Mechanistic Investigation of Iridium-Catalyzed Hydrovinylation of Olefins

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C2H3-Ir(III)(acac-O,OH)(Py) dimerizes olefins through a C–H activation mechanism. The starting catalyst first isomerizes to the cis conformer through a dissociative process, where pyridine is lost, and then adds the olefin substrate to the cis conformer. [1,2]-Insertion of the vinyl moiety into the coordinating olefin generates a Ir–CH2–CH2–CH=CH2 complex, which then isomerizes to an Ir(η3-allyl) complex through a series of β-hydride transfer reactions. The η4-allyl complex is significantly more stable than any other part of the surface and is expected to be the resting state of the catalyst. Addition of a second olefin to the η4-allyl complex leads to an Ir–(CH2–CH=CH–CH3) complex with a coordinating olefin, which can transfer a hydrogen to the product, 2-buten-1-ene, via a C–H activation transition state. This transition step is the rate-determining step, with a calculated ΔH‡ = 31.6 kcal/mol and ΔG‡ = 32.1 kcal/mol. Other pathways were found to have reasonable barriers, but are not competitive due to very facile barriers leading to the η4-allyl complex. From the allyl complex, neither 1-buten-1-ene or butadiene are feasible products. The presence of 1-buten-1-ene in the product mixture is attributed to isomerization of 2-buten-1-ene; that is, it is not a kinetic product.

1. Introduction

Carbon–carbon bond-forming reactions are among the most important types of bond constructions in organic chemistry. One potentially important class of such reactions is the hydrovinylation of olefins, which forms the basis of the Dimerol technology and the Shell higher olefin process (SHOP). These processes have been a topic of reviews and have been extended to other heterodimerization and asymmetric catalyses. Common metal choices for hydrovinylation catalysts include Rh, Ru, Pd, and Ni. The generally accepted mechanism for hydrovinylation involves a Cossee–Arlman-type migratory insertion of olefin into a metal hydride intermediate, which subsequently inserts into a second olefin to generate a metal-butenyl intermediate (see Figure 1). β-Hydride elimination yields the product, while addition of a new olefin closes the cycle. Other mechanisms involving metallacyclopentane intermediates have also been postulated. Only a related iridium complex, TP*Ir(C,H2)3H, has been shown to form a hydroxy-allyl derivative via the insertion of ethylene into the Ir–vinyl stoichiometrically, produced by the CH activation of ethylene. 

Recently, we reported that the O-ligated complex C2H3-Ir(III)(acac-O,OH)(Py) (acac-O,OH = κ2-O,O-acetylacetonate, Py = pyridine), Vinyl-Ir-Py [where –Ir– is understood to be Ir(III)(acac-O,OH)2 throughout this paper], inserts olefins and catalyzes the dimerization of olefins via a C–H activation pathway. Heating Vinyl-Ir-Py in hexafluorobenzene with ethylene at 180 °C results in the formation of 1-buten-1-ene and cis- and trans-2-buten-1-ene in a 1:2:1 ratio (TN = 32, TOF ~ 10 × 10−3 s−1). Similarly, carrying out the reaction with propylene results in the formation of various hexene isomers as observed by GC/MS analysis. Similar results are obtained when CH2-Ir-Py is used as a catalyst. This is the first system to carry out this reaction in a catalytic fashion.

We have previously reported preliminary theoretical calculations on this mechanism, where we concluded that the mech-
anism is similar to the mechanism for hydroarylation.\textsuperscript{11} The key step is a [1,2]-insertion into a complexed olefin, and product formation is realized through C–H activation. However, as the hydroarylation reaction is inhibited by the presence of excess olefin (benzene/ethene ratios > 0.2) while the hydrovinylation intrinsically has an “excess” of olefin, one cannot directly compare the mechanisms. Furthermore, the presence of multiple products indicates a significantly added complexity to the mechanism, the origin of which is not a priori clear.

In this publication we aim to present the complete computational results of the possible mechanisms for the hydrovinylation.

2. Computational Methodology

All calculations were performed using the hybrid DFT functional B3LYP as implemented by the Jaguar 5.5 and 6.0 program packages.\textsuperscript{12} This DFT functional utilizes the Becke-three-parameter functional\textsuperscript{13} (B3) combined with the correlation functional of Lee, Yang, and Parr\textsuperscript{14} (LYP) and is known to produce good descriptions of reaction profiles for transition metal containing compounds.\textsuperscript{15,16} The metals were described by the Wadt and Hay\textsuperscript{17} core-valence (relativistic) effective core potential (treating the valence electrons explicitly) using the LACVP basis set with the valence double-(relativistic) effective core potential (treating the valence electrons explicitly) using the LACVP basis set with the valence double-

Implicit solvent effects of the experimental benzene medium were calculated with the Poisson–Boltzmann (PBF) continuum approximation,\textsuperscript{19} using the parameters \(\epsilon = 2.284\) and \(r_{\text{sol}} = 2.602\) Å. Due to the increased cost of optimizing systems in the solvated phase (increase in computation time by a factor of \(\sim 4\)), solvation effects are calculated here as single-point solvation corrections to gas-phase geometries. Our previous work on the Ir(acac)\(_2\) system has shown that the total energies, geometries, frequencies, and zero-point energies were also largely unchanged when the systems were optimized in the solvation phase.\textsuperscript{11} Indeed, as these systems are essentially nonpolar systems in a nonpolar solvent, the gas-phase enthalpies were within 5 kcal/mol of the solvent enthalpies.

All energies here are reported as \(\Delta H(0 \, \text{K}) = \Delta E + \text{zero-point energy correction} + \text{solvation correction}\). 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.\textsuperscript{20} Moreover, relative energies of isoelectronic species (such as regioisomers) are considerably more accurate, since the errors largely cancel.

Free energies were calculated as \(\Delta G(473 \, \text{K}) = \Delta H(473 \, \text{K}) - T\Delta S(473 \, \text{K})\), where \(\Delta H = \Delta E(\text{gas phase}) + \Delta E(\text{solvation correction}) + ZPE + \Delta H(\text{vib}) + 3kT\Delta \gamma(n)\). The last term, \(3kT\), is a fixed value for the sum of the rotational and translational contributions to the enthalpy at 473 K, calculated to be 2.823944 kcal/mol. \(\Delta S\) terms were calculated by summing the \(\Delta S(\text{vib}) + \Delta S(\text{trans/rot}) + \Delta S(\text{conc})\). \(\Delta S(\text{vib})\) is taken from the Jaguar gas-phase calculation at 473 K, while \(\Delta S(\text{trans/rot})\) is given a fixed value of 30 cal/(mol K).

The use of \(3kT\) and 30 cal/(mol K) for the \(\Delta H(\text{trans/rot})\) and \(\Delta S(\text{trans/rot})\) terms, respectively, was made to avoid the values obtained in the gas-phase calculations of thermodynamic properties. For a solvated reaction these gas-phase values are substantially inflated,\textsuperscript{21} and accurate values most likely require a full dynamic simulation. As this is outside the scope of this paper, however, we elected to use a fixed value reflecting the experimental value for a pure liquid.

All geometries were optimized and evaluated for the correct number of imaginary frequencies through vibrational frequency calculations using the analytic Hessian. Zero imaginary frequencies corresponds to a local minimum, while one imaginary frequency corresponds to a transition structure. 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 hydrogen. Control calculations show that relative energies of intermediates and transition structures change less than 0.1 kcal/mol when methyl groups are included.

3. Results

3.1. Cis/Trans Isomerization. The first step of the mechanism is the isomerization of the trans Vinyl-Ir-Py into the cis
form. This isomerization was investigated in depth for the analogous Phenyl-Ir-L (L = H₂O, Py) catalyst and was found to isomerize through a dissociative unimolecular process.

Replacing the phenyl group with a vinyl group changes this mechanism very little. Calculations on the dissociative mechanism (Figure 2) show that 1 can easily dissociate pyridine to generate 2, with a ΔH = 15.9 kcal/mol. The five-coordinate 2 can then undergo a cis/trans isomerization (TS1) with a ΔH² = 41.0 kcal/mol (25.1 kcal/mol with respect to 2). The isomerization occurs through movement of one of the four acac ligand oxygens to a position trans to the vinyl group. TS1 is a fairly late transition state, as observed in the O–Ir−O angle of 114.1°. This is a reflection of the Hammond postulate, as the result of the isomerization (the five-coordinate species 3) is a high-energy species, 22.2 kcal/mol higher in energy than 2. The high energy of 3 is caused by the distortion of aromatic stabilization in the acac rings due to trans influence from the vinyl carbon. This has been studied in more detail in a previous publication by this group.¹¹a

3 can coordinate to either pyridine (4, ΔH = −39.9 kcal/mol) or ethene (5, ΔH = 29.3 kcal/mol). As 4 is significantly more stable than 5, this is expected to be the resting state of the catalyst. This has been confirmed experimentally for the phenyl analogue, where it was found that in the absence of an olefin 4 is formed quantitatively.⁵² Under normal experimental conditions,³² however, the concentration of ethene is significantly larger than the concentration of free pyridine, and it is thus very likely that the majority of 3 will go directly to 5.

3.2. Olefin Insertion. Insertion of the vinyl group in 5 into the olefin (TS2, Figure 3) generates a metal-butene species (6), where the double bond is in the terminal position. TS2 is a classic [1,2]-insertion transition state where an Ir−C and a C=C bond are broken while an Ir−C and a C−C bond are created simultaneously (see Figure 4). The activation energy of the insertion, 30.6 kcal/mol (22.8 kcal/mol with respect to 5), is somewhat lower than the insertion activation energy for the phenyl analogue (34.0 and 24.5 kcal/mol, respectively).¹¹b This is most likely due to the disruption of aromaticity in the phenyl transition state, which is not necessary in TS2. Consequently, the bond lengths of the breaking Ir−C and the forming C−C bonds are both shorter in TS2 than in the phenyl analogue, by 0.06 and 0.04 Å, respectively.

The product of the insertion is the chelating complex 6. The reaction is exothermic by 12.0 kcal/mol on the ΔH surface. The conversion of a double bond to two single bonds is exothermic by 29.4 kcal/mol, demonstrating the increased coordination energy due to the lack of strain. 8 is the lowest energy species on the ΔH surface, although the positive entropy term associated with the inclusion of a second olefin suggests that the conversion 6 ⇌ 8 is slightly endothermic on the ΔG surface.

**(Figure 2. Calculated pathway for isomerization of catalyst precursor. Enthalpies and free energies in kcal/mol.)**

**(Figure 3. Calculated pathway for olefin insertion. Enthalpies and free energies in kcal/mol.)**

**(Figure 4. Geometry of TS2. Distances in Å.)**

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The olefin in 8 can transfer a hydrogen to the metal-butyl species through a mechanism previously characterized as oxidative hydrogen migration (OHM) \((TS3)\). This is a concerted mechanism with a transition state similar to an oxidative addition intermediate, featuring a fully formed bond between the iridium and the migrating hydrogen (1.56 Å, see Figure 6). The distances between the hydrogen and the two carbons are 1.93 and 1.70 Å, indicative of partially formed bonds. The \(\Delta H^\circ\) of \(TS3\) is calculated to be 28.9 kcal/mol, similar in magnitude to \(\Delta H^\circ\)(\(TS2\)) at 30.6 kcal/mol. As was the case on previous occasions when an OHM style transition state was encountered, no formally Ir\(^{IV}\) intermediate could be isolated, with all attempts collapsing to either 8 or 9.

\(TS3\) yields 9, an iridium vinyl complex with the product 1-butene weakly coordinating to the metal in an agostic fashion. Generation of 9 is endothermic by 17.6 kcal/mol, reflecting the loss of coordination energy in exchanging the olefin complexation for the much less favorable agostic interaction.

With the 1-butene only weakly coordinating, loss of ligand is uphill an additional 2.9 kcal/mol, leading to the coordinatively unsaturated complex 3. Complexation of an a new ethene regenerates the catalyst and thus completes the catalytic cycle. Coordination of the ethene is exothermic by 29.3 kcal/mol, and the transformation 8 + ethene \(\rightarrow\) 5 + 1-butene is exothermic by 8.6 kcal/mol, thus providing a driving force for the latter half of the catalytic cycle.

### 3.4. Generation of 2-Butene through C–H Activation

The mechanism above cannot be the complete mechanism, however, as indicated by the experimental observance of cis- and trans-2-butene. The product distribution is caused by isomerization of the metal-butene through a methyl \(\eta^1\)-allyl moiety (13), starting from intermediate 6 (Figure 7). Instead of coordinating an olefin to the iridium-buty1 species, 6 undergoes a \(\beta\)-hydride transfer (BHT) \((TS4)\) to yield the metal-hydride butadiene species 10. The barrier for the transfer is 17.4 kcal/mol, and the thermodynamics are moderately uphill, 4.2 kcal/mol. It is likely that an agostic intermediate exists prior to \(TS4\) where the coordinating olefin has rotated outward by \(~60^\circ\), but no such intermediate could be located, via either regular optimization or IRC calculations from \(TS4\). As can be seen for structure 12, the energy of this intermediate would be very close...
to the energy of TS4 and is not expected to add to the overall barrier. TS4 is a traditional BHT transition state, with the four reacting atoms in a plane ($\varphi(\text{Ir}--\text{C}--\text{C}--\text{H}) = 1.2^\circ$). The Ir--H distance is, at 1.67 Å, fairly short (the full Ir--H bond in 10 has a distance of 1.57 Å), while the C--H distance is a fairly long, 1.41 Å.

The butadiene moiety in 10 can easily rotate around the coordinating olefin, to generate the rotamer 11. The energies of the two rotamers are identical (within the accuracy of the computational method), and the barrier for rotation (TS5) is calculated to be 6.2 kcal/mol. Technically the rotation process is a stepwise mechanism with two transition states corresponding to rotations of the olefin of ±45° (TS), ±90° (intermediate), and ±135° (TS), but only the highest energy state is shown here.

From 11 a migratory insertion (TS6) occurs, with a barrier of 13.1 kcal/mol with respect to 11 and 17.3 kcal/mol with respect to 6. Functionally, this insertion is a reverse BHT, and the transition state TS6 is very similar to TS4, with identical Ir--H and C--H bond lengths. The product of TS6 is 12, a methyl α-allyl complex where one of the hydrogens on the methyl group coordinates to the iridium in an agostic fashion. The calculated $\Delta H$ of 12 is 11.9 kcal/mol.

12 collapses easily into the methyl $\eta^2$-allyl complex 13 (see Figure 9). A transition state connecting 12 and 13 could not be located, as any deviation from the geometry of 12 immediately led to 13. A similar result has previously been reported for Ir(η$^2$-allyl)], by John et al.,[23] where only the transition state but not the intermediate could be located. Furthermore, since 12 could be found only through an IRC calculation from TS6, it appears that the hypersurface is very flat in this region, obstructing a computational separation of intermediate and transition state. However, this also means that the energy of TS7 should be very close to the energy of 12, and while this might be the highest barrier between 6 and 13, it is still significantly lower in energy than TS2.

13 is, like most metal $\eta^2$-allyls, a relatively stable complex. With a $\Delta H$ of $-12.7$ kcal/mol, the transformation of 12 $\rightarrow$ 13 is exothermic by 26.4 kcal/mol. This is somewhat more favorable than the $-21$ kcal/mol found by John et al. for the triallyl complex,[23] possibly due to the less electron donating character of the acac oxygens. The low energy of 13 establishes this as the new ground state of the system, which has some fairly drastic implications for the mechanism of this process. While the activation energy of TS2 with respect to 1 is 30.6 kcal/mol, with respect to 13 it is 42.9 kcal/mol, effectively making this pathway energetically inaccessible. This is further discussed in section 4.

Dissociation of the allyl ligand yields the five-coordinate α-butenyl species 14, with an energy of 12.8 kcal/mol. Again, no transition state connecting 13 to 14 could be found, as 14 easily collapsed back to 13. Furthermore, as 14 has no agostic interactions, it is 0.6 kcal/mol higher in energy than 12, even though the internal $\pi$-bond should confer some stability relative to the terminal $\pi$-bond in 12.

The open site enables coordination of a second ethene, leading to complex 15. Attempts at finding a concerted process for the transformation of 13 $\rightarrow$ 15 were unsuccessful, leading us to believe that even if such a process exists the energy should be similar to or higher than the dissociative process (i.e., through 14). However, it is possible that the ethene intercepts the vacant site as it is being formed, thus driving the process forward. Like 8, 15 is somewhat more stable than 13 on the $\Delta H$ surface but somewhat less stable on the $\Delta G$ surface due to a positive $\Delta S$ term.

From 15 C--H activation (TS8) forms the trans-2-butene product 16, using a transition state very similar to TS3. The activation energy is 31.6 kcal/mol from 15, suggesting that TS8 is the rate-determining step in the catalytic cycle. This also suggests that 13 and/or 15 could be trapped, as they are the resting state for the catalyst.

From the agostic complex 16 trans-2-butene is exchanged for ethene in a fashion identical with the mechanism for generation of 1-butene, and is not shown.

It should also be mentioned that all structures above show the trans-butene or anti-allyl conformation. Control calculations of the cis-butene and syn-allyl species show that these transition states and intermediates react through the same mechanism, although consistently $\sim 2$ kcal/mol higher in energy than the trans/anti pathway.

3.5. Cossee--Arlman Mechanism. The Cossee--Arlman mechanism is expected to initiate in the same fashion as the C--H activation pathway, i.e., cis/trans isomerization, coordination of olefin, and [1,2]-insertion to yield 6. As the starting catalyst contains a vinyl moiety, the catalyst must produce 1 equiv of butadiene (18) before a metal-ethyl species is formed. This would initially follow the same mechanism as isomerization of the metal-butenyl species described in section 3.4 (i.e., 6 $\rightarrow$ 10). From 10 the butadiene dissociates, leaving a five-coordinate Ir--H species (17) with a calculated $\Delta H$ of 30.2 kcal/mol. The Cossee--Arlman mechanism is summarized in Figure 10.

Coordination of a second ethene to replace the butadiene is exothermic by 33.5 kcal/mol, leading to complex 18. The calculated $\Delta H$ is of the same magnitude as the olefin coordination in the cis/trans isomerization (3 $\rightarrow$ 5, $\Delta H = -29.3$ kcal/mol), due to the similar electronic nature of iridium--hydride and iridium--vinyl bonds.
A migratory insertion from 18 occurs through TS9, with a $\Delta H^\circ = 10.9$ kcal/mol. TS9 is similar to other BHT-type transition states described above (see Figure 11) and leads to the agostic Ir-ethyl species 19. Our calculations show that 19 is 0.7 kcal/mol higher in energy than TS9, most likely due to inaccuracies in the ZPE corrections. On the $E$ surface 19 is 0.5 kcal/mol lower in energy than TS9 (in both the gas phase and solvent phase).

Rotation around the Ir-C bond in 19 leads to the five-coordinate species 20, with a $\Delta H^\circ = 5.8$ kcal/mol. The open coordination site enables association of a new ethene, with a $\Delta H^\circ = 31.7$ kcal/mol (21). Similarly to TS2, [1,2]-insertion (TS10) into the ethene ligand couples the two carbons. The $\Delta H^\circ$ of TS10 is calculated to be 33.5 kcal/mol, which is 10.7 kcal/mol higher in energy than the $\Delta H^\circ$ of TS2. This difference is most likely caused by the absence of accessible $\pi$-orbitals on the ethyl moiety, forcing the insertion into the localized $sp^3$-orbital on the migrating carbon. This is also reflected in the geometry of TS10 (see Figure 11), which has considerably longer bond lengths to the migrating carbon as compared with TS2.

As there is no unsaturated bond in the insertion product (22), the lack of a possible olefin coordination makes the insertion endothermic by 8.2 kcal/mol. 22 features an agostic interaction between the iridium and one of the $\gamma$-hydrogens, formed as the C-C bond is closed. Exchanging this interaction for an agostic interaction with a $\beta$-hydrogen (23) is exothermic by 5 kcal/mol, possibly due to hyperconjugation. BHT of this hydrogen occurs through the transition state TS11, which has a negligible barrier of 0.5 kcal/mol, and leads to the iridium hydride species 24. Investigations of possible $\gamma$-hydride eliminations from 22 did not lead to any feasible mechanisms, as scanning the breaking C-H bond showed barriers $> 30$ kcal/mol.

Dissociation of the terminal 1-butene ligand in 24 leads to the five-coordinate iridium hydride 17, thus completing the catalytic cycle. As the 1-butene binds slightly stronger to the metal than butadiene, the dissociation is exothermic by 31.8 kcal/mol.

The mechanism for generation of 2-butene is expected to follow an isomerization pattern similar to that described for the C-H activation pathway and was not further investigated.

### 3.7. Reductive Coupling

Reductive coupling, as shown by Morokuma and co-workers, was also investigated, but no stable IrV intermediate could be isolated. This is not surprising, as the presence of the OHM transition states TS3 and TS8 in lieu of regular oxidative addition intermediates indicates that other oxidative addition intermediates of similar nature would be inaccessible.

### 3.8. Free Energies

While the above sections feature discussions of the calculated $\Delta H$ values, we also calculated the free energy for each species. However, these energies are normally significantly less accurate than the $\Delta H$ energies, and as there are no experimentally determined $\Delta G$ values for these reactions, we cannot ascertain how accurate these results are.

Nevertheless, the calculated $\Delta G$ (473 K) values are included in the above diagrams, and it is clear that while the overall surface becomes higher in energy, barriers are generally of the same magnitude as the $\Delta H$ barriers. The notable exception to this, however, is the key transition of the Cossee-Arlman mechanism, which on the $\Delta H$ surface has a barrier of 34.4 kcal/mol, but on the $\Delta G$ surface is only 29.4 kcal/mol. This change

is not enough to make the Cossee–Arlman mechanism competitive, however, as outlined below.

Other changes between the \( \mathcal{H} \) and \( \mathcal{G} \) surfaces includes a change in resting states for the catalyst from 15 on the \( \mathcal{H} \) surface (–7.6 kcal/mol) to 13 on the \( \mathcal{G} \) surface (–4.3 kcal/mol). The energy difference between these two states is well within the margin of error, however.

4. Discussion

From the mechanisms in Figures 5–10, it appears that the rate-determining steps for the three potential mechanisms are 8 \( \rightarrow \) TS3 \( \rightarrow \) 9 (\( \Delta H^\circ = 28.8 \) kcal/mol, \( \Delta G^\circ = 28.8 \) kcal/mol), 13/15 \( \rightarrow \) TS8 \( \rightarrow \) 16 (\( \Delta H^\circ = 31.6 \) kcal/mol, \( \Delta G^\circ = 32.1 \) kcal/mol), and 10 \( \rightarrow \) 17 + butadiene (\( \Delta H^\circ = 34.4 \) kcal/mol, \( \Delta G^\circ = 29.4 \) kcal/mol). On this basis, we would expect that the pathway through TS3 (i.e., the one leading to 1-butene) would be the favored mechanism on both the \( \Delta H \) and \( \Delta G \) surfaces. However, this is not an accurate comparison, as during the catalytic cycle new resting states are introduced. It should be noted that since 13 and 15 change their relative order when comparing the \( \Delta H \) and \( \Delta G \) surfaces, the numbers here consistently assume the lowest of the two (13 for \( \Delta H \) and 15 for \( \Delta G \)).

By overlaying the middle part of the two mechanisms for C–H activation (i.e., the mechanisms after the insertion) in Figure 12, it can be observed that after intermediate 6 the immediate barrier to the 1-butene C–H activation mechanism is 6 \( \rightarrow \) 7, with a \( \Delta H = 26.5 \) kcal/mol (\( \Delta G = 21.8 \) kcal/mol). However, even though the absolute energy of TS3 is lower than the energy of 7, this is still the rate-determining step, as 8 \( \rightarrow \) TS3 has a barrier of \( \Delta H^\circ = 28.8 \) kcal/mol (\( \Delta G^\circ = 28.8 \) kcal/mol) due to the low energy of 8.

When looking at the mechanism for the production of 2-butene, one can readily observe that the rate-determining step, 13/15 \( \rightarrow \) TS8, has a higher absolute barrier than 8 \( \rightarrow \) TS3,
\( \Delta H^\circ = 31.6 \text{ kcal/mol} (\Delta G^\circ = 32.1 \text{ kcal/mol}) \). However, the barrier from \( 6 \rightarrow 13/15 \) through \( TS6 \) is only \( \Delta H^\circ = 17.3 \text{ kcal/mol} (\Delta G^\circ = 16.2 \text{ kcal/mol}) \) and should thus be significantly faster than \( 6 \rightarrow 7 \). The new resting state for the system thus becomes \( 13/15 \), and all barriers must be made relative to the energy of \( 13/15 \). As \( 13/15 \) is 8.5 kcal/mol (\( \Delta G = 9.1 \text{ kcal/mol} \)) lower in energy than \( 6 \), the effective barrier for formation of 1-butene is 36.5 kcal/mol (\( \Delta G = 38.9 \text{ kcal/mol} \)), i.e., significantly higher than the barrier for production of 2-butene through \( 13/15 \rightarrow TS8 \). Consequently, no 1-butene should be formed initially, and the presence of 1-butene in the final product mixture is instead attributed to isomerization of 2-butene, most likely through an allyl intermediate. This assumption is strengthened by the known isomerization of 1-hexene/2-hexene, which is \( \sim 100 \text{ times faster than hydroarylation} \).

Similarly, the Cossee–Arlman mechanism has a barrier of 34.4 kcal/mol (\( \Delta G = 29.4 \text{ kcal/mol} \)) from \( 6 \), but an effective barrier for \( 13/15 \rightarrow 17 \) of \( \Delta H = 45.0 \text{ kcal/mol} (\Delta G = 35.5 \text{ kcal/mol}) \), significantly higher than the barrier for \( 13/15 \rightarrow TS8 \) (see Figures 13 and 14). The key comparison thus becomes between the rates of butadiene liberation through \( 17 \) and conversion to the allyl intermediate through \( TS6 \). As the difference is \( \Delta H = 17.1 \text{ kcal/mol} (\Delta G = 10.2 \text{ kcal/mol}) \), this should be large enough to ensure that all catalyst is converted to \( 13 \) or \( 15 \) before any butadiene is liberated.

Thus, this catalytic system appears to be the first that dimerizes olefins through a C–H activation pathway. It is very likely this is due to the previously discussed balance between facile [1,2]-insertion and C–H activation,\(^{11} \) where it appears that factors facilitating insertion debilitates C–H activation, and vice versa. Consequently, a system with lower barriers for insertion would either become a polymerization catalyst or dimerize/oligomerize through the Cossee–Arlman mechanism, while a system with lower barriers for C–H activation would not catalyze the insertion.

It can also be observed that the C–H activation step \( TS8 \) is slightly higher in energy than the insertion transition state, \( TS2 \), and would thus be the rate-determining step.

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5. Summary

In summary, we demonstrate that our previously reported \( \text{C}_2\text{H}_3\text{-Ir(III)(acac-O,O)}_2\text{(Py)} \) system dimerizes olefins through a C–H activation mechanism. The starting catalyst first isomerizes to the cis conformer through a dissociative process, where pyridine is lost, and then adds the olefin substrate to the cis conformer. \(^{1,2}\)-Insertion of the vinyl moiety into the coordinating olefin generates a \( \text{Ir}−\text{CH}_2−\text{CH}−\text{CH}≡\text{CH}_2 \) complex, which then isomerizes to an \( \text{Ir}(\eta^3\text{-allyl}) \) complex through a series of \( \beta\)-hydride transfer reactions. The allyl complex is significantly more stable than any other part of the surface and is expected to be the resting state of the catalyst.

Addition of a second olefin to the allyl complex leads to an \( \text{Ir}−(\text{CH}_2−\text{CH}≡\text{CH}_2) \) complex with a coordinating olefin, which can transfer a hydrogen to generate the product, 2-butene, via a C–H activation transition state. This transition state is the rate-determining step, with a calculated \( \Delta H^\circ = 31.6 \text{ kcal/mol} \) and \( \Delta G^\circ = 32.1 \text{ kcal/mol} \). This is consistent with the experimentally determined rate of reaction (TOF \( \approx 10 \times 10^{-3} \text{ mol/s} \)).

Other pathways have been explored, most notably the C–H activation pathway to yield 1-butene and the Cossee–Arlman dimerization pathway, initiated by the generation of butadiene. Although both mechanisms have reasonable barriers, they were found to be not competitive due to very facile barriers leading to the \( \eta^3\)-allyl complex. From the \( \eta^3\)-allyl complex, neither 1-butene or butadiene are feasible products. The experimentally observed generation of 1-butene is suggested to occur through isomerization of 2-butene and not through initial formation.

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