



# Seminarios itinerantes

**Paul J. CHIRIK**

*Princeton University, NJ, EE.UU.*

**25 a 29 de Abril 2016**

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## ***Catalysis with Earth abundant elements***

**Lunes, 25 de Abril, Universitat Autònoma de Barcelona**

12 h, Facultat de Química ([agusti@klingon.uab.es](mailto:agusti@klingon.uab.es))

**Viernes, 29 de Abril, ICIQ, Tarragona**

12 h, ICIQ Auditorium ([ashafir@ICIQ.ES](mailto:ashafir@ICIQ.ES))

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## ***Hydrocarbon functionalization and upgrading with Earth abundant metal catalysts***

**Martes, 26 de Abril, IIQ, CSIC – Universidad de Sevilla**

12 h ([campora@iiq.csic.es](mailto:campora@iiq.csic.es))

**Jueves, 28 de Abril, ISQCH, CSIC – Universidad de Zaragoza**

12 h, Sala de Grados de la Facultad de Ciencias ([sola@unizar.es](mailto:sola@unizar.es))

**GEQO**

Grupo Especializado de Química  
Organometálica de la Real Sociedad  
Española de Química

RSEQ  
Real Sociedad Española de Química  
El Sitio de la Química en España

## Catalysis with Earth abundant elements

Transition metal catalysis has revolutionized modern society by enabling new chemical transformations with unprecedented activity and control over selectivity. Applications range from the synthesis of new silicone materials, transforming hydrocarbon fuels to accessing new building blocks for pharmaceuticals. Our laboratory has been actively engaged in developing catalysts based on earth abundant elements rather than more traditionally deployed precious metals. The inspirations for this chemistry extend beyond catalyst cost; ultimately we aim to discover new reactivity that exploits the unique electronic structures of first row transition metals. My lecture will focus on two complementary approaches to this challenge. The first explores redox-active ligands, those that engage in reversible radical chemistry with the metal center, while the second employs a more traditional strong field ligand approach to engender more electron rich metal complexes. These two extremes define a continuum of reactivity ranging from new iron catalysts for commercial silicone production (*Science* **2012**, 335, 567) to the asymmetric hydrogenation of alkenes (*Science* **2013**, 342, 1054), C-H functionalization (*J. Am. Chem. Soc.* **2014**, 136, 4133) and radiolabeling (*Nature* **2016**, 529, 195), important transformations with pharmaceutical relevance. More recently we have been focused on the discovery of new catalytic reactions for the valorization of simple alkenes – those that are now overabundant due to the development of vast natural gas reserves. An iron-catalyzed method for the diastereo- and regioselective intermolecular [2+2] cycloaddition of commodity alkenes has been discovered (*Science* **2015**, 349, 960). Through continued ligand evolution and understanding of electronic structure, we have discovered base metal catalysts that promote chemistry unknown with established precious metal variants. The mechanisms of the various catalytic transformations, the importance of electronic structure controlled through ligand manipulation and strategies for imparting air stability will be highlighted throughout.

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### Hydrocarbon functionalization and upgrading with Earth abundant metal catalysts

Transition metal catalyzed reactions have revolutionized chemical synthesis as applied to the preparation of bioactive molecules and drug compounds. Most of these transformations rely on the least abundant elements in the Earth's lithosphere – palladium, iridium and rhodium – and raise concerns about toxicity and sustainability. My lecture will focus on catalysis with Earth abundant transition metals that, in addition to cost and environmental advantages, offers unique reactivity that will enable new methods for the manipulation and functionalization of abundant hydrocarbons. Applications range from the upgrading of commodity olefins such as ethylene, propylene and butadiene (*Science* **2015**, 349, 960) to the radiolabeling of drug-like lead compounds (*Nature* **2016**, 529, 195). Rational control the electronic structure of cobalt catalysts has resulted in highly active catalysts for the C(sp<sup>2</sup>-H) (*J. Am. Chem. Soc.* **2014**, 136, 4133) and C(sp<sup>3</sup>-H) bonds (*J. Am. Chem. Soc.* **2016**, 138, 766). More recent studies have focused on both cobalt and more recently nickel compounds for the polyfunctionalization of C(sp<sup>3</sup>-H) bonds where multiple C-H bonds on a single carbon are transformed into functional groups. These methods do not rely on directing groups but rather inherent electronic and steric differences associated with specific carbon-hydrogen bonds. A third area of interest, conducted in collaboration with Bristol-Myers Squibb, explores new iron and cobalt catalysts as alternatives to palladium for the most widely applied carbon-carbon bond forming reactions utilized in the pharmaceutical industry. The structural similarity among ligand platforms culminates in a new method for one-pot site selective C-H arylation in the absence of directing groups using an Earth abundant metal catalyst. The electronic structure of the catalyst precursors, the organometallic chemistry of relevant intermediates and the mechanisms of catalytic turnover will be an emphasized throughout.



Paul CHIRIK was born in 1973 outside of Philadelphia, PA. In 1995 he earned his Bachelor of Science in Chemistry from Virginia Tech. During that time, he conducted undergraduate research with Professor Joseph S. Merola studying aqueous iridium chemistry. Chirik earned his Ph. D. with Professor John Bercaw at Caltech in 2000 and was awarded the Hebert Newby McCoy award for his dissertation on metallocene catalyzed olefin polymerization. After a brief postdoctoral appointment with Professor Christopher Cummins at MIT, Chirik began his independent career at Cornell University in 2001. In 2006, he was promoted to Associate Professor and in 2009 was named the Peter J. W. Debye Professor of Chemistry. In 2011, Chirik and his research group moved to

Princeton University where was named the Edwards S. Sanford Professor of Chemistry. His teaching and research have been recognized with an Arthur C. Cope Scholar Award, the Blavatnik Award for Young Scientists, a Packard Fellowship in science and engineering, a Camille Dreyfus Teacher Scholar Award and an NSF CAREER Award. He is currently the Editor-in-Chief of *Organometallics* and Associate Director of the Andlinger Center for Energy and the Environment.

*Edwards S. Sanford Professor of Chemistry,  
Princeton University, Frick Laboratory, 292. Princeton, NJ 08544-1023, USA*

pchirik@princeton.edu  
<http://chemists.princeton.edu/chirik/>

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