DFT calculations have been carried out to elucidate the mechanism of acceptorless dehydrogenation of alkanes RH by "pincer"-ligated Ir-catalysts (PCP)IrH$_2$. The key alkyl-hydride intermediate, (PCP)Ir(R)(H), may be formed via dissociative ($D$) or associative ($A$) paths. The $D$ path proceeds via an initial loss of H$_2$ from (PCP)IrH$_2$, followed by R-H addition to (PCP)Ir. In contrast, the $A$ path involves initial R-H activation by (PCP)IrH$_2$ and subsequent formation of a "seven-coordinate" (PCP)Ir(R)(H)$_3$ complex, followed by loss of H$_2$. Free energy considerations lead squarely to the conclusion that the dissociative pathway $D$ is operative under experimentally relevant conditions (high T, low pressure of H$_2$, bulky phosphine groups). Experimental results in support of this conclusion are presented briefly. To fully illustrate the distinctly different energy profiles of the two mechanisms, the calculations must employ realistic molecular models and include accurate simulations of experimental reaction conditions.
Introduction

Alkanes are the world’s most abundant organic resource, but methods for their use as direct precursors to higher value chemicals are severely limited. Alkenes, on the other hand, are the most versatile and important organic feedstocks in the chemical industry. (1) Direct dehydrogenation of alkanes has a very large activation energy barrier, since the reaction is highly endothermic (ca. 24-32 kcal/mol) and the synchronous removal of two hydrogens from adjacent carbon atoms is symmetry forbidden. Many heterogeneous catalysts are known to effect dehydrogenation (at elevated temperatures of ca. 500 – 900 °C), but applications are generally limited to complete and unselective dehydrogenation (e.g. ethylbenzene to styrene, ethane to ethylene). (2) Hence the selective catalytic functionalization of alkanes to the corresponding alkenes represents a potentially highly rewarding reaction and a significant challenge to the field of catalysis. The high selectivity often displayed by homogeneous catalysts, and the remarkable selectivity of transition metal complexes with respect to stoichiometric reactions of alkanes (most notably C-H bond addition), has suggested that soluble transition-metal-based systems offer great promise in this context. (3,4) Indeed, considerable progress has been made toward the development of such systems for alkane dehydrogenation. (5-8) Most examples involve transfer of hydrogen to a sacrificial olefin (eq 1) but a smaller number of catalysts have been shown effective for “acceptorless” dehydrogenation (eq 2), (9) a process that is potentially simpler and economically more favorable.

\[
\text{alkane} + \text{acceptor} \xrightarrow{\text{catalyst}} \text{alkene} + \text{H}_2\text{-acceptor} \quad \text{(transfer)} \quad (1)
\]

\[
\text{alkane} \xrightarrow{\text{catalyst}} \text{alkene} + \text{H}_2 \uparrow \quad \text{(acceptorless)} \quad (2)
\]

The catalysts reported to date that have proven most effective for both acceptorless and transfer-dehydrogenation are species of the type \((^{6}\text{PCP})\text{IrH}_2\), where \((^{6}\text{PCP})\) is the tri-coordinate "pincer" ligand \([\eta^3-2,6-(R'_2\text{PCH}_2)_2\text{C}_6\text{H}_3]\). (7-9)

The operative mechanisms for the acceptorless and transfer systems undoubtedly have several elementary steps in common. The key difference between the two mechanisms concerns the loss of H2. In the case of the transfer systems, we have shown that the \((\text{PCP})\text{IrH}_2\) dihydride loses hydrogen via
insertion of the sacrificial acceptor into the Ir-H bond, followed by C-H elimination. 

Hence, an Ir(I)/Ir(III) couple is operative in accord with independent computations by Hall and by us. The acceptorless system, however, must obviously lose free dihydrogen (eq 2). This can in principle proceed either dissociatively from the resting state of the catalyst, (PCP)IrH₂, or associatively via a highly coordinated Ir-complex, (PCP)Ir(alkyl)H₂. Elucidation of the mechanism for acceptorless dehydrogenation of alkanes, eq 2, using first-principles electronic structure calculations forms the topic of this Chapter.

**Overview of proposed mechanisms for acceptorless dehydrogenation of alkanes by (PCP)IrH₂**

Three plausible mechanisms have been proposed for catalytic acceptorless dehydrogenation of alkanes by (PCP)IrH₂ (dissociative = D; associative = A; interchange = I), as outlined in Scheme 1. The mechanisms all feature a (PCP)Ir-alkyl-hydride complex as a crucial, but as yet elusive, intermediate. The mechanisms differ in the initiation steps, which generate this alkyl hydride from the resting state of the catalyst, (PCP)IrH₂.

Scheme 1. Possible mechanisms of acceptorless alkane (RH) dehydrogenation by (PCP)IrH₂: dissociative (D), associative (A), and interchange (I) pathways.

The proposed mechanism for the dissociative pathway (D) invokes the following two steps to generate the alkyl hydride:

(D1) Reductive elimination of H₂ from (PCP)IrH₂, a process which formally changes the oxidation state of the metal from Ir(III) to Ir(I).
(PCP)IrH₂ + RH → (PCP)Ir + H₂ + RH     (D1)

(D2) Oxidative addition of the alkane RH by (PCP)Ir to form the alkyl hydride, (PCP)Ir(R)(H). The oxidation state of the metal reverts to Ir(III).

(PCP)Ir + H₂ + RH → (PCP)Ir(R)(H) + H₂     (D2)

The associative mechanism (A) also uses two steps to form the intermediate alkyl-hydride complex:

(A1) Addition of alkane RH to (PCP)IrH₂ to form a "seven-coordinate" (PCP)Ir(R)(H)₃ complex.

(PCP)IrH₂ + RH → [PCP]Ir(R)H₃     (A1)

Formally, alkane addition oxidizes the Ir atom from Ir(III) to Ir(V) if the three hydrogen atoms coordinate as classical hydrides. If they do not, i.e., if a non-classical η²-coordinated H₂ or RH molecule is present within the Ir coordination sphere, then this step involves no change in metal oxidation state.

(A2) Elimination of H₂ from (PCP)Ir(R)(H)₃ to form the alkyl hydride, (PCP)Ir(R)(H). Depending on the bonding pattern of the (PCP)Ir(R)(H)₃ species (three hydrides or η¹-H₂ or RH coordination), this may involve a reduction of the metal (Ir(V) to Ir(III)).

[PCP]IrH₃R → (PCP)Ir(R)(H) + H₂     (A2)

Recently, an interchange pathway (I) was proposed as a possible alternative to the more conventional D/A pathways. (13) The I pathway is direct and uses only one step to obtain the alkyl hydride:

(I) Reductive removal of H₂ and oxidative addition of alkane occur in a concerted reaction via a single transition state.

(PCP)IrH₂ + RH → (PCP)Ir(R)(H) + H₂     (I)

The I mechanism in essence requires the "seven-coordinate" (PCP)Ir(R)(H)₃ species to function as a TS and not as a minimum (as in the A mechanism).

To complete the mechanism for eq 2, the following two steps are proposed as common:

(3) β-H elimination from the alkyl group in (PCP)Ir(R)(H) to generate a coordinated alkene-dihydride species; no change in metal oxidation state occurs.

(PCP)Ir(R)H → (PCP)Ir(alkene)(H)₂     (3)

(4) Removal of the coordinated alkene to regenerate (PCP)IrH₂, again with

(PCP)Ir(alkene)(H)₂ → (PCP)IrH₂ + alkene     (4)

no change in metal oxidation state.

None of the intermediates proposed in Scheme 1 have been isolated for R = alkyl, but a (PCP)Ir-phenyl-hydride complex has been reported(14) and
extensively characterized (NMR,(14,15) DFT calculations,(12,14,15) and X-ray structure determination(16)). Elucidation of the acceptorless alkane dehydrogenation mechanism by non-experimental means, for example by the application of modern electronic structure techniques, thus appears to be a desirable objective. Furthermore, considering that the proposed mechanisms involve only few steps, this would appear to be a relatively easy task computationally and present an excellent opportunity to test the strength of current electronic structure methods. Indeed, two computational research groups have delved extensively into this problem using very similar methods and, yet, have arrived at different conclusions with respect to the mechanism of eq 2.(12,13,17-19) The two groups are in accord that steps (3) and (4) represent the final steps of the mechanism for acceptorless dehydrogenation and that these steps are not rate-determining. There is discord, however, as to whether the alkyl-hydride intermediate is formed by the D or by the A (or I) path, and hence the nature of the rate-determining step is in dispute.

Here we focus on calculating the energetic requirements of the two initial steps composing the D and A mechanisms using electronic structure methods based on density functional theory. We use propane as a model linear alkane, and we present results obtained with three molecular models for the (PCP)Ir species: R' = H, Me, and t-Bu. For our model systems, we have not been able to locate a transition state appropriate to an I mechanism.

We shall first consider energy profiles based on the potential energy surfaces. We subsequently acquire insight into the role entropy plays on the various elementary steps of the D and A pathways by contrasting potential and free energy profiles. There are substantial differences between the two sets of profiles (vide infra), even under standard thermodynamic conditions (STP). We then incorporate important concentration and temperature effects to more accurately simulate the very non-standard (T, P) conditions used experimentally. We briefly present some recent experimental findings relevant to distinguishing between the proposed mechanisms. Finally, we comment on the calculation of steric effects, viz. the presence of t-Bu groups in (ν₃PCP)Ir, and on the feasibility of an I mechanism for eq 2.

Potential energy profiles

There are two conformations (both of C₂ symmetry) available to the (PCP)IrH₂ species, the resting state of the catalyst in the limit of low alkene concentrations.(10) Both conformers possess a d⁶ metal configuration and a singlet ground state, but they differ in the occupancies of the Ir(d)-orbitals. The conformer of lowest energy is trigonal bipyramidal with a Y-shaped ligand arrangement in the equatorial plane and a narrow H-Ir-H angle near 60°. The higher energy conformer is pseudo-octahedral with a T-shaped ligand arrangement in the horizontal plane, a wide H-Ir-H angle close to 180°, and a vacant coordination site trans to the PCP ligand. The Y-T energy separation is
about 10 kcal/mol, and the trigonal bipyramidal conformer (Y-shaped) is thus overwhelmingly dominant, even at elevated temperatures. Hall and Niu examined in detail the elementary steps of the associative and dissociative mechanisms for both conformers (using $^{13}$PCPIrH$_2$ and methane as well as ethane as model alkanes) and found smaller activation barriers for the trigonal bipyramidal species.[17] Our own calculations agree with this assessment, and we will not consider the higher energy, T-shaped conformer further in this work.

The potential energy profile pertaining to the first two steps of the dissociative pathway for RH = propane is shown in Figure 1.

![Figure 1. Potential energy profiles (kcal/mol) for the addition of propane (Pr-H) to ($^R$PCP)IrH$_2$ along the dissociative pathway. The energy scale qualitatively corresponds to the data obtained for $R'$ = t-Bu. Fonts applied: normal, $R'$ = H; bold, $R'$ = Me; bold italic, $R'$ = t-Bu.](image)

The concerted elimination of H$_2$ from (PCP)IrH$_2$ to form free H$_2$ is fully allowed under C$_2$ symmetry, and we have not been able to locate a conventional transition state (TS) for this process. There may be a solvent-created TS for removal of H$_2$ under condensed phase conditions, but in the gas phase there is none. With no TS for H$_2$ removal from (PCP)IrH$_2$ (i.e., no activation barrier for the association reaction), we find $\Delta E^\ddagger_{D1} = \Delta E_{D1} = 27.2$ kcal/mol for $R'$ = H, 28.7 kcal/mol for $R'$ = Me, and 29.1 kcal/mol for $R'$ = t-Bu. The activation energy for H$_2$ elimination increases with increasing electron-donating ability of the phosphines ($R'$ = H < Me < t-Bu) and hence increasing "electron-richness" of the Ir metal. There does not appear to be any differential steric interactions associated with the removal of this small molecule from ($^R$PCP)IrH$_2$.

The activation energy for the oxidative addition of propane to the three-coordinate ($^R$PCP)Ir complex is $\Delta E^\ddagger_{D2} = 5.9$, 6.4, and 13.4 kcal/mol for $R'$ = H,
Me, and \(t\)-Bu, respectively. A precursor complex may form between (PCP)Ir and the alkane, but calculations by Hall and by us indicate that such a complex should be bound only weakly, \((12,13,17-19)\) and we will ignore its possible existence here. The presence of a (PCP)Ir(RH) complex will formally increase the activation energy for the C-H bond activation step slightly, but will not affect the overall energetics of the dissociative pathway. The formation of the propyl hydride intermediate from (\(^{\#}\)PCP)Ir and propane is a slightly exergonic reaction when \(R' = H\) (\(\Delta E_{D2} = -0.6\) kcal/mol) or \(R' = Me\) (\(\Delta E_{D2} = -1.4\) kcal/mol), but it is endergonic when \(R' = t\)-Bu, \(\Delta E_{D2} = 3.3\) kcal/mol.

Representation of the bulky phosphine substituents used experimentally, typically \(i\)-Pr or \(t\)-Bu, by hydrogen atoms is of course a very crude approximation for steric as well as electronic reasons. The mer-geometry attained by the (PCP)Ir fragment and the ligand enforced backbending of the P atoms (\(<\Pi r P \sim 170^\circ\) in (PCP)Ir) leaves both the face (\(trans\) to the PCP connecting carbon atom, C\(_{PCP}\)) and sides (\(cis\) to C\(_{PCP}\)) of (\(^{\#}\)PCP)Ir wide open for alkane attack. Methyl groups on the phosphorus atoms (i.e. (\(^{\#}\)PCP)Ir) capture most of the electron-donating nature of the substituent groups used experimentally. The methyl groups may also provide minimal steric hindrance, but they undoubtedly exert much less steric hindrance than \(t\)-Bu (or \(i\)-Pr) groups do. Substrates approaching \(cis\) to C\(_{PCP}\) will experience significant steric hindrance when attacking (\(^{\#}\)PCP)Ir; an approach to the less crowded site \(trans\) to C\(_{PCP}\) will clearly be favored when \(R' = t\)-Bu. Increasing electron donating ability of the phosphine substituents (\(R' = H < Me < t\)-Bu) should favor both the kinetics and thermodynamics of RH addition to (\(^{\#}\)PCP)Ir, whereas the concomitant increase in substituent steric bulk (\(R' = H \sim Me << t\)-Bu) should distinctly disfavor both the kinetics and thermodynamics of RH addition. The computed (thermodynamic) \(\Delta E_{D2}\) values (-1.4, -0.6, and 3.3 kcal/mol for \(R' = H\), Me, and \(t\)-Bu, respectively) conform well to these expectations. The transition state energies for C-H cleavage also increase in the order (\(^{\#}\)PCP)Ir \(-\) (\(^{\#}\)PCP)Ir \(<\) (\(^{\#}\)PCP)Ir \((-\) 5.9, 6.4, and 13.4 kcal/mol, respectively). Thus some steric interactions may be present in TS\(_{D2}\) even when \(R' = Me\), and these unfavorable interactions most certainly intensify when \(R' = t\)-Bu. Comparison of the reaction and activation energies shows that the change from \(R' = Me\) to \(R' = t\)-Bu engenders a larger effect on \(\Delta E_{D2}\) \((-\) 7.0 kcal/mol) than on \(\Delta E_{D2}\) \((-\) 4.7 kcal/mol). The steric interactions are less unfavorable in the reaction product than in TS\(_{D2}\), because the (PCP)Ir(alkyl)(hydride) adopts a square pyramidal geometry with the hydride in the apical position. This positions the propyl group \(trans\) to C\(_{PCP}\), exactly in the site that is the sterically least hindered. The geometry of TS\(_{D2}\) has more trigonal bipyramidal character and the propyl unit cannot avoid steric interactions with at least one phosphino \(t\)-Bu group.

Turning to the associative pathway, there are a number of potential “seven-coordinate” intermediates of formula (\(^{\#}\)PCP)Ir(R)(H). We have located five configurational isomers (A-E), shown schematically in Figure 2.\((18,19)\) Two of these isomers (C and E) are classical structures with three hydride ligands.
whereas three isomers (A, B, and D) are non-classical structures featuring an η²-coordinated H₂ molecule. The energies of isomers A-E are all in the range 13-16 kcal/mol above the reactants, (PCP)IrH₂ plus propane, when R' = H or Me. Significant steric ⁶Pr/Bu interactions destabilize those structures that have the ⁶Pr group cis to C(PCP) (structures A, B, and C) by approximately 20 kcal/mol relative to (⁶BuPCP)IrH₂ plus propane. The relative increases are only about half as large (~ 12 kcal/mol) for the two isomers in which the ⁶Pr group is approximately trans to C(PCP) (D and E). Intermediates D and E are essentially isoenergetic, independently of R', but they lie 5-10 kcal/mol below A, B, and C when R' = t-Bu. Classical and non-classical structures (e.g. D and E) may interconvert with only small activation barriers (~ 2 kcal/mol), since the potential energy surface is very flat with respect to ligand movements in the horizontal plane. Also, the barrier for internal H₂ rotation around the Ir-H₂ axis in the non-classical structures is very low (~ 1 kcal/mol).(12)

**Figure 2.** Schematic illustrations of the metal coordination in the plane perpendicular to the P-Ir-P axis for the five configurational isomers located for propane C-H addition to (⁶PCP)IrH₂. C(PCP) and Cₚ denote the carbon atoms forming the Ir-PCP and Ir-Pr linkages, respectively. Energies (in kcal/mol) relative to (⁶PCP)IrH₂ plus H₂ are shown. Fonts applied: normal, R' = H; bold, R' = Me; bold italic, R' = t-Bu.

We have located (Figure 3) three transition states for formation of isomers A-E.(18,19) Intrinsic reaction coordinate calculations show that all three transition states connect to classical product isomers. The TS in which the propane molecule enters trans to the PCP unit between the hydrides connects to isomer E and hence indirectly also to D (TS_{D/E-exo}). Approach from the side, cis to C(PCP) may lead to isomer C and hence to the A, B, C structural manifold (TS_{A/B/C}). A different initial propyl orientation, but still involving an attack from the cis side, also produces isomer E (TS_{D/E-exo}). The transition state energies fall in the narrow range of 18-22 kcal/mol (relative to (⁶PCP)IrH₂ plus propane) when R' = H or Me. When R' = t-Bu, large steric interactions occur in all three TS's. The lowest energy TS emerges clearly as the one in which the propane
molecule executes a "frontal" attack, i.e. \( \text{TS}_{D/E-\text{endo}} \). \( \text{TS}_{D/E-\text{endo}} \) lies about 5 kcal/mol below the other two transition states, but approximately 32 kcal/mol above the reactants \( ((t\text{-}Bu\text{PCP})\text{IrH}_2 + \text{propane}) \).

Figure 3. Schematic illustrations of the metal coordination in the plane perpendicular to the P-Ir-P axis for the three transition states for propane C-H addition to \((R' \text{PCP})\text{IrH}_2\); \( \text{C}_{\text{PCP}} \) and \( \text{C}_{\text{Pr}} \) are the carbon atoms forming the Ir-PCP and Ir-Pr linkages, respectively. Fonts applied: normal, \( R' = H \); bold, \( R' = \text{Me} \); bold italic, \( R' = t\text{-}Bu \).

Figure 4. Potential energy profiles (kcal/mol) for the addition of propane (Pr-H) to \((R' \text{PCP})\text{IrH}_2\) along the associative pathway. The energy scale qualitatively corresponds to the data obtained for \( R' = t\text{-}Bu \). Fonts applied: normal, \( R' = H \); bold, \( R' = \text{Me} \); bold italic, \( R' = t\text{-}Bu \).

The second step of the associative mechanism is loss of an \( \text{H}_2 \) molecule from the "seven-coordinate" intermediates \((A-E)\). As in the case of \((\text{PCP})\text{IrH}_2\), removal of \( \text{H}_2 \) from \( E \) (or from \( D \)) appears to proceed smoothly to the products \( ((\text{PCP})\text{Ir(Pr)}(H) + \text{H}_2) \) without the appearance of a conventional transition state. Measuring from intermediate \( E \), we calculate \( \Delta E_{A2}^+ = \Delta E_{A2} = 11.2, 13.7, \) and 7.2
kcal/mol for \( R' = \text{H}, \text{Me}, \) and \( t\text{-Bu} \), respectively. The low activation energy when \( R' = t\text{-Bu} \) reflects steric interactions between \( R' \) and the \( \text{cis} \) hydrogens in \( E \) (or the \( \eta^2 \)-coordinated \( \text{H}_2 \) species in \( D \)).

We illustrate in Figure 4 the potential energy profile for the associative pathway, using the transition state (\( \text{TS}_{D/E-endo} \)) and the intermediate (\( E \)) of lowest energy (\( R' = t\text{-Bu} \)) as reference points. Joint consideration of Figures 1 and 4 might seem to indicate that the favored mechanism for acceptorless dehydrogenation of linear alkanes by (PCP)IrH\(_2\) should be associative, since the \( A \) pathway (Figure 4) clearly offers the lower activation energy barrier on the potential energy surface (\( \Delta E^\ddagger_{A} = 26.6(33.1), \ 27.3(35.1), \) and \( 32.4(42.5) \) kcal/mol, for \( R' = \text{H}, \text{Me}, \) and \( t\text{-Bu} \), respectively). This conclusion, tentative (and furthermore erroneous; see later) because it is based on consideration of only potential energies, and our numerical data for \( R' = \text{H} \) agree well with results obtained by Hall and Niu on (\(^{13}\text{PCP})\text{Ir} \) and smaller substrates (methane and ethane).\(^{17}\)

Considerations based on enthalpy rather than energy would not substantially alter the appearances of Figures 1 and 4. The potential energy-to-enthalpy conversion consists primarily of vibrational zero-point energy corrections. These corrections reach their largest differential effect (~ 3 kcal/mol) on the elementary steps, where an \( \text{H}_2 \) molecule is formed (\( D1, A2 \)), but they remain small compared to the relative energy differences shown in Figs. 1 and 4.

Free energy considerations at STP

But reaction rates and equilibria are determined by differences in Gibbs free energy (\( G = H-TS \)), not by changes in potential energy (\( E \)) or enthalpy (\( H = E + PV \)). Thus, we must combine the energies (enthalpies) obtained from the electronic structure calculations with accurate estimates for the entropies of the various species involved in the catalytic process. The elementary reaction steps under consideration here include changes in molecularity and will thus show Gibbs free energy profiles that appear considerably different from the potential energy profiles shown in Figs 1 and 4. Estimates of molecular entropies may be made using standard expressions derived from statistical mechanics. The electronic structure calculations provide the fundamental quantities (vibrational and rotational frequencies) required to evaluate the partition functions, when the nature of a particular stationary point on the potential energy surface (minimum or transition state) routinely is ascertained by normal-mode analysis. It is conventional to evaluate the partition functions assuming ideal gas behavior at standard thermodynamic conditions (STP): partial pressures of \( P = 1 \) atm for all species and room temperature, \( T = 25 \) °C (298 K).

Computed free energy profiles for the associative and dissociative mechanisms at STP are shown in Figure 5. In constructing Figure 5 for the associative process, we have used the molecular species from Figure 4 (\( E \) and \( \text{TS}_{D/E-endo} \) in particular) after verifying that none of the other "seven-coordinate" intermediates or transition states become competitive.
It is most important to note that Figure 5 shows barriers in free energy for the elimination of H₂ from both (PCP)IrH₂ and (PCP)Ir(nPr)H₃, even though no conventional TS for H₂ removal could be located on the potential energy surfaces (Figs. 1 and 4). The reason behind this is as follows: As the H₂ molecule is being formed and removed from the Ir center, the free energy of the system must increase because energy (enthalpy) is required for H₂ elimination. This increase in enthalpy continues until the H₂ molecule is fully formed and is released (into solution). The significant increase in entropy (and commensurate decrease in free energy) is realized only after H₂ has been produced as a free species. The free energy barrier height for H₂ elimination is thus approximately equal to the enthalpy difference between the reacting species ((PCP)IrH₂ or (PCP)Ir(nPr)H₃) and the products ((PCP)Ir + H₂ or (PCP)Ir(nPr)H + H₂). For the loss of H₂ from (PCP)IrH₂, we compute ΔH = 25.5, 27.0, and 27.3 kcal/mol for R' = H, Me, and t-Bu, respectively. The corresponding values for loss of H₂ from (PCP)Ir(nPr)H₃ are considerably smaller, and we obtain ΔH = 8.9, 11.4, and 5.3.
kcal/mol for R' = H, Me, and t-Bu, respectively. Experimentally, activation entropies near zero have been measured for loss of H₂ from several complexes closely related to the ones under consideration here, providing support for the enthalpy/entropy view just presented.

The data presented in Figure 5 provide no particular insight into which mechanism is favored at STP. The free energy barriers for both steps on the A pathway are almost identical and they are, furthermore, essentially identical to the barriers computed for the C-H activation step (step D₂) on the D pathway. These (coincidental) similarities are independent of the phosphine substituent (R'). The free energy barriers for either pathway are computed to be in the range 32-36 kcal/mol for R' = H and Me, but increase to 45-48 kcal/mol when R' = t-Bu. The free energy of activation for the loss of H₂ from (PCP)IrH₂ (step D₁) is well below these values at STP.

Free energy considerations at catalytic conditions

Fortunately, considering that our goal is the elucidation of the mechanism for acceptorless dehydrogenation of alkanes by (PCP)IrH₂, the actual experimental conditions are far removed from the standard thermodynamic conditions applied above. The catalytic acceptorless dehydrogenation process is conducted in solution at elevated temperatures with continuous removal of the H₂ gas produced. One of the most attractive features of the pincer-Ir catalysts is their high thermal stability; experimental operating temperatures are commonly in the range 150-200 °C. Temperature changes are trivially incorporated into the statistical mechanical computations and influence both the enthalpy and entropy contributions to the free energy. Increases in temperature (above 25 °C) will of course preferentially favor the steps with positive entropy changes, i.e. those liberating or containing free H₂.

The corrections necessary to simulate the effective alkane and dihydrogen concentrations are intriguing. The alkane substrate (n-octane, cyclooctane, etc.) is also typically the solvent for the catalytic reaction and hence its concentration is on the order of 10 M rather than the 0.04 M implied by the STP partial pressure of 1 atm. We must also include a statistical factor correcting for the number of hydrogens present in the alkane and capable of undergoing reaction. For propane, this statistical factor effectively increases the concentration of potentially active C-H bonds to six times the molarity of propane. The effective concentration of C-H bonds (converted to an effective pressure using the ideal gas law) contributes a correction to the chemical potential (Gibbs free energy) of the alkane. Note that this correction will significantly lower the free energies of the TS’s for steps D₂, A₁, and A₂ (relative to (PCP)IrH₂ + propane) – in all three cases by rigorously equal amounts, since all three TS’s involve the loss of 1 mol free propane.

Finally, and most importantly, it would be impossible to dehydrogenate alkanes without the use of a sacrificial acceptor, if the partial pressure of H₂...
were equal to 1 atm. The standard free energy change for alkane dehydrogenation is of the order of 20 kcal/mol, and hence the concentration of alkene product would be miniscule at STP. In order to obtain an appreciable concentration of alkene, it is necessary to operate at high T and to remove H₂ from the solution as soon as it is produced. Hence, under catalytic conditions, the pressure of H₂ must be of the order 10⁻⁵ atm or less. This large correction in H₂ concentration (relative to STP) affects only the free energy of the TS for step D2, the only TS where free H₂ is present.

Figure 6. Gibbs free energy profiles (kcal/mol) for the addition of propane to (R'PCP)IrH₂ along the D and A pathways simulated at experimental catalytic conditions. The energy scale qualitatively corresponds to the data obtained for R' = t-Bu. Fonts applied: normal, R' = H; bold, R' = Me; bold italic, R' = t-Bu.

In Figure 6, we show the free energy profiles for A and D pathways for acceptorless dehydrogenation of propane by (PCP)IrH₂ at the simulated experimental conditions T = 200 °C, P[H₂] = 10⁻⁵ atm, and P[propane] = 2,000 atm. For the D path we obtain free energy barriers of 25.7, 27.3, and 30.3 kcal/mol for R' = H, Me, and t-Bu, respectively. In contrast, the free energy barriers along the A path are much higher (by ca. 20 kcal/mol for R' = t-Bu) at 37.3, 38.5, and 49.8 kcal/mol for R' = H, Me, and t-Bu, respectively. The rate determining step on the D pathway is predicted to be elimination of H₂ from
(\textsuperscript{t}PCP)IrH\textsubscript{2}, when R' = H or Me. When R' = t-Bu, the C-H activation step has the slightly larger computed barrier (\(\Delta G^\ddagger_{D2} = 30.3\) kcal/mol vs. \(\Delta G^\ddagger_{D1} = 27.9\) kcal/mol) at 200 \(^\circ\)C and 10\(^{-5}\) atm H\textsubscript{2}. However, the magnitude of \(\Delta G^\ddagger_{D2}\) depends on the concentration of H\textsubscript{2} (whereas \(\Delta G^\ddagger_{D1}\) does not) and a concentration of H\textsubscript{2} lower than 10\(^{-5}\) atm will further reduce the magnitude of \(\Delta G^\ddagger_{D2}\). Thus, rapid and effective expulsion of the generated H\textsubscript{2} is an essential experimental condition, which the calculations must take into account. Furthermore, the degree of efficiency of H\textsubscript{2} expulsion from solution may influence the identity of the rate-determining step within the \textbf{D} pathway.

**Experimental support for the dissociative pathway**

We have shown elsewhere that the use of a cyclic alkane, in particular cyclohexane, in DFT calculations analogous to those presented above leads to potential and free energy profiles that are almost superimposable on the ones for the linear alkane propane.\(^1\)\(^8\),\(^9\) Thus, free energy calculations simulating catalytic conditions squarely predict that the acceptorless dehydrogenation of (linear and cyclic) alkanes by (PCP)IrH\textsubscript{2} proceeds along the \textbf{D} pathway. It was noted above that the associative pathway involves non-classical intermediates in which an \(\eta^2\)-coordinated H\textsubscript{2} molecule has a very low barrier to internal rotation (~ 2 kcal/mol).\(^1\)\(^2\) If step \textit{A1} is at all feasible, the use of deuterated hydrocarbons should lead to incorporation of deuterium into the (PCP)Ir species. Indeed, perdeuterated benzene, mesitylene, and \textit{n}-decane do appear to add to (\textsuperscript{\textit{t}}PCP)IrH\textsubscript{2} with a free energy of activation near 30 kcal/mol (as evidenced by H/D exchange).\(^1\)\(^8\) However, even after one week at 180 \(^\circ\)C, no deuterium exchange between (\textsuperscript{\textit{t}}PCP)IrH\textsubscript{2} and cyclohexane-\textsubscript{d\textsubscript{12}} could be detected. The derived activation energy for the (hypothetical) C-D activation process is greater than 36 kcal/mol and thus \textit{larger} than the measured activation energy for the catalytic acceptorless dehydrogenation of cyclohexane by (\textsuperscript{\textit{t}}PCP)IrH\textsubscript{2} (ca. 31 kcal/mol). Step \textit{A1} can therefore not play a role in the dehydrogenation of cycloalkanes. Thus, in the case of the cycloalkanes there is strong experimental support for the \textbf{D} mechanism. Based on the extensive similarities between propane and cyclohexane observed in the calculations, we do strongly believe that the \textbf{D} mechanism is operative for linear alkanes as well.

**Alternative mechanism \textit{I}**

The \textit{I} mechanism was invoked in a discussion of the acceptorless dehydrogenation of cyclododecane by the (PCP)Ir pincer catalyst analog "anthraphos".\(^1\)\(^3\) Calculations on model species (experimental phosphino \textit{t}-Bu groups replaced by hydrogens, ethane used as model alkane) were presented in support of the \textit{I} mechanism being favored at moderate temperatures. At high T (250 \(^\circ\)C), all three mechanisms (\textbf{D}, \textit{A}, and \textit{I}) were found to have similar free energies of activation (partial pressures = 1 atm). We have analyzed in some
detail the TS initially proposed as representative of the I process and have found that the purported TS$_I$ is actually a TS for intramolecular rearrangement between two "seven-coordinate" species (analogues of our isomers B and C, Figure 2). Furthermore, the steric effects of the t-Bu groups presented here cast additional doubt on the feasibility of an I process. "TS$_I$" will necessarily involve a crowded "seven-coordinate" species experiencing substantial steric interactions between the alkane and the bulky phosphino alkyl group, probably to an extent very similar to what we have computed above for TS$_A$ (Figure 6).

Importantly, the entropy loss arising from addition of the alkane in "TS$_I$" cannot be mitigated by the entropy gain arising from the H$_2$ molecule being formed, because this latter entropy is not realized before the H$_2$ molecule is released into solution. Thus, an I pathway does not appear to be energetically competitive with the D pathway. Indeed, even if it is supposed that an I pathway existed, its activation enthalpy must of course be at least as great as the overall reaction enthalpy to give ($^6$PCP)Ir(R)(H) (26.6, 27.3 and 32.4 kcal/mol for R' = H, Me, and t-Bu, respectively). Thus, due to the same entropic factors that preclude the A path, even if we assume the lowest possible activation enthalpy (i.e. $\Delta H^\ddagger = 0$ in the reverse direction) an I pathway would still engender a free energy of activation no lower than that of step A2 (35.7, 36.5 and 44.3 kcal/mol for R' = H, Me, and t-Bu, respectively).

**Concluding Remarks**

We have presented results from extensive sets of electronic structure calculations on the mechanism of acceptorless dehydrogenation of alkanes by pincer ($^6$PCP)IrH$_2$ catalysts. We have analyzed two plausible mechanisms, dissociative (D) and associative (A), using propane as a model linear alkane and catalyst species exerting different steric demands (R' = H, Me, and t-Bu). We find that, independent of R', the D pathway is favored with a free energy barrier at least 10 kcal/mol lower than that for the A pathway. C-H activation by late metals, and numerous important reactions catalyzed by Group 9 metals in particular, are generally assumed to occur via low metal oxidation states. In accord with this view, in the D mechanism the metal shuttles between Ir(II) and Ir(I) oxidation states, while the A mechanism would involve Ir(III) and Ir(V) oxidation states. Bergman, however, has demonstrated that cationic Cp*Ir(III)Me can activate alkane C-H bonds, and calculations show the mechanism to proceed via an Ir(V) intermediate. But unlike the (PCP)Ir catalysts, an Ir(I) pathway is not available in the Cp*Ir(III)Me case. The deuterium exchange experiments alluded to above presumably also involve Ir(V) intermediates. Thus, Ir(V) C-H activation intermediates may certainly exist, but they are too high in free energy to play a role in the case of acceptorless dehydrogenation of alkanes by (PCP)Ir.
The data reported in Figures 1, 4, and 5 demonstrate that the magnitudes of the computed barriers depend strongly on the bulkiness of the phosphino alkyl groups. The experimentally used \( R' = t\text{-}Bu \) generates C-H activation barriers that are larger by 10 kcal/mol or more than those calculated when \( R' = H \) or Me. All data reported here are based on first principles quantum mechanical calculations on the entire molecule. It is certainly possible (indeed very likely) that DFT calculations, in combination with the small basis sets necessarily applied to cover the \( t\text{-}Bu \) groups, overestimate the steric effects of the bulky groups; note, however, that the separation in the \( D/A \) free energies under catalytic conditions is distinct, even when \( R' = H \) or Me (Figure 6). Steric effects from phosphine substituents larger than Me can only further favor \( D \) preferentially over \( A \).

Incorrect conclusions would be drawn from considerations based only on potential energy profiles. Gibbs free energies must be evaluated carefully, because the elementary steps in the mechanisms involve changes in molecularity and take place under reaction conditions that are far removed from STP. Efforts must be made to accurately simulate the actual conditions employed in the experiments, in particular the high \( T \) and low \([H_2]\). Experimental evidence shows that the \( D \) mechanism is necessarily operative in the dehydrogenation of cycloalkanes. The computed free energy profiles for cycloalkane and propane are nearly identical, as are the overall experimental catalytic barriers, providing strong support that the same conclusion applies for \( n \)-alkanes.

**Computational Details**

All calculations employed DFT with the B3LYP combination of exchange-correlation functionals.\(^{(23)}\) For species containing \((H\text{-}PCP)\text{Ir}\) and \((Me\text{-}PCP)\text{Ir}\), geometries were fully optimized with the Ir LANL2DZ ECP and corresponding basis set \((24a)\); D95(d) basis sets on the second and third row elements \((24b)\); the 311G(p) basis set for dihydrogen and hydrogen atoms in the alkane, which formally become hydrides in the product complexes; \((24c)\) and a 21G basis set for regular hydrogen atoms (BasisA).\(^{(24d)}\) Additional single-point calculations used a more extended basis set for Ir (BasisB).\(^{(24e,f)}\)

Standard statistical mechanical expressions were used to convert from purely electronic reaction or activation energies \((\Delta E, \Delta E^\dagger; T = 0 \text{ K}, \text{no } \Delta ZPE)\) to enthalpies and free energies \((\Delta H^o, \Delta H^{\ddagger}; \Delta G^o, \Delta G^{\ddagger}; \Delta ZPE \text{ included}, T = 298 \text{ K}, P = 1 \text{ atm})\). Standard formulas were also applied to obtain \( \Delta G \) and \( \Delta G^\ddagger \) at other temperature/pressure combinations. Energies for species containing \((H\text{-}PCP)\text{Ir}\) and \((Me\text{-}PCP)\text{Ir}\) are based on \( \Delta E \) \((\Delta E^\dagger)\) values from B3LYP/BasisB calculations with the electronic energy-enthalpy-free energy corrections made as appropriate in an additive fashion with data derived at the B3LYP/BasisA level. To arrive at energy data for the \((t\text{-}Bu\text{-}PCP)\text{Ir}\) containing species, we used the following approach: the energies of the relevant \((t\text{-}Bu\text{-}PCP)\text{Ir}\) and corresponding \((Me\text{-}PCP)\text{Ir}\) species were evaluated at geometries (re)optimized using
B3LYP/BasisA, except that the C and H-atoms in the phosphine alkyl groups had only a minimal STO-3G basis set (BasisC). A "best" set of energies for species containing $t$-Bu groups were then obtained in an additive fashion by matching the $(^{13}PCP)_{Ir}$ data computed at BasisB and BasisC levels.

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References


