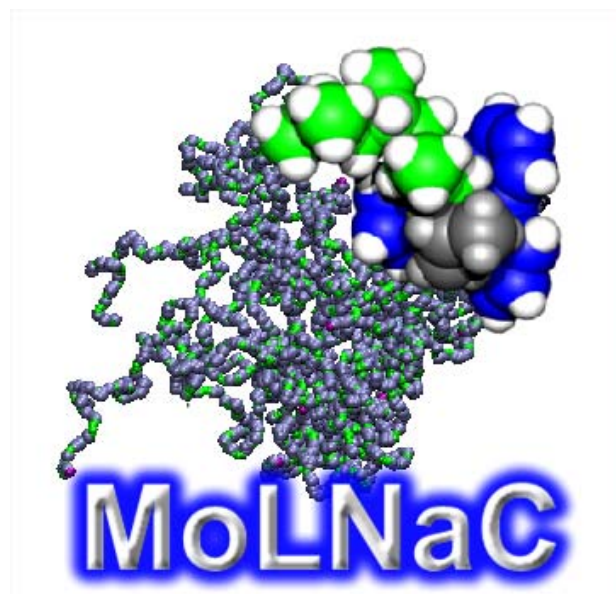


A Computational Approach to Understand the Mechanism of Ru-Catalyzed Olefin Metathesis



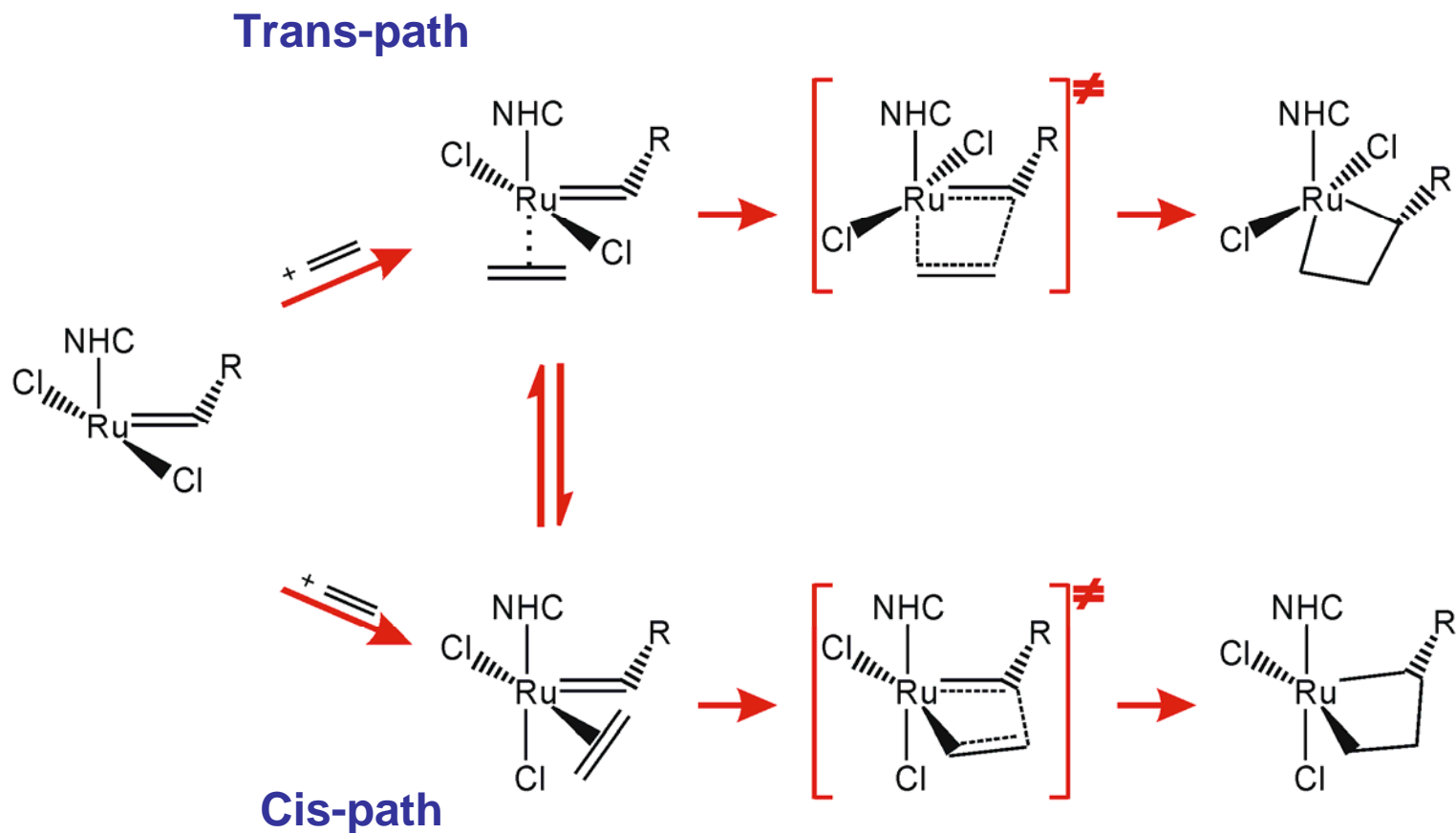
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<http://www.chem.unisa.it/groups/molnac>

Which is the “Right” Mechanism ?



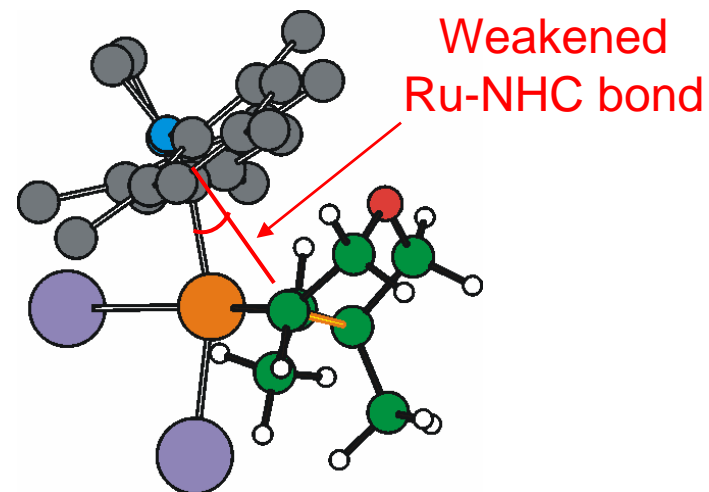
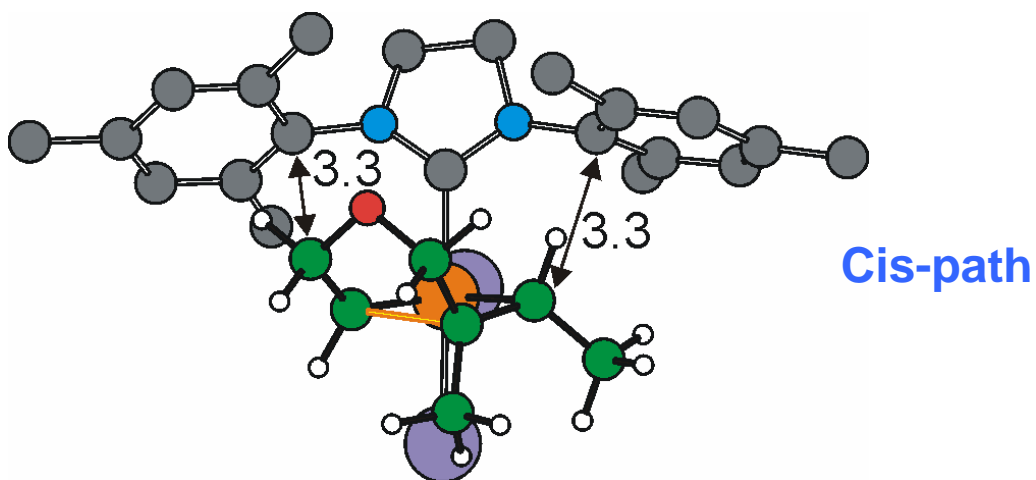
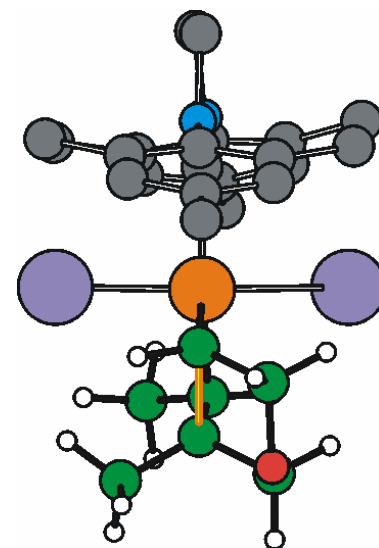
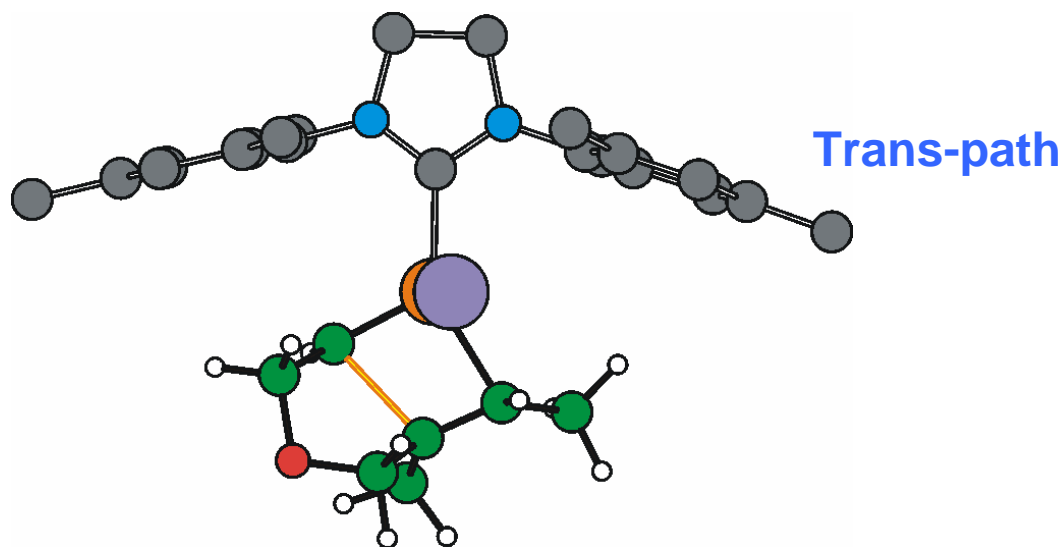
Without considering reaction pathways with two olefins coordinated

Romero & Piers JACS 2007, 129, 6198. Webster JACS 2007, 7490.

Transition state geometries

Lateral View

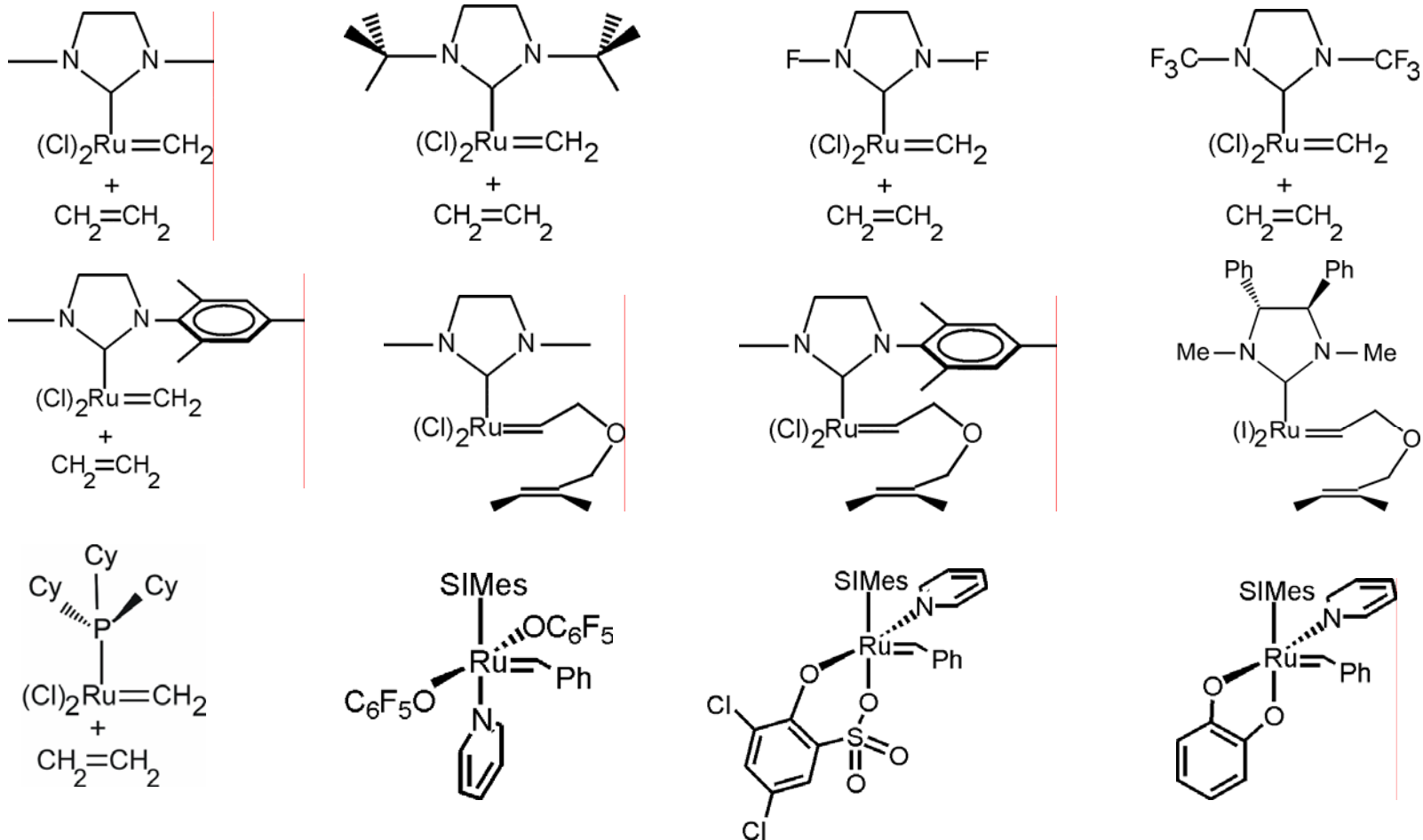
Front View



The cis path is strongly disfavored by steric interactions between the substrate and the NHC ligand. The trans path, instead, presents unstressed geometries

The Systems Investigated

The comparison between the two paths has been extended to several systems, using different substrates and ligands.



Differently from 2nd generation catalysts, calculations clearly indicated that for 1st generation catalysts the two paths are quite competitive, while for pseudohalide catalysts the cis path is strongly favored.

Conclusions

Thus, extensive investigation of several systems indicated that no path can be individued as “The Path”. Instead, the actual path followed depends on several factors. Although *there are more things in heaven and earth, than are dreamt of in our philosophy*, some general trends can be extrapolated.

