H_2 Binding to and Fluxional Behavior of $Ir(H)_2X(P^tBu_2R)_2$ (X = Cl, Br, I; R = Me, Ph)

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Abstract: The molecules $Ir(H)_2X(P^tBu_2Ph)_2$ (X = Cl, Br, I) all show low-temperature ^1H NMR spectra consistent with a structure with inequivalent hydrides, one of which is *trans* to X and one *trans* to an empty coordination site. T_1 measurements suggest that all three molecules have very similar hydride/hydride distances. Hydride rearrangement $\Delta H^\ddagger$ values show little dependence on the halide identity. The decoalescence behavior is not observed for the analogous compounds with P^tBu_2Me. While P^tBu_2Ph compounds show only T_1 and spin-saturation transfer evidence for H_2 binding, the P^tBu_2Me compounds show (at low temperature) signals for both H_2 adduct and five-coordinate species. Line shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra permits the determination of $\Delta H°$, $\Delta S°$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ for H_2 dissociation. These parameters have been determined for Cl, Br, and I and (for the chloride case) when deuterium replaces all hydrogens on Ir. The transition state for H_2 dissociation is "tight" (based on $\Delta S^\ddagger$) and it is enthalpically most accessible for the best π-donor halide, Cl. This same effect *stabilizes* the five-coordinate species most for chloride, and thus makes the activation enthalpy largest for H_2 binding. The $\Delta H°$ values for H_2 dissociation increase down the halogen group.

Introduction

A detailed study of the reactions between the formally unsaturated $Ir(H)_2X(PR_3)_2$ and H_2 is interesting for several reasons. Many η^2-H_2 complexes have been synthesized for their theoretical significance and potential importance in catalysis.[1] However, few systems are amenable to kinetic analysis of η^2-H_2 complex formation (or destruction). $M(H_2)(CO)_3(PCy_3)_2$ (M = Cr, W) is the only system to date for which both kinetic and thermodynamic parameters of H_2 binding have been determined.[2] The formation of $Ir(H)_2(H_2)Cl(PR_3)_2$ (R = Pr^i, Cy, ^{t}Bu) from $Ir(H)_2Cl(PR_3)_2$ and H_2 (eq 1) was initially described by Jensen

$$Ir(H)_2X(PR_3)_2 + H_2 \rightleftharpoons Ir(H)_2(H_2)X(PR_3)_2 \qquad (1)$$

et al.[3] We also observed this reaction as a part of complex transformations of $IrHCl_2(PR_3)_2$ (R = Pr^i, Cy) under hydrogen in solution.[4,5] A detailed understanding of the thermodynamics and kinetics of equilibrium 1 would provide a unique opportunity for a meaningful discussion of the effect of halide identity on the stability of both the unsaturated complex, $Ir(H)_2X(PR_3)_2$, and the 18e $Ir(H)_2(H_2)X(PR_3)_2$. We report here such a study.

A recent neutron diffraction study of $Ir(H)_2Cl(P^tBu_2Ph)_2$ revealed that the hydride ligands were crystallographically distinct.[5] Previous reports[3,6,7] of proton NMR spectra of molecules of this type have shown only equivalent hydrides. This raises the possibility of different structures in the solid state and in solution. Here we report the observation of inequivalent hydrides in $Ir(H)_2X(P^tBu_2Ph)_2$ by ^1H NMR spectroscopy. We will connect this observation to previous theoretical studies and discuss the effect of the halide and phosphine identity on H_2 binding in related systems.

Results and Discussion

Fluxional Behavior of $Ir(H)_2X(P^tBu_2R)_2$. (a) Decoalescence. The variable-temperature ^1H NMR spectroscopic study of $Ir(H)_2X(P^tBu_2Ph)_2$ reveals decoalescence behavior of the hydride signal. For example, in the case of a toluene-d_8 solution of $Ir(H)_2I(P^tBu_2Ph)_2$, this signal is observed as a triplet ($^2J_{PH}$ = 13 Hz) at δ −32.2 at room temperature, but it splits into two broad (145 Hz) resonances[8] at δ −20.1 and −44.4 as the temperature is lowered to −100 °C (Figure 1). The decoalescence temperature is *ca.* −65 °C, which provides[9] a free energy of activation of 8.0 kcal/mol for the hydride site exchange at −65 °C. Line shape analysis[9] of the ^1H NMR spectra recorded between −20 and −95 °C resulted in an Eyring plot (Figure 2) with $\Delta H^\ddagger$ = 7.9 ± 0.2 kcal/mol and $\Delta S^\ddagger$ = 0.1 ± 1.2 eu. This near-zero entropy change is consistent with an intramolecular mechanism, and the triplet structure at 25 °C demonstrates that there is no rupture of the Ir–H or Ir–P bonds during the fluxional process.

The low-temperature limiting hydride chemical shifts are similar to those of other relevant complexes. The hydride chemical shift of $IrHCl_2(P^tBu_2Ph)_2$, in which the hydride occupies the apical position in a square-pyramidal geometry, is −48.5 ppm.[6] The hydride chemical shift *trans* to chloride in $Ir(H)_2Cl(Cyttp)$ is −22.3 ppm.[10] Therefore, we assign the −44-ppm resonance to a hydride which is pseudo-trans to an empty coordination site and the −20-ppm resonance to a hydride which is pseudo-trans to the halide ligand. This spectroscopic assignment would also be consistent with the solid-state structure (neutron diffraction) of $Ir(H)_2Cl(P^tBu_2Ph)_2$ (Figure 3) in which one of the H–Ir–Cl angles is 156° and the other is 131°.[5]

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(8) The line width was 35 Hz in CD_2Cl_2 at −100 °C and no evidence was obtained for any large (>30 Hz) proton–proton coupling constants in the low-temperature ^1H NMR spectra of the $Ir(H)_2X(P^tBu_2Ph)_2$ complexes.

(9) Oki, M. In *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; VCH Publishers: Deerfield Beach, 1985, Chapter 1.

(10) Yang, C.; Socol, S. M.; Kountz, D. J.; Meek, D. W.; Glaser, R. *Inorg. Chim. Acta* **1986**, *114*, 119.

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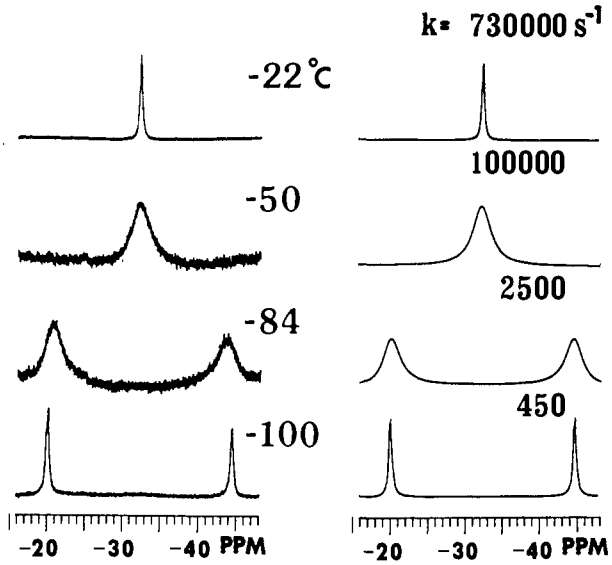

Figure 1. Experimental (left) and calculated (right, with rate constants) ^1H NMR spectra (hydride region only) for $Ir(H)_2I(P^tBu_2Ph)_2$ in toluene-d_8.

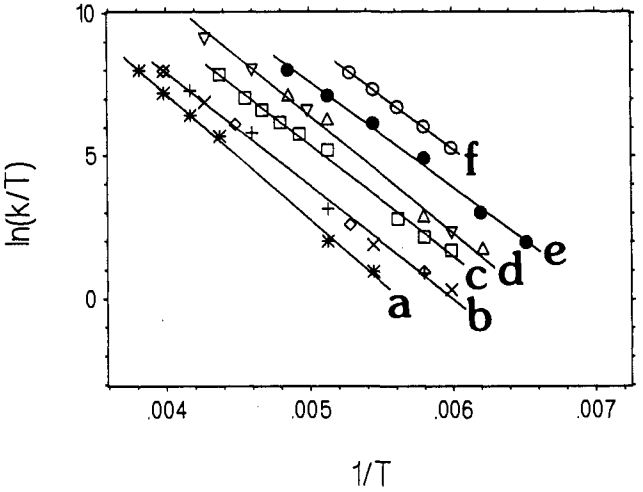

Figure 2. Eyring plots for the rate of hydride site exchange in $Ir(H)_2X(P^tBu_2Ph)_2$ for X = I (a, in CD_2Cl_2; b, in toluene-d_8), Br (c, in CD_2Cl_2; d, in toluene-d_8), and Cl (e, CD_2Cl_2; f, in toluene- d_8). Lines b and d include date derived from different concentrations of complex.

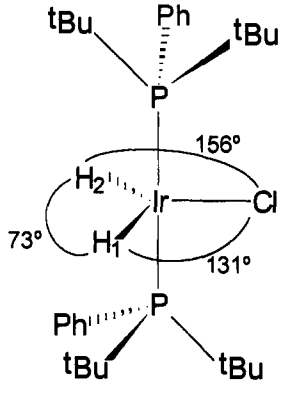

Figure 3. Structure of $IrH_2Cl(P^tBu_2Ph)_2$.

An *ab initio* study of $Ir(H)_2Cl(PH_3)_2$ provides an explanation for this distortion.[5] Although the Y structure (Scheme 1) was calculated to be the energy minimum, distortions of the H–Ir–Cl angles do not require large amounts of energy (<3.3 kcal/mol) *if* the H–Ir–H angle remains approximately 73°. Thus, pseudo-T-shaped structures are energetically accessible.

Scheme I

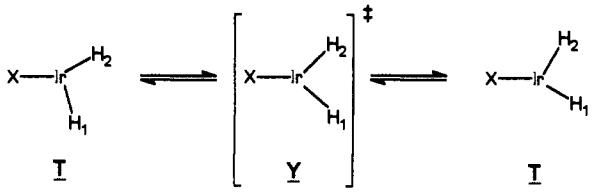

Table 1. T_1 (ms) Relaxation Time of the Hydride Ligands in $Ir(H)_2X(P^tBu_2Ph)_2$ in Toluene-d_8

	X		
T, K	Cl	Br	I
282	342	337	353
268	248	244	263
251	181	193	204
234	148	149	147
217	143	135	*a*
201	198	*a*	*a*
184	274	*a*	240

[a] T_1 was not determined because of strong broadening of the IrH_2 resonance(s).

The experimental kinetic data for $Ir(H)_2I(P^tBu_2Ph)_2$ can be rationalized in terms of the site exchange shown in Scheme1 where a ground state T-shaped structure lies 8 kcal/mol below a transition state of Y geometry. The disparity between the ground-state structure calculated (*ab initio*) for $Ir(H)_2Cl(PH_3)_2$ and that observed for examples with extremely bulky phosphines must originate in steric repulsion between phosphine substituents and the $Ir(H)_2X$ moiety. Steric interactions of this type were identified in the T-distorted ground-state structure of $Ir(H)_2Cl(P^tBu_2Ph)_2$.[5]

(b) Is the H/H Distance Dependent on the Halide Coligand? A variable-temperature T_1 study can be useful for a qualitative comparison of the H–Ir–H distances as the group X is varied in $Ir(H)_2X(P^tBu_2Ph)_2$. The relaxation rate, $1/T_1$, for the metal-bound protons is where the contributions are due to the dipole–

$$1/T_1 = 1/T_1(H...H) + 1/T_1(H...H^*)$$

dipole interactions between the phosphine protons and hydride ligands ($1/T_1(H...H^*)$) and between the hydrides themselves ($1/T_1(H...H)$).[11] The latter contribution is quite significant in the present case. In $Ir(H)_2Cl(P^tBu_2Ph)_2$, $1/T_{1min}$ is 7 s^{-1} at 300 MHz, and from the H...H distance of 1.817 Å (neutron diffraction)[5] the $1/T_{1min}(H...H)$ contribution of 3.6 s^{-1} (51% of the observed relaxation rate) can be calculated. It is reasonable to assume[12] a negligible dependence of $1/T_1(H...H^*)$ on X and any substantial changes in $1/T_1$ should be due to the $1/T_1(H...H)$ contribution which is extremely sensitive to H...H distance variations. For example, $1/T_{1min}(H...H) = (3.87 \times 10^4)\nu^{-1}r(H...H)^{-6}$, where ν is the resonance frequency in MHz and $r(H...H)$ is the distance in Å.[11] Thus, the equation predicts a 32% increase in T_{1min} if the H–Ir–H angle increases by 10° assuming the same Ir–H distances: 1.512 and 1.553 Å.

The experimental T_1 data for the hydride relaxation in $Ir(H)_2X(P^tBu_2Ph)_2$ (Table 1) are very similar at comparable temperatures. The observed differences are typically within the error limits of the technique and do not exceed 14%. This observation leads to the conclusion that the distortion of the molecular geometry which is the cause of the inequivalence of the hydrides in $Ir(H)_2X(P^tBu_2Ph)_2$ does not involve appreciable

(11) Proton–phosphorus dipole–dipole interactions are weak and can be neglected. Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 3027.

(12) A referee suggests that the constancy of the T_1 value down the halides arises from fortuitous compensation of decreasing $T_1(H- -H)$ and $T_1(H- -H^*)$. We prefer our explanation as simpler.

Table 2. Spectroscopic and Hydride-Site Exchange Activation Parameters for $Ir(H)_2X(P^tBu_2Ph)_2$

X	low-temperature δ(IrH)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Cl	*a*	7.4 ± 0.2[b]	7.7 ± 0.4[b]
Cl	−24.9; −43.1[c]	7.3 ± 0.3[c]	4.6 ± 1.5[c]
Br	−23.6; −42.4[b]	8.0 ± 0.2[b]	5.6 ± 1.4[b]
Br	−23.1; −44.9[c]	7.8 ± 0.2[c]	2.2 ± 0.9[c]
I	−20.1; −44.4[b]	7.9 ± 0.2[b]	0.1 ± 1.2[b]
I	−19.8; −45.9[c]	8.7 ± 0.2[c]	2.1 ± 0.9[c]

[a] The decoalescence was not reached in toluene-d_8; $\Delta\delta = 15.2$ ppm was assumed, based on comparison to $Ir(H)_2Br(P^tBu_2Ph)_2$ in toluene-d_8. [b] In toluene-d_8. [c] In CD_2Cl_2.

changes in the H...H distance and, thus, the H–Ir–H angle. For the latter, the actual changes should be less than 5° based on the maximum difference in the T_1 values (14%).

(c) Fluxionality for a Smaller Phosphine Analog. In contrast to the above, $Ir(H)_2X(P^tBu_2Me)_2$ compounds show only one hydride chemical shift down to −100 °C. At the lowest attainable temperature, the broadest line ($\Delta = 80$ Hz, −100 °C) was observed for $Ir(H)_2I[P^tBu_2Me]_2$ in toluene. High viscosity of the solvent is, perhaps, responsible for the line width rather than a fluxional process, since in less viscous CD_2Cl_2, this resonance was sharp enough to not obscure the proton–phosphorus coupling. For a related compound $Ir(H)_2Cl[P^iPr_3]_2$ the hydrides were found to be equivalent at 77 K by solid-state NMR.[13] Thus, the absence of the decoalescence behavior for $Ir(H_2)X[P^tBu_2Me]_2$ most probably reflects undistorted Y-shaped structure for this smaller phosphine.

(d) Halide Dependence of the Fluxionality Barrier. The ^1H NMR spectroscopic and kinetic data for the full range of halide complexes $Ir(H)_2X(P^tBu_2Ph)_2$ are summarized in Table 2. The rate of intramolecular exchange significantly accelerates in the order I < Br < Cl. For example, $k_{Cl}/k_I = 143$ and $k_{Br}/k_I = 12$ in toluene at 200 K. Surprisingly, however, the effect is *not enthalpic* in origin. As it is seen from Table 2 and from the nearly-identical slopes in Figure 2, the $\Delta H^{\ddagger}$ values do not depend (significantly) on X, changing only from 7.4 to 8.0 kcal/mol in toluene.

We have expended the effort to look for solvent effects on the site exchange rate. There are two reasons to anticipate only small solvent effects on the activation parameters (Table 2) when comparing CH_2Cl_2 and aromatic solvents. First, the $Ir(H)_2X(P^tBu_2R)_2$ molecules are very crowded due to the large phosphines, leaving no site for solvent incorporation. In addition, the hydride motion occurs with very little structural reorganization of the $IrX(P)_2$ atoms and thus the solvent sheath should be very similar throughout the rearrangement. Indeed, $\Delta H^{\ddagger}$ values show no major changes on comparing the two solvents. Any solvent effect is reflected in the ratio $k(\text{toluene-}d_8)/k(CD_2Cl_2)$, which is between 2.9 and 3.8 for $Ir(H)_2X(P^tBu_2Ph)_2$ at 200 K.[14]

Significantly positive $\Delta S^{\ddagger}$ values of 7.7 ± 0.4 and 5.6 ± 1.4 eu found for the hydride exchange in $Ir(H)_2Cl(P^tBu_2Ph)_2$ and $Ir(H)_2Br(P^tBu_2Ph)_2$, respectively, seem at first glance to be inconsistent with an intramolecular process. At the same time, they are inconsistent with a bimolecular process, where a substantially negative $\Delta S^{\ddagger}$ is expected. In general, it is unreasonable to suspect that different site exchange mechanisms can operate in $Ir(H)_2X(P^tBu_2Ph)_2$ depending on the halide identity. Experiments with different concentrations of the complexes (Figure 2, X = Br, I) show no concentration dependence, strongly supporting the intramolecular character of the exchange. We believe that quantum-mechanical tunneling of the hydride ligands can operate, to a varying degree, in all $Ir(H)_2X(PR_3)_2$ complexes, precluding correct determination of the $\Delta S^{\ddagger}$ values.[15,16]

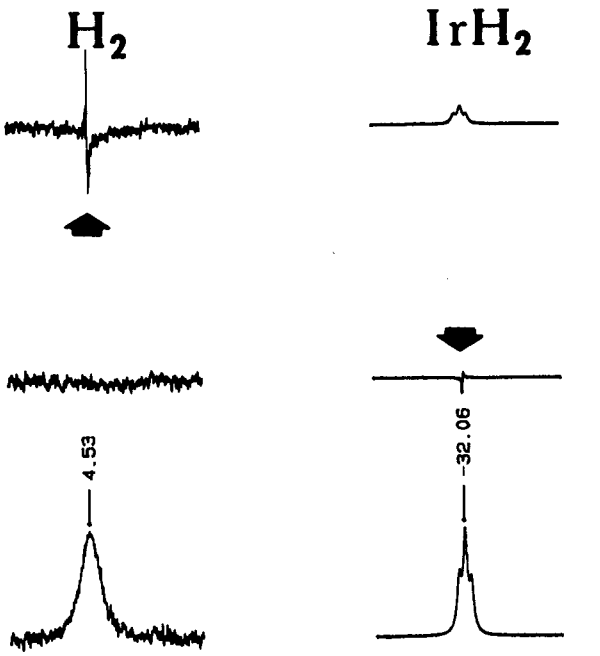

Figure 4. Effects of saturation transfer in ^1H NMR spectra (free H_2 and hydride regions) of $Ir(H)_2Cl(P^tBu_2Ph)_2$ under 700 Torr of H_2 in toluene-d_8 at −5 °C. Saturation was applied at the indicated positions or, in the case of the reference (bottom) spectrum, between the resonances. All spectra were measured and plotted under otherwise identical conditions.

H_2 Binding to $Ir(H)_2X(P^tBu_2Ph)_2$ (X = Cl, Br, I). The extreme steric bulk of P^tBu_2Ph strongly disfavors H_2 binding by these molecules. For each halide, spectroscopic evidence supports equilibrium 1, but lying very far to the left. At room temperature, the ^1H NMR of all $Ir(H)_2X(P^tBu_2Ph)_2$ molecules under H_2 show broadened resonances of dissolved hydrogen (Δ = 56–62 Hz) at δ 4.5 and that of $Ir(H)_2$ (Δ = 40–46 Hz) at ca. δ −32. Above −20 °C, the T_1 relaxation measurements give identical T_1 values for dissolved hydrogen and for the hydrides. The T_1 values for the H_2 signals (200–300 ms at −10 °C) are appreciably shorter than those of free H_2 in the absence of the metal complex (>1 s). Only at temperatures below −20 °C are the relaxation times for dissolved H_2 increased because of slowing the rate of equilibrium 1 on the relaxation time scale. The most convincing evidence for the existence of equilibrium 1 is obtained by a spin saturation-transfer experiment for $Ir(H)_2Br(P^tBu_2Ph)_2$. At +10 °C, CW decoupling at δ 4.5 effectively saturates the $Ir(H)_2$ peak at δ −32.7 and vice versa. This clearly shows that protons of the dihydride complex and H_2 are exchanging quickly in the unobserved fluxional $Ir(H)_2Br(H_2)(P^tBu_2Ph)_2$. Figure 4 shows this behavior for the chloride complex. In all cases, in the temperature range 20 to −90 °C, no detectable amount of $Ir(H)_2X(H_2)(P^tBu_2Ph)_2$ is directly observed by ^1H and $^{31}P\{^1H\}$ NMR. While this precludes further kinetic and thermodynamic study, the averaging and shortening of T_1 for free H_2 and for coordinated hydrides represents a phenomenon useful for proving the existence of a hydride/dihydrogen compound when direct

(13) Wishniewski, L. L.; Mediati, M.; Jensen, C. M.; Zilm, K. W. *J. Am. Chem. Soc.* **1993**, *115*, 7533.

(14) (a) There is currently an inability of physical theories to account quantitatively for solvent effects on rates. A decrease in reaction rate upon increasing solvent polarity is commonly associated[14b,c] with a transition state of lower polarity than the ground state. Ground-state stabilization by the more coordinating solvent (CD_2Cl_2 *vs* toluene-d_8) can be an alternative explanation to purely polarity-based considerations. (b) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH Publishers: New York, 1988, Chapter 5. (c) Connors, K. A. *Chemical Kinetics: The Study of Reaction Rates in Solution*; VCH Publishers: New York, 1990.

(15) Bell, R. P. In *The Tunnel Effect in Chemistry*, Chapman and Hall: London and New York, 1980, Chapter 3.

(16) We attempted to slow any quantum tunnelling contribution by replacement of H by deuterons. The ^2H NMR spectrum of $Ir(D)_2Cl(P^tBu_2Ph)_2$ shows no decoalescence at −102 °C in CH_2Cl_2. Since the resonance frequency is reduced by a factor of 6.5 compared to the protio compound, this factor overwhelms any change in site exchange rate and thus leaves the experiment inconclusive.

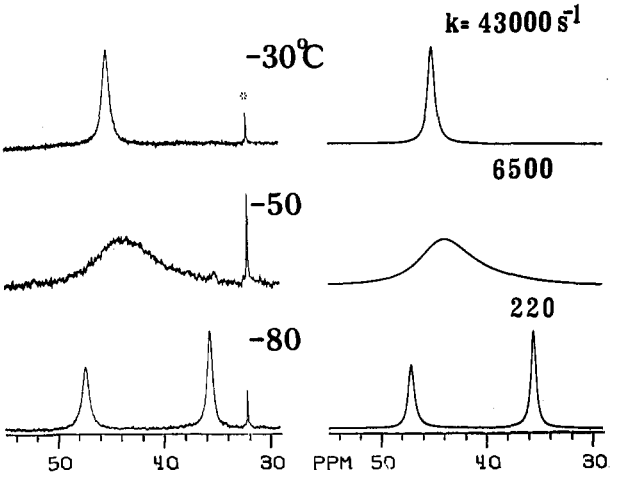

Figure 5. Observed (left) and calculated (right, with rate constants for H_2 loss from $Ir(H)_2Cl(H_2)(P^tBu_2Me)_2$) variable-temperature $^{31}P\{^1H\}$ NMR spectra of $Ir(H)_2Cl(P^tBu_2Me)_2$ under 700 mm of H_2 in toluene-d_8. The resonance of $Ir(H)_2Cl(H_2)(P^tBu_2Me)_2$ appears at 35.5 ppm. The asterisk indicates an inert impurity at 32 ppm.

observation is not possible (e.g., when the equilibrium population is low).

Kinetics of H_2 Binding to $Ir(H)_2X(P^tBu_2Me)_2$ (X = Cl, Br, I). Below 20 °C, variable-temperature ^1H and $^{31}P\{^1H\}$ NMR study demonstrates appreciable H_2 binding by all of these halide compounds, consistent with the smaller size of P^tBu_2Me (i.e., dominant steric effect).[17] A significant steric influence on the extent of H_2 binding has been demonstrated previously in $Ir(H)_2Cl(PR_3)_2$ systems.[3b] Rate data for loss of H_2 from $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ obtained by fitting the experimental variable-temperature $^{31}P\{^1H\}$ NMR spectra (see, for example, Figure 5) using the simulation program DNMR5 are displayed in an Eyring plot in Figure 6. Data obtained for the dissociation of D_2 from $Ir(D)_2(D_2)Cl(P^tBu_2Me)_2$ are also compared to those for loss of H_2 from $Ir(H)_2(H_2)Cl(P^tBu_2Me)_2$ in an Eyring plot in Figure 6. Activation parameters obtained by linear least-squares fitting of the data are shown in Table 3.

The $\Delta S^\ddagger$ values are all positive but of small magnitude consistent with a process with only slightly increased degrees of freedom in the transition state as a result of the departing H_2 molecule. The values show that the transition state is reached with only a small amount of bond breaking. Perhaps the higher entropy of D_2 *vs* H_2 is reflected in a higher $\Delta S^\ddagger$ for $Ir(D)_2Cl(D_2)(P^tBu_2Me)_2$ than for $Ir(H)_2Cl(H_2)(P^tBu_2Me)_2$. Unfortunately, the relatively large error makes further quantitative comparisons impossible. The compounds $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ are among the most unstable known dihydrogen complexes and the $\Delta H^\ddagger$ values listed in Table 3 are at the lower limit of values found for the loss of H_2. Comparable activation parameters of 8.8 ± 0.1 and 12.1 ± 1.0 kcal/mol were reported for $[Ru(H_2)(H)_3(PPh_3)_3]^+$ and $Cr(H_2)(CO)_3(PCy_3)_2$, respectively.[2b,18] In the case of the kinetically more stable $W(H_2)(CO)_3(PCy_3)_2$ and $Ru(H_2)(H)_2(PPh_3)_3$, $\Delta H^\ddagger$ values are noticeably higher: 16.9 ± 2.2 and 17.9 ± 0.2 kcal/mol, respectively.[2c,14] Unfortunately, meaningful comparison of the activation entropies is practically impossible because of the large error (several cal mol^{-1} K^{-1}) in the $\Delta S^\ddagger$ data available in the literature. The error, perhaps, is mainly responsible for the strongly different values reported for $[Ru(H_2)(H)_3(PPh_3)_3]^+$ (−12 eu), $Cr(H_2)(CO)_3(PCy_3)_2$ (−2.1 eu), $W(H_2)(CO)_3(PCy_3)_2$ (+10.4 eu), and $Ru(H_2)(H)_2(PPh_3)_3$ (+3 eu).[2b,c,15]

(17) It is not possible that the P^tBu_2Ph analog binds H_2 poorly due to a phenyl *o*-hydrogen interaction because the neutron diffraction structure[5] shows these to be absent. Also, the −44 ppm hydride chemical shift is diagnostic of hydride *trans* to an *empty* coordination site.

(18) Halpern, J.; Cai, L. S.; Desrosiers, P. J.; Lin, Z. R. *J. Chem. Soc., Dalton Trans.* **1991**, 717.

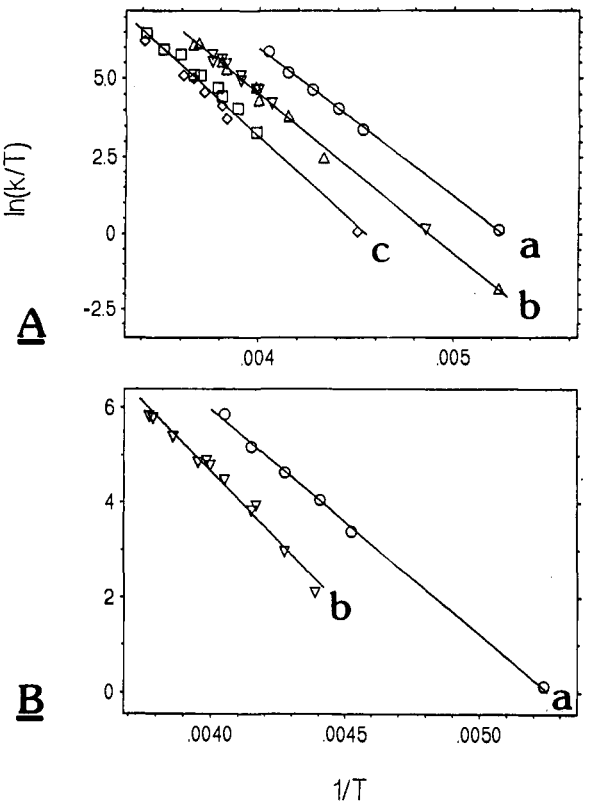

Figure 6. (A) Eyring plot of rate data for H_2 loss from $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ for chloride (a), bromide (b), and iodide (c). Lines b and c contain data for two different concentrations of complex (identified by different symbols) and show the concentration independence of *k*. (B) Eyring plots for dissociation of D_2 from $Ir(D)_2(D_2)Cl(P^tBu_2Me)_2$ (b) and H_2 from $Ir(H)_2Cl(H_2)(P^tBu_2Me)_2$ (a).

Table 3. Kinetic and Thermodynamic Data for H_2 and D_2 Loss from $Ir(H)_2(H_2)X(P^tBu_2Me)_2$ (X = Cl, Br, I) and $Ir(D)_2(D_2)Cl(P^tBu_2Me)_2$ in Toluene-d_8

	M (×10⁻²)	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	ΔH°, kcal/mol	ΔS°, eu
Cl	41	9.4 ± 0.2	2.3 ± 0.9	6.8 ± 0.2	19.2 ± 0.7
Br	29	10.2 ± 0.2	2.4 ± 1.0		
				7.9 ± 0.9[a]	19.7 ± 3.2[a]
	47	10.1 ± 0.2	2.4 ± 0.9		
I	22	10.8 ± 0.5	2.8 ± 2.0		
				9.3 ± 0.2[a]	22.7 ± 0.8[a]
	35	11.3 ± 0.3	3.7 ± 1.1		
Cl[b]	28			–	–
		11.7 ± 0.5[a]	8.7 ± 2.2[a]		
	41			7.7 ± 0.5	20.7 ± 1.8

[a] Parameters were determined combining the data at two concentrations when less than five data points were measured for one concentration. [b] Data for $Ir(D)_2Cl(D_2)(P^tBu_2Me)_2$.

As could be expected for a process involving bond rupture, the kinetic isotope effect found for the D_2 loss from $Ir(D_2)(D)_2Cl(P^tBu_2Me)_2$ is relatively high; k_H/k_D are 1.8 and 6 at 20 °C and −50 °C, for example. These values are within the range of k_H/k_D for $W(H_2)(CO)_3(PCy_3)_2$, $Cr(H_2)(CO)_5$, and $IrHCl_2(H_2)(PCy_3)_2$: 1.7 (25 °C), 5 (room temperature) and 6–7 (−60 to −70 °C), respectively.[2c,4,19]

$\Delta H^\ddagger$ values increase in the order Cl < Br < I. The dissociative transition state could be expected to show the opposite trend based purely on size of the halide, with the larger iodide[20] promoting a decrease in coordination number. Therefore, the data indicate that electronic factors dominate steric considerations. We suggest a transition state in which a halide lone pair interacts

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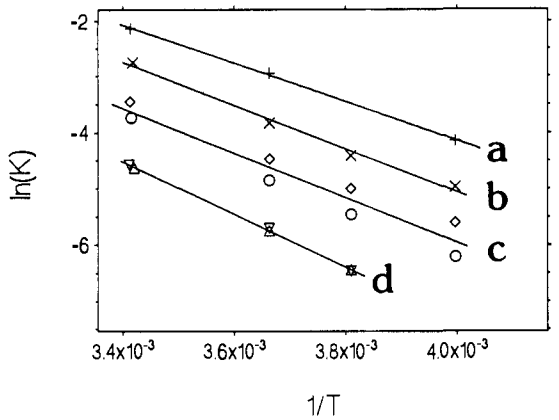

Figure 7. Equilibrium constants for H_2 dissociation from $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ displayed as ln K vs $1/T$. Lines a, c, and d are for I, Br, and Cl, respectively. Line b is for D_2 binding to $Ir(D)_2Cl(P^tBu_2Me)_2$. Lines c and d include data collected at two different concentrations of complex.

constructively with the metal center, partially displacing the dihydrogen ligand. The $\Delta H^{\ddagger}$ values contain evidence for the existence of increasing **multiple-bond character** between the iridium metal center and the halide ligands in the transition state with the established[21] capacity for π-bonding (Cl > Br > I) determining the trend.

Thermodynamics of H_2 Loss from $Ir(H)_2X(P^tBu_2Me)_2$ (X = Cl, Br, I). The π-donation invoked to explain the trends in $\Delta H^{\ddagger}$ should also influence the thermodynamics of H_2 binding to $Ir(H)_2X(P^tBu_2Me)_2$ complexes. Thermodynamic data were obtained at temperatures above −30 °C due to the slow rate of H_2 transport into and out of toluene in an NMR tube at temperatures below −30 °C. Data obtained for dissociation of $Ir(H_2)(H)_2X(P^tBu_2Me)_2$ are displayed in a plot of ln K *vs* $1/T$ in Figure 7.

Values obtained by linear least-squares fitting of the data are contained in Table 3. The ΔS° values are large and positive, as expected for a dissociative reaction. The magnitude of ΔS° also compares well with previously obtained values: 23.2 ± 1, 23.8 ± 2.1, and 25.6 ± 1.7 eu for $Ru(H_2)HCl(CO)(P^iPr_3)_2$,[22] $Mo(H_2)(CO)_3(PCy_3)_2$,[2a] and $Cr(H_2)(CO)_3(PCy_3)_2$,[2b] respectively. These same complexes, having been characterized by ΔH° of 7.7 ± 0.2, 6.5 ± 0.2, and 7.3 ± 0.1 kcal/mol, respectively, have thermodynamic stability similar to that of $Ir(H)_2Cl(H_2)(P^tBu_2Me)_2$. The adduct is enthalpically favored for all halides. The magnitude of the ΔH° values show the same trend as the $\Delta H^{\ddagger}$ values: Cl < Br < I.

Investigation of the D_2 addition to $Ir(D)_2Cl(P^tBu_2Me)_2$ reveals an equilibrium isotope effect, K_D/K_H = 2.7 at 260 K. At this temperature, the ratio is 2 for the only other case of $H_2(D_2)$ coordination, $IrHCl_2(PCy_3)_2 + H_2(D_2)$, where the isotope effect has been measured so far.[4] A similar effect with K_D/K_H = 1.9 (260 K) was found for an oxidative addition of $H_2(D_2)$ to $WI_2(PMe_3)_4$, where the W–D bonds in the product were shown to be *ca.* 1.8 kcal/mol stronger than the W–H bonds.[23] The last available example is $Cp_2Ta(\mu\text{-}CX_2)_2Ir(CO)(PPh_3)$, where for the oxidative addition of H_2 (X = H) and D_2 (X = D), K_D/K_H = 2.3 (260 K).[24] It is interesting to note that in these cases the isotope effects are enthalpic in origin: $\Delta H^{\circ}(D) - \Delta H^{\circ}(H) = 0.9 \pm 0.7$ ($Ir(H)_2Cl(P^tBu_2Me)_2$), 1.9 ± 1.3 ($WI_2(PMe_3)_4$), 1.0 ± 0.6 kcal/mol ($Cp_2Ta(\mu\text{-}CX_2)_2Ir(CO)(PPh_3)$). Both M–D and M–($D_2$) bonds seem to be substantially stronger than the corresponding M–H or M–(H_2) bonds.

In general, a great thermodynamic difference between the reactions of dihydrogen coordination or oxidative addition should not be expected. A higher enthalpy change can, perhaps, be associated with the latter reaction. The few entropy unit change found for the equilibria $M(H_2)L_n \rightleftharpoons M(H)_2L_n$ clearly shows that the intramolecular part of an oxidative addition of H_2 is not significantly "entropy consuming".[1] Thus, ΔS° should be mainly determined by the loss of the rotational freedom of H_2 on "adduct" formation. The "adduct" can be a stable dihydrogen complex or a transition state if further (oxidative) reaction occurs. Unfortunately, the existing literature data are too limited to argue either for or against these considerations. If for the oxidative addition of H_2 to $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)(PPh_3)$ the ΔS° of −23.7 ± 0.6 eu is "reasonable", the example with $WI_2(PMe_3)_4$ gave a very large ΔS° of −45 ± 2 eu.[23,24]

Reactivity of H_2 with $IrH_2F(P^tBu_2R)_2$ (R = Me). We have shown[25] that late transition metal fluorides are often quite different from Cl, Br, and I in their binding and also in their reactivity. For example, $RuHF(CO)(P^tBu_2Me)_2$ reacts with H_2 to eliminate HF whereas this behavior was not observed for the other halides. We were therefore interested in obtaining kinetic and thermodynamic information on H_2 binding to iridium dihydride fluorides. Unfortunately, $IrH_2F(P^tBu_2Ph)_2$ reacts in an analogous fashion to the ruthenium fluoride mentioned above producing $IrH_5(P^tBu_2Ph)_2$ (^{31}P and ^1H NMR evidence) and HF (through observation of glass etching), precluding further study. The common reactivity for these different compounds underscores the high Brønsted basicity of fluoride in the presumed dihydrogen complexes $RuHF(H_2)(CO)(P^tBu_2Me)$ and $Ir(H)_2F(H_2)(P^tBu_2Ph)_2$. It is also worth highlighting the low acidity of HF under these conditions as evidenced by the lack of significant back reaction between IrH_5L_2 and HF.

Conclusion

The data obtained here are best represented graphically. In Figure 8 reaction coordinate profiles of all of the compounds measured are superimposed with the transition state enthalpy fixed at the same energy for the purpose of comparing $\Delta H^{\ddagger}$ values. The ordering of halides is reversed in the five- and the six-coordinate sides precisely because what *assists* during *dissociation* of H_2 (X → Ir π-donation) *inhibits binding* of H_2 (or any Lewis base). The magnitude of this effect upon H_2 addition is modest (<0.9 kcal/mol difference from iodide to chloride). The magnitude of the effect upon H_2 dissociation is larger (1.6 kcal/mol). This correlates with the fact that X-ligand lone pairs do not simply stabilize the H_2-loss transition state, but they *destabilize* the H_2 adduct ground state, by filled/filled repulsions with the filled d_π iridium orbitals. Since the transition state has been established as "tight" (still rigid by the $\Delta S^{\ddagger}$ criterion), such ground-state destabilization should significantly augment the transition state stabilization. Finally, while these π-effects are systematically detectable in our data, their subtle magnitude is evident in the fact that the change to D from H exceeds the change from one halide to another.

The same conclusion has been articulated[26] concerning the X-dependence of the thermodynamics of H_2 addition to $IrX(CO)(PH_3)_2$: π-donation by X dominates over σ-effects, and increased π-donation makes H_2 addition less exothermic. Paradoxically, criteria of electron density at Ir such as ν(CO) and oxidation potentials *fail* to correlate these ΔH° trends.

The small size of $\Delta S^{\ddagger}$ for a dissociative process leads to the surprising conclusion that the transition state has little increase in degrees of freedom. That $\Delta S^{\ddagger}$ is only 10% of ΔS° indicates that most of the degrees of freedom remain to be gained along

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(25) Poulton, J. T.; Sigalas, M. P.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.*, submitted for publication.
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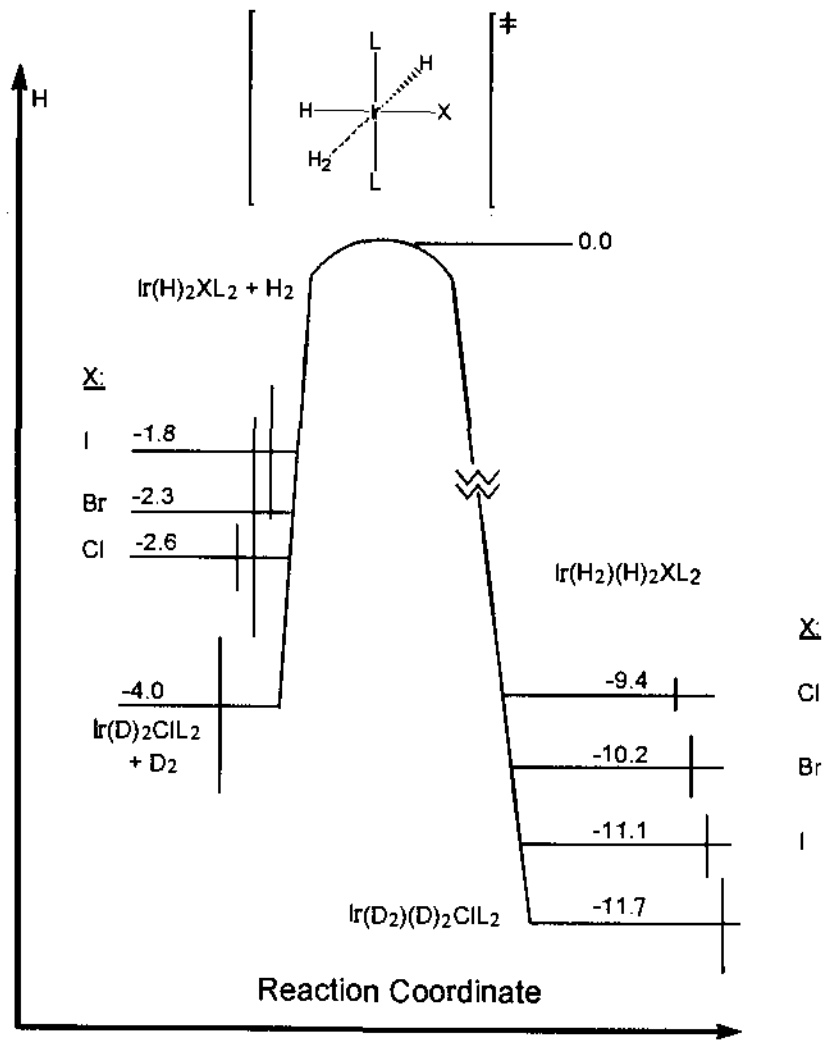
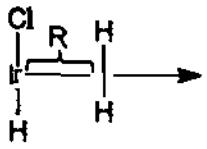


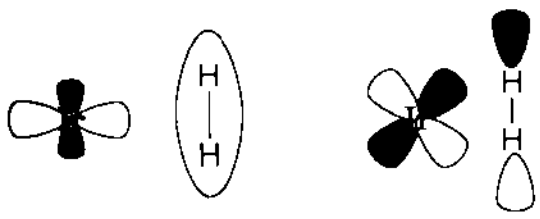
Figure 8. Reaction profile (enthalpies of reaction, kcal/mol, in toluene, with error bars shown to scale) for the reaction $Ir(H)_2X(P^tBu_2Me)_2 + H_2 \rightleftharpoons Ir(H)_2X(H_2)(P^tBu_2Me)_2$. Errors accumulate in $\Delta H^\ddagger$ for H_2 binding since they are derived by subtraction of $\Delta H^\ddagger$(dissociation) and ΔH°.

the reaction coordinate after the free energy turns downward again. The reaction coordinate is anticipated to be with H_2 perpendicular to, but along the vector shown in **Q**. We propose



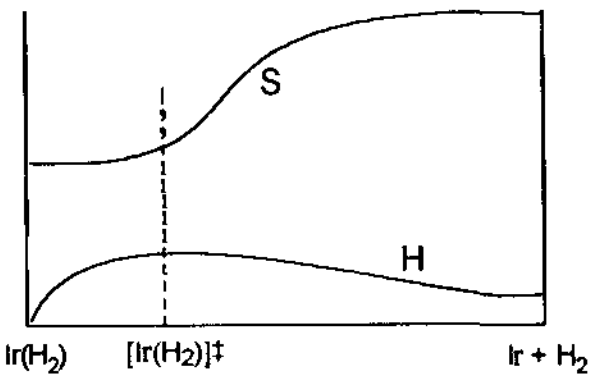
Q

that the free energy turns down at a relatively short distance R as a consequence of the character of the M–(H_2) bond. The π back bonding from Ir to H_2 falls off more quickly with distance than it does in a typical σ bond because of the side-to-side character of the overlap. Peculiar to H_2 is the fact that $H_2 \rightarrow Ir$ σ bonding does not involve a directed ligand lone pair, but instead the filled σ(H–H) orbital, whose density is directed perpendicular to the Ir–(H_2 center-of-mass). Its overlap with a metal orbital will



thus decrease more rapidly with distance than if this ligand were PH_3 or NH_3. As a result, along the reaction coordinate (increased R), enthalpy will immediately rise but entropy will rise only for larger values of R.[27]

(27) After completion of this manuscript, relevant work has appeared on the activation parameters for H_2 loss from $Ir(H)_2X(H_2)(P^iPr_3)_2$ where X = Cl, Br, and I. Le-Husebo, T.; Jensen, C. M. *Inorg. Chem.* **1993**, *32*, 3797. The halide dependence of $\Delta G^\ddagger$ is comparable to that reported here, although their intepretation of the cause is different.



Experimental Section

General. All manipulations were carried out using standard Schlenk and glovebox techniques under prepurified argon. Toluene-d_8 was dried over sodium metal and vacuum distilled prior to use. CD_2Cl_2 was dried over $CaCl_2$ and distilled before use. H_2 (Air Products, Ultra High Purity Grade) and D_2 (Matheson) were used without further purification. All gas transfers were performed on a calibrated gas manifold.

$^{31}P\{^1H\}$ and ^{19}F NMR spectra were recorded on a Nicolet NT360 spectrometer at 146.2 and 339.7 MHz, respectively. ^1H NMR spectra were recorded on a Varian XL300 spectrometer at 299.9 MHz. Positive ^{31}P NMR chemical shifts are downfield from the external 85% H_3PO_4 reference. The standard inversion recovery sequence 180–τ–90 was used to determine T_1. All temperatures were carefully calibrated by using the ^1H NMR chemical shifts of methanol. Negative ^{19}F NMR chemical shifts are upfield from external $CFCl_3$. $Ir(H)_2Cl(P^tBu_2Ph)_2$, $Ir(H)_2I(P^tBu_2Ph)_2$, and $Ir(H)_2Cl(P^tBu_2Me)_2$ have all been prepared previously.[6] $Ir(H)_2Br(P^tBu_2Ph)_2$ and $Ir(H)_2Br(P^tBu_2Me)_2$ were prepared by stirring the respective chlorides with NaBr in toluene overnight and filtering. $Ir(H)_2I(P^tBu_2Me)_2$ was prepared by stirring $Ir(H)_2Cl(P^tBu_2Me)_2$ with NaI in toluene overnight and filtering. Yields for all halide exchanges were essentially quantitative.

Synthesis of $Ir(H)_2F(P^tBu_2Ph)_2$. A solution of $Ir(H)_2Br(P^tBu_2Ph)_2$ in benzene was mixed with CsF and stirred overnight. Little conversion was observed by $^{31}P\{^1H\}$ NMR assay. 18-Crown-6 was then added to the solution which was then stirred overnight. Nearly complete[28] conversion to $Ir(H)_2F(P^tBu_2Ph)_2$ is observed. $^{31}P\{^1H\}$ NMR in C_6D_6: 61.7 (s). ^1H NMR in C_6D_6: 1.49 (vt, 12 Hz), –32.0 (dt, $^2J_{FH}$ = 46 Hz, $^2J_{PH}$ = 12 Hz). ^{19}F NMR in C_6D_6: –204 (t, $^2J_{FH}$ = 46 Hz).

Reactivity of $Ir(H)_2F(P^tBu_2Ph)_2$ with H_2. An NMR tube containing a C_6D_6 solution of $Ir(H)_2F(P^tBu_2Ph)_2$ was freeze–pump–thaw degassed three times. The head space of the tube was filled with 700 Torr of H_2 gas. The tube was then sealed with a flame. Within 15 min, the only observable product by $^{31}P\{^1H\}$ NMR was $Ir(H)_5(P^tBu_2Ph)_2$. The glass of the tube became etched over time, indicating the production of HF.

Sample Preparation. All samples were prepared by transfer of a weighed amount of the solid organometallic compound into an NMR tube. Toluene-d_8 (500 μL) was then added by syringe, and the tube was connected to a gas adapter via Tygon tubing. The solvent was freeze–pump–thaw degassed five times. H_2 (or D_2) gas (700 Torr) was allowed to fill the space above the frozen toluene solution. The gas adapter was then closed and the majority of the tube was immersed in liquid nitrogen. The tube was then sealed with a torch and stored at –15 °C prior to study.

Kinetic Modeling. Between 25 and –90 °C, $^{31}P\{^1H\}$ NMR spectra (Figure 5) of an equilibrium mixture of $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ and $Ir(H)_2X(P^tBu_2Me)_2$ show variable-temperature behavior characteristic of a two-site exchanging system.[9] Two sharp resonances can be observed at –90 °C, but on raising the temperature, they broaden and coalesce, and the resulting averaged signal finally sharpens. In the case of a true two-site exchange (eq 2), the lifetimes of sites τ_A and τ_B can be expressed

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad (2)$$

using the rate constant k_1: $\tau_A = 1/k_1$ and $\tau_B = 1/k_{-1} = R/k_1$ where R is the ratio [B]/[A], i.e., the equilibrium constant.[9] It can be easily shown that for an equilibrium between $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ (A) and $Ir(H)_2X(P^tBu_2Me)_2$ (B) (eq 3), the same definitions for the lifetimes, $\tau_A = 1/k_1$ and $\tau_B = R/k_1$ (R = [B]/[A]), are valid and can be obtained using the following conventional formulae: $\tau_B = (k_1[H_2])^{-1}$ and $K = [B][H_2]/[A] = k_1/k_{-1}$. Thus, equilibria 2 and 3 are spectroscopically

(28) Attempts to use this method to synthesize $Ir(H)_2F(P^tBu_2Me)_2$ failed.

Table 4. NMR Data (in C_6D_6, 25 °C)

	$\delta(^{31}P)$	$\delta(^1H, {}^tBu)$	$\delta(^1H, Me)$	$\delta(^1H, IrH)$
$Ir(H)_2Br(P^tBu_2Me)_2$	48 (s)	1.16 (vt, 12 Hz)	1.65 (br s)	−32.7 (t, 12 Hz)
$Ir(H)_2I(P^tBu_2Me)_2$	48 (s)	1.12 (vt, 13 Hz)	1.97 (br s)	−32.5 (t, 14 Hz)
$Ir(H)_2(H_2)Cl(P^tBu_2Me)_2$[a]	35.5 (br s)	c	c	−10.8 (br s)
$Ir(H)_2(H_2)Br(P^tBu_2Me)_2$[a]	33 (s)	c	c	−10.8 (br s)
$Ir(H)_2(H_2)I(P^tBu_2Me)_2$[a]	29 (s)	c	c	−10.7 (br s)
$Ir(H)_2Cl(P^tBu_2Ph)_2$[b]	67 (s)	1.43 (vt, 13 Hz)		−32.1 (t, 14 Hz)
$Ir(H)_2Br(P^tBu_2Ph)_2$[b]	68 (s)	1.41 (vt, 13 Hz)		−32.7 (t, 13 Hz)
$Ir(H)_2I(P^tBu_2Ph)_2$[b]	70 (s)	1.39 (vt, 13 Hz)		−32.2 (br t, 13 Hz)

[a] −80 °C, in toluene-d_8. [b] Phenyl resonances fall within the range 8.15–7.02 ppm. [c] Not determined due to coalescence with the five-coordinate complex.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B + H_2 \qquad (3)$$

identical in $^{31}P\{^1H\}$ NMR and the two parameters, R and k_1, are sufficient to characterize and simulate the variable-temperature $^{31}P\{^1H\}$ NMR spectra.[29]

The [B]/[A] ratio (R) can be determined experimentally. To avoid the difficulties with integration of strongly broadened lines, we preferred the determination of R at temperatures above the coalescence point, where

$$\delta = a\delta_A + b\delta_B$$

$$a + b = 1$$

δ is the chemical shift of the exchange-averaged resonances, and a and b are the mole fractions of $Ir(H)_2X(H_2)(P^tBu_2Me)_2$ and $Ir(H)_2X(P^tBu_2Me)_2$, respectively.

Care was taken to assure that the chemical shift and peak width at half-height of the $^{31}P\{^1H\}$ NMR signals were constant over the time of one spectrum acquisition (5–10 min). Peak widths at half-height and chemical shifts for broadened signals were conveniently obtained by use of a curve-fitting program from the Nicolet software. In each case, a small (<5%) sharp impurity peak believed to be an iridium carbonyl compound was used as an internal reference (Figure 5). The origin of this compound is unknown. Complete line shape analysis of the variable-temperature $^{31}P\{^1H\}$ NMR spectra was done using DNMR5 (QCMP 059) available from the QCPE at Indiana University.

Thermodynamic Determinations. Transport of H_2 (or D_2) into and/or out of solution proved to be slow at temperatures below −30 °C. Therefore, samples were held at the desired temperature for at least 5 h before spectral measurement in order to assure that both H_2 saturation and equilibrium were attained. The literature data[30] on hydrogen solubility were used in the calculations of the equilibrium constants.

Acknowledgment. This work was supported by the National Science Foundation. D.G. is a recipient of a fellowship from the U.S. National Academy of Sciences/AID.

(29) This conclusion can be expressed in a qualitative way: the phosphorus nuclei do not "know" what kind of changes in the environment make them resonate at two different frequencies.

(30) Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*, John Wiley & Sons: Chichester, 1991.