

Contents

Special Issue: Theory and Mechanistic Studies

Publisher's note	4333
Editorial	4335

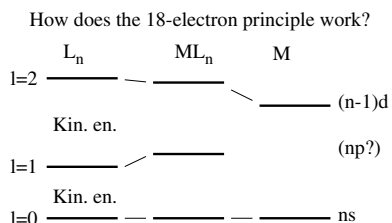
Regular papers

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.

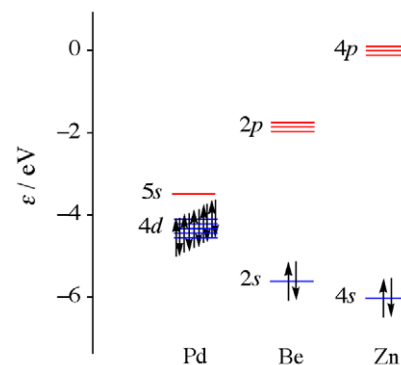


G. Theodoor de Jong, Ruud Visser, F. Matthias Bickelhaupt

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.

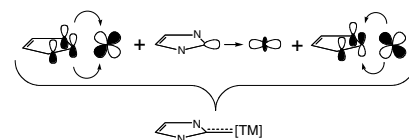


Heiko Jacobsen, Andrea Correa, Chiara Costabile, Luigi Cavallo

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.

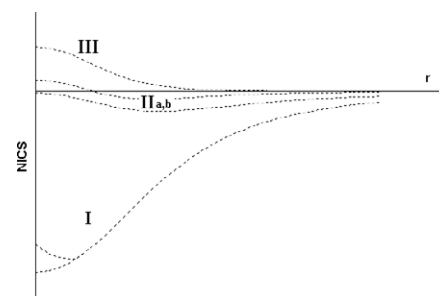


**J. Oscar C. Jiménez-Halla, Eduard Matito,
Juvencio Robles, Miquel Solà**

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.

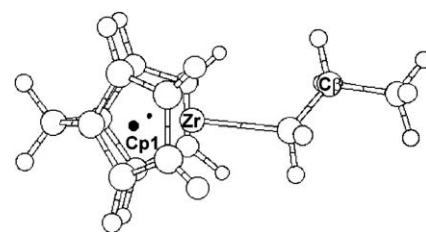


**Martin Graf, Klaus Angermund, Gerhard Fink,
Walter Thiel, Vidar R. Jensen**

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 $[\{H_2C(Cp)_2\}Zr-^iBu]^+$ (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).

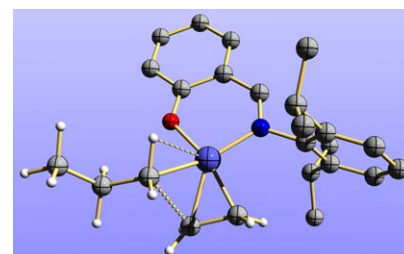


Alexander Zeller, Thomas Strassner

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.

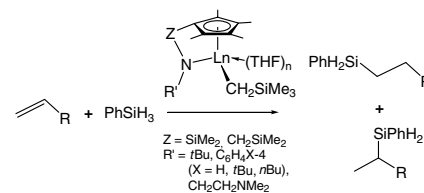


**Dominique Robert, Alexander A. Trifonov,
Peter Voth, Jun Okuda**

J. Organomet. Chem. 691 (2006) 4393

“Constrained geometry” catalysts of the rare-earth metals for the hydrosilylation of olefins

A series of rare-earth metal alkyl complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{ZNR}'\text{-}\kappa\text{N})(\text{CH}_2\text{SiMe}_3)(\text{THF})_n]$ ($\text{Ln} = \text{Y, Lu}$; $\text{Z} = \text{SiMe}_2, \text{CH}_2\text{SiMe}_2$; $\text{R}' = t\text{Bu, Ph, C}_6\text{H}_4\text{-}t\text{Bu-4, C}_6\text{H}_4\text{-}n\text{Bu-4}$) was examined for catalytic activity in the hydrosilylation of 1-decene and styrene under standard conditions using PhSiH_3 . A significant influence of the ligand structure on the catalytic property (turnover frequency, regioselectivity) was observed.

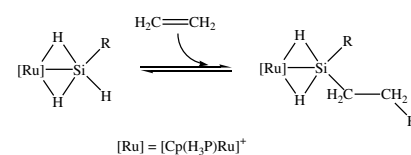


Uwe Böhme

J. Organomet. Chem. 691 (2006) 4400

Hydrosilylation vs. [2 + 2]-cycloaddition: A theoretical study with iron and ruthenium complexes

The mechanism of hydrosilylation with the model complex $[\text{Cp}(\text{H}_3\text{P})\text{Ru}(\text{H})_2\text{Si}(\text{H})\text{Ph}]^+$ and possible alternative pathways are investigated with quantum chemical methods. The analysis of the electron density distribution of the catalytic active complex shows surprising bond features between Ru and Si. It is necessary to make drastic changes in the ligand environment of the transition metal-silicone complex to observe cycloaddition reactions.

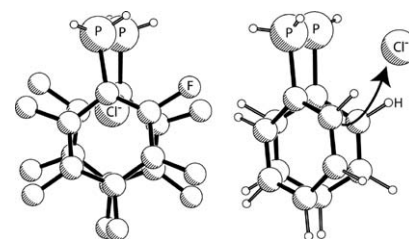


**Marcella Gagliardo, Remco W.A. Havenith,
Gerard van Klink, Gerard van Koten**

J. Organomet. Chem. 691 (2006) 4411

(*P*-Bis(pentafluorophenyl) substituted) PCP-pincer Ru(II) complexes: A theoretical study of the molecular structure and electronic properties

A theoretical study of the molecular structure of complex $[\text{RuCl}\{\text{C}_6\text{H}_3(\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2)_2\text{-2,6}\}(\text{PPh}_3)]$ ($[\text{RuCl}(\text{PCP}^{\text{H}})(\text{PPh}_3)]$, **1**) and its tetrakis-pentafluorophenyl substituted analogue $[\text{RuCl}\{\text{C}_6\text{F}_5(\text{CH}_2\text{P}(\text{C}_6\text{F}_5)_2)_2\text{-2,6}\}(\text{PPh}_3)]$ ($[\text{RuCl}(\text{PCP}^{\text{F}20})(\text{PPh}_3)]$, **2**) has been carried out to rationalise the observed structural changes observed in **2** compared to **1** upon replacement of C_6H_5 - by C_6F_5 -groups. The results of the calculations, performed on the models $[(\text{C}_6\text{F}_5\text{PH}_2)_2\text{Cl}]^-$ and $[(\text{C}_6\text{H}_5\text{PH}_2)_2\text{Cl}]^-$, show that in complex **2** the chloride ligand interacts with the axial fluorinated phenyl rings. The spectroscopic features of both complexes have been interpreted with the TD-DFT method.

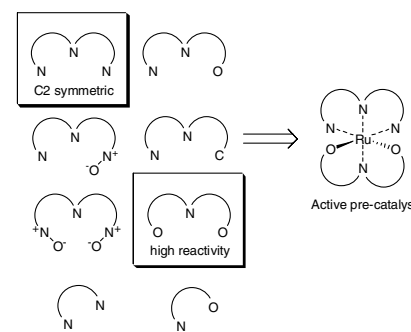


**Man Kin Tse, Haijun Jiao,
Gopinathan Anilkumar, Bianca Bitterlich,
Feyissa Gadissa Gelalcha, Matthias Beller**

J. Organomet. Chem. 691 (2006) 4419

Synthetic, spectral and catalytic activity studies of ruthenium bipyridine and terpyridine complexes: Implications in the mechanism of the ruthenium(pyridine-2,6-bisoxazoline)(pyridine-2,6-dicarboxylate)-catalyzed asymmetric epoxidation of olefins utilizing H_2O_2

Possible active intermediates of the ruthenium-catalyzed epoxidation of olefins using H_2O_2 are proposed based on synthetic, spectral, catalytic activity and computational studies of ruthenium bipyridine and terpyridine complexes. This fragment based analysis of the catalytic system suggests also reasons for low catalytic activity and low enantiomeric induction of some catalysts. A simple catalytic system utilizing UHP has also been developed in which all six classes of aromatic olefins can be epoxidized in moderate to good yields with good chemoselectivity.

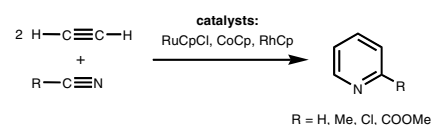


**Georg Dazinger, Marta Torres-Rodrigues,
Karl Kirchner, Maria José Calhorda,
Paulo J. Costa**

J. Organomet. Chem. 691 (2006) 4434

Formation of pyridine from acetylenes and nitriles catalyzed by RuCpCl, CoCp, and RhCp derivatives – A computational mechanistic study

The mechanism of the catalytic formation of pyridines from the coupling of two alkynes and the nitriles $\text{N}\equiv\text{CR}$ ($\text{R} = \text{H}, \text{Me}, \text{Cl}, \text{COOMe}$) with the fragments CpRuCl, CpCo, and CpRh has been investigated by means of DFT/B3LYP calculations.

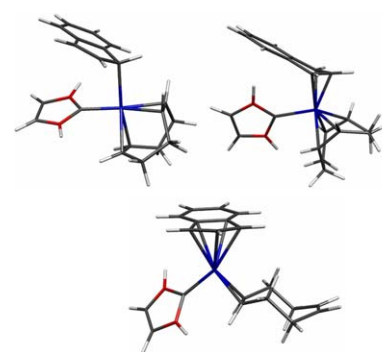


**Martina Prinz, Luís F. Veiros,
Maria José Calhorda, Carlos C. Romão,
Eberhardt Herdtweck, Fritz E. Kühn,
Wolfgang A. Herrmann**

J. Organomet. Chem. 691 (2006) 4446

Structural preferences of cyclopentadienyl and indenyl rings in iridium(I) carbene complexes

Although both $[\text{Ir}(\eta^4\text{-COD})(\text{NHC}^{\text{Cy}})(\eta^1\text{-Cp})]$ and $[\text{Ir}(\eta^2\text{-COD})(\text{NHC}^{\text{Me}})(\eta^5\text{-Cp})]$ have been characterized as derivatives of the $\text{Ir}(\eta^4\text{-COD})(\text{NHC}^{\text{R}})$ fragment, the only indenyl complex isolated for this system was $[\text{Ir}(\eta^4\text{-COD})(\text{NHC}^{\text{R}})(\eta^1\text{-Ind})]$. DFT calculations showed that the energies of $\eta^1\text{-Ind}$, $\eta^3\text{-Ind}$, and $\eta^5\text{-Ind}$ complexes are close enough to be consistent with a fluxional behavior in solution.

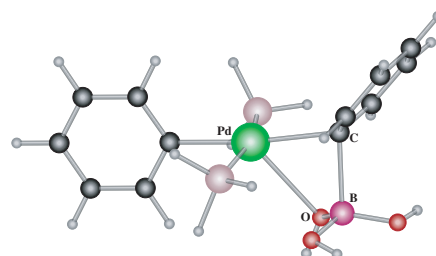


**Ataulpa A.C. Braga, Nelson H. Morgon,
Gregori Ujaque, Agustí Lledós, Feliu Maseras**

J. Organomet. Chem. 691 (2006) 4459

Computational study of the transmetalation process in the Suzuki–Miyaura cross-coupling of aryls

DFT calculations confirm that the palladium-catalyzed Suzuki–Miyaura cross-coupling between phenyl bromide and phenylboronic acid requires the presence of a base, and suggest that the mechanism starts with the attack of the base on the organoboronic acid.

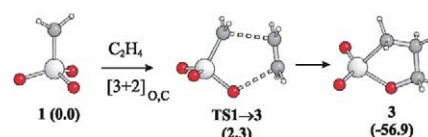


**Daniel Cappel, Sandor Tüllmann,
Christoph Loschen, Max C. Holthausen,
Gernot Frenking**

J. Organomet. Chem. 691 (2006) 4467

Ethylene addition to $\text{OsO}_3(\text{CH}_2)$ – A theoretical study

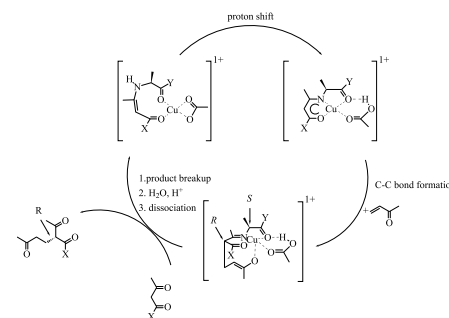
Quantum chemical calculations of the reaction profile for addition of ethylene to $\text{OsO}_3(\text{CH}_2)$ show that there are several reactions pathways besides the most favorable $[3+2]_{\text{O,C}}$ addition.



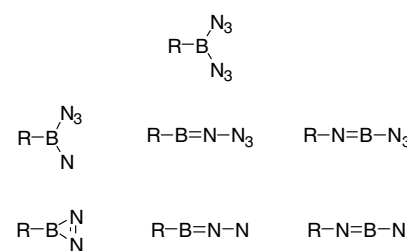
Julia Borowka, Christoph van Wüllen*J. Organomet. Chem.* 691 (2006) 4474

Computational studies on the copper(II) catalyzed Michael reaction

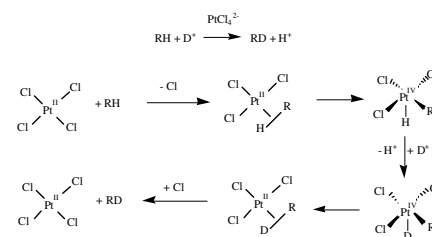
The copper(II) catalyzed Michael reaction of enamines derived from 1,3-diketones and amino acids most likely involves as a key intermediate an aza-enolate coordinated to three sites of a square planar copper centre.

**Holger F. Bettinger***J. Organomet. Chem.* 691 (2006) 4480Dinitrogen extrusion from diazidophenylborane: Computational analysis of PhBN_x ($x = 6, 4, 2$) isomers

Energies and structures of PhBN_6 , PhBN_4 , and PhBN_2 isomers are investigated computationally.

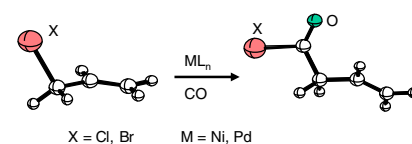
**Hongjuan Zhu, Tom Ziegler***J. Organomet. Chem.* 691 (2006) 4486A theoretical study of the original Shilov reaction involving methane activation by platinum tetrachloride (PtCl_4^{2-}) in an acidic aqueous solution

Density functional theory (DFT) has been employed to investigate the rate-determining step for the Shilov reaction in which PtCl_4^{2-} can catalyze H-D exchange of alkanes in acidic aqueous solution. C-H activation and methane uptake are the two possible candidates.

**Andrea Bottoni, Gian Pietro Miscione, M. Angels Carvajal, Juan J. Novoa***J. Organomet. Chem.* 691 (2006) 4498

The mechanism of transition metal catalyzed carbonylation of allyl halides: A theoretical investigation

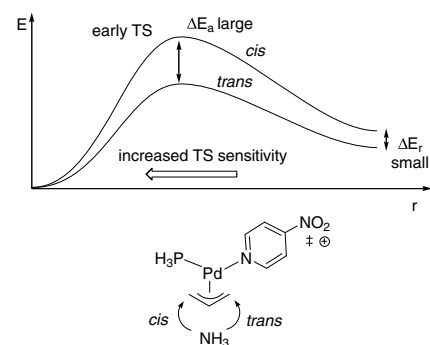
The computational study of the carbonylation of allyl substrates catalyzed by nickel and palladium, shows interesting mechanistic features. In particular, irrespective of the metal used in the catalysis, the favored path is very similar in the two cases (i.e., a direct attack of the halogen on the metal).



Bernd Goldfuss*J. Organomet. Chem.* 691 (2006) 4508

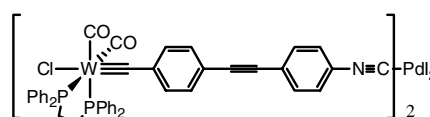
Electronic differentiations in palladium-catalyzed allylic substitutions

In Pd-catalyzed allylic substitutions, the sensitivity for electronic differentiation is higher for earlier transition structures, due to closer Pd-C_α contacts. This even overcompensates smaller intrinsic differentiation with *para*-nitro pyridine ligands, which yields the highest *cis* vs. *trans* differentiation and selectivity.

**Marie Pui Yin Yu, Vivian Wing-Wah Yam, Kung-Kai Cheung, Andreas Mayr***J. Organomet. Chem.* 691 (2006) 4514

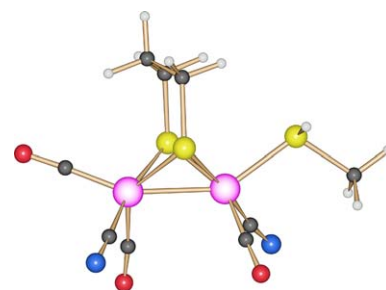
Electronic communication between tungsten alkyidyne and metal isocyanide complex fragments across phenyleneethynylene bridges

Heteronuclear metal complexes such as [Cl(CO)₂(dppe)W≡C(-C₆H₄-C≡C)_p-C₆H₄-N≡C-]₂PdI₂ (*p* = 0–3) have been prepared. The electronic interaction between the remote metal centers has been probed by a variety of spectroscopic techniques.

**Prabha Jayapal, Mahesh Sundararajan, Ian H. Hillier, Neil A. Burton***J. Organomet. Chem.* 691 (2006) 4532

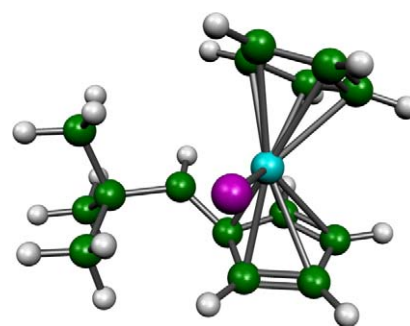
Structure and ionization energies of some analogues of iron-only hydrogenases studied by density functional theory methods

Density functional theory calculations are used to predict the structure and the ionization energies of some analogues of iron-only hydrogenases.

**Rainer Koch, Eva Bölter, Jörg Stroot, Rüdiger Beckhaus***J. Organomet. Chem.* 691 (2006) 4539

Theoretical studies on titanium pentafulvene complexes

Six titanium pentafulvene complexes are theoretically investigated and indicate a gradual change of the fulvene ligand coordination to the titanium center for dianionic η^5, η^1 - to olefinic η^6 -coordination. Time-dependant DFT calculations reproduce the experimental UV data reasonably well. The absorption maxima correspond to a ligand-to-metal charge transfer from the HOMO to the LUMO+1 of the complexes.

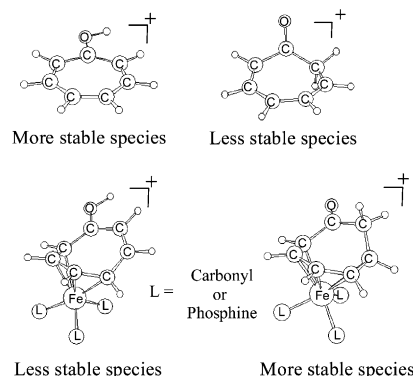


Alireza Ariafard, Zhenyang Lin

J. Organomet. Chem. 691 (2006) 4545

Theoretical studies on the protonation behavior of tropone and its metal complexes

Structures and stabilities of tropone and troponeiron complexes, (tropone)Fe(CO)₃, (tropone)Fe(CO)₂(PH₃) and (tropone)Fe(PH₃)₃, and their protonated species have been theoretically investigated. While the oxygen-protonated tropone is more stable than the carbon-protonated tropone, on the contrary, the carbon-protonated species of the tropone-iron complexes are more stable than the oxygen-protonated species.

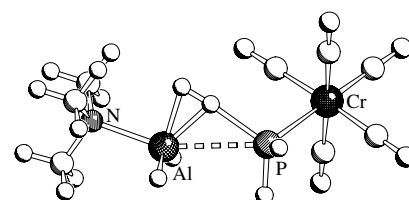


Ulf Vogel, Alexey Y. Timoshkin, Karl-Christian Schwan, Michael Bodensteiner, Manfred Scheer

J. Organomet. Chem. 691 (2006) 4556

The formation of Lewis acid/base stabilised phosphanyltriellanes – A theoretical and experimental study

Mechanistic investigations on the reaction mechanism and thermochemistry of the formation reactions of Lewis acid/base stabilised phosphanyltriellanes via H₂-elimination have been conducted. For the elements aluminium and gallium a five-coordinate transition state was determined, which gives an answer to the question why this reaction cannot be observed for boron containing molecules.



Isabella Hyla-Kryspin, Yong Nie, Hans Pritzkow, Walter Siebert

J. Organomet. Chem. 691 (2006) 4565

Molecular and electronic structure of (η⁵-pentaalkyl-2,3-dihydro-1,3-diboroly)(η⁵-penta-methylcyclopentadienyl)metal complexes, M = Fe, Ru

The X-ray diffraction study of the Ru sandwich derivative **2b** revealed a folding along the B···B vector of the heterocycle of 40.7°, which is due to electronic factors. The molecular and electronic structure of iron and ruthenium complexes have been studied by density functional theory (DFT) with the B3LYP functional and extended triple-ζ basis sets. The model complexes with a planar diboroly ligand **1'** (M = Fe) and **2'** (M = Ru) are by 24.9 and 24.5 kcal/mol less stable than the equilibrium folded structures of **1** and **2**, respectively.

