Relationship of Hydride Fluxionality in $Ir(H)_2L(phosphine)_2^{n+}$ to Properties of L: An Exceptional Range of Barrier Heights

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Introduction

Transition metal polyhydrides are central to the study of homogeneous hydrogenation and hydroformylation catalysis,[1] coordination and activation of molecular hydrogen,[2] and quantum exchange coupling (QEC).[3] Metal hydride/dihydrogen complexes have been characterized by a combination of methods (neutron and X-ray diffraction and solid state and solution NMR spectroscopy)[2] and studied by theoretical methods.[4]

Polyhydride complexes of the general formula MH_xL_y often display dynamic NMR spectra which are consistent with rapid (on the NMR time scale) site exchange between hydride ligands.[5] Using low-temperature ^{1}H NMR at high (300+ MHz) magnetic fields, the decoalescence of hydride signals may be achieved if the free energy of activation ($\Delta G^{\ddagger}$) is above ca. 6 kcal/mol. Line shape analysis of the NMR spectra can be used to measure the rate of hydride site exchange at various temperatures, leading to the determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ by a standard Eyring analysis.[6]

In most cases, the small $\Delta G^{\ddagger}$ for exchange between chemically inequivalent hydride ligands causes the coalescence temperature to be below 25 °C. We report here that, by virtue of incorporation of ligands L with varying steric and electronic properties, in a homologous series, the $\Delta G^{\ddagger}$ value can, in fact, be altered over an unexpectedly wide range. In one case, a square-pyramidal structure shows inequivalent ^{1}H NMR signals for apical and basal hydrides even at 25 °C.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk and glovebox techniques under argon. $CHCl_3$ was distilled from P_2O_5 under argon. Diglyme-d_{14}, THF-d_8, and toluene-d_8 were dried over sodium metal and vacuum distilled before use in a glovebox. CD_2Cl_2 and $CDCl_3$ were dried over CaH_2 and vacuum distilled before use in a glovebox. ^{1}H (referenced to residual solvent impurity), ^{13}C, ^{31}P (referenced to external 85% H_3PO_4), and ^{19}F (referenced to external $CFCl_3$) NMR spectra were collected on Varian Gemini-300 and Inova-400 spectrometers using methanol to calibrate the probe temperature. IR spectra were collected on a Nicolet 510T FT-IR spectrometer. $[H(Et_2O)_2][BAr'_4]$ and $Na[BAr'_4]$ ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) were prepared according to a literature procedure[7] ($[H(Et_2O)_2][BAr'_4]$ was stored under argon at −20 °C). $Ir(H)_2X(P^tBu_2Ph)_2$ ($X = NHC(O)CH_3$, N_3, OSO_2CF_3),[8] $Ir(H)_2Cl(CO)(P^tBu_2Ph)_2$,[9] $[IrH(\eta^2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)][BAr'_4]$,[10] and $[Ir(H)_2L_3][BAr'_4]$ ($L = PCy_2Ph$, P^iPr_2Ph)[10] were prepared according to literature procedures.

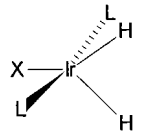
$[Ir(H)_2(CO)(P^tBu_2Ph)_2][BAr'_4]$. A solution of $Ir(H)_2Cl(CO)(P^tBu_2Ph)_2$ (325 mg, 0.46 mmol) in $CHCl_3$ (20 mL) was added to $Na[BAr'_4]$ (410 mg, 0.46 mmol) to form a colorless suspension. This was stirred for 30 min at room temperature, developing a light yellow color during this time. The solution was filtered and the solvent removed in vacuo to yield a light yellow solid (665 mg, 93%). ^{1}H NMR ($CDCl_3$, 25 °C): 7.71 (m), 7.59 (s) 7.51−7.34 (m), 1.31 (vt, J_{PH} = 7.5 Hz), −2.0 (br s), −36.5 (br s). ^{13}C{^{1}H} NMR (THF-d_8, −60 °C): 188.13 (br s), 163.11 (m), 136.11 (m), 136.61 (t, J_{PC} = 4.9 Hz), 135.56 (s), 132.65 (s), 130.58 (m), 130.27 (m), 129.95 (m), 129.64 (s), 129.56 (m), 126.93 (s), 124.26 (s), 121.52 (s), 118.55 (m), 39.79 (t, J_{PC} = 11.8 Hz), 37.47 (t, J_{PC} = 12.6 Hz), 29.95 (s), 29.22 (br s). ^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C): 61.9 (s). ^{19}F NMR ($CDCl_3$, 25 °C): −63.4 (s). IR ($CDCl_3$): ν(CO) 2031 cm^{-1}.

$[Ir(H)_2(HN_3)(P^tBu_2Ph)_2][BAr'_4]$. In an NMR tube was dissolved $Ir(H)_2(N_3)(P^tBu_2Ph)_2$ (25 mg, 0.037 mmol) in 0.6 mL of a 7:3 mixture of THF-d_8/toluene-d_8. To this orange solution was added $[H(Et_2O)_2][BAr'_4]$ (35 mg, 0.037 mmol). Upon mixing, the solution darkened slightly. ^{1}H NMR (7:3 THF-d_8/toluene-d_8, 25 °C): 7.95 (m), 7.81 (m), 7.63 (br s), 7.42−7.38 (overlapping m), 1.20 (vt, J_{PH} = 6.4 Hz), −33.9 (br t). ^{31}P{^{1}H} NMR (7:3 THF-d_8/toluene-d_8, 25 °C): 72.1 (s).

$[Ir(H)_2(H_2)(P^tBu_2Ph)_2][BAr'_4]$. In an NMR tube, fitted with a Teflon stopcock, was dissolved $[IrH(\eta^2\text{-}C_6H_4P^tBu_2)(P^tBu_2Ph)][BAr'_4]$ (25 mg, 0.016 mmol) in 0.6 mL CD_2Cl_2. This orange solution was degassed three times (freeze−pump−thaw) and cooled to −78 °C in a dry ice/acetone bath. H_2 (760 Torr) was added to the solution. The solution was agitated for 10 min at −78 °C, quickly changing color from orange to light yellow. The sample was inserted into a NMR probe which had been precooled to −90 °C. ^{1}H NMR (CD_2Cl_2, −90 °C, hydride and dihydrogen ligands only): −0.02 (br s, 2H), −10.0 (br s, 1H), −41.2 (br s, 1H). ^{31}P{^{1}H} NMR (CD_2Cl_2, −90 °C): 58.3 (s).

Results and Discussion

Determination of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for $[Ir(H)_2LL'_2]^{n+}$ Hydride Site Exchange. Complexes with the formula $Ir(H)_2XL_2$ (X = halide, L = bulky phosphine) have been reported to contain only one resonance in the room temperature ^{1}H NMR spectrum for the hydride ligand.[11] This is consistent with a C_{2v} symmetric structure (**I**) for the $Ir(H)_2XL_2$ core, which would make the



I

hydrides equivalent by symmetry. However, the solid-state

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Scheme 1

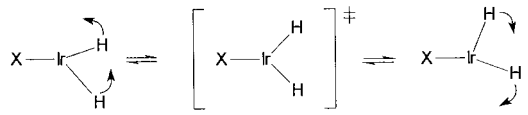

Table 1. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for $[Ir(H)_2LL'_2]^{n+}$ Hydride Site Exchange

L	L′	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (eu)[a]	T range[h] (°C)
Cl[c]	P^{t}Bu$_2$Ph	7.4 ± 0.2[b]	7.7 ± 0.4[b]	
Br[c]	P^{t}Bu$_2$Ph	8.0 ± 0.2[b]	5.6 ± 1.4[b]	
I[c]	P^{t}Bu$_2$Ph	7.9 ± 0.2[b]	0.1 ± 1.2[b]	
OSO_2CF_3[d]	P^{t}Bu$_2$Ph	6.3 ± 0.6	−1.9 ± 1.5	−120 to −50
HN_3[d]	P^{t}Bu$_2$Ph	7.1 ± 0.3	−2.3 ± 0.7	−100 to −10
CO[e]	P^{t}Bu$_2$Ph	11.6 ± 0.3	−3.5 ± 0.8	0 to +120
H_2[f]	P^{t}Bu$_2$Ph	8.6 ± 0.9	−4.2 ± 2.5	−80 to −60
$NHC(O)CH_3$[c]	P^{t}Bu$_2$Ph	9.4 ± 0.1	−5.7 ± 0.2	−50 to +50
P^{i}Pr$_2$Ph[g]	P^{i}Pr$_2$Ph	4.8 ± 0.2	−16.3 ± 1.1	−110 to +30
PCy$_2$Ph[g]	PCy$_2$Ph	5.0 ± 0.4	−18.6 ± 1.1	−110 to +50

[a] "eu", cal mol^{-1} K^{-1}. [b] From ref 6. [c] In toluene-d_8. [d] In 70:30 THF-d_8/toluene-d_8. [e] In diglyme-d_{14}. [f] In CD_2Cl_2. [g] In THF-d_8. [h] Temperatures between which rate constants were obtained.

structure of $Ir(H)_2Cl(P^tBu_2Ph)_2$, determined by neutron diffraction, has revealed the complex adopts a structure in which the hydrides are *not* equivalent.[12] The variable-temperature ^{1}H NMR spectra of $Ir(H)_2X(P^tBu_2Ph)_2$ (X = Cl, Br, I) suggest a fluxional process in which the inequivalent hydrides participate in a two-site exchange process through a transition state with C_{2v} symmetry (Scheme 1; the phosphines, which lie out of the plane of the paper, have been omitted). The activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were obtained from the variable temperature ^{1}H NMR spectra but show no clear dependence on the properties of the halide ligand.[6]

A recently devised synthetic methodolgy[8] and halide abstraction reactions[10,13] have afforded a number of new $[Ir(H)_2LL'_2]^{n+}$ complexes which we now find to exhibit hydride site-exchange fluxionality which can be decoalesced. From line shape analysis[14] of variable-temperature ^{1}H NMR spectra of these complexes, the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have been determined (Table 1). We find no solvent dependence of these kinetic parameters upon changing from CD_2Cl_2 to THF-d_8. The large number of examples assist in identification of several trends regarding the influence of the steric and electronic characteristics of ligands L and L′ on the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for $[Ir(H)_2LL'_2]^{n+}$ hydride site exchange.

The $\Delta H^{\ddagger}$ values (L ≠ phosphine) range from 6.3 (L = OSO_2CF_3) to 11.6 (L = CO) kcal/mol. Assuming only a small contribution from $\Delta S^{\ddagger}$ (close to zero for OSO_2CF_3 and CO), these define the limits of the barrier ($\Delta G^{\ddagger}$) to dynamic processes which are amenable to measurement by variable temperature ^{1}H NMR. At 300 MHz, the hydrides of $Ir(H)_2(OSO_2CF_3)(P^tBu_2Ph)_2$ decoalesce at −90 °C, while the coalescence of the hydrides in $[Ir(H)_2(CO)(P^tBu_2Ph)_2][BAr'_4]$ does not occur until +100 °C. This is a remarkably varied range of fluxionality controlled by the ligand L in these molecules.

Effect of the Electronic Character of Ligand L on $\Delta H^{\ddagger}$. The presence of a weak Ir−O bond in $Ir(H)_2(\eta^2\text{-}NHC(O)CH_3)(P^tBu_2Ph)_2$,[8] which must dissociate in the transition state, raises the $\Delta H^{\ddagger}$ for hydride site exchange in this complex. Other examples that show high $\Delta H^{\ddagger}$ are purely five-coordinate $[Ir(H)_2LL'_2]^+$ (L = CO and H_2) which have π-acidic ligands L. For these complexes, a high barrier is not unexpected, because moving toward a C_{2v} symmetrical transition state (**I**) lowers the amount of back-bonding to the π-acid ligands L. The large difference in the π-acidity of the two ligands (CO stronger than H_2) is reflected in the higher, by 3.0 kcal·mol^{-1}, $\Delta H^{\ddagger}$ for hydride site exchange in $[Ir(H)_2(CO)L'_2]^+$ vs $[Ir(H)_2(H_2)L'_2]^+$. For comparison to these values, the $\Delta H^{\ddagger}$ for hydride site exchange in isoelectronic $Ru(H)_2(CO)(P^tBu_2Me)_2$ is found to be 7.6 (±0.2) kcal/mol.[15] That this enthalpy of activation is significantly lower than that for cationic $Ir(H)_2(L)(P^tBu_2Ph)_2^+$ (L = H_2 or CO) is evidence for increased destabilization of the C_{2v} transition state caused by the relatively weak back-bonding ability of the cationic iridium centers in comparison to $Ru(H)_2(CO)(P^tBu_2Me)_2$. Thus, the $\Delta H^{\ddagger}$ for hydride site exchange is dependent on both the π-acidity of ligand L (CO vs H_2) and the π-basicity of the metal (cationic Ir vs neutral Ru).

While a C_{2v} transition state minimizes back-bonding to π-acidic ligands L, raising $\Delta H^{\ddagger}$ for site exchange, this geometry actually maximizes the available π-donation[16] from L.[12] $Ir(H)_2L(phosphine)_2$ (π-donor L = Cl, Br, I, OSO_2CF_3, HN_3) complexes adopt a ground state with inequivalent hydrides but there is no electronic destabilization of a C_{2v} transition state to hydride site exchange. The net result of the electronic contributions of ligands L to the C_{2v} transition state is to lower the $\Delta H^{\ddagger}$ for hydride site exchange involving complexes with π-donor ligands and raise $\Delta H^{\ddagger}$ for complexes with π-acid ligands.

Effects of Steric Contributions from Ligands L and L′ on $\Delta S^{\ddagger}$. Analysis of the $\Delta S^{\ddagger}$ values yields important information about the effect of steric congestion on the barrier to hydride site exchange. Increased steric bulk in the ligands L and L′ of $[Ir(H)_2LL'_2]^{n+}$ results in increasingly negative values of $\Delta S^{\ddagger}$. When only two phosphines are present in $[Ir(H)_2LL'_2]^{n+}$, $\Delta S^{\ddagger}$ ranges from +7.7 to −5.7 cal mol^{-1} K^{-1}. The bulkier phosphines of $Ir(H)_2(CO)(P^tBu_2Ph)_2^+$ yield a $\Delta S^{\ddagger}$ of −3.5 eu compared to $\Delta S^{\ddagger}$ = 6.5 (±1) eu for hydride site exchange in $Ru(H)_2(CO)(P^tBu_2Me)_2$. Upon coordination of three bulky phosphines (i.e., the last two entries in Table 1), a decrease of over 10 cal mol^{-1} K^{-1} is observed. The rearrangement of Scheme 1 is significantly impeded by axial/equatorial phosphine congestion. The larger cone angle of PCy_2Ph[17] makes $\Delta S^{\ddagger}$ more negative by 2.3 cal/mol K in $[Ir(H)_2L_3]^+$ compared to less bulky P^{i}Pr$_2$Ph. A more negative $\Delta S^{\ddagger}$ corresponds to greater organization in the transition state, characteristic of the need of phosphine ligands to reorient bulky alkyl substituents. In a steric environment as crowded as that found for $[Ir(H)_2L_3]^+$ (L = PCy_2Ph, P^{i}Pr$_2$Ph), the open (equatorial) coordination site represents a "vacant area" for occupation by phosphine alkyl groups. Thus, the crystal structure of $[Ir(H)_2(PCy_2Ph)_3][BAr'_4]$, but not its P^{i}Pr$_2$Ph analogue, shows an agostic interaction from a cyclohexyl group, which is promoted by the steric bulk of the phosphines.[10] In the proposed transition state for hydride site exchange, a hydride ligand is moving toward the empty coordination site, prompting the need to move any alkyl groups *from* this area of the coordination sphere of the metal. At the same time, the motion of the hydride ligands opens space on the other side of

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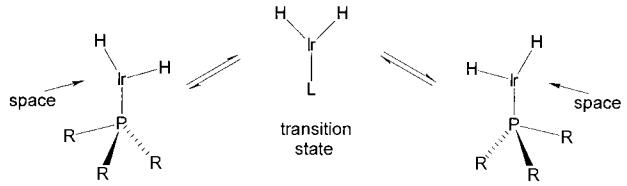
Scheme 2



the coordination sphere, ultimately resulting in a "new" space for occupation by phosphine alkyls (Scheme 2).

Conclusions

The energetics of the rearrangement in Scheme 1[18] are shown to vary by more than a factor of 2 in $\Delta H^{\ddagger}$, and this can be reasonably attributed to dominant contributions by π-acidity or π-donation by L and by steric effects of L′ interfering with L (when the latter is itself a phosphine). While the $T\Delta S^{\ddagger}$ term (at 273 K) is generally within ± 2 kcal/mol of zero, the very congested cases when L = $P^{i}Pr_2Ph$ or PCy_2Ph show an entropy cost of 4−5 kcal/mol in going to the transition state. Although only the latter of these has an agostic (axial) phosphine substituent (cyclohexyl), this factor is apparently less important than are steric repulsions, since $\Delta H^{\ddagger}$ is indistinguishable between these two phosphines.

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