

**MS80.29.4***Acta Cryst.* (2005). A61, C102**14-Electron Metal Complexes Stabilized by  $M \cdots \eta^3\text{-H}_2\text{C}$  Agostic Interactions**

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The coordination of inert C-H bonds to a transition metal center is of fundamental interest for stoichiometric and catalytic reactions, with particular regard to the problem of alkane functionalization via C-H bond activation. Unfortunately, information on the nature of the primary adduct is still very scarce, since saturated hydrocarbons are notoriously very poor ligands.

By use of the phosphine  $\text{PR}_2(2,6\text{-Me}_2\text{C}_6\text{H}_3)$  (R = Ph, Cy), bearing two methyl groups in the *ortho* position, rare examples of 14-electron Ru(II) and Pt(II) complexes have been isolated [1]. Solid state studies, using both X-ray and neutron diffraction techniques, reveal that non-classical  $M \cdots \eta^3\text{-H}_2\text{C}$  agostic interactions take place and this result is in agreement with a structural survey on Cambridge databank, data in solution and a computational analysis. The reactivity of these complexes is reported, as well as the use of the Ru system as precursor for the preparation of highly active transfer hydrogenation catalysts.

[1] a) Baratta W., Mealli C., Herdtweck E., Ienco A., Mason S. A., Rigo P., *J. Am. Chem. Soc.*, 2004, **126**, 5549; b) Baratta W., Herdtweck E., Rigo P., *Angew. Chem. Int. Ed.*, 1999, **38**, 1629; c) Baratta W., Stoccoro S., Doppiu A., Herdtweck E., Zucca A., Rigo P., *Angew. Chem. Int. Ed.*, 2003, **42**, 105.

**Keywords:** agostic interactions, C-H activation, neutron structural determination

**MS80.29.5***Acta Cryst.* (2005). A61, C102**Asymmetric Hydrogenation: Novel Rh(I) Catalysts & Predictive DFT Calculations**

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Recent advances in the calculation of molecular energetics based on Density Functional Theory (DFT) have raised the hope that both properties and transition state energy profiles could be predicted.<sup>1</sup> We have been investigating homogeneous Rhodium(I) catalysts coordinated to novel carbohydrate-phosphinite ligands and now report our attempts to predict by calculation the enantiomeric excess (ee) values for hydrogenation using variants of these ligands. We have characterized by X-ray diffraction analyses two components: "CandyPhos"(1D-3,4-bis(O-diphenylphosphino)-1,2,5,6-tetra-O-methyl-chiro-inositol) and the active complex (CandyPhos)( $\eta^4\text{-}(Z,Z)\text{-cyclo-octa-1,5-diene}$ )-rhodium(I) tetrafluoroborate  $\text{CHCl}_3$  solvate.

DFT calculations have been carried out using the Amsterdam Density Function programme suite<sup>2</sup> utilizing these diffraction coordinates and the previous in-depth analysis by Feldgus & Landis<sup>3</sup>. We will report the crystallographic details and the interim calculation results for model enamides in comparison with our in-house determined ee values. We acknowledge with gratitude the support of Professor Tom Ziegler & Dr Michael Seth of the University of Calgary, Calgary, Canada.

[1] Ziegler T., *Can. J. Chem.*, 1995, **73**, 743-761. [2] SCIENTIFIC COMPUTING & MODELLING NV, ADF Program Suite, Vrije Universiteit, Theoretical Chemistry, Amsterdam, The Netherlands. [3] Feldgus S, Landis C.R., *J. Am. Chem. Soc.*, 2000, **122**, 12714-12727.

**Keywords:** asymmetric synthesis, theoretical structural modelling, X-ray diffraction crystallography

**MS81 TIME-RESOLVED POWDER DIFFRACTION FOR MATERIALS PRODUCTION AND PROCESSING***Chairpersons:* Eric Kisi, Paul Barnes**MS81.29.1***Acta Cryst.* (2005). A61, C102**Investigating Fast Solid State Reactions with Time-resolved Constant Wavelength Neutron Powder Diffraction at D20**

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D20 provides highest intensity in neutron powder diffraction. The incident flux on the sample reaches up to  $10^8$  n/s/cm<sup>2</sup> at 1.3 Å wavelength. A stationary, curved linear position sensitive detector covers continuously 153.6° in 2θ with 1536 cells in parallel. This makes D20 an ideal tool for *in-situ* diffraction studies with time constants even below a second and encourages the use of difficult sample environments. 4 vertically focusing monochromators, 15 take-off angles, and optional Soller collimators provide a large choice in Q-space, resolution, wavelength (0.8 to 2.4 Å), and flux, adapting D20 to various levels of crystallographic complexity and rapidity of an observed phenomenon. The continuous and simultaneous detection of series of complete diffraction patterns is necessary for the investigation of phase transitions during variation of a parameter like pressure or temperature (*thermodiffraction*). *One-shot* experiments study the structural evolution of solids *in situ* during a chemical reaction with single diagrams of down to 400 ms, quantifying short-living intermediate phases and elucidating subtle structural changes. High-resolution patterns can be obtained in a few minutes at high take-off angle. Faster, cyclic phenomena are observable in a stroboscopic acquisition mode. Time resolution is limited by the travel time of neutrons through sample and detection gap,  $\approx 10$  μs for thermal neutrons. An oscillating radial collimator with a focus aperture of 22 mm and full angular coverage suppresses background from sample environment.

**Keywords:** neutron powder diffraction, in-situ time-resolved powder diffraction, instrumentation

**MS81.29.2***Acta Cryst.* (2005). A61, C102**Time-resolved Studies on Materials using Synchrotron Radiation at the ESRF**

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Time-resolved studies at the European Synchrotron Radiation Facility in Grenoble are becoming more and more important and span a wide range of fields of applications. The talk will outline the possibilities at the ESRF including X-ray sources, beamlines, detectors and auxiliary equipment.

The talk will be illustrated by examples of work performed on self-generated high temperature synthesis, batteries, annealing processes, phase transitions, grain growth as well very fast reactions on photo-dissociation.

**Keywords:** synchrotron radiation, time-resolved studies, chemical reactions

**MS81.29.3***Acta Cryst.* (2005). A61, C102-C103**In-situ X-ray Diffraction Studies into Pressure Acid Leaching of Lateritic Ores**

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Nickel is the earth's 22<sup>nd</sup> most abundant element but it is not found in its native form other than in meteorites. Increasing world demand for nickel is reflected by its recent price increase. The majority of nickel is refined from sulphide ores but the oxide ores or laterites (sapolite, nontronite, limonite) represent the largest reserves