Abstract: The mechanism of hydroarylation of olefins by a homogeneous Ph-Ir(acac)$_2$(L) catalyst is elucidated by first principles quantum mechanical methods (DFT), with particular emphasis on activation of the catalyst, catalytic cycle, and interpretation of experimental observations. On the basis of this mechanism, we suggest new catalysts expected to have improved activity. Initiation of the catalyst from the inert trans-form into the active cis-form occurs through a dissociative pathway with a calculated $\Delta H(0 K)^\ddagger = 35.1$ kcal/mol and $\Delta G(298 K)^\ddagger = 26.1$ kcal/mol. The catalytic cycle features two key steps, 1,2-olefin insertion and C–H activation via a novel mechanism, oxidative hydrogen migration. The olefin insertion is found to be rate determining, with a calculated $\Delta H(0 K)^\ddagger = 27.0$ kcal/mol and $\Delta G(298 K)^\ddagger = 29.3$ kcal/mol. The activation energy increases with increased electron density on the coordinating olefin, as well as increased electron-donating character in the ligand system. The regioselectivity is shown to depend on the electronic and steric characteristics of the olefin, with steric bulk and electron withdrawing character favoring linear product formation. Activation of the C–H bond occurs in a concerted fashion through a novel transition structure best described as an oxidative hydrogen migration. The character of the transition structure is seven coordinate Ir$^{IV}$, with a full bond formed between the migrating hydrogen and iridium. Several experimental observations are investigated and explained: (a) The nature of L influences the rate of the reaction through a ground-state effect. (b) The lack of $\beta$-hydride products is due to kinetic factors, although $\beta$-hydride elimination is calculated to be facile, all further reactions are kinetically inaccessible. (c) Inhibition by excess olefin is caused by competitive binding of olefin and aryl starting materials during the catalytic cycle in a statistical fashion. On the basis of this insertion-oxidative hydrogen transfer mechanism we suggest that electron-withdrawing substituents on the acac ligands, such as trifluoromethyl groups, are good modifications for catalysts with higher activity.

1. Introduction

The synthesis of straight-chain alkyl benzenes is generally complicated by the almost 100% selectivity toward the branched isomer in conventional Friedel–Crafts alkylation. Even though the use of shape selective zeolites has met some limited success, the method of choice is normally a Friedel–Crafts acylation followed by reduction. Recently, Matsumoto$^2$–$^4$ and Periana$^5$ reported the synthesis of a novel Ir complex, [Ir($\mu$-acac-O$_2$O)$_2$-acac-C$_3$)$_2$, 4, that catalyses arylation of an unactivated olefin by benzene, generating a mixture of linear and branched alkyl benzenes (see Figure 1). Although potentially a very useful catalyst, several unresolved issues impede commercialization. Foremost among these are the low activity (turn-over-frequency (TOF) of $10^{-3}$ s$^{-1}$ at 200 $^\circ$C), but there are also problems with selectivity, cost, and stability.

Here, we explore the mechanism of hydroarylation of olefins by a Ph-Ir(acac)$_2$(L) catalyst on the $\Delta H(0 K)$ and $\Delta G(298 K)$ surfaces. In particular, the following questions will be addressed: (i) How is the catalytic cycle initiated?

![Figure 1. Arylation of olefin catalyzed by 4.](Image)

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(ii) What is the mechanism of the catalytic cycle?
(iii) What is the rate-determining step?
(iv) What is the origin of the regioselectivity for olefin insertion?
(v) By what mechanism is the C–H bond activated?
(vi) Why is no β-hydride elimination observed to form unsaturated products?
(vii) Why is the reaction inhibited by excess olefin?
(viii) How can the activity and selectivity of the catalyst be improved?

Matsumoto and Periana have conducted mechanistic studies, showing that C–H activation is involved and excluding several potential mechanisms. However, an unambiguous mechanism for the C–H activation and other critical steps has not yet been determined. Matsumoto concluded that the mechanism is not related to the Friedel–Crafts mechanism, and measured the free energy of activation for the unsubstituted reaction to be 28.7 kcal/mol. Both selectivity and activity change when substituted olefins are used, whereas activity changes with substituted aryls. The reaction exhibits complex kinetic behavior with nonzero order in ethene at low ethene/benzene ratios, but a negative dependence at higher ratios, indicating competitive inhibition by ethene. Periana showed, Figure 2, that the active catalyst is most likely a mononuclear Ph-Ir(acac)$_2$ or Ph-Ir(acac)$_2$(L) compound formed from arene C–H activation, where L is a coordinating ligand such as H$_2$O or pyridine. This hypothesis was strengthened by the independent synthesis of several mononuclear Ph-Ir(acac)$_2$(L) compounds, Figure 3, all of which have catalytic activities similar to 4. Furthermore, the mechanism does not appear to contain any charged species or breaking of Ir–O bonds between Ir and the acac ligands, which significantly reduces the number of potential mechanistic pathways.

The mechanism suggested by Periana features activation of the starting catalysts, which includes isomerization of the trans-Ph-Ir(acac)$_2$(L) to a cis-Ph-Ir(acac)$_2$(L) compound and coordination of the olefin. 1,2-Migration of the phenyl group to ethene, as observed in the Heck reaction, and coordination of a second benzene leads to a covalently bound Ir-alkyl species. C–H activation and hydrogen migration yields alkyl benzene and an Ir-phenyl compound. The C–H activation was expected to proceed either through a seven-coordinate Ir$^+$ intermediate or through a σ-bond metathesis pathway, as suggested for analogous C–H activations by the groups of Bergman and Maitlis.

Replacement of the alkyl benzene with an olefin completes the catalytic cycle. The identity of the rate determining step or the basis for the varying activities and selectivities observed with different olefinic substrates and additives have not yet been experimentally determined.

2. Computational Methodology

All calculations were performed using the hybrid DFT functional B3LYP as implemented by the Jaguar 4.1 program package. This DFT functional utilizes the Becke three-parameter functional (B3) combined with the correlation functional of Lee, Yang, and Parr (LYP) and is known to produce good descriptions of reaction profiles for transition metal containing compounds. The Ir was described by the Wadt and Hay core-valence (relativistic) effective core potential (treating the 17 electrons explicitly) using the LACVP basis set with the valence double-ζ contraction of the basis functions, LACVP*. All electrons were used for all other elements using a modified variant of Pople's 6-31G* basis set, where the six d functions have been reduced to five.

Implicit solvent effects of the experimental benzene medium were calculated with the Poisson–Boltzmann (PBF) continuum approximation, using the parameters $\epsilon = 2.284$ and $r_{	ext{sol}} = 2.602\,\text{Å}$. Due to the increased cost of optimizing systems in the solvated phase (increase in computation time by a factor of ~4) solvation effects are calculated here as single point solvation corrections to gas-phase geometries. Control calculations on structures 7 and TS2 show that energies change only 0.12 and 0.33 kcal/mol, respectively, when optimized in solution.
Geometries, frequencies, and zero point energies were also largely unchanged (see the Supporting Information for structures with and without solvation). Furthermore, control calculations of TS2(2,2)-propene and TS2(1,2)-propene in solution changed $\Delta \Delta H(0 \text{ K})$ less than 0.1 kcal/mol.

Energies on the $\Delta H(0 \text{ K})$ surface are reported as $\Delta E + \text{zero point energy corrections}$ at 0 K + solvation correction. Energies on the $\Delta G(298 \text{ K})$ surface are reported as $\Delta E + \text{zero point energy corrections}$ at 0 K + solvation correction + $\Delta G$ corrections at 298 K.

Relative energies on the $\Delta H(0 \text{ K})$ surface are expected to be accurate to within 3 kcal/mol for stable intermediates, and within 5 kcal/mol for transition structures. Moreover, relative energies of iso-electronic species (such as regio-isomers) are considerably more accurate, since the errors largely cancel.

Relative energies on the $\Delta G(298 \text{ K})$ surface are significantly less accurate, due to the use of the PBF model. Consequently, relative energies on the $\Delta G(298 \text{ K})$ surface can at best be considered qualitative, and should only be considered when comparing fairly similar species. This is further discussed in section 3.9.

All geometries were optimized and evaluated for the correct number of imaginary frequencies through vibrational frequency calculations using the analytic Hessian. Zero imaginary frequencies correspond to a local minimum, whereas one imaginary frequency corresponds to a transition structure. Due to a documented bug in the Jaguar implementation of frequency calculations on Ir,17 all imaginary frequencies between 0 and $-30 \text{ cm}^{-1}$ were ignored. This bug has subsequently been corrected in Jaguar 5.0. Although the singlet states are expected to be the lowest energy spin states, we also investigated higher spin states for select geometries, and invariably found the singlet as the lowest energy state.

To reduce computational time the methyl groups on the acac ligands were replaced with hydrogens. Control calculations show that relative energies of intermediates and transition structures change less than 0.1 kcal/mol when methyl groups are included. Regioselectivities are also largely unaffected. The use of a truncated acac group is here labeled acac$^1$.

3. Results and Discussion

3.1 Preliminaries. 3.1.1 Net Reaction. The reaction of benzene (1) and ethene (2) to generate ethyl benzene (3), illustrated in eq 1, is calculated to be exothermic with $\Delta H(0 \text{ K}) = -21.7 \text{ kcal/mol}$ and $\Delta H(289.15 \text{ K}) = -23.9 \text{ kcal/mol}$, which corresponds very well to the experimental value of $\Delta H(289.15 \text{ K}) = -25.2 \text{ kcal/mol}$.18 We calculate $\Delta G(289.15 \text{ K}) = -15.4 \text{ kcal/mol}$, very close to the experimental value of $-16.1 \text{ kcal/mol}$.18 Adding single point solvation correction to the gas-phase geometries reduces the exothermicity by 0.9 kcal/mol. This small correction reflects the similar hydrophobicity of starting materials and reactants. No experimental value could be found for the reaction in benzene.

$$\text{C}_2\text{H}_4 + \text{C}_6\text{H}_6 \rightarrow \text{ethyl benzene} \Delta H(289.15 \text{ K}) = -23.9 \text{ kcal/mol}$$

3.1.2 Character of the Bonding. Species such as 5–8 are generally described as Ir$^{10}$, which assumes that the acac ligands each get one electron from the metal while the phenyl or C-bonded acac group gets another for a total of three oxidations of the Ir. This is an oversimplification, because the Ir–C bonds are quite covalent.QM calculations show that the two electron

Ir–C sigma bond has about one electron in an Ir orbital with dominantly $dz^2$ character and the other in a $sp^3$ orbital on the carbon. This single bond has a length of 2.11, 2.16, 2.01, and 2.03 Å in 5–8, respectively. The bonding to each acac can be thought of as a resonance of two configurations each with a covalent bond, say in the x direction, and a donor–acceptor in the y direction. This leads to an average bond distance of 2.04, 2.05, 2.04, and 2.05 Å for 5–8, which can be thought of as an average of a single bond of $\sim 1.90 \text{ Å}$ and a $\sigma$–$\pi$ bond of $\sim 2.20 \text{ Å}$. This uses a combination of 6s and 5d$x^2$-$y^2$ character. The Ir has, in addition to the three electrons involved in the covalent bonds, 2 electrons each in the $dz_y$, $dz_x$, and $dxy$ orbitals for a total of 9 electrons. In this Generalized Valence Bond (GVB) model the notation Ir$^{10}$ refers to the three covalent bonds.

The ligand trans to the Ir–C localized covalent bond cannot make a partially covalent bond, thus in the cis compound 11 discussed below, the acac$^1$ O trans to the Ir–C bond becomes pure DA, with a bond distance of 2.21 Å, whereas the other bond to this acac$^1$ decreases to 2.04 Å. Thus, this acac$^1$ favors just the one resonance configuration. Simultaneously the bonds to the second acac$^1$ (still in the xy plane) favor slightly the resonance configuration with the lone pair trans to the 2.04 Å bond of the first acac$^1$.

3.2 Ground-State Effects. In the results reported by Matsumoto$^2$–$^4$ and Periana,$^5$ it was noted that starting with different catalyst compositions based on the Ir$^{III}$ (acac)$_2$ fragment led to varying catalytic rates, but that the ratio of linear to branched alkyl arene addition product was independent of the catalyst composition. This strongly indicates that different catalyst compositions share a common rate determining step, and most likely share catalytic cycles.$^{19}$ In this scenario, the change in catalyst rates with different starting catalysts is assumed to be caused by a ground state effect. This assumption was confirmed through theoretical calculations on the catalysts illustrated in Figure 3, which were experimentally investigated by Periana.$^5$ To compare the starting catalysts we report their relative energies. These relative energies can be considered

(17) Cao, Y.; Schrodingier, Inc., Portland, Oregon, Personal communication
(19) During review, one of the referees pointed out that the distribution of n-propyl benzene vs i-propyl benzene corresponds to the thermodynamic equilibrium distribution. However, this appears to be coincidental. Preliminary experimental studies show that i-propyl benzene is not susceptible to isomerization, either to n-propyl benzene or other products, when heated to 200 °C with the catalyst, 7, in liquid benzene (with or without ethylene). This shows that the reaction cannot be under thermodynamic control. Preliminary calculations also show that the product distribution from higher alkenes do not correspond to the thermodynamic distribution. For example, the equilibrium distribution of 2-methyl-propyl benzene vs tert-butyl benzene is calculated to 97: 3, whereas the distribution observed in ref 3 is reported as 82:18.
Rearrangement of the trans species From the Arrhenius equation, the natural logarithm of the turnover frequency (TOF) by the Arrhenius equation, is the relative energy of the rate determining step. If for each catalyst \( x \) should be given by the expression \( q_{E_{rds}} \) implicit reaction energies: the relative energy of, for example, 7 vs 5 is thus defined as the reaction energy of \( 7 + C_2H_5N \rightarrow 5 + H_2O \). The results of these calculations are summarized in Table 1, with the relative energy of 7 arbitrarily set to 0.

The activation energy of a catalyst is linearly related to the natural logarithm of the turnover frequency (TOF) by the Arrhenius equation, \( k = A e^{-\Delta E_{rds}/RT} \). If the catalysts share the same rate determining step, then the activation energy, \( \Delta E_{rds} \), for each catalyst \( x \) should be given by the expression \( \Delta E_{rds} = E_{act} - E_x \), where \( E_x \) is the relative energy of the catalyst \( x \), and \( E_{act} \) is the relative energy of the rate determining step. If \( E_{act} \) is the same for all the catalysts, then \( E_{act} \) will be constant and we should thus expect to obtain a linear correlation between the natural logarithm of the experimentally derived TOFs and the calculated relative energies.

As can be seen in Figure 5, such a linear correlation for the monomeric catalysts 5-8 is clearly observed. The dimeric catalyst 4 is slightly off, which we believe is caused by chelating effects in the dimeric catalyst. This confirms our hypothesis of a common rate-limiting step regardless of starting catalyst. On the basis of these results and the similarities in product ratios, it is reasonable to expect that catalysts 4-8 proceed through a similar reaction mechanism, illustrated in Figure 6, involving activation and cis-trans isomerization to the active catalyst 9. As the above catalysts feature common mechanisms, we elected to limit this study to the most active catalyst, 7.

### 3.3 Catalyst Activation by Cis–Trans Isomerization of Catalyst Precursor

There are several plausible mechanisms for the activation and conversion of 7 to 9, the energetics of which are summarized in Figure 7. They all start with a barrierless dissociation of the \( H_2O \) ligand to yield the 5-coordinate, 16\(^e\) species 10. 11.9 kcal/mol higher in energy than 7. From 10, one can continue on the dissociative pathway by rearrangement of the trans species 10 to the iso-electronic cis species, 11. Species 11 is 19.6 kcal/mol higher than the iso-electronic 10. This is due to the loss of resonance stabilization in 1 as described in section 3.1.2. The transition structure TS\(_{1A} \) (see Figure 8) connecting 10 and 11 has an activation energy of 23.2 kcal/mol relative to 10, (35.1 kcal/mol relative to the resting state 7) and a negative mode of \(-93 \text{ cm}^{-1} \), corresponding to a movement of the O–Ir–O angle. As 11 is significantly uphill in energy, it is not surprising that TS\(_{1A} \) is a late transition structure with an O–Ir–O angle of 115.5° and an Ir–O bond length of 2.18 Å.

Species 10 can also continue via an associative pathway where it coordinates an ethene to give 12, which is exothermic by 6.8 kcal/mol. From 12, we explored the possibility of a concerted mechanism in which one of the Ir–O bonds would switch place with the Ir–(C\(_2\)H\(_4\)) group. However, we could not find a transition state connecting 12 and 9. Forcing the O–Ir–O angle to go continuously from 180° to 90° invariably caused breaking of one of the Ir–O bonds. Likewise, forcing the (C\(_2\)H\(_4\))–Ir–Ph angle from 180° to 90° led to dissociation of C\(_2\)H\(_4\), regenerating 10. Consistent with the experimental work showing lack of exchange of the acac ligands, deliberately breaking one of the Ir–O bonds gave structure 13, 41.2 kcal/mol uphill from 12. The magnitude of the barrier for this isomerization can be compared to the experimental values for racemization of the related Ru(acac)\(_3\) and Rh(acac)\(_3\), which are measured to be > 40 kcal/mol.

We also considered that coordination of C\(_2\)H\(_4\) to TS\(_{1A} \) might yield a transition structure TS\(_{1B} \) (see Figure 8) that would bypass the high energy 11. Simply adding a C\(_2\)H\(_4\) to TS\(_{1A} \) did not lead to a stable structure, however, so a more extensive mapping of the hypersurface was undertaken, and transition

Image 5

**Table 1.** Activity and Relative Energy of Catalysts 4–8

<table>
<thead>
<tr>
<th>Complex</th>
<th>TOF ( \times 10^{-4} \text{s}^{-1} )</th>
<th>Isomer Ratio</th>
<th>( \Delta H(0 \text{K}) ) (kcal/mol)</th>
<th>( \Delta G(298 \text{K}) ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>110</td>
<td>61:39</td>
<td>3.3</td>
<td>9.5</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>61:39</td>
<td>-1.0</td>
<td>4.6</td>
</tr>
<tr>
<td>6</td>
<td>24</td>
<td>61:39</td>
<td>-9.9</td>
<td>-2.4</td>
</tr>
<tr>
<td>7</td>
<td>130</td>
<td>61:39</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>32</td>
<td>61:39</td>
<td>-7.0</td>
<td>-5.0</td>
</tr>
</tbody>
</table>

\( ^a \) From ref 5. \(^b \) Linear:branched product.

**Figure 5.** Plot of ln(TOF) vs \( \Delta H \) of catalysts 4–8. Line fitted to 5–8 with \( R^2 = 0.989 \), 4 not included due to chelating effects.

**Figure 6.** Suggested pathways for initiation of 4–8.
respectively, indicating that TS1A entropy and temperature corrections are required to obtain an experimental activation energy of 28.7 kcal/mol. However, this is significantly higher than the TS1A 35.1 kcal/mol and 34.0 kcal/mol. This is comparable to the experimental value of 28.7 kcal/mol at 413–473 K.

Figure 7. Pathways for converting the catalyst precursor 7 to the active catalyst 9, deduced from QM calculations. The lowest energy pathway on the ΔG(298 K) surface is added in a simplified dotted line. The rate determining step is through TS1A with ΔH(0 K) = 35.1 kcal/mol and ΔG(298 K) = 26.1 kcal/mol. This is comparable to the experimental value of 28.7 kcal/mol.

Figure 8. TS1A and TS1B.

structure TS1B was eventually located. TS1B has an activation energy of 22.1 kcal/mol relative to 10, (34.0 kcal/mol relative to the resting state 7), an O–Ir–O angle of 130.1° and a negative mode of −132 cm⁻¹, corresponding to movement of the O–Ir–O angle. The distances between the Ir and the carbons of the incoming C₂H₄ are calculated to 3.48 Å and 3.50 Å.

As 7 and 9 are quite close in energy, we also explored the possibility of adding C₂H₄ directly to 7, which would lead to a transition structure TS1C. In this case, the incoming C₂H₄ could both stabilize the transition state and also induce the cis–trans isomerization. However, we could not locate TS1C, as all attempts of constraining the C₂H₄–Ir distance and the O–Ir–O angle resulted in breaking the Ir–O bond, at relative energies several kcal/mol higher than TS1A and TS1B.

Thus, the lowest energy pathways on the ΔH(0 K) surface are through TS1A or TS1B, with total activation energies of 35.1 and 34.0 kcal/mol. This is significantly higher than the experimental activation energy of 28.7 kcal/mol. However, including temperature and entropy corrections, we obtain ΔG values of 26.1 and 34.4 kcal/mol for TS1A and TS1B, respectively, indicating that TS1A is the preferred pathway. Although not quantitatively correct, it is clear that inclusion of entropy and temperature corrections are required to obtain an accurate picture of cis–trans isomerization. These estimates of entropy terms in liquid-phase assume the free translation and free rotation of dissociated products, which could cause errors of several kcal/mol. Nevertheless, the final energetics are in reasonable agreement with experiment, i.e., lower in energy than the experimental activation energy of 28.7 kcal/mol.

3.4 Catalytic Cycle. The important steps in the catalytic cycle derived from the QM calculations are given in Figure 9 (energy profile) and Figure 10 (structures), respectively.

3.4.1 Starting Point (9). The catalytic cycle starts with 9, an Ir¹¹¹ species featuring two acac¹ groups cis to each other, a covalently bound phenyl group and a coordinating C₂H₄ ligand. The C–C axis in the C₂H₄ ligand in 9 is parallel to the Ph–Ir–O axis, facilitating the migratory insertion found to be the first step in the catalytic cycle. The Ir–C1 and Ir–C2 distances are 2.25 Å, whereas the C1–C2 bond length is 1.40 Å. This indicates some small amount of iridium d → π* back-bonding or of metallacyclop propane character. 21

3.4.2 Migratory Insertion (9 → TS2 → 14). The migratory insertion proceeds via the transition structure TS2, with a relative energy of 27.0 kcal/mol. TS2 is a four membered transition structure, featuring the simultaneous breaking of the Ir–C3(σ) and C1–C2(π) bonds and the creation of Ir–C1(σ) and C2–C3(σ) bonds. The geometric changes are as follows:

- The Ir–C3 distance increases from 2.05 Å in 9 to 2.20 Å at TS2 to 2.41 Å in the product 14.
- The C1–C2 distance increases from 1.40 Å in 9 to 1.47 Å in TS2 to 1.54 Å in 14.
- The Ir–C1 distance decreases from 2.25 Å in 9 to 2.08 Å in TS2 to 2.0 Å in 14.
- The C2–C3 distance decreases from 2.25 Å in 9 to 1.90 Å in TS2 to 1.52 Å in 14.

Thus TS2 has essentially fully formed Ir–C1 and C1–C2 single bonds, but half order bonds from C3 to Ir and to C2. TS2 has one imaginary frequency of ~348 cm⁻¹, corresponding to free rotation of dissociated products, which could cause errors of several kcal/mol. Nevertheless, the final energetics are in reasonable agreement with experiment, i.e., lower in energy than the experimental activation energy of 28.7 kcal/mol.

to a slipping of the C₂H₄ toward the phenyl group and closure of the C₂C₃ distance.

The product of TS₂ is the intermediate 14 with a relative energy of 5.6 kcal/mol, 3.1 kcal/mol higher in energy than 9. 14 features intramolecular coordination of the bound phenyl group, with Ir–C distances of 2.42 Å and 2.63 Å. The asymmetry in the coordination is caused by ring strain in the four membered ring formed by Ir–C₁–C₂–C₃.

When compared with 15, we consider that the coordination of the bound phenyl group is worth 10.1 kcal/mol, whereas comparing 9 with 11, we can consider the coordination of the C₂H₄ group in 9 to be worth 29 kcal/mol (with Ir–C distances of 2.21 Å). Because the exothermicity to insert a free ethylene into the C–H bond of benzene [eq 1] is 23.9 kcal/mol, 14 has gained this amount by conversion of a σ bond to a π bond, but also lost 26.6 – 10.1 = 16.5 through the much weaker coordination of the phenyl vs the C₂H₄ group. Thus, if the Ir–C sp² bond in 9 were the same strength as the Ir–C sp³ bond in 14, we would have expected 14 to be 5.0 kcal/mol stable than 9, rather than 3.1 kcal/mol less stable. This difference of 8.1 kcal/mol represents an increased strength of bonding in 9 due to the Ir–C sp³ bond and π interactions with the phenyl group.

3.4.3 Addition of Benzene (14 → 15 → 16). The weak coordination of the phenyl group in 14 enables the next step in the cycle to be energetically accessible. Rotation around the C₂–C₃ bond leads to dissociation of the coordinating phenyl to form intermediate 15. The energy cost is 10.1 kcal/mol uphill (with no additional barrier).

Association of a benzene to 15 to form 16 is exothermic by 11.1 kcal/mol, which can be compared to the 26.6 kcal/mol bond of ethylene to 11. This is consistent with the Ir–C bonds of 2.39 and 2.40 Å for benzene in 16, compared with the 2.21 Å Ir–C distances in 9. The lack of steric strain in 16 makes it 1.0 kcal/mol more stable than 14. The steric strain is most likely worth more than 1.0 kcal/mol, but the coordinated benzene moiety in 14 also features a small substituent effect from the electron donating –CH₂ group, which increases the stabilization. A better measure of the coordination might be found by comparing the relative energy of the analogue of 15 with a coordinating toluene instead of benzene.

3.4.4 Hydride Transfer (16 → TS₃ → 17). The final step in the functionalization is the transfer of a hydride from the coordinating benzene to C₁. In the catalytic cycle suggested by Periana et al.,² two possible mechanisms for the hydride transfer were presented, one stepwise mechanism featuring a seven coordinate IrV intermediate and one concerted σ-bond metathesis type mechanism. We were not able to locate any stable intermediates, as all starting geometries eventually converged to 16 or 17. However, a transition state TS₃ connecting 16 and 17 was easily located. 16 → TS₃ has an

Figure 9. Calculated mechanism for generation of ethyl benzene.

Figure 10. Structures of 9, 14–18, TS₂–TS₄. Distances in Angstroms (Å).
energy barrier of 12.0 kcal/mol and a negative eigenvalue of $-391 \text{ cm}^{-1}$ corresponding to movement of the hydride. However, TS3 does not correspond to a $\sigma$-bond metathesis transition state.

The structure for TS3 in Figure 8 shows that the Ir$-$H distance is only 1.58 Å, which is a normal Ir$-$H sigma bond. However, the H$-$C bond being broken on the benzene has increased from 1.09 Å to 1.99 Å, whereas the benzene C$-$Ir bond has decreased from 2.39 Å to 2.09 Å, essentially a full H$-$C$-$Ir bond. At the same time, the new C$-$H bond is 1.69 Å while the Ir$-$C1 bond being broken has increased from 2.10 Å to 2.21 Å. The C$-$H$-$C angle is 154°. TS3 is consequently best described as IrV with three covalent bonds to phenyl, H, and C1 in addition to the two to acac$^\text{'}$s. The H has essentially no bond to either C1 or to the phenyl. Clearly this is not a $\sigma$-bond metathesis. This process of 16 $\rightarrow$ TS3 $\rightarrow$ 17, we refer to as "oxidative hydrogen migration". This is the first documented example of this type of transition state, which will be further discussed in section 3.6.

The product of TS3 is the intermediate 16, which now features a covalently bound phenyl and an ethyl benzene loosely coordinated through an H$-$Ir Lewis acid-Lewis base (LA$-$LB) interaction. The net energy change from 16 to 17 is 0.1 kcal/mol downhill.

3.4.5 Product Formation (17 $\rightarrow$ 11 + 3). Dissociation of the ethyl benzene from 17 to yield the product 3 is uphill by 2.9 kcal/mol, but barrierless. This involves breaking the CH$-$Ir LA$-$LB bond, which is partially compensated by the energy gained through the Ir$-$Ph back-bonding.

3.4.6 Regeneration of the Catalyst (11 + ethylene $\rightarrow$ 9). Coordination of a C$_2$H$_4$ molecule to the vacant site of 11 is exothermic by 26.6 kcal/mol (and barrierless), leading back to 9 and completing the catalytic cycle. The final energy for 9 + 3 in Figure 7 is 21.7 kcal/mol lower than the 9 in Figure 6, corresponding to the calculated exothermicity of the reaction.

We find that the rate-determining step for the catalytic cycle is going through TS2, the migratory insertion. For catalyst 7 we calculated this activation energy to be 27.0 kcal/mol. We also calculated TS2 for the 4 catalyst, where we obtain 25.2 kcal/mol, corresponding to the ground-state effect discussed in section 3.2.

The experimentally determined activation energy for 4 is 28.7 kcal/mol, in excellent agreement with the calculated value of 25.2 kcal/mol.

3.5 Regioselectivity of Olefin Insertion. On the basis of our calculated mechanism, the origin of the regioselectivity rests in the geometries of the various conformers in TS2. To confirm this, we carried out calculations of TS2 with several substituted olefins and compared the relative energy barriers with the experimentally measured ratios. Pertinent geometry values and relative energies are given in Table 2.

The simplest substituted olefin investigated by Periana and Matsumoto is propene, which gives linear and branched propyl benzene in a 61:39 ratio, which at 180 °C (453 K) corresponds to a $\Delta G$ of 0.4 kcal/mol in favor of the linear product. Our calculations of TS2-propene show that the lowest energy isomer of TS2-propene, labeled TS2(1,2)-propene, has a relative energy of 29.8 kcal/mol and is expected to yield linear propyl benzene. The lowest energy isomer that leads to a branched propyl benzene is TS2(2,2)-propene, with a relative energy of 30.2 kcal/mol. Other isomers of TS2 were optimized, but were found to be over 1 kcal/mol higher in energy and will not be further discussed. Our calculated $\Delta H$ (0 K) value is thus 0.4 kcal/mol, remarkably close to the experimental $\Delta G$ value.

Calculations of TS2(1,2)-isobutene and TS2(2,2)-isobutene gave structures with relative energies of 34.1 and 34.8 kcal/mol, respectively, and a $\Delta H$ (0 K) of 0.7 kcal/mol, which should be compared to the experimental value of 1.4 kcal/mol. Inclusion of $\Delta G$ terms yields a $\Delta G$ (453 K) of 1.2 kcal/mol. Both $\Delta H$ and $\Delta G$ are very close to the experimental value.

Our investigation of TS2-styrene was limited to the isomers TS2(2,2)-styrene and TS2(1,2)-styrene, with the expectation that these are the lower energy structures of each pathway. The relative energy of TS2(1,2)-styrene and TS2(2,2)-styrene are calculated to 31.8 and 34.1 kcal/mol, respectively, which gives a $\Delta H$ (0 K) value of 2.3 kcal/mol. Inclusion of $\Delta G$ terms yields a $\Delta G$ (453 K) of 2.5 kcal/mol. With an experimental $\Delta G$ (453 K) value of 3.5 kcal/mol, both $\Delta H$ and $\Delta G$ are $\sim$ 1 kcal/mol from the experimental value. This error could be due to a well known problem in DFT for the correct treatment of Van der Waals interactions, particularly for pi-stacking systems like TS2(2,2)-styrene. However, it could also be experimental error in the original publication. The ratio of 1,2-diphenylethane:1,1'-diphenylethane is reported as 98:2, which corresponds to a $\Delta G$ (453 K) of 3.5 kcal/mol. The value 2.4 kcal/mol corresponds to a ration of 95:5, possibly within the margin of error. Nevertheless, it is clear that our calculations reproduce both the trend and the magnitude of experimental $\Delta G$ values.

We also considered the underlying causes of the regioselectivity. One factor is the steric bulk of the olefin substituents.
The bond lengths in Table 2 show that the calculated Ir--C3 and C1--C2 distances are essentially identical for all four olefins investigated here, independent of regio-isomer. On the other hand, the Ir--C1 and C2--C3 distances are affected just as would be expected for steric crowding, i.e., increasing when the carbon center is substituted. Furthermore, using TS2-ethene as a base point, we see that substitution at C1 results in deviations $\pm 0.04$ Å, whereas substitution at C2 yields C=Ph changes of $\pm 0.07$ Å. Consequently, we expect substitutions at C1 to be advantageous. Inspection of the optimized geometry of TS2(1,2)-propene suggests that the substituent fits into the empty space above the acac$^+$ unit, whereas the substituent in TS2(2,2)-propene is crowded against the phenyl group.

However, sterics alone do not account for the substantially higher linear/branched ratio of styrene vs. isobutene. Phenyl is less bulky than methyl, and insertion in styrene should thus be less selective. Consequently, there must be an electronic factor, which we believe is an electron-donating/withdrawing character. Iridium is more electron rich than carbon, and it would thus be more advantageous for an olefin with an electron withdrawing substituent to form TS2(1,2) over TS(2,2). This is consistent with the substituents explored above, as the linear/branched ratio increases in the order propene $\prec$ isobutene $\prec$ styrene.

Neither methyl or phenyl are particularly electron withdrawing; however, to explore our hypothesis, we sought more electronically active substituents. The only available substituent in ref 5 is methyl ethyl-phenyl ester, which has an experimental linear/branched ratio of 69:31. However, although the ester group is electron withdrawing, it is also significantly less bulky than methyl or phenyl, which most likely causes the low selectivity. With a $\Delta G$ value of merely 0.7 kcal/mol this substituent is not a suitable target for testing of our hypothesis.

Instead, we optimized the regio-isomers of vinyl trifluoromethyl, VTFM, and vinyl methyl ether (VME). VTFM is a very electron poor olefin and should consequently give a high percentage of linear products, whereas VME is an electron rich olefin which should give high percentage of branched products. Our results, summarized in Table 2, show that TS2(2,2)-VTFM and TS2(1,2)-VTFM have calculated relative energies of 30.9 and 24.8 kcal/mol, respectively, which gives a $\Delta \Delta H(0 \text{ K})$ of 6.1 kcal/mol. TS2(2,2)-VME and TS2(1,2)-VME have calculated relative energies of 26.0 and 30.0, respectively, which gives a $\Delta \Delta H(0 \text{ K})$ of $-4.0$ kcal/mol. This suggests that electron donating character is much more important than steric bulk, to the point of reversing regio-selectivity for a particularly electron donating substituent. These theoretical predictions are currently awaiting experimental verification.

The electronic trend calculated above closely mirrors the trend observed in the Heck reaction. This is not surprising, since both reactions undergo a 1,2-insertion with similar geometries (see Figure 12).

What makes this catalyst unique is that unlike the Heck reaction, it also features C--H activation. As such, the activation mechanism deserves further consideration, even though it is not the rate determining step. In the catalytic cycle suggested by Periana et al., two possible mechanisms for the C--H activation were presented, one stepwise mechanism featuring a seven coordinate Ir$^+$ intermediate and one concerted $\sigma$-bond metathesis type mechanism. On the basis of precedents from the groups of Bergman and Maitlin, we expected the stepwise mechanism to be the lower energy pathway. However, our calculations do not lead to seven coordinate Ir$^+$ intermediates. Depending on starting structure, all starting geometries converged to either 15 or 16.

To ensure that this result is not an artifact of the computational methods employed in this study, we optimized the seven coordinate Ir$^+$ intermediate $[\text{Cp}^+(\text{PH}_3)\text{Ir}(\text{CH}_3)\text{H}]^+$ from ref 6, and found that our geometries corresponded very closely to the Ir$^+$ geometries characterized by the groups of Chu$^{23}$ and Hall.$^{24}$

We suggest that there are two major differences between the Bergman and Periana compounds responsible for this very different behavior.


First: the presence of the η-5 aromatic Cp* ligand in the Bergman compound is less bulky than the three separate ligands in the Periana compound. All published examples of seven coordinate L₄ Ir V (R)(H)(R) species have either Cp* or cyclooctadiene present as L₁ or L₂, respectively.

Second: the electron densities on the iridium atoms are quite different. The ligands in the Bergman compound [Cp*(PH₃)]Ir(CH₃)₂⁺ are electron donating, resulting in a calculated Mulliken charge of −0.29 electrons on the iridium. In contrast, the Mulliken charge on the iridium in 11 (the structure corresponding most closely to [Cp*(PH₃)]Ir(CH₃)⁺) is 0.76 electrons, a difference of over one electron. Clearly, oxidizing IrIII to IrV is less favorable for a structure with a much higher positive charge on the metal center.

It is interesting that Chu and Hall concluded that there is no concerted transition structure on the [Cp*(PH₃)]Ir(CH₃)⁺ + CH₄ hyper surface, which is in stark contrast to our finding of the asymmetric transition structure TS3. We suspect that TS3 has much more in common with the intermediate [Cp*(PH₃)]Ir(CH₃)₂⁺ than any of the transition states in the Chu and Hall studies. With an electron rich IrIII center, the mechanism for C–H activation is stepwise and low in energy, while reducing electron density gradually increases the relative energy of the intermediate until the mechanism obtains concerted character, as illustrated in Figure 13.

3.7 β-Hydride Elimination as an Alternative Mechanism. β-Hydride elimination is normally quite facile for late transition metals, and there is no reason to believe Ir to be an exception. Indeed, it is the major reactive pathway for (PCP)Ir catalyzed dehydrogenation of ethane as reported by Goldman and co-workers. β-hydride elimination leading to styrene is also thermodynamically feasible (eq 2) in the ethylene/benzene system if a second ethylene is used as a sacrificial hydrogen acceptor. Nevertheless, as seen in the publications of Matsumoto and Periana, no styrene byproducts were observed from arylation of olefins with catalysts 4–8. However, Matsumoto et al. reported that adding O₂/Cu(OAc)₂ (a potential hydride scavenging oxidizing agent) to catalyst 1 in a mixture of benzene and ethene generated exclusively styrene and vinyl acetate, but with significantly lowered yield.

\[
\text{C}_2\text{H}_4 + \text{C}_8\text{H}_6 \rightarrow \text{styrene} + \text{C}_2\text{H}_6 \Delta H^\circ = -29.7 \text{ kcal/mol} \tag{2}
\]

It is thus relevant for us to consider β-hydride processes to understand these experiments and to ensure that we have considered all plausible reactions. We investigated the production of styrene from benzene and ethene with the results summarized in Figure 14, where we have indicated with dotted lines the catalytic cycle for reference purposes. The structures of TS4 and 18 are shown in Figure 10.

As 15 is the only coordinately unsaturated intermediate in the catalytic cycle, we assumed that β-hydride elimination would occur from this part of the hypersurface. However, the energy of the optimized transition structure for this elimination, TS4, is 7.6 kcal/mol lower than 15, indicating that 15 need not play a role in β-hydride elimination.

The only prerequisite for TS4 is an Ir–C–C–H dihedral of ~0°, and this can be achieved through a rotation around the Ir–C–C–Ph dihedral in 14 by ~81°. The actual Ir–C–C–H dihedral in TS4 is 5.6°, reflecting a small steric interaction between the phenyl group and one of the acac-rings. TS4 is an early transition structure, with almost unchanged Ir–C and C–C distances of 2.07 Å and 1.48 Å, respectively. The breaking C–H bond is increased to 1.36 Å and the forming Ir–H bond is decreased to 1.70 Å.

Completing the process yields structure 18 with an energy of 9.5 kcal/mol below 14. In 18 the styrene is strongly coordinated with short Ir–C distances of 2.16 and 2.25 Å, much like the ethene in 9 with 2.21 Å. Thus, dissociating styrene from 18 to form 19 + 20 is 28.5 kcal/mol uphill, about the same as the bond of 26.6 of ethene to 11.

Because the maximum barrier from 14 through TS3 to ethyl benzene product in Figure 7 is 11.0 compared to 19.0 kcal/mol for the barrier to form styrene, we consider that styrene should not have formed under the conditions we consider here. It should be pointed out that this is contrary to the conclusions drawn from the ΔG surface, where styrene formation through 19 + 20 is favored by 3.3 kcal/mol compared to TS3. However, as discussed in sections 2 and 3.9, the accuracy of the ΔG surface deteriorates rapidly when the number of species changes in the solution, and we believe that the ΔH surface is considerably more reliable.

However, we also calculated potential products of 19. Isomerization of the cis hydride 19 to the trans hydride 23 goes through TS5 with a barrier of 2.6 kcal/mol. This cis to trans reaction is exothermic by 20.7 kcal/mol, which can be compared to 19.6 kcal/mol for the phenyl case (11 versus 10). Finally, coordination of an ethene to 23 gives structure 24, which is downhill by 3.9 kcal/mol.

Instead of isomerizing to the trans-acac geometry, 19 could coordinate directly with an ethene, leading to structure 21 which is exothermic by 32.9 kcal/mol. 21 could form an Ir–C₂H₃ structure, 22, via ethene insertion in the Ir–H bond. This is endothermic by 3.9 kcal/mol and may have an additional barrier. 22 could in turn react with a benzene via a transition structure similar to TS3. The product of this reaction chain could potentially regenerate the catalyst into 9, with the use of a sacrificial ethene to yield ethane.

This reaction pathway is calculated to be exothermic by 27.0 kcal/mol, which is 5.3 kcal/mol more exothermic than the production of ethyl benzene. That this thermodynamically favored product is not observed is consistent with our result that the barrier from 18 to 21 is much higher than that from 14 through TS3.

However, a hydride scavenging agent such as Cu(OAc)₂ would likely react with a hydride intermediate such as 18 to generate a five coordinate IrIII cation, which could react further to regenerate the catalyst. This would bypass the high-energy
pathway through 19, resulting in exclusive formation of styrene and byproducts. More detailed theoretical and experimental investigations of the Cu(OAc)$_2$ and related systems are warranted and planned for future studies. We are also currently trying to confirming the rapid equilibrium between 15 and 18 by labeling studies.

3.8 Inhibition by Ethene. Although the TOF is reported to rise with increased ethene/benzene molar ratio at low ratios, it drops again above a ratio of $\sim 0.20$. As our calculations of intermediates 9 and 12 shows, a ground state effect is not the cause of the inhibition, which leaves inhibition of a key mechanistic step as the cause of the inhibition. The only likely candidate for this step is the five coordinate intermediate 15.

Our calculations show that coordination of an ethene to 15 gives structure 25, (see Figure 15) which is exothermic by 29.2 kcal/mol (similar to the 26.6 kcal/mol for 11 to 9). This is significantly more favorable than the next intermediate on the catalytic cycle, 16. However, since the coordination of either ethene or benzene to 15 is barrierless, we estimate that the relative rate of formation of 16 vs 25 should be proportional to the ratio of ethene to benzene concentrations in a purely statistical fashion.

From 25, we considered three mechanisms. The first is simply reversal of the previous step, i.e., dissociation of the ethene molecule to regenerate structure 15, which would then be followed by association of either ethene or benzene.

Figure 14. Mechanism for $\beta$-hydride elimination of 14 to form styrene. *Energies include loss of styrene †Energies include loss of styrene and addition of ethene.

Figure 15. Inhibition by ethylene. Mechanistic pathway from section 3.4 included in dotted line. Insertion pathway from 25 in dashed line, hydrogen migration pathway from 25 in solid.
the dissociation is barrierless, we can consider the difference in energy between 25 and 15 as the activation energy of this process, which would then be 29.2 kcal/mol.

The second possibility is a reaction analogous to 9 → TS2 → 14, where the −CH3− group is inserted into the π bond via the transition structure TS6. 30.7 kcal/mol higher in energy than 25. The slightly higher activation energy (24.5 kcal/mol for 9 → TS2, compared to 30.7 for 25 → TS6) reflects the somewhat lower migratory aptitude of a −CH3− vs a -phenyl moiety. This can also be seen in the geometry of TS6 (see Figure 16), where the relevant bond distances are Ir−C′ = 2.06 Å, C1′−C2′ = 1.46 Å, C2′−C3′ = 1.99 Å and C3′−Ir = 2.39 Å, which should be compared to the bond distances in TS2: 2.07, 1.47, 1.90, and 2.20 Å, respectively. It is clear that C3′ in TS6 is significantly further away from both Ir and C2′ than C3 in TS2 is from Ir and C2. TS6 leads to the longer chain phenyl alkane complex 26, which could potentially undergo further reaction either with benzene or ethene.

The third possible reaction is a hydrogen migration analogous to 16 → TS3 → 17, where one of the hydrogens from the ethene migrates to the −CH3− moiety via TS7. 28.7 kcal/mol higher in energy than 25. This transition structure is very similar to TS3, with a Ir−H distance of 1.56 Å and C−H distances of 1.93 Å and 1.67 Å (see Figure 16). The significantly higher activation energy of 25 → TS7 (28.7 kcal/mol) than 16 → TS3 (12.0 kcal/mol) is caused by ground-state stabilization.

Comparing the activation energies of the dissociation (29.2 kcal/mol), insertion (30.7 kcal/mol) and hydrogen migration (28.7 kcal/mol), we conclude that hydrogen migration is the most favorable. However, we must note that the difference in calculated activation energies is at most 2.0 kcal/mol, which is within the margin of error for these types of calculations. Nevertheless, it is encouraging to see that our calculations show a higher energy for TS6 than either TS7 or 15, as this is consistent with the lack of polymerization products. Furthermore, the preference of hydrogen migration over dissociation is of little practical significance, as both mechanisms eventually yield structures 3 and 9. The complete mechanism of the subsequent steps has also been calculated and will be discussed in a future publication.

It is clear that regardless of mechanism, the association of ethene causes inhibition. The lowest calculated activation energy for reaction of 25, 28.7 kcal/mol, is higher than the activation energy of the rate-determining step in the catalytic cycle, TS2, at 27.0 kcal/mol. As such, the association of ethene introduces a new rate determining step in the reaction which is consistent with the experimental observation. We are currently trying to isolate or independently synthesize intermediate 25 for further experimental verification.

Because the energy of TS3 is similar to 15, we expect about half the 16 formed will proceed through TS3 to form ethyl benzene product, whereas the other half might revert back to 15, making it vulnerable again to ethene inhibition. If the energy of TS3 were significantly higher than 15, this reasoning would suggest that the catalyst might become inactive, even though TS3 is lower in energy than TS2. Consequently, for the reaction to proceed at a reasonable rate in the presence of significant amounts of ethylene, the catalyst should have a TS3 with equal or lower relative energy than 15. This naturally poses additional difficulties in designing catalyst with improved activity than the ones previously characterized.

3.9 Discussion of Accuracy. 3.9.1 ΔG Calculations. The ΔH and ΔG values are fairly similar for reactions having the same number of reacting molecular fragments, as the translational and rotational components are similar. Thus, the process 7 + C2H4 → 9 + H2O has a calculated ΔH(0 K) of 2.5 kcal/mol, and a calculated ΔG(298 K) of 4.5 kcal/mol. This total ΔG correction of 2.0 kcal/mol most likely reflects a lower rotational barrier for the H2O group. In addition, the relative energy change from 7 to TS2 is ΔH = 27.0 and ΔG = 29.3 kcal/mol, which is consistent with the experimentally determined activation energy of 28.7 kcal/mol.

However, for a process such as association of benzene to 15 to form 16 there are much larger corrections. For 15 + C6H6 → 16 is ΔH(0 K) = −11.1 kcal/mol, whereas ΔG(298 K) = +0.5 kcal/mol. Similarly 16 → TS3 has activation energies of ΔH = 15.6 and ΔG = 30.7 kcal/mol, because TS3 is very constrained. As a result the ΔG for TS3 is 1.4 kcal/mol higher in energy than TS2, whereas ΔH is 10.4 kcal/mol lower.

However, we should point out that the entropies have been calculated for the gas-phase system. We have not tried to include the vibration energies of the molecules in solvation, nor the diffusional motions, both of which will decrease the free entropy for the free reagents, making the results closer to the ΔH numbers.

3.9.2 Concentration Effects. We have made no attempt to correcting our free energies for concentration effects. For example, the 15 + C6H6 → 16 has a calculated ΔG = 0.5 kcal/mol. Correcting for the concentrations according to eq 3, reduces the free energy by RT ln([C6H6]−1), which in neat benzene is equal to 1.4 kcal/mol.

\[ ΔG = ΔG^0 − RT \ln ([16] \cdot [15]^{-1} \cdot [C_6H_6]^{-1}) \]  (3)

3.9.3 Solution Corrections. For a molecule in a solvent, there will be entropy corrections from the vibrational states. This is not included in the continuum solvent approximation. These corrections could be included using molecular dynamics with explicit solvents, which unfortunately is beyond the scope of this study.

3.10 Rational Improvement of Catalyst Activity. The ultimate goal of this mechanistic study is to improve the catalyst. On the basis of our understanding of the mechanism of 1,2-insertions, we expect that a catalyst with less electron density on the metal would have a lower activation energy. To confirm this assumption, we optimized two analogues to 7 and TS2-ethene, where the acac\textsuperscript{−} groups were modified with electron donating and electron withdrawing groups. The results of these studies are summarized in Figure 17.
3.10.1 Electron Donating Substituents. In compound 4N, the carbonyls of the two acac’s are replaced with imines, which are more electron donating. We find that this increases the $\Delta H(0 K)$ for $7$ to $TS2$ from 27.0 to 34.8 kcal/mol. Thus, electron donating substituents should substantially decrease the rate.

3.10.1 Electron Withdrawing Substituents. In the second system, labeled 4CF$_3$, the four hydrogen groups of the acac† were replaced with electron withdrawing –CF$_3$ groups. We find that this reduces the $\Delta H(0 K)$ for $TS2$ from 27.0 to 23.0 kcal/mol, which should substantially improve the rates. Control calculations on $TS3$ showed only marginal change, with $\Delta H(0 K)$ going from 16.6 to 15.9 kcal/mol.

4. Summary and Conclusions

We find that (L)Ir(acac’)$_2$ catalyzed arylation of olefins reacts through a mechanism with two key steps, 1,2-insertion and oxidative hydrogen migration.

The insertion is rate determining, with a calculated $\Delta H(0 K)$ of 25.2 kcal/mol for the dimeric catalyst 4. The activation energy increases with increased electron density on the coordinating olefin, as well as increased electron donating character on the ligand system. The regioselectivity is shown to depend on the electronic and steric character of the olefin, where steric bulk and electron withdrawing character favors linear product formation.

Activation of the C–H bond occurs through a novel concerted oxidative hydrogen transfer mechanism in which a hydrogen migrates from a coordinating benzene to the covalently bound phenyl alkyl through a transition structure in which the H is bonded to the metal and not either carbon. The metal transforms from Ir$^{III}$ to Ir$^{V}$ in establishing this unusual transition state.

Activation of the precatalyst occurs through a dissociative pathway, where the ligand L first dissociates, followed by a rearrangement of the trans-acac’groups into a cis conformation, which is stabilized by association of an ethylene. The calculated $\Delta H(0 K)$ is 35.1 kcal/mol and $\Delta G(298 K)$ is 26.1 kcal/mol. The nature of L influences the speed of the reaction through a ground-state effect—a high energy Ir–L coordination lowers the relative energy of the starting catalyst, but does not affect the relative energy of the rate determining step.

We investigated the possibility of a $\beta$-Hydride elimination mechanism. We find that it is facile but reversible, with all further reactions kinetically unfavorable.

We also considered inhibition by excess olefin which we find is caused by competition between olefin and aryl for an intermediate in the catalytic cycle.

Although we calculated the $\Delta G$ values for the various processes, we are not confident that the entropy in solvation is adequately treated. In addition, we have not corrected for concentration effects.

On the basis of the mechanism, we suggest that including electron withdrawing substituents on the acac ligands, such as trifluoromethyl groups, would increase the activity.

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Supporting Information Available: Tables of geometries, imaginary frequencies, and absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.