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Heterolytic dihydrogen activation in an iridium complex with a pendant basic group

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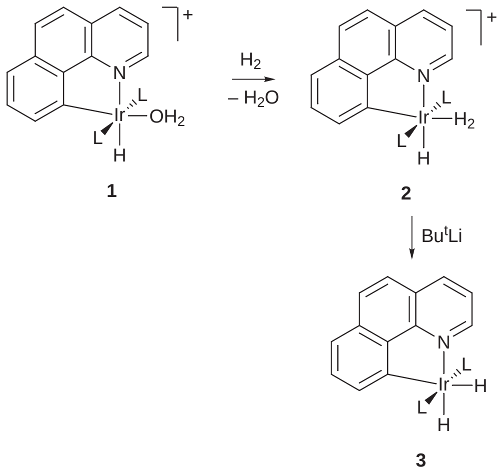
Experimental and theoretical studies show that H_2 reacts with an Ir phosphine complex having a basic pendant amino group to give either an H_2 or an Ir–H···H–N hydrogen-bonded hydride complex, depending on the basicity of the phosphine ligands.

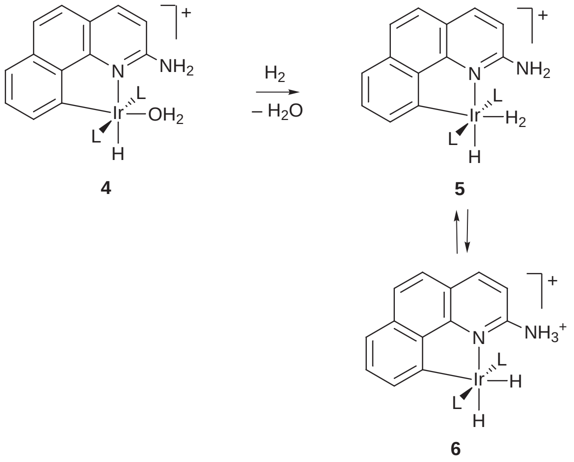
Heterolytic hydrogen activation by a transition metal complex can occur by deprotonation of an intermediate dihydrogen complex by an external base, as shown in several studies.[1–6] We have shown that appending an NH_2 group at the 2-position of a cyclometalated 7,8-benzoquinolinate ligand (bq-NH_2) can lead to ligand binding *via* both M–L bonds and –N–H···L hydrogen bonds.[7] Since the pendant NH_2 group is basic, we have now examined the possibility that the pendant group can act as an internal base to deprotonate an adjacent H_2 ligand.

We have compared the reactivity of a series of bq-NH_2 complexes with that of the corresponding unsubstituted benzoquinolinate analogue (bq-H) that lacks the pendant group. In the comparison bq-H system, the known cationic aqua complex, $[IrH(bq\text{-}H)(OH_2)(PPh_3)_2]BF_4$ **1**, reacts with H_2 to give a cationic H_2 complex, **2**, previously characterized in detail.[8] Addition of Bu^tLi as base leads to deprotonation of the H_2 ligand to form the known neutral dihydride, $[IrH_2(bq\text{-}H)(PPh_3)_2]$ **3** (Scheme 1).



Scheme 1

The aqua complex, $[IrH(bq\text{-}NH_2)(OH_2)(PPh_3)_2]BF_4$ **4a**, in the new pendant amine system also reacts with H_2 to give, not the corresponding H_2 complex, **5a**, but *via* heterolytic activation to give the dihydride, **6a**, instead (Scheme 2). Complex **6a** was fully characterized as $[IrH_2(bq\text{-}NH_3)(PPh_3)_2]BF_4$ and its identity is shown, for example, by the spectral data. The reaction is accompanied by the loss of both the ^1H NMR triplet hydride resonance at δ −16.4 and the amino resonance at δ 6.1 characteristic of **4a**, and the appearance of two sharp, mutually coupled (dt, $^2J_{HH'}$ 8.5; $^2J_{PH}$ 14.6 Hz) hydride resonances at δ −23.2 and −25.7, and a broad resonance at δ 3.8, which are respectively assigned to the *cis*-hydrides and the NH_3^+ protons.

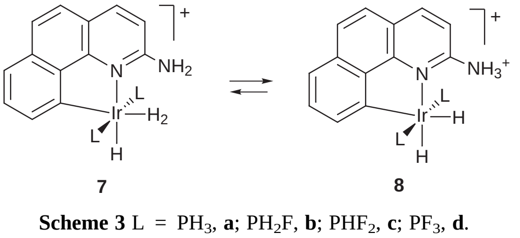


Scheme 2 L = PPh_3, **a**; $PMePh_2$, **b**; PEt_2Ph, **c** or PBu^n_3, **d**.

This conversion is completely reversible: removing the dihydrogen gas from the solution with a stream of dinitrogen causes the resonances at δ −23.2 and −25.7 to disappear, and the signal at δ −16.1 to reappear in the ^1H NMR spectrum. Complex **6a** readily loses H_2 in the solid state, and as a result we were unable to isolate it for elemental analysis or IR studies.

Theoretical work (DFT-B3PW91)† on the model systems $[IrH(bq\text{-}NH_2)(H_2)(PH_3)_2]^+$ **7a** and $[IrH_2(bq\text{-}NH_3)(PH_3)_2]^+$ **8a** gave the unexpected result that the H_2 complex is the more stable form by 12 kcal mol^{-1}, contrary to the result in the experimental system. In considering why there might be a difference between the experimental pair **5**/**6** and the theoretical model pair **7**/**8** (Scheme 3), we considered the possibility that the change from PPh_3 to PH_3 was responsible. If so, we felt that the more basic alkyl phosphines would be a better experimental comparison.

Accordingly, we studied the species, $[IrH(bq\text{-}NH_2)(OH_2)(PBu^n_3)_2]BF_4$ **4d**, made *via* the standard route,[7,8] where the aryl groups have been replaced by alkyls. Hydrogen was passed for 1 min at −80 °C in the presence of anhydrous $MgSO_4$ to facilitate removal of water. Even with such a small change, we find that the H_2 complex, **5d**, is now formed on reaction with H_2, not the dihydride **6d**. The identity of the H_2 complex followed from the ^1H NMR data, which show two separate resonances below 230 K, a broad one at δ −4.7 for the coordinated H_2 molecule and a sharp one at δ −17.2 for the



Scheme 3 L = PH_3, **a**; PH_2F, **b**; PHF_2, **c**; PF_3, **d**.

Table 1 IR data for $[IrH(bq\text{-}NH_2)(CO)(L)_2](BF_4)$ which shows the order of donor power of the phosphines studied

Ligand (L)	ν_{CO}/cm^{-1}
PPh_3 (**9a**)	2026.5
$PMePh_2$ (**9b**)	2021.8
PEt_2Ph (**9c**)	2015.3
$PBu^n{}_3$ (**9d**)	2004.6

classical hydride. These chemical shifts are close to those for the unsubstituted analogue $[IrH(bq\text{-}H)(H_2)(PPh_3)_2]BF_4$ **2**.[8] The HD complex (d^1-**5b**)shows a $^1J_{HD}$ coupling of 29.3 Hz.

Similar results were obtained with other basic phosphines, PEt_2Ph and $PMePh_2$, so the result is general. In no case was an equilibrium seen between dihydrogen complex **5** and hydride **6**. This implies that moving to a more basic phosphine decreases the acidity of the coordinated H_2 ligand in **5** and correspondingly increases the basicity of the terminal hydride in **6**. This results in the proton moving completely from the $NH_3{}^+$ group of **6** to the terminal hydride to give **5** on changing from PPh_3 to any of the more basic phosphines.

This large change of structure is rather surprising for such a relatively small change in ligand, and we wanted to verify that the basicity of the phosphines was indeed varying in the expected manner. Reaction of the aqua complex, **4** with CO (1 atm) in CH_2Cl_2 gave the carbonyl species $[IrH(bq\text{-}NH_2)(CO)(L)_2]BF_4$ (**9**, L = PPh_3, **a**; $PMePh_2$, **b**; PEt_2Ph, **c**; $PBu^n{}_3$, **d**). The IR data obtained for these complexes (Table 1) verifies that the basicity is indeed higher for the more highly alkylated phosphines. Having only one CO but two L groups makes this system much more sensitive to change of phosphine than Tolman's $LNi(CO)_3$ system,[9] but the trends are essentially the same.

Returning to the theoretical work, we have a rare case where the quantum model PH_3 is inadequate to reproduce the experimental observations on a PPh_3 complex. In order to model the more electron-accepting PR_3 groups, we have now moved to PFH_2 (**7b**/**8b**), PF_2H (**7c**/**8c**), and PF_3 (**7d**/**8d**); of course these are far more electron-withdrawing than the experimental PPh_3 group, but we were only interested in seeing if the correct trends could be reproduced. Indeed, as shown in Table 2, the calculated energies for **7** and **8** do alter in the expected fashion, confirming that the acid/base character of the Ir–H/Ir–(H_2) system shows an unexpectedly strong dependence on the nature of the phosphine.

Table 2 The theoretical structural (Å) and energetic parameters (kcal mol^{-1}) of dihydrogen complex **7** and dihydride **8** with change of phosphine

	7		**8**		
Ligand	d_{HH}	$d_{H\cdots H}$	d_{NH}	$d_{H\cdots H}$	ΔE^a
PH_3	0.861	1.854	1.135	1.412	−12
PFH_2	0.851	1.829	1.090	1.548	−2.5
PF_2H	0.856	1.873	1.093	1.502	+0.5
PF_3	0.847	1.849	1.073	1.618	+3.0

^{a} $E(\mathbf{8}) - E(\mathbf{7})$ is reported, so negative values imply the dihydrogen complex is more stable.

The structural parameters of **7** and **8** from the theoretical work (Table 2) are in good agreement with the solid state structure of $[IrH(bq\text{-}NH_2)(CO)(L)_2]PF_6$ for which experimental structural data is available.[10] For all phosphine ligands, **7** and **8** both correspond to energy minima. In **7**, the dihydrogen ligand is always coplanar with the *cis*-Ir–H bond and the pendant NH_2 group is coplanar and conjugated with the bq ligand. As expected, the H–H distance in **7** decreases (from 0.861 to 0.847 Å) with increasing F substitution on the phosphine (Table 2) showing the effects of the diminished back-donation along the series. In **8**, the N–H bond interacting with the hydride *via* a dihydrogen bond[11] is elongated, especially for PH_3 (d_{NH} = 1.135 Å) where the hydride is the most basic and the dihydrogen bond distance is the shortest ($d_{H\cdots H}$ = 1.412 Å). The compounds cannot be isolated because they lose hydrogen too readily, consistent with the presence of a strong N–H···H–Ir interaction. This 1.4 Å H···H distance is significant because it is considerably shorter than any so far suggested for a dihydrogen bond, consistent with a particularly strong interaction, and is even in the range proposed for stretched dihydrogen complexes, so the species could even be considered as representing an arrested intermediate stage of heterolytic H_2 activation. Going from PH_3 to PF_3 leads to an elongation of $d_{H\cdots H}$ to 1.618 Å, however, beyond the upper limit of 1.6 Å proposed for stretched H_2 complexes, showing the strong sensitivity of the structure to the nature of the phosphine.

This work shows that the very strong dependence[1,2,20] of the pK_a of the H_2 ligand has interesting effects on the reactivity of these complexes toward H_2 and on the structure of the resulting hydrides even with relatively small changes in the ligand sphere. The pK_a of the H_2 ligand seems to be unusually sensitive to back bonding effects, even though the changes in d_{HH} are relatively modest (Table 2). From a theoretical standpoint, great care should be taken in modelling such systems.

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Notes and references

† *Computational details*: All the calculations were performed with the Gaussian 94 set of programs[12] at the B3PW91 level[13,14] level. Iridium was represented with the Hay–Wadt relativistic core potential (ECP) for the 60 innermost electrons and its associated double-ζ basis set.[15] Phosphorus atoms were also represented with Los Alamos ECPs and their associated double-ζ basis set[16] augmented by a polarisation d function.[17] A 6-31G(d,p) basis set[18,19] was used for the atoms bound directly to Ir (H, C, and N) and for the atoms of the amido group (N and H), all the other atoms have been described with a 6-31G basis set.[18] Full geometry optimisations within C_s symmetry (the bq-NH_2 ligand is planar) have been carried out within the framework of DFT (B3PW91).

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