

Non-innocent role of the CNHC ligand on the isomerization of cationic $[\text{Ir}(\text{CNHC})(\text{CH}_3\text{CN})_2(\text{P}^i\text{Pr}_3)]^+$ complex: A DFT Approach

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The dihydrido-iridium (III) cationic complex **A** has proved to be an excellent catalyst especially in alkene and imine hydrogenations.^{1, 2} Its reaction with an excess of ethylene followed by diallylamine leads to a mixture of two isomeric compounds, **B-kin** and **B-ther**, which slowly evolves at room temperature to the thermodynamic isomer **B-ther**.³

Such an isomerization seems to entail a non-innocent role of the NH moiety since the analogous reaction in the presence of methyldiallylamine forms an analogue of **B-kin** as single and final product. The use of Density Functional Theory (DFT) to study elementary steps such as solvent dissociation, NH protonation and deprotonation, and proton shuttled tautomerizations is in process and aims the rationalization of the formation of **B-ther** and its reactivity.

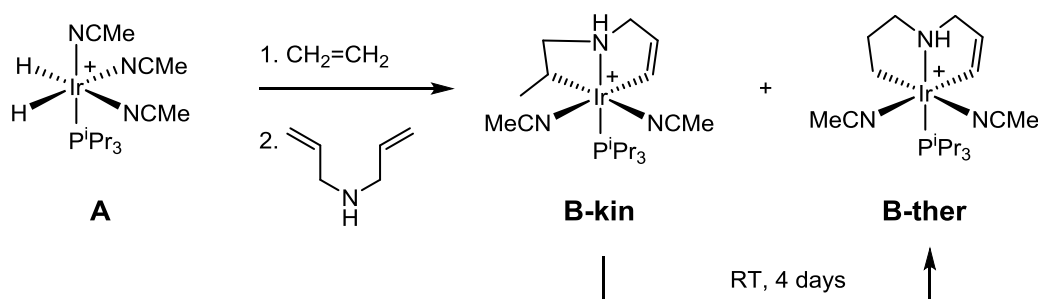


Figure 1 – Synthesis and isomerization of Iridium **B-kin** and **B-ther** isomers from $[\text{IrH}_2(\text{NCMe})_2(\text{P}^i\text{Pr}_3)]^+$ complex.

1. Sola, E.; Navarro, J.; López, J. A.; Lahoz, F. J.; Oro, L. A.; Werner, H. *Organometallics* **1999**, *18*, 3534.
2. Martín, M.; Sola, E.; Tejero, S.; Andrés, J. L.; Oro, L. A. *Chem. Eur. J.* **2006**, *12*, 4043.
3. Salom, A.; Martín, M.; Sola, E.; *unpublished results*