

Mechanism of Ru(II)-Catalyzed Olefin Insertion and C–H Activation from Quantum Chemical Studies

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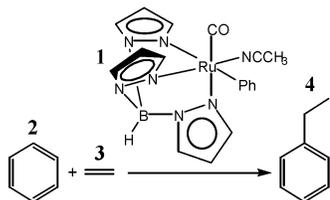
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One of the more challenging goals of transition metal catalysis is the catalytic activation and functionalization of C–H bonds.¹ Recent years have seen remarkable improvements in this area, particularly in the catalytic hydroarylation of olefins. The first system to catalyze the coupling of an unactivated arene to an unactivated olefin was the binuclear complex $[\text{Ir}(\mu\text{-acac-O})(\text{acac-O},\text{O})(\text{acac-C}^3)]_2$ $[\text{Ir}(\text{acac})_3]_2$ reported by Matsumoto et al.,² with an activation energy of 28.7 kcal/mol.

Later variations of this system by Periana et al. featured several mononuclear Ir compounds of the form $\text{Ir}(\text{acac-O},\text{O})_2(\text{R})(\text{L})$, where R is either (acac-O,O,C³) or Ph, and L is either H₂O or pyridine.³ Both the binuclear and the mononuclear systems were explored computationally by Oxgaard et al.⁴ and were found to react through a common mechanism.

Recently, Gunnoe and co-workers reported a new catalyst for this reaction.⁵ Heating a solution of $\text{TpRu}(\text{CO})(\text{Me})(\text{NCCH}_3)$ (**1**) (Tp = hydridotris (pyrazolyl) borate) and 0.17 MPa of ethene (**2**) in benzene (**3**) at 90 °C yielded ethyl benzene (**4**) with a TOF of $3.5 \times 10^{-3} \text{ s}^{-1}$. Comparing this TOF to a TOF for the $[\text{Ir}(\text{acac})_3]_2$ complex extrapolated to 90 °C suggests that system **1** is ~200 times faster than previous systems.



The rational design of more active, selective, and robust catalysts requires a fundamental understanding of the relevant mechanisms. Consequently, we carried out quantum mechanical calculations of the Ru^{II}-catalyzed hydroarylation reaction, illustrated in Figure 1. For comparison purposes, the calculated hypersurface for the $[\text{Ir}(\text{acac})_3]_2$ -catalyzed reaction⁴ is illustrated as a dotted line.

All calculations used B3LYP density functional theory with the Hay and Wadt LACVP** basis and effective core potential treatment of the Ru (16 explicit electrons), as implemented by the Jaguar 5.0 package.⁶ Geometries were optimized in the gas phase and corrected for zero point energies and solvation [single point calculation using the Poisson–Boltzmann continuum solvent method ($\epsilon = 2.284$ and probe radius = 2.60219 Å)]. All reported energies are solvent corrected enthalpies at 0 K.

The structure of **1** is octahedral, with the (negative) Tp ligand occupying the coordinating sites on one face. The Ru–N distances are 2.11 Å (bond trans to NCCH₃), 2.20 Å (trans to CO), and 2.27 Å (trans to Ph). The Ru–C(CO) distance is 1.87 Å, while the Ru–C(Ph) distance is 2.09 Å, with the plane of the Ph ligand in the same plane as the Ru–N(NCCH₃) bond (2.05 Å).

The catalyst is activated through dissociation of the NCCH₃ ligand, with a ΔH of 21.9 kcal/mol, to yield the coordinatively unsaturated complex **5**. Removal of the mildly trans-influencing ligand shortens the Ru–N bond distance to 2.04 Å, but other structural parameters are largely unchanged.

Association of ethene leads to complex **6**, with a ΔH of –18.1 kcal/mol. The C₂H₄ ligand in **6** has a C–C bond length of 1.39 Å with Ru–C(C₂H₄) bond lengths of 2.25 and 2.27 Å, indicating σ -donating character. The C₂H₄ ligand has the π bond aligned along the Ph–Ru axis, orienting it for insertion. The energy of **6** + free acetonitrile is 3.8 kcal/mol higher than that of **1** + ethene, which is consistent with complex **6** not being observed experimentally.

The insertion occurs through transition state **TS1**, with a relative energy of 24.9 kcal/mol as compared to **1**. **TS1** features a four-membered ring with a C1–C2 bond length of 1.46 Å, equally far from intermediate **6** (where C1–C2 is a double bond) and the product, intermediate **7** (where C1–C2 is a single bond).

With substituted olefins as substrates, Gunnoe et al. reported a moderate amount of anti-Markovnikov regioselectivity.⁵ For example, propene yielded linear versus branched propyl benzene in a 1.6:1 ratio. Visual inspection of **TS1** (Figure 2) suggests that the explanation for this selectivity is that substituents at C1 are significantly less crowded than substituents at C2 (which face steric interactions from two pyrazolyl rings cis to the phenyl and the hydrogens in the phenyl β position).

Intermediate **7** features the newly formed covalent Ru–CH₂R bond with intramolecular coordination of the phenyl unit. Aromatic rings are poorly coordinating ligands, which is reflected in the long Ru–C distances, 2.63 and 2.82 Å. The weak coordination facilitates dissociation through rotation around the C1–C2 bond, to give the coordinatively unsaturated intermediate **8**, uphill 5.3 kcal/mol.

Coordination of free benzene to **8** yields intermediate **9**, downhill 4.5 kcal/mol. The benzene in **9** coordinates through a CH (agostic) bond (Ru–H = 2.03 Å), which orients complex **9** for subsequent C–H activation.

C–H activation occurs through a concerted mechanism of unusual character, which we refer to as oxidative hydrogen migration (OHM).^{4,7} While the OHM transition structure, **TS2**, has oxidative character, it is not an oxidative addition, because there is no stable Ru^{IV} intermediate.

The OHM transition structure, **TS2**, features: (a) one imaginary frequency at –1137 cm^{–1}, corresponding to the H going from C(Ph) to C1; (b) a fully formed bond between the H and the Ru (Ru–H = 1.61 Å and a vibrational frequency of 2110 cm^{–1}); (c) weak bonds between this H and both carbons (H–C1 = 1.65 Å, H–C(Ph) = 1.56 Å); (d) a half-order Ru–C1 bond (2.27 Å, 479 cm^{–1}); and (e) a half-order Ru–C(Ph) bond (2.17 Å, 1033 cm^{–1}). The half-order bonds should be compared to the full Ru–C1 in **8** (2.12 Å, 529 cm^{–1}), and Ru–C(Ph) in **5** (2.07 Å, 1085 cm^{–1}), respectively.

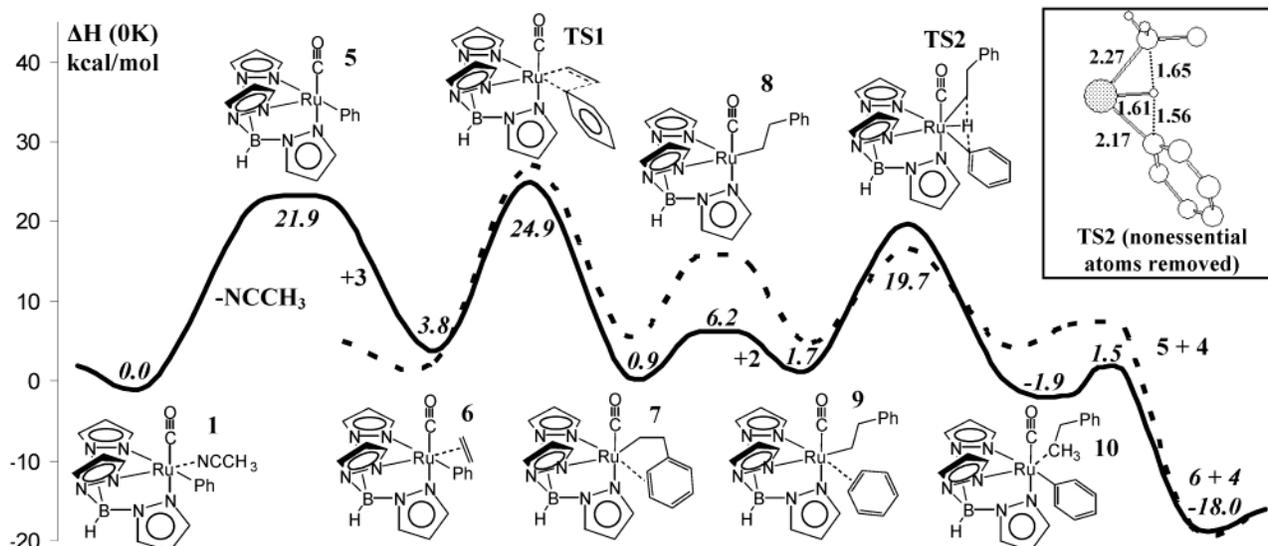


Figure 1. Calculated mechanism for hydroarylation by Ru(Tp)(CO)(Ph)(NCCH₃). The dotted line shows the hypersurface for Ir(acac)₃.

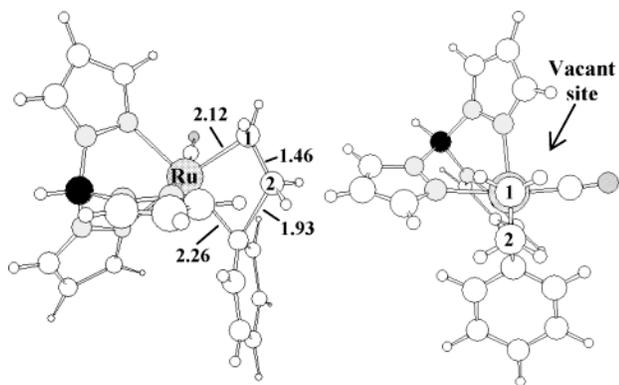


Figure 2. Insertion transition structure, side and top view.

The activation energy of TS2 is 18.0 kcal/mol relative to **9**, and 19.7 kcal/mol relative to **1**.

Hydrogen migration leads to intermediate **10**, 3.6 kcal/mol lower in energy than **9**. **10** is very short-lived, with a barrier of 3.4 kcal/mol for dissociation to ethyl benzene and intermediate **5**. Complexation of a new ethene to **5** (down by 18.4 kcal/mol) regenerates intermediate **6**. The overall exothermicity of the reaction is 21.9 kcal/mol.

The calculated mechanism closely mirrors the mechanism of the [Ir(acac)₃]₂ system, as illustrated in Figure 1. The Ru-based system follows a lower energy pathway than the Ir-based system in all respects except C–H activation. The rate-determining step, TS1, is 3.8 kcal/mol lower in energy than the 28.7 kcal/mol of the (Ir(acac)₃)₂ complex, which corresponds to a rate enhancement of 193 times at 90 °C, very close to the enhancement of ~200 times extrapolated from experiment. The origin of this rate enhancement is not clear. The Ru is less electrophilic (the calculated Mulliken charge on Ru is +0.07e vs +0.45e for the Ir), yet it is more active. We believe that the difference has an electronic origin related to the role of the Mⁿ⁺² oxidation state. We are currently investigating this effect.

The C–H activation step, on the other hand, is higher in energy in the Ru system. Because the mechanism of the activation is related to oxidation, it seems natural to assume that a more accessible Mⁿ⁺² state would lead to lower energy activation.

The opposing trends in the two key steps indicate that catalytic hydroarylation involves a balancing act. Improving C–H activation

would most likely impede insertion and thus overall rate, while improving insertion and impeding C–H activation would most likely lead to faster rates but extensive polymerization.

Indeed, polymerization is predicted to be problematic in the current Ru system. Preliminary calculations show a viable polymerization pathway, 15 kcal/mol lower in energy than the C–H activation. However, this pathway is first order in ethene, while the C–H activation is first order in benzene, and it is probably not noticeable at the low olefin concentration of 0.17 MPa used in ref 4. We do suggest that this prediction be tested experimentally, possibly by running the reaction at the ~1.72 MPa used in ref 3.

Even with this balance in mind, the catalyst can likely be improved. Elimination of the ground-state effect by replacing the acetonitrile in **1** with a less donating ligand, such as H₂O, might improve the energy by 3.8 kcal/mol, depending on concentration. An alternative is to reduce electron density on the metal, by introducing electron-withdrawing groups (such as CF₃) on the Tp ligand or by replacing the CO with a more π-accepting group (such as PF₃).

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Supporting Information Available: Tables of coordinates, absolute energies, zero point energy corrections, and imaginary frequencies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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