16-Electron, non-π-stabilized $Ir(H)_2(H_2)(PBu^t_2Ph)_2{}^+$ and 18-electron $Ir(H)_2(H_2)_2(PBu^t_2Ph)_2{}^+$: fluxionality and H/D exchange as independent processes‡

Alan C. Cooper,[a] Odile Eisenstein*,[b] and Kenneth G. Caulton*,[a]

[a] *Department of Chemistry Indiana University, Bloomington, Indiana 47405-4001, USA*
[b] *LSDSMS (UMR 5636), Université de Montpellier 2, 34095 Montpellier Cedex 5, France*

Variable-temperature ^1H NMR studies and *ab initio* (B3LYP) calculations have revealed hydride site exchange in $[Ir(H)_2(H_2)(PBu^t_2Ph)_2][BAr'_4]$ $[Ar' = C_6H_3(CF_3)_2\text{-}3,5]$ as well as fluxional and HD formation processes in $[Ir(H)_2(H_2)_2(PBu^t_2Ph)_2][BAr'_4]$ that occur *via* independent mechanisms.

Transition-metal polyhydrides and complexes containing coordinated molecular hydrogen have been the subjects of extensive study.[1] Among the subset containing both hydride and dihydrogen ligands, many coordinatively saturated complexes have been characterized by a combination of methods (neutron and X-ray diffraction, solid-state and solution NMR spectroscopy) and studied by theoretical methods.[2] However, there have been few experimental or theoretical studies of coordinatively *unsaturated* dihydrogen complexes, and these few examples are all similar in containing a π-donating[3] halide or pseudo-halide ligand.[4]

In contrast, a coordinatively unsaturated dihydrogen complex which does not contain any π-donor ligands is formed quantitatively (by ^1H and $^{31}P\{^1H\}$ NMR) in the reaction of $[IrH(\eta^2\text{-}C_6H_4PBu^t_2)(PBu^t_2Ph)][BAr'_4]$ (1) $[Ar' = C_6H_3(CF_3)_2\text{-}3,5]$ with an excess of H_2 (760 torr) in CD_2Cl_2 at 193.8 K. This complex, $[Ir(H)_2(H_2)(PBu^t_2Ph)_2][BAr'_4]$ (2), is persistent in solution at temperatures below *ca.* 213 K. Above this temperature, binding of an additional H_2 ligand becomes apparent (*vide infra*). Therefore, the sequential addition of H_2 to 1 allows for the synthesis of 2 in a way that cannot be achieved by protonation of $IrH_5(PR_3)_2$.[5]

The dihydrogen ligand of 2 is found in the ^1H NMR spectrum at -0.02 ppm as a broad singlet from 183–213 K. The two hydride resonances (-10.0 and -41.2 ppm, *trans* to H_2 and *trans* to the empty coordination site respectively) broaden *equally* (i.e., without coalescing with the -0.02 ppm signal) as the temperature is raised from 183 to 213 K, indicative of a two-site hydride exchange process.[6] Simulation of the variable-temperature ^1H NMR spectra[7] resulted in an Eyring plot with activation parameters $\Delta H^\ddagger = 8.6\ (\pm 0.9)$ kcal mol^{-1} and $\Delta S^\ddagger = -4.5\ (\pm 2.5)$ e.u. (nearly zero and indicative of an intramolecular process) for this exchange.

The optimized structure† (Fig. 1) of $IrH_4(PH_3)_2{}^+$ (GS$_{H4}$) is a dihydrogen adduct of the 14-electron species, $Ir(H)_2(PH_3)_2{}^+$, in which H_2 coordinates *trans* to one hydride ligand to yield a square-based pyramidal ground-state structure with inequivalent hydrides. Owing to the poor capability of this unsaturated Ir^{III} center for backbonding to the dihydrogen ligand,

the H—H bond remains short (0.800 Å). The experimental H—H distance of 0.85 Å in 2 {derived from the J_{HD} value[9] in $[Ir(H)_{2-x}(D)_x(HD)(PBu^t_2Ph)_2][BAr'_4]\}$ is among the shortest observed for known dihydrogen complexes.[1b,10] The H_2 ligand prefers to be perpendicular to the plane of Ir and the two hydrides, although the rotational barrier is very small (0.2 kcal mol^{-1}).
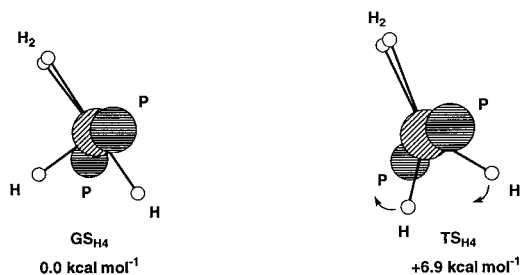
A transition state for hydride exchange (TS$_{H4}$) has been located at 6.9 kcal mol^{-1} above the ground state (Fig. 1 and Scheme 1, at far right), close to the experimental value of 8.6 kcal mol^{-1}, and well below the calculated binding energy of H_2 to $Ir(H)_2(PH_3)_2{}^+$ (11.8 kcal mol^{-1}). The calculated energy of TS$_{H4}$ is probably a lower limit to the experimental value since an agostic interaction may have to be broken in reaching the transition state; $Ir(H)_2(PBu^t_2Ph)_2{}^+$ has two agostic interactions from Bu^t groups.[11] The geometry of TS$_{H4}$ (Fig. 1) has an acute angle between the two hydrides (73.8°), similar to that in $IrH_2Cl(PH_3)_2$.[12] In this geometry (Y-shaped), H_2 needs to be perpendicular to the molecular mirror plane to benefit from the back-donation by the occupied metal d orbital. It is quite remarkable that such a structure is energetically accessible despite the absence of a π-donor ligand and the relatively weak binding energy of H_2 to the metal center.

The reaction of 1 or $[Ir(H)_2(PBu^t_2Ph)_2][BAr'_4]$[11] with H_2 (760 torr) at 298 K for 10 minutes, followed by cooling to 243 K results in the appearance of a broad signal in the ^1H NMR spectrum at -7.4 ppm.‡ Upon decreasing the temperature, this signal broadens and below 213 K a 2 : 1 mixture of 2 and $[Ir(H)_2(H_2)_2(PBu^t_2Ph)_2][BAr'_4]$ [3, decoalesced high-field ^1H NMR signals: -3.75 (br, s, 4H) and -14.8 ppm (s, 2H)] is observed. These ^1H NMR resonances of 3 are very similar to those reported for $Ir(H)_2(H_2)_2(PCy_3)_2{}^+$ (Cy = C_6H_{11}) at low temperature.[5] The broad signal at -7.4 ppm in the 243 K ^1H NMR spectrum is assigned to the coalesced signal for the two hydrides and the two dihydrogen ligands of 3. Indeed, the calculated chemical shift of the coalesced resonance, based upon the decoalesced chemical shifts of the hydrides and dihydrogen ligands of 3, is -7.4 ppm. The hexacoordinated $IrH_6(PH_3)_2{}^+$ (GS$_{H6}$) is calculated (Scheme 1) to have an octahedral structure with two *cis* dihydrogen ligands coordinated to the metal; there is almost no barrier for rotation of the H_2 ligands. The larger binding energy of H_2 to $Ir(H)_2(H_2)(PH_3)_2{}^+$

Fig. 1 Optimized structures and relative energies for $Ir(H)_4(PH_3)_2^+$: GS_{H4} (ground-state structure) and TS_{H4} (transition state for hydride site exchange). Arrows in TS_{H4} indicate schematically the motion of atoms (transition-state vector) from TS_{H4} to GS_{H4}. PH_3 hydrogens omitted for clarity

$(13.3 \text{ kcal mol}^{-1})$ compared to the H_2 binding energies of $6.8–9.3$ kcal mol^{-1} measured for $Ir(H)_2(H_2)X(PBu^t_2Ph)_2$ $(X = Cl, Br \text{ or } I)^{13}$ is due to the lack of a π-donor ligand at the metal. Substituting PMe_3 for PH_3 increases the binding energy of H_2 to $Ir(H)_2ClL_2$ by 2 kcal mol^{-1} due to stronger σ-donation by PMe_3.[14] Thus, the actual binding energy of H_2 to **2** is likely to be higher than 13.3 kcal mol^{-1}.

The rapid site exchange between hydrides and dihydrogen ligands of **3** might provide a mechanism for the formation of HD upon reaction of $[Ir(H)_2(PBu^t_2Ph)_2][BAr'_4]$ with D_2. A transition state, TS_{H6}, associated with the cleavage of *one* of the dihydrogen ligands of $Ir(H)_2(H_2)_2(PH_3)_2^+$ has been located 15.7 kcal mol^{-1} above GS_{H6} (Scheme 1). TS_{H6} (Fig. 2) has pentagonal-bipyramidal geometry (C_{2v} symmetry) with a coordinated H_2 ligand (H—H distance 0.81 Å). As indicated by the direction of the transition-state vector (which shows the motion of atoms from TS to reactants or products), this transition state is implicated in the cleavage and formation of a H—H bond *cis* to the intact H_2 ligand. This transition state can serve to coalesce the hydride and dihydrogen resonances of **3** in the ^1H NMR spectrum at 243 K, since all H centers will be alternatively hydrides and part of dihydrogen ligands. However, this transition state cannot account for the formation of free or coordinated HD because it accomplishes pairwise exchange of one H_2 with *two* hydrides (Scheme 1). To form HD, *one* hydride must exchange with H_2. Such a process is effected by transition state, $TS_{H6'}$, 8.4 kcal mol^{-1} above TS_{H6}. This accomplishes exchange of the intact H_2 (or D_2) with a *cis* hydride (Fig. 2, at right). In $TS_{H6'}$ (C_{2v} symmetry), the intact H_2 and a *cis* hydride are brought into close proximity $[H(1)\cdots H(6)$ and $H(5)\cdots H(6)$ separation of 1.12 Å]. The
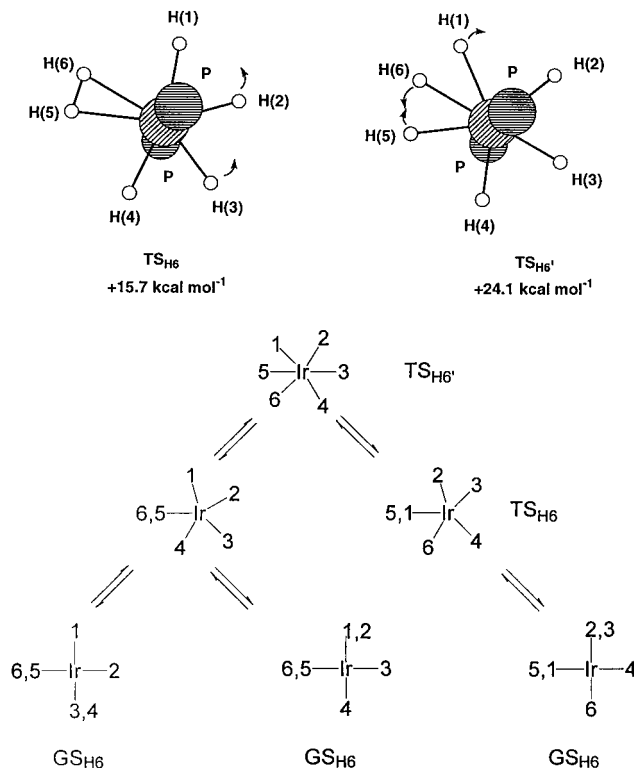

Fig. 2 Optimized structures and relative energies, in reference to the ground state (not shown), of the two transition states (TS_{H6} and $TS_{H6'}$) involved in fluxionality and HD formation in $Ir(H)_6(PH_3)_2^+$. Arrows indicate schematically the motion of atoms (transition-state vector) when going from $TS_{H6'}$ to TS_{H6} to the ground state. PH_3 hydrogens omitted for clarity. Selected bond angles (°) for TS_{H6}: H(1)—Ir—H(2), 62.7; H(1)—Ir—H(6), 70.6; H(2)—Ir—H(3), 69.1 and $TS_{H6'}$: H(1)—Ir—H(2), 73.9; H(1)—Ir—H(6), 37.7; H(2)—Ir—H(3), 68.5. The bottom of the figure illustrates some site changes accomplished by these transition states

three other hydrides remain outside of bonding distance from any other hydride. This process has been suggested[15] to account for hydride site exchange in $Re(H)_4L_3(CO)^+$, and has been calculated as the TS for site exchange in $FeH_2(H_2)(PR_3)_4^+$.[16] The transition-state vector (Fig. 2) indicates that $TS_{H6'}$ permits the formation of HD (Scheme 1). Indeed, addition of 760 torr of D_2 to a degassed solution of $[Ir(H)_2(PBu^t_2Ph)_2][BAr'_4]$ in CD_2Cl_2 results in the formation of a small amount of free HD after 30 minutes at 298 K. The ^1H NMR spectra of this solution at 183 K show signals consistent with coordinated HD in $[Ir(H)_{2-x}(D)_x(HD)-(PBu^t_2Ph)_2][BAr'_4]$ $(-0.02$ ppm, $J_{HD} = 34$ Hz) and $[Ir(H)_{2-x}(D)_x(HD)_2(PBu^t_2Ph)_2][BAr'_4]$ $(-3.75$ ppm, $J_{HD} = 32$ Hz).

The involvement of all six hydrogen atoms in the transition state for the formation of HD suggests that replacing one of the dihydrogen ligands of $IrH_6(PH_3)_2^+$ by PH_3 could inhibit the formation of HD. Calculations for such a $IrH_4(PH_3)_3^+$ species have found no low-energy transition state allowing the formation of HD. Indeed, the ^1H NMR spectrum of the reaction of $[Ir(H)_2(PCy_2Ph)_3][BAr'_4]$ (**4**) with an excess of D_2 in CD_2Cl_2 for 24 hours at 298 K shows *no* production of free HD.§ Related conclusions have been used to account for the solid-state NMR spectra of $IrH_2(H_2)Cl(PPr_3)_2$.[17]

Fluxionality and HD formation in **3** are therefore two independent processes. The idea that fluxionality renders all H
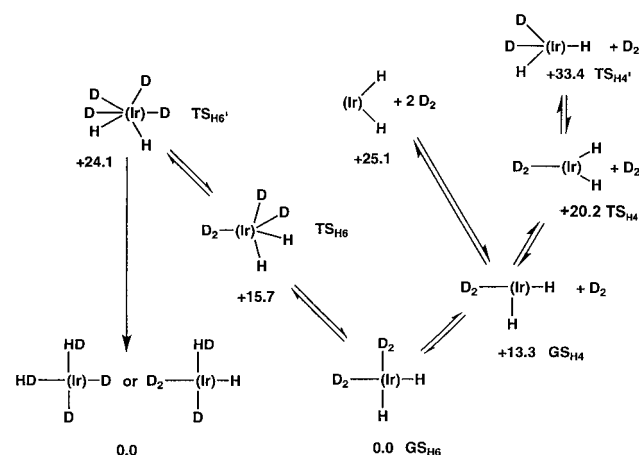
Scheme 1 Energy scheme (kcal mol^{-1}) showing fluxionality and HD formation pathways in $Ir(H)_2(D_2)_2(PH_3)_2^+$ and $Ir(H)_2(D_2)(PH_3)_2^+$ from calculations performed on the all-H_2 systems. D_2 is used for highlighting the HD formation mechanisms. (Ir) $= Ir(PH_3)_2^+$

equivalent in **3** but does not permit the indiscriminate formation of a bond between any pair of hydrides may be counter-intuitive and illustrates the importance of full understanding of the path connecting transition states to products. Scheme 1 summarizes the possible reaction paths involved in fluxionality and HD formation in $Ir(H)_2(H_2)L_2^+$ and $Ir(H)_2(H_2)_2L_2^+$. In particular, the loss of a coordinated D_2 could lead to another located transition state, $TS_{H4'}$, which also permits formation of HD through the central H (or D) making a bond to either of the two outside H ligands. However $TS_{H4'}$ is a 16-electron complex without π-donor ligands, and is calculated to be 33.4 kcal mol^{-1} above $Ir(H)_2(H_2)_2(PH_3)_2^+$ and thus significantly higher than $TS_{H6'}$. While the absolute activation energies calculated with model PH_3 as phosphine are probably upper limits of the real energies, the lower energy for TS_{H6} compared to $TS_{H6'}$ accounts well for the ^1H NMR coalescence occurring at a lower temperature than HD formation. Agostic interactions will modify the energies in Scheme 1 modestly, but no fundamental reversals are expected.

Acknowledgements

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