

The Role of Electronic and Geometric Factors in Rhodium-Catalyzed Selective Hydrogenation of Enones

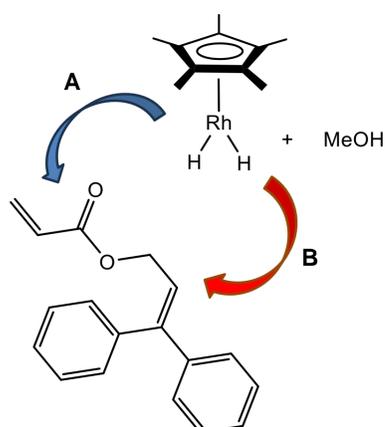
Ferran Acuña-Parés^a

^aEscuela Superior de Ingeniería y Tecnología (ESIT), Universidad Internacional de la Rioja (UNIR), Logroño, Spain

INTRODUCTION & AIM

The selective hydrogenation of α,β -unsaturated carbonyl compounds (enones) vs. isolated double bonds is a reaction of considerable interest in organic synthesis, particularly in the pharmaceutical and fine chemical industries. Previous studies have elucidated the mechanism of this reaction, which is catalyzed by the $\text{Cp}^*\text{Rh}(2\text{-}(2\text{-pyridyl})\text{phenyl})\text{H}$ complex in methanol^{1,2}. However, computational research has primarily focused on substrates containing a single reactive group, neglecting systems with both enone and olefin functionalities.² Moreover, the origins of the preference for enone hydrogenation remain insufficiently explored.

This project explores the electronic and structural reasons behind this selectivity using a dual-functional substrate and DFT tools.



Why does Rh prefer enones over simple olefins?

METHOD

Geometries

- B3LYP/def2SVP
- Methanol solvent \rightarrow SMD model and explicit molecule
- Dispersion effects \rightarrow Grimme-D₃ correction
- Frequency and IRC calculations ($\xi \equiv$ intrinsic coordinate)

Reaction force profile (RFP) and reaction work (W) (kcal/mol)

$$F(\xi) = -\frac{dE(\xi)}{d\xi}$$

$$W_1 = -\int_{\xi_R}^{\xi_1} F(\xi) d\xi > 0 \quad W_2 = -\int_{\xi_1}^{\xi_2} F(\xi) d\xi > 0$$

$$W_3 = -\int_{\xi_2}^{\xi_1'} F(\xi) d\xi < 0 \quad W_4 = -\int_{\xi_1'}^{\xi_P} F(\xi) d\xi < 0$$

Reaction Energies (kcal/mol)

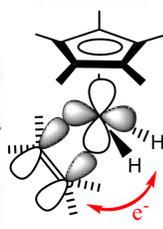
$$G = E(\text{B3LYP})_{\text{def2TZVP}} + G_{\text{Thermal}} + G_{\text{Solvation}} + G_{\text{Grimme}}$$

Electronic Structure Analysis

Density-driven

Hirshfeld charges

QTAIM/ELF
 $H(r)$ evaluated at CPs

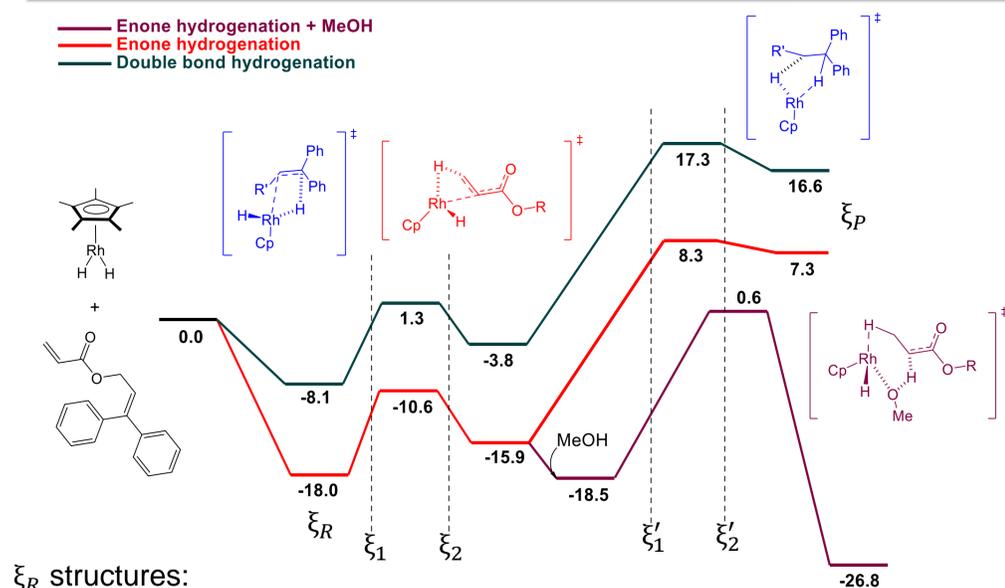


Orbital-driven

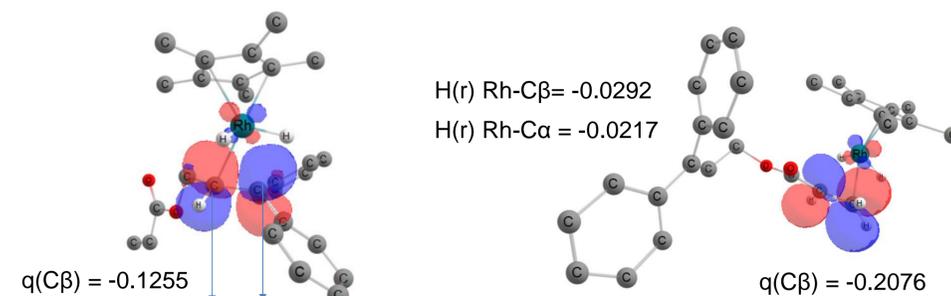
NBO

Orbital overlap & interference

RESULTS & DISCUSSION



ξ_R structures:



$$H(r) = -0.0168 \quad H(r) = -0.0279$$

$$E_{\pi(\text{C}=\text{C})} \rightarrow \text{sp}(\text{Rh}) = 26.03 \text{ kcal/mol}$$

$$E_{\pi(\text{C}=\text{C})} \rightarrow \sigma^*(\text{Rh}-\text{C}) = 49.08 \text{ kcal/mol}$$

$$E_{\pi(\text{C}=\text{C})} \rightarrow \pi^*(\text{C}=\text{O}) = 20.17 \text{ kcal/mol}$$

$$E_{\text{d}(\text{Rh})} \rightarrow \pi(\text{C}\alpha=\text{C}\beta) = 34.56 \text{ kcal/mol}$$

$$E_{\pi(\text{C}\alpha=\text{C}\beta)} \rightarrow \text{sp}(\text{Rh}) = 69.25 \text{ kcal/mol}$$

$$E_{\pi(\text{C}\alpha=\text{C}\beta)} \rightarrow \sigma^*(\text{Rh}-\text{C}) = 52.13 \text{ kcal/mol}$$

$$E_{\pi(\text{C}\alpha=\text{C}\beta)} \rightarrow \text{p}(\text{C}_{\text{carbonyl}}) = 33.46 \text{ kcal/mol}$$

$\xi_R - \xi_2$ regions	Reactant rearrangement (W_1)	Electronic (TS region, $W_2 + W_3$)	Product rearrangement (W_4)
Enone	4.6	0.5	-4.6
Double bond	2.1	-3.0	6.0

$\xi_1' - \xi_P$ regions	Reactant rearrangement (W_1)	Electronic (TS region, $W_2 + W_3$)	Product rearrangement (W_4)
Enone*	3.6	-0.1	-13.8
Double bond	12.2	8.6	-0.4

*Enone + MeOH mechanism.

The enone forms a synergistic interaction with Rh via π -donation, π -backdonation, and enhanced donor-acceptor resonance, which polarizes the π -system and localizes negative charge at $\text{C}\beta$. QTAIM $H(r)$ values confirm stronger $\text{Rh}-\text{C}\beta$ covalent character. Therefore, $\text{C}\beta$ becomes more electrophilic and orbital-accessible, favoring hydride transfer from the polarized $\text{Rh}-\text{H}$ bond. While the olefin shows greater TS electronic work, the enone benefits from product stabilization and methanol-assisted selectivity.

CONCLUSION

Enone selectivity arises from better orbital overlap, greater charge polarization and favorable structural relaxation due to resonance and MeOH coordination. These key electronic and geometric features offer valuable insights for guiding ligand design to further optimize this transformation.

FUTURE WORK/REFERENCES

Analyze the electronic structure of the maxima/minima in the RFP. Propose ligand modifications to enhance enone, or olefin, selectivity, and broaden substrate scope.

1. Gu, Y. et al. *J. Am. Chem. Soc.* **2021**, *143*, 9657–9663.
2. Zhang, Y.; Li, X. *ChemPhysChem* **2022**, *23*, e202200562.