in eq 2 is relevant here and that the isotopic perturbation effects arise primarily from non-statistical occupancy of two different sites within a single structure.

Qualitatively, the observation that HD species generally resonate downfield of HH complexes is consistent with non-statistical concentration of D in the site *trans* to solvent, giving $K_{eq} > 1$ for the equilibrium of eq 2. If we make certain assumptions regarding the limiting chemical shifts of the two hydride sites, we can estimate a value for K_{eq}. Assuming as noted above that H *trans* to solvent has a chemical shift of −42 ppm (δ_x) and that H *trans* to carbon has a chemical shift of −10 ppm (δ_y), we anticipate an average chemical shift of −26 ppm for the dihydride complex. This is close to the actual observed chemical shift in Freon at low temperature. The chemical shift δ_{HH} is strongly temperature dependent, shifting to higher field as the temperature is lowered, probably due to a shifting of equilibrium 1 to the right. At the lowest observation

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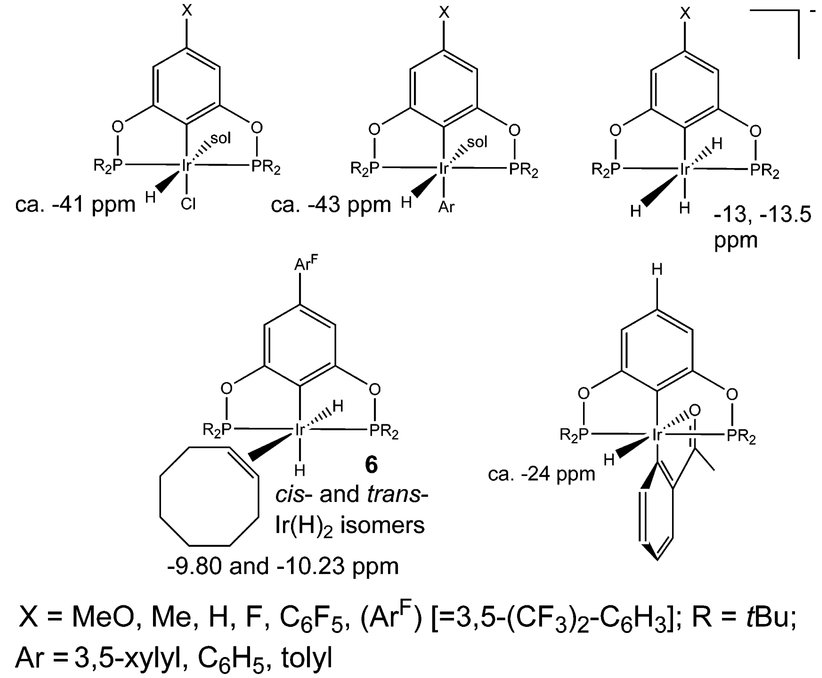
[15] Heinekey, D. M.; van Roon, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134−12140.

[16] Hartwig, J. F.; De Gala, S. *J. Am. Chem. Soc.* **1994**, *116*, 3661−3662.

Scheme 1. Examples of Hydride Chemical Shifts in Related POCOP Complexes



temperature, δ_{HH} appears to be asymptotically approaching a value of *ca.* −22 ppm, so the estimated values for the limiting chemical shifts seem reasonable.

The equilibrium depicted in eq 2 is described by eq 3.[15]

$$\Delta\delta = \delta_{HD} - \delta_{HH} = \frac{(\delta_x - \delta_y)(1 - K)}{2(K + 1)} \qquad (3)$$

Using the data for complex **6** in Table 3, assuming that $\delta_x - \delta_y = -32$ ppm, K_{eq} at 253 K is calculated to be 1.19. There is thus a slight preference for D to occupy the site *trans* to solvent. The large $\Delta\delta$ of 1.3 ppm can be attributed to the unusually large chemical shift difference between the two hydride environments. As the temperature is lowered, the values of K_{eq} increase, reaching 1.68 at 133 K.

With respect to the temperature dependent J_{HD}'s of complexes **1**−**6**, several other examples of similar observations have been reported. Whereas $[Ru(HD)(C_5Me_5)(dppm)]^+$ exhibits an increasing J_{HD} with decreasing temperature,[17] *trans*-$[Os(HD)(H)(dppe)_2]^+$,[8] *trans*-$[Os(HD)(Cl)(dppe)_2]^+$,[7] and $[Ir(HD)(C_5Me_5)(dmpm)]^{2+}$[6e] show decreasing J_{HD} values with decreasing temperature. Calculations on a truncated model complex for $[Ru(\eta^2\text{-}H_2)(C_5Me_5)(dppm)]^+$ led to a model featuring population of excited vibrational states in a highly anharmonic potential to account for the temperature-dependent couplings.[18] An even more anharmonic potential for the H−H elongation within the η^2-H_2 ligand was also calculated for the truncated analogue of *trans*-$[Os(H_2)(Cl)(dppe)_2]^+$ which exhibits increasing J_{HD}'s with increasing temperature.[9b]

Our observations suggest that in the case of Ir complexes **1**−**6**, the observed temperature-dependent couplings are the result of shifts in an equilibrium between two structures, best described as a solvated dihydride of Ir(III) and a dihydrogen complex of Ir(I). In this respect, the situation closely resembles that reported for $[Ir(H_2)(C_5Me_5)(dmpm)]^{2+}$. This complex is believed to have two minima on the potential energy surface corresponding to a dihydride and a dihydrogen form.[6e]

Summary

(*p*-XPOCOP)IrH_2 complexes (**1**−**6**) exhibit a highly solvent- and temperature-dependent geometry in solution on the basis of a series of NMR spectroscopic deuterium labeling studies. (*p*-Ar^FPOCOP)IrHD (**6**-d_1) is an Ir(III) hydride in CD_2Cl_2 or $CDCl_2F$ solvent with $J_{HD} = 0$ and exhibits very large isotopic shift differences caused by an IPE. In contrast, relaxation time and HD coupling data suggest that the same complex in pentane or toluene is best described by an equilibrium between an elongated dihydrogen complex of Ir(I) and an Ir(III) dihydride complex. The pronounced temperature dependence of J_{HD} of complexes **1** in pentane and toluene, especially that of complex **1** in toluene-d_8 in combination with the respective T_1(min) confirm that complexes **1**−**6** exist in a rapidly established equilibrium between two distinct structures.

Experimental Section

General. All manipulations were carried out using standard Schlenk techniques or in an argon-filled drybox. Argon was purified by passage through columns of BASF R3−11 (Chemalog) and 4 Å molecular sieves. Benzene-d_6 and toluene-d_8 were dried over sodium. CD_2Cl_2 was dried over P_2O_5. $CDFCl_2$ was prepared by the procedure of Siegel and Anet[19] and stored over P_2O_5. NMR spectra were recorded on Bruker DRX 400 and AMX 300 instruments. Complexes **1**−**6** were prepared as previously reported.[10a]

Procedure for the Generation of Deuterium-Labeled Complexes 1−6-d_{0-2}. Ten mmol of the respective complex **1**−**6**-h_2 was loaded into a thick walled J. Young tube in the glovebox. Benzene (0.6 mL) was added, and the tube was removed from the glovebox and cooled to −78 °C. The tube was evacuated under high vacuum (−78 °C, 10^{-3}

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[17] (a) Law, J. K.; Mellows, H.; Heinekey, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 1024−1030. (b) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677−7681.

[18] Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *J. Am. Chem. Soc.* **1997**, *119*, 9840−9847.

[19] Siegel, J. S.; Anet, F. A. *J. Org. Chem.* **1998**, *53*, 2629−2631.

mbar), backfilled with HD gas (prepared by reaction of NaH in THF with D_2O) and allowed to react for 30 min at 23 °C, whereas isotopic mixtures of **1**−**6**-d_{0-2} and their respective tetrahydrides were formed. After careful sublimation of the frozen benzene at 0 °C for 2.5 h under high vacuum (10^{-3} mbar), the sample was cooled to −78 °C and the desired solvent was vacuum transferred into the J. Young tube to leave isotopic mixtures of **1**−**6**-d_0, -d_1, and -d_2 in >95% yield by NMR. Labeled samples of compounds **1**−**6** at 23 °C, even in the solid state, slowly transfer their "hydridic" deuterium label into the *tert*-butyl groups. Therefore, samples have to be prepared immediately prior to the NMR studies.

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