

# Carbon–Carbon bond activation of epoxides by a (dtbpm)Pt fragment - A theoretical study.

Philipp N. Plessow,<sup>1,2</sup> Jorge J. Carbó,<sup>3,4</sup> Ansgar Schäfer,<sup>2</sup> Peter Hofmann<sup>1,4</sup>

<sup>1</sup>Catalysis Research Laboratory (CaRLa), Heidelberg, Germany

<sup>2</sup>BASF SE, Quantum Chemistry, Ludwigshafen, Germany

<sup>3</sup>Department de Química Física i Inorgànica, Universitat Rovira i Virgili, Tarragona, Spain

<sup>4</sup>Organisch–Chemisches Institut, Ruprecht–Karls–Universität, Heidelberg, Germany

Platinum complexes with the bis(di-tert-butylphosphino)-ligand (dtbpm) are the only known complexes that selectively activate epoxides at the carbon–carbon bond. Here we study this reaction theoretically using the random phase approximation. We find that the reactivity is kinetically controlled and is caused by the formation of a monodentate (dtbpm- $\kappa^1P$ )Pt fragment rather than the (dtbpm- $\kappa^2P$ )Pt chelate complex. Insertion into the epoxide C–C bond occurs without energy barrier. The competing reactions, C–O and C–H activation, both proceed via formation of a  $\sigma$ -complex, followed by small but significant barriers for the insertions. A reversible formation of the  $\sigma$ -complexes would perfectly explain the observed reactivity. For an irreversible formation we find that intramolecular rearrangement of these  $\sigma$ -complexes towards C–C activation is faster than both C–O and C–H activation. The same reactivity is expected for other mono-coordinated platinum phosphine complexes. However, only the specific properties of dtbpm make the formation of this intermediate and the subsequent, rapid closing of the chelate ligand favourable.