Available online at www.sciencedirect.com
ScienceDirect
Volume 691, issue 21, 15 October 2006
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Contents

Special Issue: Theory and Mechanistic Studies

Publisher's note 4333
Editorial 4335

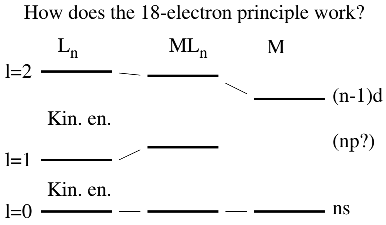
Regular papers

Pekka Pyykkö

J. Organomet. Chem. 691 (2006) 4336

Understanding the eighteen-electron rule

The 18-electron principle can be explained by invoking s and d bonding contributions at the metal M, combined with the nodal structure of the ligand system, L_n. No metal p orbitals are necessarily required.

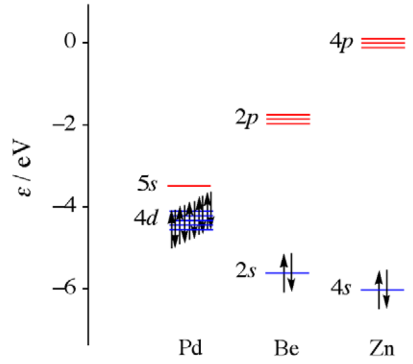


G. Theodoor de Jong, Ruud Visser,
F. Matthias Bickelhaupt

J. Organomet. Chem. 691 (2006) 4341

Oxidative addition to main group versus transition metals: Insights from the Activation Strain model

The transition metal Pd is intrinsically more reactive towards oxidative insertion into a C–X bond than alkaline earths and group-12 transition metals. This can be mainly ascribed to palladium's excellent electron-donating and accepting capabilities associated with the high-energy 4d HOMO and low-energy 5s LUMO.

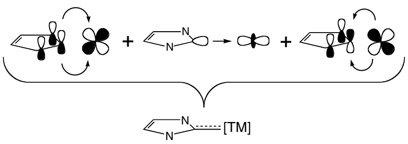


Heiko Jacobsen, Andrea Correa,
Chiara Costabile, Luigi Cavallo

J. Organomet. Chem. 691 (2006) 4350

π-Acidity and π-basicity of *N*-heterocyclic carbene ligands. A computational assessment

Based on DFT calculations the NHC–[TM] bond is analyzed in terms of σ-donation, π-backdonation and π-donation contributions.



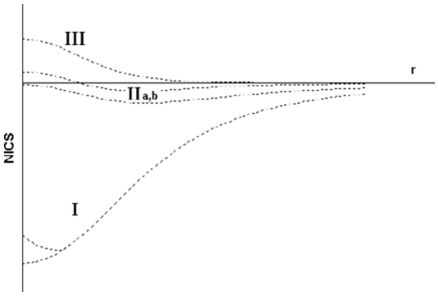
Elsevier B.V.
doi:10.1016/S0022-328X(06)00728-5

J. Oscar C. Jiménez-Halla, Eduard Matito, Juvencio Robles, Miquel Solà

J. Organomet. Chem. 691 (2006) 4359

Nucleus-independent chemical shift (NICS) profiles in a series of monocyclic planar inorganic compounds

NICS profiles have been calculated for a series of monocyclic planar inorganic compounds by performing hybrid DFT calculations. According to their profiles, the systems studied can be classified in three groups depending on their aromatic, non-aromatic or antiaromatic character.

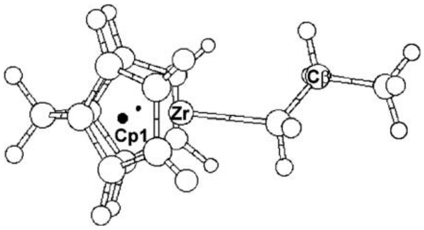


Martin Graf, Klaus Angermund, Gerhard Fink, Walter Thiel, Vidar R. Jensen

J. Organomet. Chem. 691 (2006) 4367

Site epimerization in *ansa*-zirconocene polymerization catalysts

Density functional calculations address site epimerization in $[\{H_2C(Cp)_2\}Zr–Pr]^+$ (Pr = *n*-propyl) and $[\{H_2C(Cp)_2\}Zr–{}^iBu]^+$ (^{i}Bu = *iso*-butyl). For both catalysts, the rate-limiting step is an inversion connecting two α-agostic intermediates, with computed free-energy barriers of 11 kcal/mol. According to the computed barriers, insertion is favored over epimerization in the *n*-propyl case (retention of active site stereochemistry), while both processes are competitive in the *iso*-butyl case (possible stereoerrors).

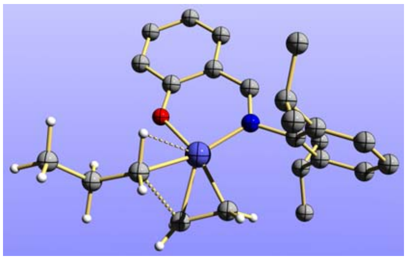


Alexander Zeller, Thomas Strassner

J. Organomet. Chem. 691 (2006) 4379

The mechanism of ethylene polymerization by nickel salicylaldiminato catalysts – Agostic interactions and their kinetic isotope effects

A previously unknown α-agostic interaction was identified by DFT calculations for the insertion transition state of a neutral nickel polymerization catalyst. The resulting kinetic isotope effects are described.



Selina C. Wang, Dean J. Tantillo

J. Organomet. Chem. 691 (2006) 4386

Metal promoted vinylcyclopropane–cyclopentene rearrangements: Reactions ripe for mechanism-based catalyst design

This brief review describes experimental and theoretical data relevant to the mechanisms of transition metal promoted vinylcyclopropane–cyclopentene rearrangements. In particular, reactions utilizing Pd(0), Rh(I), and Ni(0) are highlighted and compared to analogous reactions not involving transition metals.