Computational study of ethene hydroarylation at [Ir(κ²-OAc)(PMe₃)Cp]+

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Abstract
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Reference

DOI: 10.1039/c0dt00409j
This article is published as part of the *Dalton Transactions* themed issue entitled: 

**Dalton Discussion 12: Catalytic C-H and C-X Bond Activation**

Published in *issue 43, 2010* of *Dalton Transactions*

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Computational study of ethene hydroarylation at \([\text{Ir}(\kappa^2\text{-OAc})(\text{PMe}_3)\text{Cp}]^+\)†‡

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Received 3rd May 2010, Accepted 17th June 2010
DOI: 10.1039/c0dt00409j

Density functional theory calculations have been employed to model ethene hydroarylation using an \([\text{Ir}(\kappa^2\text{-OAc})(\text{PMe}_3)\text{Cp}]^+\) catalyst, I. The reaction proceeds via: (i) an acetate-assisted C–H activation of benzene via an AMLA-6 transition state; (ii) rate-limiting insertion of ethene into the Ir–Ph bond; and (iii) protonolysis of the β-phenylethyl species by HOAc. A range of competing processes are assessed, the most important of which are the C–H activation of ethene at I and trapping of the β-phenylethyl intermediate with ethene. The former process gives rise to Ir–vinyl species which can then access further ethene insertion to give stable allyl by-products. A comparison with other ethene hydroarylation catalysts reported in the literature is presented.

Introduction

A range of different transition metal systems have now been shown to be capable of C–H bond activation.1 This reaction can proceed via several different mechanisms which depend on the metal fragment involved and can range from oxidative addition at electron rich late transition metal centres to σ-bond metathesis at electrophilic early metal systems. Computational studies2 have made a particularly important contribution to understanding mechanism in this area and have shown that σ-bond metathesis can also be extended to late metal centres. More recently, the activation of C–H bonds at electrophilic, late transition metal centres bearing either a heteroatom ligand, X, with an available lone pair or an intramolecular chelating base has been particularly prominent. We have shown that the synergic combination of C–H activation of ethene at M···M agostic interaction with C–H···X H-bonding can provide particularly facile C–H bond cleavage via ambiphilic metal-ligand activation; such reactions may involve 4-membered (AMLA-4) or 6-membered (AMLA-6) transition states (Scheme 1).2a,3

Increasingly, the emphasis of research into C–H activation has shifted towards integrating this step into catalytic cycles, such that the C–H ‘functional group’ can be exploited in synthesis.4 Such processes would allow cheap hydrocarbons to be exploited directly as feedstocks and promise a high atom economy, both highly desirable features from a Green Chemistry point of view. Significant progress in this area has been achieved in the intramolecular cyclisation reactions of substituted aryl halides in the presence of carboxylate or carbonate bases.5 In these processes C–halide activation first anchors the substrate and directs the metal toward intramolecular C–H activation. C–C coupling then completes the cyclisation process. Intramolecular base-assistance is central to the success of these reactions, although in some cases it has been proposed that external base may play an equivalent role.5b,c

Related intermolecular C–H functionalisation has also been achieved,6 most notably by Fagnou and coworkers who reported the catalytic arylation of electron deficient arenes. These reactions are promoted by the acidic C–H bonds present in such species. Progress with unactivated substrates has also been made, with the groups of Gunnoe7 and Periana8 reporting the hydroarylation of ethene at \(\{\text{TpRu(Ph)L(NCMe)}\} (\text{L} = \text{CO, PMe}_3)\) and \(\{\text{Ir(acac)}_2(\text{Ph})\}\) fragments. Although these processes require high temperatures and suffer from low turnovers, they do provide ‘proof of concept’. The mechanisms of these reactions have been the focus of parallel computational studies by Cundari7b,c,9 and Goddard,10 respectively, that have highlighted the subtle factors that control catalytic efficiency, as well as probing the accessibility of a number of competing side reactions.

We have previously shown that acetate and other carboxylate co-ligands can be particularly effective in promoting intramolecular C–H activation at both Pd2–11,12 and Ir2+ 13,14 metal centres. Indeed, C–H bond cleavage is not the difficult step in such processes, but rather the initial \(\text{k}^2\)-\(\text{k}^1\) displacement of the acetate that makes available a pendant basic oxygen (see Scheme 2). C–H activation then proceeds through an AMLA-6 process typically with a minimal barrier.15 Alternative reactions based on oxidative addition or an AMLA-4 process (with H-transfer onto the inner acetate arm) are much higher in energy. The promising features...
of these acetate-assisted C–H activation reactions prompted us to undertake a computational study of ethene hydroarylation incorporating this step. For this study we have chosen the [Ir(κ²-OAc)(PMe₃)Cp]⁺ as a model catalyst.¹⁶

Results

Computed catalytic cycle for ethene hydroarylation.

The basis for our work is shown in the model catalytic cycle in Scheme 3. Addition of benzene to [Ir(κ²-OAc)(PMe₃)Cp]⁺, 1, results in displacement of one arm of the acetate ligand to give adduct [Ir(κ¹-OAc)(C₆H₆)(PMe₃)Cp]⁺, 2. C–H activation then gives phenyl intermediate 3, with substitution of acetic acid by ethene allowing migratory insertion in 4 to give β-phenylethyl species 5. Protonolysis of acetic acid gives 6, from which protonolysis releases the ethylbenzene product and regenerates catalyst 1.

Details of the initial C–H activation of benzene at 1 are given in Fig. 1, where here and throughout all energies are quoted relative to the sum of 1, free benzene and ethene. The computed structure of 1 shows a symmetrically bound κ²-acetate ligand with similar Ir–O distances around 2.16 Å. C–H activation then proceeds through TS(1–2) (E = +15.8 kcal mol⁻¹) in which one arm of the acetate ligand is displaced by benzene to form the κ¹-intermediate, 2 (E = +9.9 kcal mol⁻¹). This involves elongation of the Ir–O₁ distance and rotation about the Ir–O₂ bond, such that the acetate ligand adopts an upright orientation in 2. This rotation is quantified by the C₁–O₂–Ir–X torsion angle, where X is the Cp ring centroid. Cp and PMe₃ H atoms are omitted for clarity.

Overall, the C–H activation of benzene at 1 is slightly endothermic and proceeds with a barrier of 15.8 kcal mol⁻¹ that reflects the...
ease of κ²-κ¹ displacement of acetate rather than the cleavage of the C–H bond. A similar pattern has been computed previously for the cyclometallation of dimethylbenzylamine (DMBA-H) in [Ir(DMBA-H)(κ²-ΟAc)Cp]⁺, where an overall barrier of 13.4 kcal mol⁻¹ was computed, again corresponding to κ²-κ¹ displacement of acetate. The C–H activation step in that case had a minimal barrier of only 0.9 kcal mol⁻¹. Accordingly, an earlier C–H activation transition state was computed in the DMBA-H system, with barely any elongation of the C–H bond (1.12 Å), but much longer H···O and Ir···C contacts (2.12 Å and 2.46 Å respectively). Cyclometallation is also more favourable as it is both exothermic by 5.6 kcal mol⁻¹ and not significantly affected by entropy considerations. This is not the case for the intermolecular activation of benzene, the associative nature of which means that all stationary points become significantly less accessible on the free energy surface. The κ²-κ¹ displacement remains the highest point on the C–H activation profile (G = +28.4 kcal mol⁻¹), but this is now only marginally above the C–H cleavage transition state (G = +28.1 kcal mol⁻¹) and the overall C–H activation is significantly endergonic (ΔG = +16.6 kcal mol⁻¹). Stoichiometric activation of benzene would therefore not be expected to occur at 1, although this does not rule out catalysis, as long as the subsequent steps are kinetically accessible and lead to a net thermodynamic stabilisation.

The following step in the ethene hydroarylation pathway requires substitution of acetic acid by ethene to form [Ir(Ph)(C₂H₅)(HOAc)(PMe₃)Cp]⁺, 4 (E = −0.9 kcal mol⁻¹, see Fig. 2). The structure of 4 and the subsequent stationary points associated with migratory insertion are standard. Thus TS(4–5) (E = +18.5 kcal mol⁻¹) is a 4-centred transition state featuring elongation of the Ir–Ph bond (Ir···Ph = 2.23 Å), a decrease in the C2···C4 distance (to 1.96 Å) and lengthening of the C4–C5 distance (from 1.42 Å in 4 to 1.47 Å). These tendencies are completed in the β-phenylethyl complex 5 (E = −3.9 kcal mol⁻¹; C2–C4 = 1.53 Å, C4–C5 = 1.54 Å) in which the formally 16e Ir metal centre is stabilized by an η¹-interaction with the phenyl substituent, as evidenced by two short contacts (Ir···C2 = 2.52 Å, Ir···C3 = 2.40 Å) and a slight elongation of the C2–C3 bond (1.44 Å). Migratory insertion proceeds with a barrier of 19.4 kcal mol⁻¹ and is slightly exothermic (ΔE = −3.0 kcal mol⁻¹). The intramolecular nature of this step means that the energetics are not significantly affected by entropic effects.

The final step in our proposed hydroarylation cycle involves protonolysis of 5 by the acetic acid formed in the initial C–H activation of benzene. We have modelled this by first adding HOAc to the Ir centre and displacing the weakly bound phenyl moiety (see Fig. 3). This step produces [Ir(CH₂CH₂Ph)(HOAc)(PMe₃)Cp]⁺, 6 (E = −18.3 kcal mol⁻¹), and is favourable (ΔE = −14.4 kcal mol⁻¹, ΔG = −2.5 kcal mol⁻¹). Protonolysis then proceeds with a barrier of 15.3 kcal mol⁻¹ via TS(6–7) (E = −3.0 kcal mol⁻¹). In this transition state the transferring proton is equidistant between acetate and the alkyl groups (O1···H2 = H2···C5 = 1.40 Å) and shows a short contact with Ir of 1.98 Å. The Ir···C5 distance also increases by over 0.2 Å as it begins to cleave. TS(6–7) leads to structure 7 in which ethylbenzene is effectively fully dissociated from the metal complex (the shortest contact being well over 4 Å) and the acetate ligand adopts a κ¹-binding mode (Ir···O1 = 3.14 Å). A barrier of 4.3 kcal mol⁻¹ (calculated separately in the absence of ethylbenzene) must be cleared to reform 1 with a κ¹-acetate. Protonolysis of 6 to form 1 and free ethylbenzene is exothermic (ΔE = −7.3 kcal mol⁻¹) and is further favoured by the dissociative nature of this step (ΔG = −21.9 kcal mol⁻¹).

Fig. 2 Computed reaction profile (kcal mol⁻¹) for the migratory insertion of ethene in [Ir(Ph)(C₂H₅)(PMe₃)Cp]⁺, 4, with selected geometrical parameters (Å, degrees) and computed free energies shown in italics. Cp and PMe₃ H atoms are omitted for clarity.

Fig. 3 Computed reaction profile (kcal mol⁻¹) for protonolysis of [Ir(CH₂CH₂Ph)(HOAc)(PMe₃)Cp]⁺, 6, with selected geometrical parameters (Å, degrees) and computed free energies shown in italics. Cp and PMe₃ H atoms are omitted for clarity.

The overall reaction profile computed for ethene hydroarylation catalysed by 1, is shown in Fig. 4. The overall process is thermodynamically favourable (ΔE = −25.6 kcal mol⁻¹, ΔG
\[ \Delta G = -14.6 \text{ kcal mol}^{-1} \]. The profile shows the highest lying transition state along the cycle corresponds to ethene insertion (TS(4–5), \( E = +18.5 \text{ kcal mol}^{-1} \)) and that this step also has the highest individual barrier (19.4 kcal mol\(^{-1}\)). The barriers associated with initial C–H activation and protonolysis are 15.8 kcal mol\(^{-1}\) and 15.3 kcal mol\(^{-1}\) respectively. Both the initial benzene activation and ethene insertion steps are disfavoured on the free energy surface, although the latter remains the highest point along the profile (\( G = +32.3 \text{ kcal mol}^{-1} \)). This is therefore the overall rate determining step for the hydroarylation process.

### Competing side reactions

A number of competing processes may occur during the hydroarylation catalytic cycle and the fact that significant barriers are associated with each of the C–H activation, alkene insertion and protonolysis steps means that the precursors involved (1, 4 and 5 respectively) may be vulnerable in this respect. Possible side reactions derived from each of these species will therefore be considered in turn below.

#### C–H activation of ethene at 1

In addition to the C–H activation of benzene, catalyst 1 may undergo an analogous reaction with ethene to give the vinyl species [Ir(C\(_2\)H\(_3\))(HOAc)(PMe\(_3\))Cp]\(^+\), 9 (see Fig. 5). \( \kappa^2-\kappa^1 \)-displacement of acetate in this case proceeds with a barrier of 14.3 kcal mol\(^{-1}\) and forms intermediate 8 (\( E = -4.2 \text{ kcal mol}^{-1} \)). 8 features a relatively strong Ir-\( \eta^2 \)-ethene interaction (Ir–C2 = 2.21 Å; Ir–C3 = 2.21 Å, C2–C3 = 1.41 Å) which must be disrupted in order for C–H activation to occur. As a result C–H activation via TS(8–9) has a significant barrier of 15.0 kcal mol\(^{-1}\). This step is also endothermic by 3.1 kcal mol\(^{-1}\), although the overall process, the formation of 9 from 1 and ethene remains slightly exothermic (\( AE = -1.1 \text{ kcal mol}^{-1} \)). Entropic effects will again disfavour the C–H activation, with the free energy barrier increasing to 26.3 kcal mol\(^{-1}\) and the process becoming endergonic by 10.7 kcal mol\(^{-1}\). Overall, the energetics of the C–H activation of ethene at 1 are similar to those computed for benzene and the main difference between the systems is the much more stable intermediate formed with ethene.
Ethene insertion at 9 and methylallyl formation.

The above study indicates that the C–H activation of ethene at 1 would be reversible and so the significance of this process as a side reaction will depend on whether the vinyl species formed, 9, can access further reactivity. One possibility is the insertion of a second ethene molecule into the Ir–vinyl bond; the butenyl species thus formed could then isomerise to a methylallyl complex. Such a process has been observed experimentally in other ethene hydroylation reactions\(^\text{a}\) and is implicated in ethene hydrovinylation.\(^\text{a}\) The computed profile for methylallyl formation in the current system is summarized schematically in Fig. 6. Structural details of all species are given in the ESI.\(^\ddagger\)

The initial HOAc/C\(_2\)H\(_4\) substitution in 9 gives 10 and is a favourable process (\(\Delta E = -4.5\) kcal mol\(^{-1}\), \(\Delta G = -4.0\) kcal mol\(^{-1}\)).\(^\text{b}\) Ethene insertion then proceeds with a barrier of 18.7 kcal mol\(^{-1}\) to give Ir–butenyl species 11 (\(E = -13.8\) kcal mol\(^{-1}\)). This barrier is similar to that computed above for ethene insertion into the Ir–Ph bond of 4 (\(\Delta E^1 = 19.4\) kcal mol\(^{-1}\)), although the insertion with 10 is more favourable thermodynamically (\(\Delta E = -8.2\) kcal mol\(^{-1}\), cf. -3.0 kcal mol\(^{-1}\) for 4 to 5) as the vinyl moiety of the butenyl ligand interacts more strongly with the Ir centre. Isomerisation to the methylallyl species involves \(\beta\)-H transfer via TS(11–12) (\(E = +8.2\) kcal mol\(^{-1}\)) which can be accessed by rotation about the central C–C bond of the butenyl ligand. This forms the hydrido-butadiene species 12 (\(E = -20.0\) kcal mol\(^{-1}\)) which can then reinsert into the Ir–H bond via TS(12–13). This final step has an activation barrier of 24.4 kcal mol\(^{-1}\) and forms methylallyl complex 13 at -33.4 kcal mol\(^{-1}\). Overall the reaction of 10 to 13 consists of a series of thermodynamically favourable steps, each of which involve barriers comparable to those of the main hydroylation pathway. The stability of methylallyl complex 13 means that the reverse process to reform 9 would require an overall barrier of 46.5 kcal mol\(^{-1}\) (\(\Delta G^2 = +45.8\) kcal mol\(^{-1}\)). Therefore methylallyl formation is predicted to be a significant competing reaction to ethene hydroylation.

C–H activation of ethene at 4

\([\text{Ir}(\text{Ph})(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cp}]^+\), 4, is the key precursor to the ethene insertion step, however, this species could also undergo C–H activation of ethene to generate \([\text{Ir}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_4)(\text{PMe}_3)\text{Cp}]^+\), 15. C\(_6\)H\(_5\)/C\(_2\)H\(_4\) substitution would then form 10 and provide an alternative route to the stable methylallyl species 13. The computed reaction profile for this process is shown in Fig. 7; geometries are again fairly standard throughout and are given in the ESI.\(^\ddagger\)

Starting from 4, C–H activation requires initial isomerisation to 4b (\(E = +20.3\) kcal mol\(^{-1}\)) in which the ethene ligand exhibits an \(\eta^2\)-C–H binding mode (a transition state for this process was also located but was less than 0.5 kcal mol\(^{-1}\) above 4b and so is omitted from Fig. 7 for clarity). H transfer is then a 2-step process involving Ir(\(\nu\))-hydride intermediate 14 (\(E = +24.4\) kcal mol\(^{-1}\)). A similar process has been computed previously for C–H activation at \{Ir(R)\((\text{PR}_3)_2\)\text{Cp}\}\(^+\) fragments\(^\text{a}\) and has been observed experimentally.\(^\text{b}\) From 14, the subsequent C–H reductive coupling occurs via TS(14–15) and forms vinyl complex 15 (\(E = +18.2\) kcal mol\(^{-1}\)) which features an \(\eta^2\)-C–H bound benzene. C\(_6\)H\(_5\)/C\(_2\)H\(_4\) substitution then gives 10. The transformation of 4 to 10 via ethene C–H activation is controlled by TS(14–15) and the high energy of this species (\(E = +25.5\) kcal mol\(^{-1}\), \(G = +38.8\) kcal mol\(^{-1}\)) means

**Fig. 6** Computed reaction profile (kcal mol\(^{-1}\)) for formation of [Ir(\(\eta\)-C\(_6\)H\(_5\)Me)(PMe\(_3\))Cp]\(^+\), 13. Free energies are given in italics.

**Fig. 7** Computed reaction profile (kcal mol\(^{-1}\)) for C–H activation of ethene at [Ir(Ph)(C\(_2\)H\(_4\))(PMe\(_3\))Cp]\(^+\), 4. Free energies are indicated in italics.
that this process should not compete with the productive ethene insertion step via the more accessible \( \text{TS}(4-5) \) \((E = 18.5 \text{ kcal mol}^{-1}, +32.3 \text{ kcal mol}^{-1})\).

**Alternative reactions of 5**

In the hydroarylation cycle intermediate 5 undergoes protonolysis with HOAc to give 1 and ethylbenzene. These products are thermodynamically stable \((E = -25.6 \text{ kcal mol}^{-1}, G = -14.6 \text{ kcal mol}^{-1})\) and are accessed through \( \text{TS}(6-7) \) \((E = -3.0 \text{ kcal mol}^{-1}, G = +24.2 \text{ kcal mol}^{-1})\) as the rate-limiting transition state. Any side reactions derived from 5 need therefore to be compared against these energetic benchmarks.

One possibility direct from 5 itself is \( \beta\)-H elimination and the computed reaction profile for this is shown in Fig. 8. \( \beta\)-H transfer in 5 is accessed via rotation about the \( \text{C}^{\alpha}\text{-C}^{\beta} \) bond and occurs through \( \text{TS}(5-20) \) \((E = +6.3 \text{ kcal mol}^{-1}, G = +19.5 \text{ kcal mol}^{-1})\) without any \( \beta\)-H agostic intermediate being located. This forms hydrido-styrene complex 20 \((E = -17.7 \text{ kcal mol}^{-1}, G = -4.8 \text{ kcal mol}^{-1})\) which can then liberate styrene to form \( \text{Ir(H)(PMe}_{3}\text{Cp)}^{+} \). The computed free energies suggest that both \( \text{TS}(5-20) \) and the overall \( \beta\)-H elimination reaction will be kinetically competitive with protonolysis by HOAc. In principle \( \beta\)-H elimination could be reversible, although trapping of the 16e species 21 with another ligand could instigate further processes that would effectively remove Ir from the catalyst pool.

Further reactions of 5 are based on the addition of either benzene or ethene to form 17 or 18 respectively (see Fig. 9). 17 and 18 can each undergo C–H activation resulting in protonolysis of the Ir–alkyl bond to liberate ethylbenzene. These reactions both involve Ir(v) intermediates and are very similar to the C–H activation of ethene in 4 outlined above in Fig. 7. In addition 18 can undergo a second insertion of ethene to give 24. Fig. 9 summarises the key energy changes associated with each of these processes, where for brevity only the energy of the highest-lying transition state along each reaction profile is indicated. In 17 \((E = -0.8 \text{ kcal mol}^{-1}, G = +25.4 \text{ kcal mol}^{-1})\) the benzene ligand is weakly bound in an \( \eta^{3}\text{-C}==\text{C} \) mode and its addition is actually disfavoured relative to 5, suggesting that the interaction of the \( \beta\)-phenyl group with the Ir centre in 5 is more stabilising. C–H activation in 17 has a low barrier \((\Delta E^f = 5.7 \text{ kcal mol}^{-1}, \Delta G^f = 5.6 \text{ kcal mol}^{-1})\), but the intrinsically high energy of 17 means that the key transition state involved \((E = +4.9 \text{ kcal mol}^{-1}, G = +31.0 \text{ kcal mol}^{-1})\) lies well above \( \text{TS}(6-7) \). Neither the formation of 17 nor its subsequent C–H activation reaction are therefore likely to be important competing processes.

In contrast, ethene addition to 5 is extremely favourable and the species formed, 18, is very stable \((E = -25.8 \text{ kcal mol}^{-1}, G = -0.3 \text{ kcal mol}^{-1})\). This again reflects the ability of the smaller ethene ligand to interact strongly with the \( \text{Ir(R)(PMe}_{3}\text{Cp)}^{+} \) moiety. By the same token both C–H activation and insertion of ethene require the disruption of this strong interaction and both processes have high activation barriers in excess of 27 kcal mol\(^{-1}\). The transition states involved are therefore higher in energy than \( \text{TS}(6-7) \) and so neither reaction will compete with protonolysis by HOAc. However, ethene adduct 18 is computed to be more stable than the HOAc adduct 6, \((E = -18.3 \text{ kcal mol}^{-1}, G = +7.3 \text{ kcal mol}^{-1})\). As a result under catalytic conditions 18 would be expected to be the dominant species that is formed from 5 and this may well inhibit catalysis, especially when ethene is present in high concentration.

**Discussion**

**Comparison with other ethene hydroarylation systems**

To date two other catalysts have been developed for ethene hydroarylation, trans-[Ir(acac)\(_2\)Ph(L)] (Iracac\(_2\), \( L = \text{H}_2\text{O, pyridine})\) and [TpRu(Ph)(L)(MeCN)] (TpRuL, \( L = \text{CO, phosphine})\).\(^3\) Computational studies suggest a common mechanism operates in these systems that consists of (i) initial ligand substitution of L by \( \text{C}_\text{H}_2\) in Iracac\(_2\), or of MeCN by \( \text{C}_\text{H}_2\) in TpRuL, (ii) insertion of ethene into the M–Ph bond and (iii) C–H activation of benzene to form ethylbenzene and regenerate the active M–Ph species. The Iracac\(_2\) system also requires an additional isomerisation step to form the active \( \text{cis} \) isomer which entails a substantial barrier.

The identity of the rate-determining step in these systems varies depending on the interpretation of the computational results.
and can either be viewed as the ethene insertion (in terms of computed enthalpies),\(^1\) or the C–H activation (if the free energies are considered).\(^2\) More generally, these two processes appear close in energy and the factors controlling them are interrelated and counter-directing. In both the \textit{Iracac}, and \textit{TpRuL}, systems C–H activation is computed to proceed \textit{via} a one-step \(\sigma\)-bond metathesis in which the transition state exhibits a M–H bonding interaction, indicative of a degree of Ir\((\nu)\) or Ru\((\nu)\) character. As a result the barrier to C–H activation can be lowered by a more electron rich metal centre. Unfortunately, however, this increases the barrier to insertion, a ground state stabilisation effect due to stronger ethene binding to a more electron releasing metal centre. It has been suggested that these counter-directing effects on C–H activation and ethene insertion will make optimisation of these catalysts problematic. The occurrence of side reactions makes this even more difficult and different degrees of oligomerisation, allyl formation and \(\beta\)-H elimination have all been observed depending on the precise nature of the catalyst employed.

The catalytic cycle proposed here has a number of differences to these previous systems. Most fundamentally, the C–H activation step involves deprotonation by acetate and so does not necessitate an increase in metal oxidation state (see Fig. 1). It may therefore be possible to decouple the energetics of the C–H activation and ethene insertion steps. The C–H activation process also incorporates the formation of a vacant site at the metal centre, a step which actually has a higher transition state than C–H activation. We have previously shown that this process can be facilitated by use of a more weakly coordinating base (e.g. trifluoroacetate or triflate) without making the C–H activation step significantly harder.\(^3\)

In the final step of the hydroarylation cycle acetate returns the proton by addition to the phenylethyl ligand (see Fig. 3). This occurs \textit{via} TS(6–7) and is a more accessible process than many of the possible competing reactions derived from intermediate 5. \(\beta\)-H elimination from 5 may still be an important competing process, however.

Between these two H-transfer processes, the ethene insertion step \textit{via} TS(4–5) remains the rate limiting process of the computed ethene hydroarylation cycle. The computed barrier of around 19 kcal mol\(^{-1}\) for this step is somewhat lower than those computed with the \textit{Iracac}, and \textit{TpRuL}, systems, although the different methodologies employed in these studies makes direct comparison difficult.

As well as the promising features described above, our study also highlights a number of issues that might hamper the development of 1 as an ethene hydroarylation catalyst. Most prominent among these is the facile C–H activation of ethene (see Fig. 4). Overall this process has similar energetics to the C–H activation of benzene, with a similar barrier for the \(\kappa^2\)-\(\kappa^1\) displacement of acetate and being close to thermoneutral. The major difference is the formation of a stable ethene complex 8. The difficulty with this process is that it provides access to Ir–vinyl complexes that can react on \textit{via} ethene insertion to form stable allyl by-products (e.g. 10 to 13, Fig. 6).

Another intrinsic difficulty seen in all ethene hydroarylation schemes is the trapping of the \(\beta\)-phenylethyl intermediate by ethene. In the present case this forms complex 18 and, although the direct reactions of this species (C–H activation or insertion of ethene) are predicted to be inaccessible, the stability of 18 means that it may act as a thermodynamic sink, trapping out the active intermediate 5. One positive aspect of the current system is that the precursor to protonolysis, HOAc adduct 6, is only \(ca.\) 7 kcal mol\(^{-1}\) less stable than 18. This is an improvement over the \textit{Iracac}, and \textit{TpRuL}, systems where protonolysis involves a high energy benzoate adduct; for example [Ir(acac),(CH\(_2\)CH\(_2\)Ph)(C\(_2\)H\(_4\))] lies over 17 kcal mol\(^{-1}\) above [Ir(acac),(CH\(_2\)CH\(_2\)Ph)(C\(_2\)H\(_4\))]. Despite the greater accessibility of 6 in the current system, ethene hydroarylation is still likely to be retarded at higher ethene concentrations.

In conclusion, density functional calculations have been employed to define the energetics of ethene hydroarylation with a [Ir(\(\kappa^2\)-OAc)(PM\(_3\)Me)\(_2\)Cu\(^{+}\)] catalyst, 1. This system has a number of promising features, mostly derived from the role of acetate in mediating the necessary proton transfer steps. Significant challenges still remain however, in particular the competitive C–H activation of ethene and irreversible ethene binding during catalysis. Biasing the C–H activation step in favour of the arene centre is therefore a key task and preliminary calculations suggest that use of electron donating para substituents may facilitate this step. The balance between alkene and HOAc binding may also be controlled by varying the steric environment around the metal centre. However, the consequences of perturbing one step in the catalytic cycle on the other processes involved are difficult to predict \textit{a priori}. Computational studies are ideally placed to provide an overall picture of such effects and so will play a central role in catalyst design in the future.

**Computational details**

All geometries were optimised without constraints using Gaussian 03, Revision C.02\(^2\) employing the BP86 functional.\(^2\) The SDD relativistic ECPs and the associated basis sets was used for Ir and P,\(^24\) with a set of d-orbital polarisation functions added for P.\(^25\) Basis sets were employed for all other atoms.\(^26\) Stationary points were confirmed as either minima or transition states through analytical frequency calculations and characterised through IRC calculations and subsequent geometry optimisation. All energies include a correction for zero-point energies and free energies were computed at 298.15 K and 1 atm.

**Acknowledgements**

We thank the EPSRC for funding (AIPB) and Heriot-Watt University and the University of Leicester for support.

**References**


