

Computational and experimental studies of the mechanism of (PCP)Ir-catalyzed acceptorless dehydrogenation of alkanes

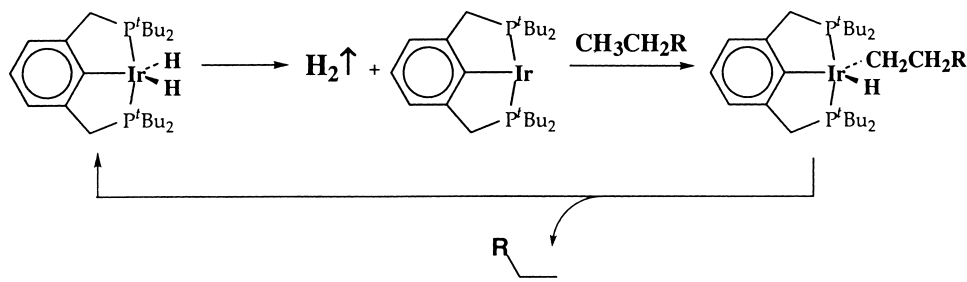
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Abstract

(PCP)IrH₂ efficiently catalyzes the “acceptorless” dehydrogenation of alkanes. The key step in the reaction cycle is calculated (DFT/B3LYP) to be dissociative loss of H₂ to afford an Ir(I) intermediate; this conclusion is supported by experimental results.



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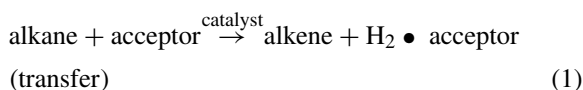
Keywords: Alkanes; Acceptorless dehydrogenation; DFT; IR; Homogenous catalysis; Pincer complexes

1. Introduction

Alkanes are the world’s most abundant organic resource, but they have little value as direct precursors of higher-value chemicals. In contrast, alkenes are the most versatile and important feedstocks in the petrochemical industry [1]. The dehydrogenation of alkanes to give alkenes is thus a reaction of great potential significance. Although this conversion can be effected

by heterogeneous catalysts with ethane or (somewhat less efficiently) propane [2], it remains a challenging goal in the context of higher alkanes and cycloalkanes [3].

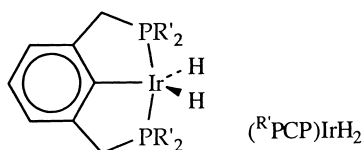
Several transition metal complexes have been found capable of catalyzing alkane transfer-dehydrogenation using a mole of olefin as sacrificial hydrogen-acceptor (Eq. (1)) [4,5]. The most promising to date are the iridium “pincer” complexes of the type (R’PCP)IrH₂, where (R’PCP) is [η³-2,6-(R’₂PCH₂)₂C₆H₃]Ir [6,7]:



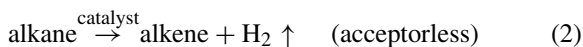
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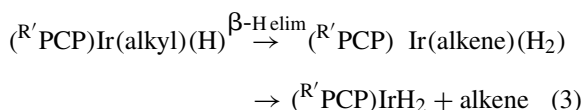


Acceptorless dehydrogenation (Eq. (2)) [8–10] is a reaction that is even more economically attractive, not only because a mole of olefin (hydrogen acceptor) is not consumed but also because of the potentially simpler operating procedures involved:

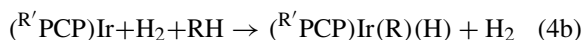


In this case, too, the most efficient catalysts reported to date are the (R'PCP)Ir complexes.

Presumably, the (R'PCP)Ir-catalyzed acceptorless and transfer-dehydrogenation cycles share several common steps, in particular those subsequent to the formation of (R'PCP)Ir(alkyl)(H) (Eq. (3)):

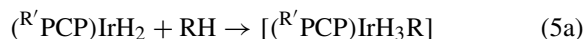


The major difference between the two cycles presumably involves the loss of hydrogen from (R'PCP)IrH₂. In the case of transfer-dehydrogenation, the loss is accepted to proceed via insertion of sacrificial olefin into the metal–hydride bond, followed by elimination of hydrogenated acceptor to give the Ir(I) species (R'PCP)Ir [7,11,12]. For the acceptorless reaction, the loss of dihydrogen could conceivably involve any of the several different transition states and/or intermediates, but the most obvious possible pathways may be most simply grouped into two classes, associative (A or I_A) [13] and dissociative (D). In the case of the D pathway, elimination of H₂ (with little or no assistance from incoming hydrocarbon) gives the same Ir(I) intermediate (Eq. (4a)) that is involved in the transfer-dehydrogenation; this three-coordinate species then adds an alkane C–H bond (Eq. (4b)):



The associative pathway could potentially proceed via a classical Ir(V) intermediate or via non-classical

Ir(III) intermediates [14]. Alternatively, a concerted pathway (I_A [13]) could involve a transition state (TS) with either Ir(V) or Ir(III) character [15]:



In either case, the overall reaction is that shown in Eq. (6); the mechanism of this reaction is the focus of this paper:



Using (MePCP) as our model pincer ligand we have previously calculated that the D pathway for Eq. (6) is the most favorable for a number of different hydrocarbon substrates [12,16]. We have also calculated associative (A) pathways that proceed via both Ir(V) and non-classical Ir(III) intermediates. These pathways were found to be less favorable than the D pathway. The barrier for alkane addition to (R'PCP)IrH₂ (Eq. (5a), A pathway) is calculated to be higher than the overall barrier of the D path. However, an even higher barrier along the A pathway is calculated for the loss of H₂ (Eq. (5b)) to give (MePCP)Ir(alkyl)(H); thus, elimination of H₂ is calculated to be the rate-determining step along the A pathway [12,16]. In all reported experimental work [6,7,9,10], the PCP ligands have contained groups spatially larger than methyl, most commonly *t*-butyl. In this contribution, we review briefly our previous mechanistic work on acceptorless dehydrogenation [12,16], and we analyze the critical steps of both the A and D pathways using the full (*t*-BuPCP) ligand in our calculations.

2. Prior results obtained with MePCP and general considerations

With (MePCP) as a model pincer ligand and RH = cyclohexane, we previously calculated that the energy barrier (ΔE^\ddagger) for the D pathway for Eq. (6) (ca. 36 kcal/mol) is significantly *higher* than that for the A pathway (ca. 27 kcal/mol). When the addendum is propane, the corresponding energy barriers are $\Delta E^\ddagger = 35.3$ and 28.0 kcal/mol for the D (Fig. 1) and A (Fig. 2) pathways, respectively [12,16].

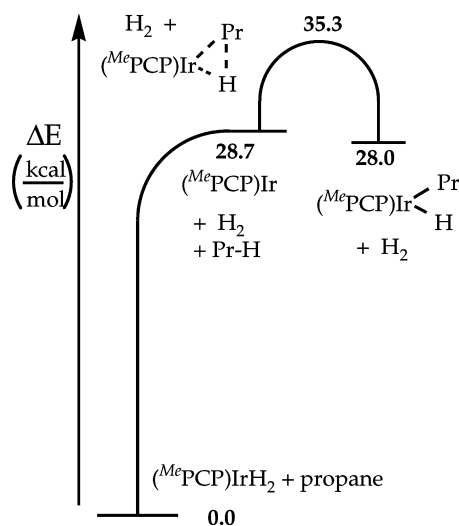


Fig. 1. Energy profile for the dissociative pathway of Eqs. (4a) and (4b) ($R = n$ -propyl).

These latter results are in accord with earlier calculations by Niu and Hall [14] using smaller PCP-models and alkanes. However, we calculated that the *free-energy* barrier (ΔG^\ddagger) for the reaction of cyclohexane with $(\text{MePCP})\text{IrH}_2$ was slightly *lower* (by ca. 4 kcal/mol) for the D path than for the A path under standard thermodynamic conditions (STP). Additionally, and quite importantly, we noted that the assumption of standard conditions is not truly relevant to the catalytic system, since the acceptorless dehydrogenation of alkanes is thermodynamically possible only under H_2 pressures much less than 1 atm [12,16]. At temperature/pressure conditions under which alkane dehydrogenation is possible (for example, $T = 150^\circ\text{C}$ and $P(\text{H}_2) = 10^{-7}$ atm)²[17], the overall free energy barrier to Eq. (6) is calculated to be more than 9 kcal/mol lower for the D path than for the

A path; for example, $\Delta G_D^\ddagger = 27.2$ kcal/mol versus $\Delta G_A^\ddagger = 36.6$ kcal/mol for $R'\text{PCP} = \text{MePCP}$, $R = n$ -propyl, $T = 150^\circ\text{C}$, $P(\text{H}_2) = 10^{-7}$ atm (Fig. 3 and Tables 1–3).

As can be seen in Fig. 3, our calculations indicate that the rate-limiting step for Eq. (6) is loss of H_2 for either the D or the A pathway (Eqs. (4a) and (5b), respectively). In the case of the D pathway, elimination of H_2 occurs from the dihydride, $(\text{MePCP})\text{IrH}_2$. In the case of the A pathway, elimination may be from any of five species (configurational isomers) of the composition $[(\text{MePCP})\text{Ir}(\text{R})(\text{H}_3)]$ for which we have located distinct structures as minima on the energy hypersurface [16]. For both D and A pathways, there is apparently no barrier (ΔE^\ddagger) to the reverse of the H_2 eliminations (i.e. H_2 addition; reverse of Eqs. (4a) and (5b)). Thus, the energy barriers (ΔE^\ddagger) for these H_2 eliminations are equal to the reaction energies (ΔE). This absence of a barrier to H_2 addition to $(R'\text{PCP})\text{Ir}$ is consistent with previous theoretical studies on H_2 addition to $d^8 \text{ML}_2\text{X}$ systems ($M = \text{Rh}, \text{Ir}$) [18,19]. In the case of addition to $(R'\text{PCP})\text{IrRH}$, qualitative experimental observations reveal that addition of H_2 to the analogous dihydrides, $(R'\text{PCP})\text{IrH}_2$, is very fast [20]. Since there is no internal electronic energy barrier to H_2 addition, it may be assumed that the enthalpy barrier is likewise absent or, at most, quite small.

Our electronic structure computer simulations have an idealized gas phase system as reference and find no energy barriers present to either of the H_2 additions under consideration. Hence, conventional molecular transition states cannot be located for these very endothermic elimination reactions. In the absence of a conventional transition state, it is not possible to directly calculate the entropy of activation from a standard electronic structure program, so the activation entropy for H_2 elimination (in solution) must be estimated. Fortunately, activation entropies have been determined experimentally for numerous H_2 eliminations. Of particular note, activation entropies have been determined for elimination of H_2 from various neutral seven-coordinate d^4 species and their non-classical d^6 isomers, i.e. close analogues of the species $(\text{MePCP})\text{Ir}(\text{R})(\text{H})_3$ and $(\text{MePCP})\text{Ir}(\text{R})(\text{H})(\text{H}_2)$ (the reaction intermediates produced in Eq. (5a)). We have found experimental activation parameters for eight different known species in this class, and

² For example, for the dehydrogenation of n -hexane_(liq) to give 1-hexene and *trans*-2-hexene, the respective values of ΔG at 25°C are 20.97 and 18.37 kcal/mol [17]; at 1.0 M hexene and 10 M n -hexane, the equilibrium pressures of H_2 at 25°C are thus 4.21×10^{-15} and 3.40×10^{-13} atm, respectively. At 150°C , the respective pressures are 1.49×10^{-8} and 3.27×10^{-7} atm. At 200°C , the respective pressures are 6.63×10^{-7} and 1.05×10^{-5} atm. Throughout the course of this work we use 10^{-7} atm at 150°C and 10^{-5} atm at 200°C .

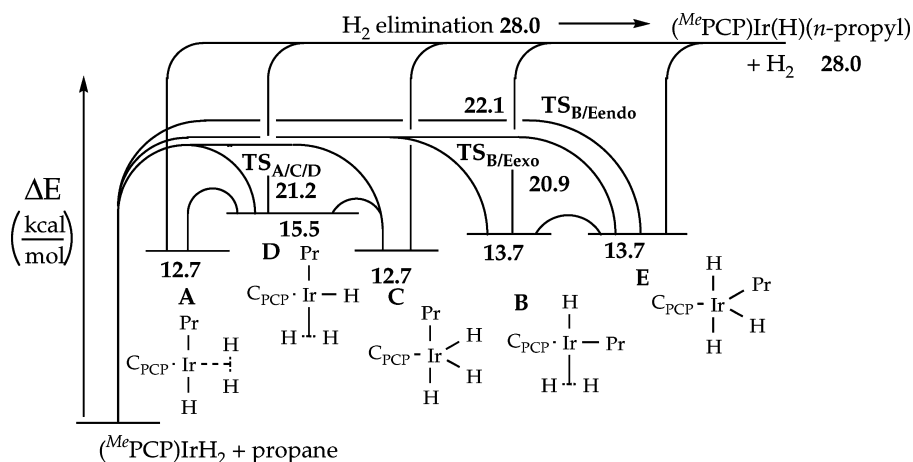


Fig. 2. Energy profile for the associative pathway of Eq. (5) ($R = n\text{-propyl}$). The structures of the five calculated energy minima (in the plane perpendicular to the P-Ir-P axis) are shown schematically.

the experimental activation entropies, ΔS^\ddagger , range in value from -2 ± 4 to 3.7 ± 1.1 eu [21].³ Thus, we can estimate the activation entropy for H_2 loss from $(MePCP)Ir(R)(H)_3$ (Eq. (5b)) as 0 ± 6 eu. At $T = 150^\circ\text{C}$, for example, the estimated uncertainty of ± 6 eu in ΔS^\ddagger corresponds to ± 2.5 kcal/mol in ΔG^\ddagger . Although to our knowledge there are no reported values of activation entropies for elimination of H_2 from five-coordinate d^0 species, we will use this same estimate, $\Delta S^\ddagger = 0 \pm 6$ eu, for Eq. (4a).

The enthalpy of activation for the C–H addition to $(MePCP)IrH_2$ on pathway A ($\Delta H^\ddagger = 20.8$ kcal/mol at STP, $RH = \text{propane}$; Eq. (5a); Table 2) was previously found to be slightly lower than the enthalpy of the products formed by H_2 elimination from the C–H addition intermediate $(MePCP)Ir(R)(H)_3$ (24.9 kcal/mol at STP, $RH = \text{propane}$; Eq. (5b); Table 3). For $RH = \text{cyclohexane}$, the corresponding barrier heights are 18.4 and 25.3 kcal/mol. The two “transition states” under consideration may be viewed as transition states

for elimination of R–H and of H_2 , respectively, from the $(MePCP)Ir(R)(H)_3$ complex (see Fig. 3, A pathway free-energy profile). This calculated result, that the barrier to H_2 loss should be greater than the barrier to C–H elimination, is consistent with available experimental comparisons. The elimination of alkane from an alkyl hydride is generally much more facile than the elimination of H_2 from a dihydride analogue [22].

Throughout the remainder of this paper, we will assume that the above noted condition is maintained, namely that the TS for Eq. (5a) is lower in enthalpy than the barrier (“transition state”) for Eq. (5b). Since no enthalpic barrier is calculated for H_2 addition to $(R^iPCP)Ir(R)(H)$ (the reverse of Eq. (5b)), the overall activation enthalpy for an A or I_A pathway is then simply equal to the overall reaction enthalpy (ΔH_6). In view of the above noted points concerning entropies of H_2 elimination, we can then employ the following equations:

$$\Delta H_A^\ddagger = \Delta H_6 \quad (7)$$

$$\Delta S_A^\ddagger = \Delta S_{5a} + \Delta S_{5b}^\ddagger = \Delta S_{5a} \quad (8)$$

$$\Delta G_A^\ddagger = \Delta H_A^\ddagger + T \Delta S_A^\ddagger = \Delta H_6 + T \Delta S_{5a} \quad (9)$$

Since we assume that ΔH_{5a}^\ddagger is less than ΔH_6^\ddagger , and thus neglect any contribution to the activation enthalpy from ΔH_{5a}^\ddagger , all values we obtain for ΔH_A^\ddagger , and thus for ΔG_A^\ddagger , must be regarded as lower limits.

³ For example, activation entropies for H_2 loss have been determined for a series of “seven-coordinate” iridium complexes, $(PR_3)_2IrX(H)_2(H_2)$ which are particularly closely related to the non-classical intermediates calculated in this work. Six values were determined for ΔS^\ddagger , ranging from 0.7 ± 1.0 to 3.7 ± 1.1 eu [21a,b]. Another highly relevant study was conducted on the neutral seven-coordinate complexes $Ru(H)_2(H_2)(PR_3)_3$ and $Os(H)_4(PR_3)_3$. ΔS^\ddagger values for elimination of H_2 from these complexes were determined to be 3 ± 1 and -2 ± 4 eu, respectively, [21c].

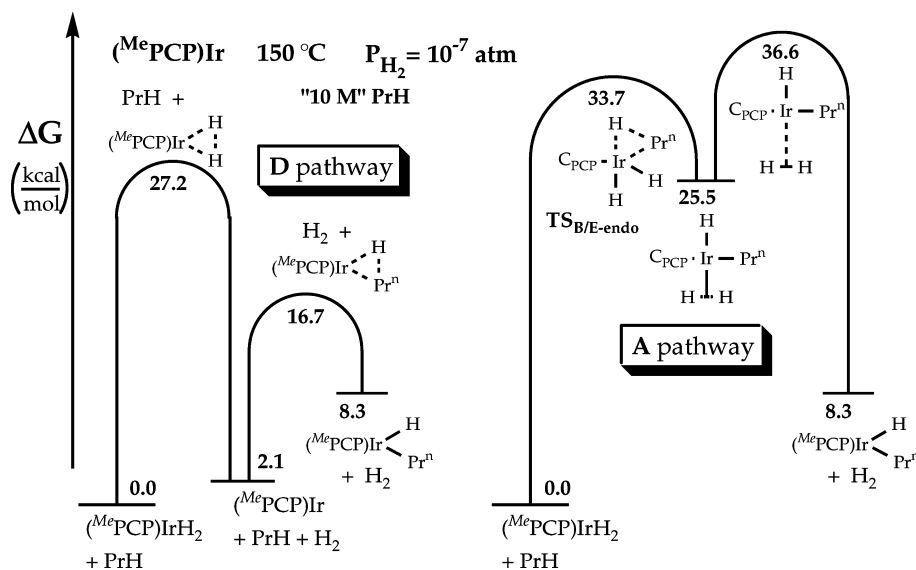


Fig. 3. Free-energy profiles for D and A pathways at 150°C , $P(\text{H}_2) = 10^{-7}\text{ atm}$ and 10 mol/l propane for the reaction of propane with $(\text{MePCP})\text{IrH}_2$. Note that under these conditions (in contrast with STP) the rate-determining step for the D pathway is calculated to be loss of H_2 , not C–H addition.

Since it will be seen that the values of $\Delta G_{\text{A}}^\ddagger$ so obtained are higher than those found for the D pathway ($\Delta G_{\text{D}}^\ddagger$), these lower limits are sufficiently high to enable us to determine that the D pathway should be operative. Thus, the assumption that $\Delta H_{5\text{a}}^\ddagger < \Delta H_6$

does not in any way affect the validity of our conclusions. Likewise, if an energy/enthalpy barrier to H_2 addition does in fact exist in solution, this would also lead to an increase in $\Delta H_{\text{A}}^\ddagger$, and thus it would not affect the validity of our calculated values representing

Table 1
Activation and thermodynamic parameters of individual reaction steps of the D pathway (Eqs. (4a) and (4b))

Reaction	T/P^a	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	ΔH	ΔS	ΔG
$(\text{MePCP})\text{IrH}_2 \rightarrow (\text{MePCP})\text{Ir} + \text{H}_2$	STP	27.0	0	27.0	27.0	26.8	19.0
$(\text{MePCP})\text{Ir} + \text{PrH} \rightarrow (\text{MePCP})\text{Ir}(\text{Pr})(\text{H})$	STP	4.7	-38.0	16.0	-2.2	-37.0	8.8
$(\text{MePCP})\text{Ir} + \text{CyH} \rightarrow (\text{MePCP})\text{Ir}(\text{Cy})(\text{H})$	STP	5.4	-39.8	17.2	-1.7	-40.0	10.2
$(t\text{-BuPCP})\text{IrH}_2 \rightarrow (t\text{-BuPCP})\text{Ir} + \text{H}_2$	STP	27.6	0	27.6	27.6	25.5	20.0
$(t\text{-BuPCP})\text{Ir} + \text{PrH} \rightarrow (t\text{-BuPCP})\text{Ir}(\text{Pr})(\text{H})$	STP	10.9	-48.1	25.3	2.4	-46.1	16.2
$(t\text{-BuPCP})\text{Ir} + \text{CyH} \rightarrow (t\text{-BuPCP})\text{Ir}(\text{Cy})(\text{H})$	STP	14.5	-48.5	28.9	10.7	-48.8	25.2
$(\text{MePCP})\text{IrH}_2 \rightarrow (\text{MePCP})\text{Ir} + \text{H}_2$	150	27.2	0	27.2	27.2	59.4	2.1
$(\text{MePCP})\text{Ir} + \text{PrH} \rightarrow (\text{MePCP})\text{Ir}(\text{Pr})(\text{H})$	150	5.0	-22.6	14.6	-2.3	-20.1	6.2
$(\text{MePCP})\text{Ir} + \text{CyH} \rightarrow (\text{MePCP})\text{Ir}(\text{Cy})(\text{H})$	150	5.8	-22.8	15.5	-1.2	-22.5	8.4
$(t\text{-BuPCP})\text{IrH}_2 \rightarrow (t\text{-BuPCP})\text{Ir} + \text{H}_2$	150	27.8	0	27.8	27.8	58.5	3.1
$(t\text{-BuPCP})\text{Ir} + \text{PrH} \rightarrow (t\text{-BuPCP})\text{Ir}(\text{Pr})(\text{H})$	150	11.2	-29.8	23.8	2.3	-26.6	13.5
$(t\text{-BuPCP})\text{Ir} + \text{CyH} \rightarrow (t\text{-BuPCP})\text{Ir}(\text{Cy})(\text{H})$	150	14.9	-28.9	27.1	11.3	-28.7	23.4

Enthalpies and free energies are in kcal/mol; entropies in eu.

^a STP: $T = 298.15\text{ K}$, all reactants and products at $P = 1\text{ atm}$; 150: $T = 423.15\text{ K}$, $P(\text{H}_2) = 10^{-7}\text{ atm}$, RH pressures selected to give C–H bond densities approximating that of solvent.

Table 2

Activation and thermodynamic parameters of individual reaction steps of the A pathway (Eqs. (5a) and (5b))

Reaction	T/P^a	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	ΔH	ΔS	ΔG
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{PrH} \rightarrow [(^{\text{Me}}\text{PCP})\text{IrPrH}_3]$	STP	20.8	-43.7	33.9	13.5	-43.0	26.3
$[(^{\text{Me}}\text{PCP})\text{IrPrH}_3] \rightarrow (^{\text{Me}}\text{PCP})\text{IrPrH} + \text{H}_2$	STP	11.4	0	11.4	11.4	32.9	1.6
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{CyH} \rightarrow [(^{\text{Me}}\text{PCP})\text{IrCyH}_3]$	STP	18.4	-46.5	32.2	15.1	-40.8	27.3
$[(^{\text{Me}}\text{PCP})\text{IrCyH}_3] \rightarrow (^{\text{Me}}\text{PCP})\text{IrCyH} + \text{H}_2$	STP	10.2	0	10.2	10.2	27.5	1.9
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{PrH} \rightarrow [(^{\text{Me}}\text{PCP})\text{IrPrH}_3]$	150	20.1	-30.4	32.9	12.2	-30.2	25.0
$[(^{\text{Me}}\text{PCP})\text{IrPrH}_3] \rightarrow (^{\text{Me}}\text{PCP})\text{IrPrH} + \text{H}_2$	150	12.7	0	12.7	12.7	69.5	-16.7
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{CyH} \rightarrow [(^{\text{Me}}\text{PCP})\text{IrCyH}_3]$	150	18.6	-30.1	31.3	15.4	-23.6	25.6
$[(^{\text{Me}}\text{PCP})\text{IrCyH}_3] \rightarrow (^{\text{Me}}\text{PCP})\text{IrCyH} + \text{H}_2$	150	10.4	0	10.4	10.4	60.5	-15.1

Enthalpies and free energies are in kcal/mol; entropies in eu.

^a STP: $T = 298.15$ K, all reactants and products at $P = 1$ atm; 150: $T = 423.15$ K, $P(\text{H}_2) = 10^{-7}$ atm, RH pressures selected to give C–H bond densities approximating that of solvent.

lower limits. Indeed, our conclusion regarding the non-favorable A pathway is only *strengthened*, if either of these simplifying assumptions does not hold.

Finally, we note that Eq. (6) is an isogyric reaction (number of electron pairs is conserved) [23]. Thus, we would expect relative energies to be well reproduced by calculations, and the computed value of ΔH_A^\ddagger should be quite reliable as a lower limit. The entropy terms, ΔS_{5a} , are consistent with values expected in bimolecular reactions, and the uncertainty limits associated with these terms are much too small to affect the major conclusions of this work.

3. Calculations using the full *t*-BuPCP ligand

3.1. The D pathway for the reaction of (*t*-BuPCP)IrH₂ with alkanes

The value of ΔE for loss of H₂ from (*t*-BuPCP)IrH₂ is calculated as 29.6 kcal/mol. The corresponding value of ΔH_{4a} is 27.6 kcal/mol, which is therefore also the value of ΔH_{4a}^\ddagger and the approximate value of ΔG_{4a}^\ddagger . The thermodynamic free energy of the H₂ loss, ΔG_{4a} , is calculated as 20.0 kcal/mol at STP (Table 1).

At “experimental” conditions (high temperature and, most importantly, very low H₂ pressure), for example $T = 150$ °C and $P(\text{H}_2) = 10^{-7}$ atm, ΔG_{4a}^\ddagger

Table 3

Activation and thermodynamic parameters of overall reaction, A pathway

Reaction	T/P^a	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	ΔH	ΔS	ΔG
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{PrH} \rightarrow (^{\text{Me}}\text{PCP})\text{IrPrH} + \text{H}_2$	STP	24.9	-43.0	37.7	24.9	-10.2	27.9
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{CyH} \rightarrow (^{\text{Me}}\text{PCP})\text{IrCyH} + \text{H}_2$	STP	25.3	-40.7	37.5	25.3	-13.2	29.2
$(^t\text{-BuPCP})\text{IrH}_2 + \text{PrH} \rightarrow (^t\text{-BuPCP})\text{IrPrH} + \text{H}_2$	STP	30.0	-54.3	46.2	30.0	-20.7	36.2
$(^t\text{-BuPCP})\text{IrH}_2 + \text{CyH} \rightarrow (^t\text{-BuPCP})\text{IrCyH} + \text{H}_2$	STP	38.3	-55.6	55.6	38.3	-23.4	45.3
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{PrH} \rightarrow (^{\text{Me}}\text{PCP})\text{IrPrH} + \text{H}_2$	150	24.9	-27.6	36.6	24.9	39.3	8.3
$(^{\text{Me}}\text{PCP})\text{IrH}_2 + \text{CyH} \rightarrow (^{\text{Me}}\text{PCP})\text{IrCyH} + \text{H}_2$	150	26.1	-23.6	36.0	26.1	36.9	10.5
$(^t\text{-BuPCP})\text{IrH}_2 + \text{PrH} \rightarrow (^t\text{-BuPCP})\text{IrPrH} + \text{H}_2$	150	30.1	-35.6	46.2	30.1	31.9	16.6
$(^t\text{-BuPCP})\text{IrH}_2 + \text{CyH} \rightarrow (^t\text{-BuPCP})\text{IrCyH} + \text{H}_2$	150	39.1	-38.3	55.3	39.1	29.7	26.5

Activation parameters are for loss of H₂, relative to iridium dihydride plus alkane. Thermodynamics parameters refer to Eq. (6). Enthalpies and free energies are in kcal/mol; entropies in eu.^a STP: $T = 298.15$ K, all reactants and products at $P = 1$ atm; 150: $T = 423.15$ K, $P(\text{H}_2) = 10^{-7}$ atm, RH pressures selected to give C–H bond densities approximating that of solvent.

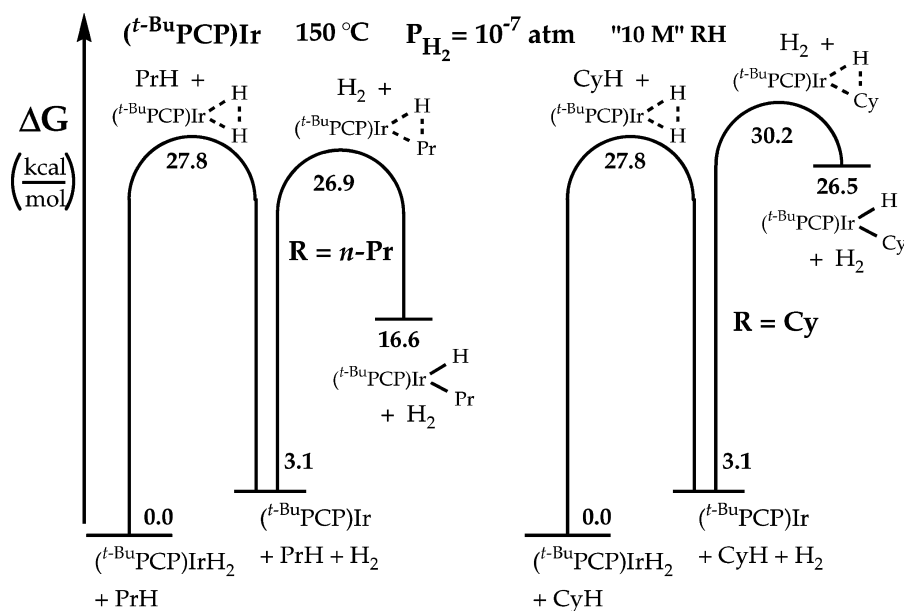


Fig. 4. Free-energy profiles for D pathways at 150 °C, $P(\text{H}_2) = 10^{-7}$ atm and 10 mol/l alkane for the reaction of alkane with $(t\text{-BuPCP})\text{IrH}_2$.

is essentially unchanged, 27.8 kcal/mol. However, the thermodynamic free energy, ΔG_{4a} , is found to be only 3.1 kcal/mol under such conditions (Fig. 4; Table 1). The correction for H_2 pressure, completely rigorous and necessary in terms of basic thermodynamic principles, follows from the simple relationship for chemical potential:

$$\mu_A = \mu_A^\circ + RT \left[\ln \left(\frac{P_A}{P_A^\circ} \right) \right] \quad (10)$$

Thus, for example, for a state that includes free H_2 , the use of $P(\text{H}_2) = 10^{-7}$ atm instead of 1.0 atm results in a ΔG change equal to $T[R \times \ln(10^{-7})]$ (13.5 kcal/mol at 150 °C) or, equivalently, an entropy change of $\Delta S = R \times \ln(10^{-7}) = 32.0$ eu.

ΔG_{4b}^\ddagger for addition of the propane primary C–H bond to $(t\text{-BuPCP})\text{Ir}$ has a calculated value of 23.8 kcal/mol at 150 °C. This value includes a correction for the density of C–H bonds from 1 atm (STP) to a density approximately equal to that of neat solvent.⁴ The same correction is applied to

mechanism A, so it does not affect the relative barriers of Eqs. (4b), (5a) and (5b); however, Eq. (4a) is unaffected by this correction, since it does not involve alkane. For addition of cyclohexane to $(t\text{-BuPCP})\text{Ir}$, $\Delta G_{4b}^\ddagger = 27.1$ kcal/mol, which is 3.3 kcal/mol greater than ΔG_{4b}^\ddagger for propane. The difference is presumably due largely to steric effects, since the difference in activation energies between the two alkanes in the case of addition to $(\text{MePCP})\text{Ir}$ was found to be only 0.9 kcal/mol (15.5 – 14.6 kcal/mol = 0.9 kcal/mol, Table 1).

For addition of Pr–H and Cy–H to $(\text{MePCP})\text{Ir}$ and for Pr–H addition to $(t\text{-BuPCP})\text{Ir}$, the free energy of the transition state is calculated to be less than that for H_2 elimination. The free energy for Cy–H addition

calculations only take into account a single H atom of the hydrocarbon, we must also correct for the greater number of C–H bonds per molecule, that may add to iridium. Thus, when the addendum is cyclohexane we include a statistical factor of $\ln(12 \times 10/0.041)$. Although this correction is less rigorous than the one used for the hydrogen pressure, it is also less important in the context of differentiating between the A and D pathways; for both A and D pathways, the respective C–H addition transition states are favored by the same factor and so the factor cancels out in evaluating the difference between these two transition states.

⁴ Neat alkane solvent has a concentration of ca. 10 mol/l (e.g. 9.3 mol/l for cyclohexane), whereas the standard calculations assume 1 atm or 0.041 mol/l. Since the basic statistical mechanical

to (*t*-BuPCP)Ir is calculated to be slightly higher than that for H₂ elimination, even under experimental conditions (Fig. 4). Thus, Eq. (4b) would appear to be rate limiting in this case. However, DFT/B3LYP is known to determine energies associated with long range interactions inaccurately due to the absence of dispersion interactions [24]. The numerous van der Waals-type interactions present in the C–H addition/elimination transition state in question are most likely estimated as too repulsive, and the binding energies associated with the long Ir–C, Ir–H, and C–H distances in the transition state are most likely underestimated. It is thus very probable that the actual transition state for R–H addition lies somewhat lower than calculated here and, consequently, that the rate-determining step of the D pathway is actually the loss of H₂ from (*t*-BuPCP)IrH₂ (Eq. (4a), not Eq. (4b)).⁵ Furthermore, we can only determine an upper limit for the effective H₂ pressure under experimental conditions (10⁻⁷ atm at 150 °C). Lower actual H₂ pressures are certainly possible in the catalytic runs; this would lead to lower values for the height of the barrier to C–H addition, since the Gibbs free energy of free H₂ is included in that value (see Fig. 4). In any case, it is worth noting that calculated barriers for both H₂ loss and C–H addition are in reasonably good agreement with the experimental value for the free energy of the catalytic dehydrogenation of cycloalkanes ($\Delta G^\ddagger = 30.0$ kcal/mol for cyclooctane at 151 °C; 32.4 kcal/mol for cyclodecane at 201 °C) [9].⁶ Since the calculated values for Eq. (6) via pathway D are slightly lower than the experimental values for the catalytic reaction of Eq. (2), the calculations are fully consistent with experiment. The barrier to Eq. (6) can be lower than that for Eq. (2), since Eq. (6) is only a segment of the full catalytic cycle of Eq. (2).

⁵ The energy of (*t*-BuPCP)IrH₂ may also be slightly overestimated (i.e. the H₂ binding energy may be underestimated), though probably to a lesser degree than that for the C–H addition transition states, since the metal–ligand bond distances are shorter and van der Waals interactions presumably less significant. This would lead to an underestimation of the “TS” free energy for H₂ elimination, since this value is not calculated directly but is obtained from the enthalpy required to remove H₂. In comparing the transition states (pathway D) for H₂ elimination and C–H addition, however, any such errors would cancel, since the free energy of the TS for C–H addition includes the free energy of the prior loss of H₂.

⁶ Rates of (*t*-BuPCP)IrH₂-catalyzed dehydrogenation of cyclooctane (151 °C) and cyclodecane (201 °C) are 11 and 42.5 h⁻¹ corresponding to $\Delta G^\ddagger = 30.0$ and 32.4 kcal/mol, respectively [9].

3.2. The A pathway for the reaction of (*t*-BuPCP)IrH₂ with alkanes

The calculated enthalpy of Eq. (6) at STP is 30.0 kcal/mol for the reaction of (*t*-BuPCP)IrH₂ with propane yielding (*t*-BuPCP)Ir(*n*-Pr)(H) and free H₂. Addition of propane to (*t*-BuPCP)IrH₂ to give (*t*-BuPCP)Ir(*n*-Pr)(H)₃ has a reaction entropy of approximately -54 ± 4 eu at STP^{7,8} [25]. Correcting

⁷ We have calculated the transition states and products of cyclohexane and propane (1°) C–H addition to (*t*-BuPCP)IrH₂ (Eq. (5a)). Specifically, we have calculated the analogues of the isomers that were found to be energetically most favorable in the case of (^{Me}PCP)IrH₂. Both ΔG_{5a}^\ddagger and ΔG_{5a} are found to be much higher than is consistent with a viable A pathway for reaction (6) (54.8 and 49.1 kcal/mol for ΔG_{5a}^\ddagger and ΔG_{5a} for propane at 150 °C; 60.0 and 53.7 kcal/mol for cyclohexane). Although these results certainly support the main conclusion of this work (the non-favorability of the A pathway) we have chosen not to rely strongly on this data to support our conclusion for two reasons. Firstly, it has been claimed that DFT/B3LYP yields energies that are too high for complexes in which the metal is in a high oxidation state [15]. Secondly, it would be computationally too demanding to explore the entire energy hypersurface including, at the very least, the analogues of the five energy minima, which we discovered for R–H addition to (^{Me}PCP)IrH₂. However, in the case of addition to (^{Me}PCP)IrH₂, we found that the entropies of the different isomers do not vary widely (± 4 eu), and therefore, a best estimate for the entropy of R–H addition to (*t*-BuPCP)IrH₂ can be obtained by using the entropy obtained for the calculated isomer of the (*t*-BuPCP)IrH₂ addition reactions (-38.0 and -32.3 eu for propane and cyclohexane, respectively, at 150 °C, corrected for solvent C–H bond densities).

⁸ The entropies of C–H addition may seem unusually unfavorable (negative) upon initial consideration. For example, for the C–H addition of propane to (^{Me}PCP)Ir, the entropy at STP is -37.0 eu which appears slightly more negative than a typical ligand addition (1 atm). If correction is made for the number of primary C–H bonds (6) this corresponds to -27.1 eu at 1.0 M. These values may be viewed as a thermodynamic combination of entropies of alkane coordination and C–H addition (even if the reaction does not actually proceed via an alkane complex). We find computationally that formation of the propane complex has an entropy of -29.2 eu (STP) corresponding to -19.3 eu at 1.0 M at 25 °C after correcting for the number of C–H bonds (this value is certainly not very negative for a bimolecular reaction). The conversion of the corresponding propane complex to the propyl hydride has an entropy of -7.8 eu. This result is in very good agreement with studies by Bergman and Moore who found that the entropy of C–H addition of a range of alkane complexes Cp^{*}Rh(CO)(RH) averages -10.5 eu (-10 ± 2 when RH is propane). Thus, extrapolation to solution-phase densities of C–H bonds (ca. 10 M, 6 C–H bonds) gives a value of -22.5 eu for propane C–H addition at 25 °C, from which ca. 8 eu is attributable to C–H addition of the coordinated

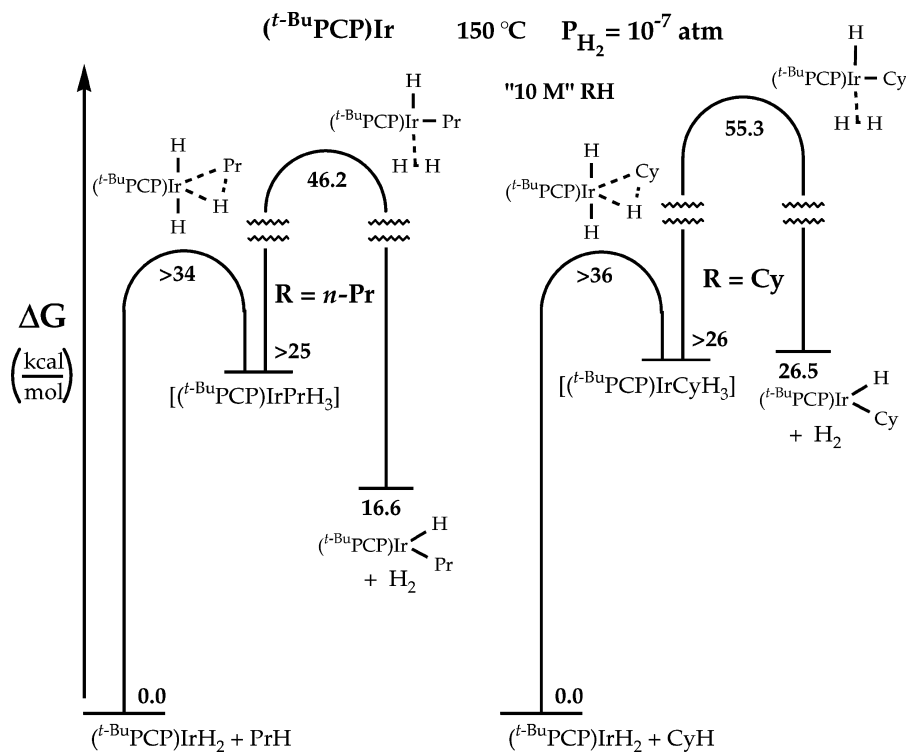


Fig. 5. Free-energy profiles for A pathways at 150 °C, $P(\text{H}_2) = 10^{-7}$ atm and 10 mol/l alkane for the reaction of alkane with $(t\text{-Bu})\text{PCP})\text{IrH}_2$.

for the effective density of C–H bonds in solution lowers the entropic cost to -36 ± 4 eu ($T = 150$ °C). Applying Eqs. (7)–(9) then gives a value of $\Delta G_{\text{A}}^{\ddagger} \sim 46.2$ kcal/mol at 150 °C (Fig. 5). Using the combined entropy errors of the C–H addition (± 4 eu) and the H_2 elimination (± 6 eu) gives an uncertainty in $\Delta G_{\text{A}}^{\ddagger}$ of ± 3.1 kcal/mol. The final value thus obtained for $\Delta G_{\text{A}}^{\ddagger}$ is 46.2 ± 3.1 kcal/mol. We emphasize again that this value must be considered a lower limit for two reasons: (i) We assume, based on results with $(\text{Me})\text{PCP})\text{Ir}$ (see above), that $\Delta G_{\text{A}}^{\ddagger}$ for C–H addition to $(t\text{-Bu})\text{PCP})\text{IrH}_2$ (Eq. (5a)) is lower than the barrier to H_2 elimination from $[(t\text{-Bu})\text{PCP})\text{Ir}(\text{R})(\text{H})_3]$. If the barrier to C–H addition is actually the greater (which may well be the case (see Footnote 7)), that barrier value would constitute the overall barrier to the A pathway. (ii) The calculations indicate the absence of an en-

thalpic barrier for H_2 addition to $(\text{Me})\text{PCP})\text{Ir}(\text{R})(\text{H})$. If there is in fact an enthalpic barrier for H_2 addition to $(t\text{-Bu})\text{PCP})\text{Ir}(\text{R})(\text{H})$, the magnitude of that barrier would be added to the value obtained above for $\Delta G_{\text{A}}^{\ddagger}$.

Thus, although the calculated values of $\Delta G_{\text{A}}^{\ddagger}$ involve two simplifying assumptions, these assumptions do in no way detract from the reliability of our computed $\Delta G_{\text{A}}^{\ddagger}$ values to serve as lower limits. The value of the lower limit, $\Delta G_{\text{A}}^{\ddagger} = 46.2 \pm 3.1$ kcal/mol ($\text{R}' = t\text{-Bu}$; $\text{R} = n\text{-propyl}$) is much greater than the value obtained for $\Delta G_{\text{D}}^{\ddagger}$, 27.8 kcal/mol (Fig. 4).

For the reaction of cyclohexane with $(t\text{-Bu})\text{PCP})\text{IrH}_2$, Eq. (6) is found to be significantly more endothermic than for propane: $\Delta H = 39.1$ kcal/mol. Inclusion of the corrected entropy term (-38 ± 4 eu in this case) yields a value for $\Delta G_{\text{A}}^{\ddagger} \sim 55.3 \pm 3.1$ kcal/mol at 150 °C. Not only is this value ca. 25 kcal/mol greater than the calculated value of $\Delta G_{\text{D}}^{\ddagger} = 30.2$ kcal/mol, it is also more than 20 kcal/mol greater than the experimental value for $(t\text{-Bu})\text{PCP})\text{Ir}$ -catalyzed cycloalkane

alkane. Additions to the iridium dihydride and additions to the $(t\text{-Bu})\text{PCP})\text{Ir}$ complexes are slightly more entropically unfavorable (see Table 2); this is presumably due to steric crowding.

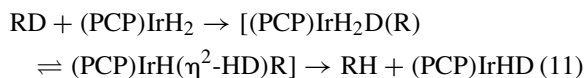
dehydrogenation at 151 °C ($\Delta G^\ddagger = 30.0$ kcal/mol, see Footnote 6) [9]. Obviously, a catalytic cycle cannot include any reaction steps with a barrier greater than that of the overall catalytic cycle. Thus, even the lower limits of the free energies calculated in this work are completely inconsistent with an A (or I_A) pathway or any variation thereof, which involves loss of H₂ to give (*t*-BuPCP)Ir(R)(H) as a segment within the full pathway for (*t*-BuPCP)Ir-catalyzed acceptorless dehydrogenation.

4. Experimental determination of the barrier to the A pathway: H/D exchange

The problem of experimentally testing the conclusions of these calculations is quite intriguing. The reaction in question (Eq. (6)) yields an intermediate, which has never been observed for RH = alkane; indeed, formation of the alkyl hydrides (even from free (^RPCP)Ir) is calculated to be endothermic and, in addition, the alkyl hydrides are presumably subject to relatively rapid β-hydrogen elimination. Even for an observable model species, such as (*t*-BuPCP)Ir(Ph)(H) [26], Eq. (6) is highly endothermic (calculated $\Delta H = 15$ kcal/mol [16]), effectively precluding kinetic measurements. Thus, direct measurement of the barrier of Eq. (6) seems a formidable task. However, the nature of the associative pathway—irrespective of the calculated values of ΔG_A^\ddagger —suggests a way to determine at least an upper limit to the rate.

The calculated intermediates of the associative pathway are either dihydrogen complexes or species that are in rapid equilibrium with dihydrogen complexes. For example, the intermediate of lowest energy is the dihydrogen complex *trans*-(^{Me}PCP)Ir(*n*-Pr)(H)(H₂) (intermediate A; see Fig. 2). We have calculated the activation parameters for the conversion of this species to the Ir(V) isomer (*cis*-(^{Me}PCP)Ir(*n*-Pr)(H)₃; intermediate C) as follows: $\Delta E^\ddagger = 2.3$ kcal/mol; $\Delta H^\ddagger = 1.0$ kcal/mol; $\Delta G^\ddagger = 0.8$ kcal/mol. The barrier to rotation of the dihydrogen ligand in *trans*-(^{Me}PCP)Ir(*n*-Pr)(H)(H₂) is also calculated to be quite low: $\Delta E^\ddagger = 2.3$ kcal/mol; $\Delta H^\ddagger = 1.7$ kcal/mol; $\Delta G^\ddagger = 2.5$ kcal/mol. These barriers are significantly lower than that for elimination of propane from intermediate A: $\Delta E^\ddagger = 8.5$ kcal/mol; $\Delta H^\ddagger = 7.7$ kcal/mol; $\Delta G^\ddagger = 7.3$ kcal/mol. Thus,

deuteroalkane C–D addition to (^{Me}PCP)IrH₂ should reliably lead to H/D scrambling:



Note that H/D exchange should occur regardless of whether the intermediate adduct undergoes reversible H₂/HD loss subsequent to addition. Observation of (or failure to observe) H/D exchange affords no information about the rate of Eq. (5b) per se and is indicative only of the rate of Eq. (5a). As noted above, the calculations suggest that the barrier to loss of H₂ from the C–H addition products (Eq. (5b)) is slightly higher than that for C–H addition/elimination, Eq. (5a) (see Fig. 2). Thus, the rate of H/D exchange (Eq. (11)) should be faster than overall reaction (5), but it should provide in any case a good *upper limit* estimate to the rate of associative exchange, Eq. (5). In other words, ΔG_{11}^\ddagger is a lower limit for ΔG_5^\ddagger .

The addition of benzene to (^{Me}PCP)Ir is calculated to be much more thermodynamically favorable than addition of alkanes; accordingly, the corresponding substitution of H₂ by R–H (Eq. (6)) is thermodynamically much more favorable for benzene. Addition to (^{Me}PCP)IrH₂ to produce the (^{Me}PCP)IrRH₃ intermediate is also thermodynamically more favorable for benzene (by 13 kcal/mol) than for cyclohexane, and the associative transition state for benzene addition (25 °C) is calculated to be 8 kcal/mol lower than that for cyclohexane [12]. These results are in accord with all previous experimental comparisons revealing that addition of benzene to late metal centers is both kinetically and thermodynamically much more favorable than addition of alkanes⁹ [27]. The barrier ($\Delta G^{\ddagger\circ}$) for benzene addition to (^{Me}PCP)IrH₂ is calculated to be 24.2 kcal/mol, when corrections are applied for the C–H bond concentration of neat benzene. The reverse reaction (elimination of benzene from the lowest energy intermediate, A) has a barrier of ca. 11 kcal/mol, which is substantially greater than the barriers calculated for rotation of H₂ in this and other works [28]. Thus, H/D exchange between C₆D₆ and (^{Me}PCP)IrH₂

⁹ For some reviews of alkane C–H bond activation by organometallic complexes, see [27a–e]. Some more recent papers that have addressed selectivity in particular and provide good lead references include [27f–i].

Table 4

Experimental rates and free energies of H/D exchange (Eq. (11)), and corresponding calculated ΔG_{5a}^\ddagger values of C–H addition to (^{Me}PCP)IrH₂ (Eq. (4a))

Calculated		Experimental				
R–H	ΔG_{5a}^\ddagger (kcal/mol)	R–H	<i>T</i> (°C)	<i>k</i> ₁₁ (M ⁻¹ s ⁻¹)	Rate _{5a} (s ⁻¹)	ΔG_{11}^\ddagger (kcal/mol)
Benzene	20.9 at 25 °C (21.1 at 30 °C)	Benzene	30	1.1×10^{-4}	2.5×10^{-3}	21.4
Toluene	24.5 at 25 °C (27.5 at 110 °C)	Mesitylene	110	7.2×10^{-5}	1.0×10^{-3}	27.9
Pr–H(1°)	29.1 at 25 °C (32.3 at 130 °C)	<i>n</i> -C ₁₀ H ₂₁ –H	130	8.0×10^{-5}	8.2×10^{-4}	29.5
CyH	27.6 at 25 °C (32.3 at 180 °C)	CyH	180	$<3 \times 10^{-6}$	$<2.8 \times 10^{-5}$	>36.4

From [16]. Rates determined by kinetics simulations (see [16] for experimental and simulation details).

is calculated to occur with a barrier of 24.2 kcal/mol at 25 °C (before adjusting for isotope effects and for statistical terms that would account for non-productive addition/elimination). Accordingly, H/D exchange between C₆D₆ and (^{*t*}-BuPCP)IrH₂ is experimentally observable even at 25 °C (Table 4).

H/D exchange with other hydrocarbons, specifically mesitylene-d₁₂ and decane-d₂₂, requires significantly higher temperatures than C₆D₆ to achieve conveniently measured rates. Our most significant experimental result regarding H/D exchange is a negative one. Even at 180 °C, cyclohexane-d₁₂ undergoes no observable H/D exchange with (^{*t*}-BuPCP)IrH₂ after 1 week, indicating that addition of cyclohexane-d₁₂ C–D bonds to (^{*t*}-BuPCP)IrH₂ does not occur on this time scale. We can thereby determine a lower limit for the free energy of activation for Cy–H addition to (^{*t*}-BuPCP)IrH₂ (Eq. (4a)) as $\Delta G_{5a}^\ddagger > 36.4$ kcal/mol (see Table 4).

The resulting exchange rates for the different hydrocarbons decrease in the following order: phenyl-H > benzyl-H > *n*-alkyl-H > cycloalkyl-H. This trend is familiar in the context of C–H activation, especially by late metal centers; indeed, to our knowledge, every study involving C–H addition of these substrates has yielded this exact order for both kinetics and thermodynamics¹⁰ (see Footnote 9) [27].

¹⁰ The relative differences in the addition rates among different alkane substrates for kinetic measurements is usually much smaller than observed in the present case. This is probably because direct measurements of addition rates necessarily involve exoergic additions, whereas in this case the rate-determining step is endoergic. Thus, the transition state is late and, perhaps more importantly, our kinetic barriers include a thermodynamic barrier. Thermodynamic variations among additions of various hydrocarbons are often found to be of the same order of magnitude as in the present case.

Consequently, the relative barriers to exchange are all consistent with the assumption that the exchange rate is a measure of the addition rate of the corresponding C–H bond.

The experimentally determined activation barriers are useful in two distinct respects. Firstly, they provide a comparison with the computationally predicted values. It can be seen from Table 4, that the agreement is quite good, although the calculated free energies of activation appear to be somewhat overstated¹¹ [29].

Secondly—and independent of the good agreement with the calculated values—the experimental values for H/D exchange fully confirm the major conclusion drawn from the calculations (i.e. that the catalytic reaction proceeds via a dissociative pathway) by direct comparison with *experimentally* measured catalytic rates. For cyclooctane dehydrogenation catalyzed by (^{*t*}-BuPCP)IrH₂ at 151 °C the catalytic turnover rate is 11 h⁻¹ (3.1×10^{-3} s⁻¹), corresponding to 30.0 kcal/mol. For cyclodecane dehydrogenation, the turnover rate is 90 h⁻¹ (2.5×10^{-2} s⁻¹) at 201 °C, corresponding to 32.4 kcal/mol. The failure of cyclohexane-d₁₂ to undergo any observable H/D exchange with (^{*t*}-BuPCP)IrH₂, even after 1 week at 180 °C, indicates a barrier to C–H addition to (^{*t*}-BuPCP)IrH₂ that is significantly higher than the experimentally determined barrier to the overall catalytic reaction. (Note that cyclohexane has been reported by Bergman and co-workers to undergo addition *more* readily than cyclooctane, in separate

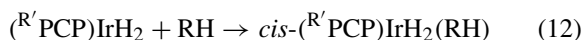
¹¹ Many of the currently available functionals (including B3LYP) underestimate intermolecular binding energies and charge-transfer effects at long range. It is possible, that the B3LYP functionals differentially overestimate the energies in metal complexes with high coordination numbers and in the transition states, which lead to the formation of these complexes.

reactions with two different iridium species [30].) Since a catalytic cycle obviously cannot proceed more rapidly than any single step in the cycle, these results are clearly inconsistent with an associative pathway for the catalysis or, at the very least, are inconsistent with the associative pathways calculated in this work by us and calculated by others for smaller substrates [14], since such pathways are also calculated to lead to H/D exchange. Thus, the cycloalkane dehydrogenations must proceed via the D pathway with an overall barrier of ca. 31 kcal/mol. No step within the overall pathway, including Eq. (6), can have a barrier greater than that. The barrier for dissociative H₂ loss (Eq. (4a)) should be independent of alkane, while the barrier to Eq. (4b) for *n*-alkanes should be lower than that for cycloalkanes, based on either our calculations or literature precedent for selectivity in C–H activation (see Footnote 9 [27]). Thus, if the dissociative pathway for Eq. (6) operates with cycloalkanes with a barrier = 30 kcal/mol, it must be at least equally accessible for *n*-alkanes. The fact that *n*-alkanes are less easily dehydrogenated is presumably due to steps subsequent to alkyl hydride formation or, very possibly, a more rapid back reaction (hydrogenation) of the linear olefins.

5. Dissociative interchange pathway

We have discussed to this point only associative mechanisms that lead directly to the alkyl hydrides (^{R'}PCP)Ir(R)(H) (either A or I_A pathways). We have also begun to investigate an alternative pathway, which can be labeled I_D. Using the nomenclature of Langford and Gray [13], an I_D pathway is one in which the metal center interacts only weakly with the incoming ligand. In the specific case of Eq. (6), one could envision a weakly binding alkane interacting with the departing dihydrogen molecule or, in other words, an “alkane-assisted” H₂ elimination. However, arguments very similar to those used to demonstrate that the A and I_A pathways are unfavorable, can also be applied to show that the I_D pathway should be less favorable than a fully dissociative pathway.

We begin by calculating the thermodynamics of alkane coordination to (^{Me}PCP)IrH₂:



Results are shown in Table 5. Although an energy minimum may be located for an octahedral species (^{Me}PCP)Ir(H)₂(RH), its energy is slightly higher than that of the unbound state ((^{Me}PCP)IrH₂+RH). Consequently, the energy required to rearrange the hydrides to open a vacant coordination site is greater than the binding energy of the resulting alkane complex. ΔG₁₂ for alkane binding is of course significantly positive. Surprisingly, the (^{*t*-Bu}PCP) complex binds propane more favorably (probably due to van der Waals interactions); however, the enthalpy of binding is approximately zero and the free energy remains quite positive.

Not surprisingly, the coordination of alkane to three-coordinate (^{Me}PCP)Ir shows a favorable binding energy:



However, the value is quite small; ΔE = −5.1 kcal/mol (propane) in good agreement with results by Niu and Hall [14]. The enthalpy of binding is found to be of similar magnitude, ΔH = −4.4 kcal/mol. This enthalpy is insufficient to compensate for even a modest entropy of binding, calculated as −31.6 eu at 1 atm, which corresponds to −16.0 eu after corrections are made for solvent density, the number of C–H bonds per molecule, and temperature (150 °C). Consequently, the free energy of coordination to (^{Me}PCP)Ir is positive: +2.9 kcal/mol at T = 150 °C. In the case of propane binding to (^{*t*-Bu}PCP)Ir, the enthalpy of binding is even less negative, −1.3 kcal/mol, and the free energy change is +6.3 kcal/mol at 150 °C (Table 5).

The coordination of alkane to either (^{R'}PCP)IrH₂ or to free (^{R'}PCP)Ir is thus found to be unfavorable in terms of free energy, even in the least hindered case (R' = Me). Particularly in view of the positive free energy of binding to free (^{R'}PCP)Ir, it seems highly unlikely that incoming alkane could make a favorable contribution to the departure of the H₂ molecule. Indeed, the binding of alkane to a complex in which the H₂ molecule is still present, even when very weakly bound, is presumably far more unfavorable than alkane binding to the fully open coordination site of free (^{R'}PCP)Ir.

DFT calculations with all commonly used functionals tend to underestimate the magnitudes of the binding energies for weakly bound states, so it is possible that the binding energy of the alkane is

Table 5

Calculated thermodynamics of propane binding to (R^{\prime} PCP)Ir and to (R^{\prime} PCP)IrH₂

Propane complex	ΔE	ΔH_{STP}	ΔS_{STP}	ΔG_{STP}	ΔH_{150}	ΔS_{150}	ΔG_{150}
(^{Me} PCP)Ir(C ₃ H ₈)	−5.1	−4.4	−31.6	5.1	−3.8	−16.0	2.9
<i>cis</i> -(^{Me} PCP)Ir(H) ₂ (C ₃ H ₈)	1.2	0.1	−29.4	8.9	0.6	−13.9	6.5
(^{t-Bu} PCP)Ir(C ₃ H ₈)	−2.3	−1.3	−32.7	8.4	−0.7	−16.7	6.3
<i>cis</i> -(^{t-Bu} PCP)Ir(H) ₂ (C ₃ H ₈)	−1.4	−3.3	−31.0	6.0	−2.8	−14.9	3.5

Values of ΔE , ΔH and ΔG are in kcal/mol; values of ΔS in eu. ΔG_{150} refers to $T = 150^{\circ}\text{C}$ and C–H bond densities approximately equal to that of typical alkane solvent (ca. 10 M; six primary C–H bonds per molecule).

somewhat more favorable than that calculated by ourselves and by others [14]. However, even allowing for significantly stronger binding of alkane to the three-coordinate complex, and even if the free energy of binding were slightly negative, the free-energy contribution to a state in which molecular H₂ is still present is presumably quite insignificant at best. Thus, even if alkane participation does take place, the calculations very strongly suggest that it would not have any significant effect on the energetics of H₂ elimination.

6. Summary

(R^{\prime} PCP)IrH₂ has been found to efficiently catalyze both acceptorless and transfer-dehydrogenation of alkanes. The critical step distinguishing the acceptorless reaction is the loss of free dihydrogen. Under those experimental conditions where molecular H₂ is efficiently expelled from solution, this loss of H₂ is presumably the rate-determining step.

We have previously shown that the free-energy barrier to the addition of alkanes to (^{Me}PCP)IrH₂ (the initial step of an A pathway) is significantly higher than the overall barrier calculated for a purely dissociative (D) pathway; however, the barrier to subsequent loss of H₂ along the A pathway was found to be higher still. In this work, we report calculations on the actual (^{t-Bu}PCP)Ir complexes. As anticipated [12,16], the presence of the *t*-butyl groups raises the free energy of the much more crowded “transition state” for H₂ elimination from the (R^{\prime} PCP)Ir(R)H₃ complexes significantly more (relative to (R^{\prime} PCP)IrH₂) than the free energy of the “transition state” for dissociative loss of H₂ from (R^{\prime} PCP)IrH₂. With *t*-butyl groups on phosphorus, the D pathway is favored over an A or

I_A pathway by ca. 20 kcal/mol at 150 °C as compared with ca. 9 kcal/mol, when the reaction is modeled with methyl groups.

The essential general points that demonstrate the non-favorable aspects of A or I_A pathways are the following: R–H addition to (free) (R^{\prime} PCP)Ir to give (R^{\prime} PCP)Ir(R)(H) has a ΔH value that is either positive or negligible (−0.2 kcal/mol for *n*-Pr–H addition to (^{Me}PCP)Ir). Therefore, as (R^{\prime} PCP)Ir(R)(H) is approached along the reaction coordinate by elimination of H₂ from the R–H addition product (i.e. any species of the composition [(R^{\prime} PCP)Ir(R)H₃]), the enthalpy that is asymptotically approached must be higher or comparable to the enthalpy approached when H₂ dissociates from (R^{\prime} PCP)IrH₂. In addition, the entropy of the “transition state” for H₂ elimination from [(R^{\prime} PCP)Ir(R)H₃] is much less favorable than that for H₂ elimination from (R^{\prime} PCP)IrH₂, since the latter does not contain a bound alkane molecule. The entropic price of alkane C–H addition (−23 to −38 eu at solvent-densities, see Footnote 8) [25] corresponds to free energy changes of 10–16 kcal/mol at 150 °C, and accordingly greater values at higher temperatures. For (^{Me}PCP)Ir, ΔG^{\ddagger} is approximately 5 kcal/mol greater for the A pathway than for loss of H₂. For (^{t-Bu}PCP)Ir, the A pathway is even more unfavorable: the combined entropic and enthalpic penalties result in a barrier to the A pathway that is more than 15 kcal/mol greater than that for H₂ dissociation. Of course, the enthalpic and entropic barrier to C–H addition must be “paid” after the H₂ dissociation event in the case of the D pathway. However, the very high entropy achieved by H₂ liberation under the low hydrogen pressures—the same factor that allows alkane dehydrogenation to be thermodynamically possible—results in a very low free energy of the intermediate state ((R^{\prime} PCP)Ir plus free dihydrogen). This entropy

of free H₂ is sufficient to ensure that the free energy of the transition state for R–H addition to (R'PCP)Ir (the second step of the D pathway) is lower than or comparable to the “transition state” for H₂ elimination from (R'PCP)IrH₂ ($\Delta G^\ddagger = 27.8$ kcal/mol).

We also explored the possibility of an alkane-assisted, primarily dissociative (I_D) pathway for Eq. (6). For reasons very closely related to those considered above for the A and I_A paths (an entropic cost combined with negligible or even unfavorable enthalpic factors), the I_D path is less favorable than the D path.

In conclusion, we note that the energy and enthalpy values that we calculate for the (MePCP)Ir reactions are not very different from values calculated by other workers [11,14,15], in spite of differences such as the use of hydrogens instead of methyls on the ligating P-atoms, different functionals, or an anthrathos-type pincer ligand. The difference in the conclusions that we draw stems largely from, a consideration of entropy effects under the conditions relevant to catalysis. In addition, even though a transition state has not been located for H₂ loss subsequent to (or concertedly with) C–H addition, we have considered the energetics of this critical reaction step in detail. Finally, in this work we have also considered steric factors by conducting calculations with full *t*-butyl groups on phosphorus. Steric factors are found to further increase the favorability of the D path relative to either A or I_A paths by an additional 8–18 kcal/mol.

7. Computational methods

We use computational methods based on density functional theory [31] as implemented in the GAUSSIAN98 series of computer programs [32]. The calculations made use of the three-parameter exchange functional developed by Becke [33] and the correlation functional of Lee, Yang and Parr [34] (B3LYP). All calculations also employed the Hay–Wadt relativistic, small-core effective core potential and corresponding basis sets (split valence double-zeta) for the Ir atom (LANL2DZ model) [35]. This 60-electron ECP releases the penultimate valence electrons (5s²5p⁶ for Ir) for explicit coverage by basis functions along with the valence electrons (6s²5d⁷). In the reference calculations involving MePCP, we used all-electron, full double-zeta plus polarization function basis sets for

the elements C (Dunning–Huzinaga D95(d)) [36] and P (McLean–Chandler) [37]; hydrogen atoms in H₂ or a hydrocarbon, which formally become hydrides in the product complexes, were described by the triple-zeta plus polarization 311G** basis set [38]; regular hydrogen atoms present in the PCP ligand or in alkyl substrate groups carried a double-zeta quality 21G basis set [39]. Reactant, transition state and product geometries were fully optimized with the combination of functionals, ECP and basis sets described above (B3LYP/BasisA). Additional single-point calculations on the B3LYP/BasisA geometries at the B3LYP level used a more extended basis set for Ir in which the default LANL2DZ 6p functions were replaced by the functions reoptimized by Couty and Hall [40], and sets of diffuse d functions (exponent = 0.07) and *f* functions (exponent = 0.938) [41] were added (B3LYP/BasisB).

All stationary points were characterized further by normal mode analysis at the B3LYP/BasisA level. The (unscaled) vibrational frequencies formed the basis for the calculation of vibrational zero-point energy (ZPE) corrections. Thermodynamic corrections based on standard partition function expressions were made to convert from purely electronic reaction or activation energies (ΔE , ΔE^\ddagger ; no ΔZPE) to enthalpies and free energies (ΔH , ΔH^\ddagger ; ΔG , ΔG^\ddagger ; ΔZPE included at STP: $T = 298$ K, $P = 1$ atm) [42]. Enthalpies, entropies, and free energies at T , P combinations other than STP were similarly evaluated using (ideal gas) partition functions. We arrive at a set of “best” energies, enthalpies, and free energies for all the reference calculations on (MePCP)Ir-containing species by adding the differential energy changes from the B3LYP/BasisB calculations in a purely additive fashion to the complete sets of data derived at the B3LYP/BasisA level. These are the values used in the text, unless otherwise noted.

The use of methyl groups attached to the phosphorus atoms (i.e. PR₂ = PMe₂) represents a compromise between the use of hydrogen atoms, common in many computational investigations of phosphine-containing transition metal complexes, and the alkyl groups actually employed experimentally in the catalytic systems (*i*-Pr or *t*-Bu). Methyl groups capture most of the electronic effects of the larger alkyl groups, but they cannot fully model the steric bulk exerted by these groups [43]. In an attempt to better assess the ener-

getic effects arising from bulky phosphines (t -BuPCP versus Me PCP), we reoptimized all structures with the functionals, ECP and basis sets listed above as BasisA except that the Me or t -Bu groups on P now carried only STO-3G basis sets (B3LYP/BasisC). We also did normal mode analysis on these structures to arrive at enthalpies and free energies. “Best” (t -BuPCP)Ir data were then obtained in a purely additive fashion; for example, $\Delta G(t\text{-BuPCP}; \text{any } T, P \text{ combination}) \approx \Delta G(t\text{-BuPCP}; \text{BasisC, STP}) - \Delta G(Me\text{PCP}; \text{BasisC, STP}) + \Delta G(Me\text{PCP}; \text{best value; any } T, P \text{ combination})$.

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