Redox activity of carbene ligands;

Convergent and divergent radical-type pathways of 'carbene radicals'

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28 de Marzo de 2017
12:00
Sala de Grados de la Facultad de Ciencias

CICLO CONFERENCIAS **ISQCH** 2017

Instituto de Síntesis Química y Catálisis Homogénea
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C/ Pedro Cerbuna, 12. Zaragoza 50009. Spain
CSIC Consejo Superior de Investigaciones Científicas
Universidad Zaragoza
Facultad de Ciencias Universidad Zaragoza
GEQO Grupo Especializado de Química Organometálica de la Real Sociedad Española de Química
RSEQ Real Sociedad Española de Química

Redox activity of carbene ligands; Convergent and divergent radical-type pathways of 'carbene radicals'

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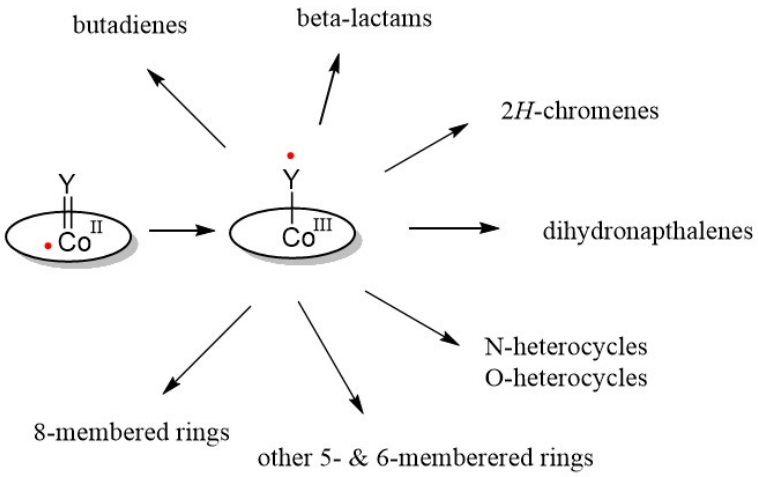
Radicals are intrinsically reactive, and were long believed to be "too reactive to be selective". However, in the coordination sphere of transition metals highly selective radical-type processes are certainly possible. In fact, radical-type reactions are tremendously important in several bio-synthetic pathways mediated by metallo-enzymes. Nature solves its most difficult and most interesting bio-synthetic problems with radical-reactivity. Yet, despite their radical-nature, these reactions proceed with ultrahigh precision and selectivity.



Inspired by such intriguing catalytic radical-type transformations mediated by metallo-enzymes, we are investigating new catalytic radical-type transformations mediated by synthetic (open-shell) organometallic catalysts. This presentation is focused on the diverse radical-type reactivity of cobalt-carbene (and nitrene) complexes, in which the transient reactive moieties act as redox active ligands producing discrete carbene (and nitrene) radicals. Such species provide unique opportunities in developing new catalytic ring-closure protocols. Here we report on their diverse radical-type pathways, revealing both convergent pathways and unique divergent routes to a variety of desirable organic ring products.

Bas de BRUIN studied chemistry at the University of Nijmegen from 1989-1994. He obtained his Ph. D. (April 20, 1999) from the same university (Rh Mediated Olefin Oxygenation). He did his postdoc in the group of Wieghardt at the Max-Planck Institut für Bioanorganische Chemie (Mülheim a/d Ruhr, Germany, April 1999-April 2000) for which he obtained an *Alexander-von-Humboldt fellowship* in 1999. After his postdoc he returned to the University of Nijmegen as an assistant professor in Inorganic Chemistry (Metal-Organic Chemistry), where he was involved in several research activities ranging from olefin oxygenation, radical organometallic chemistry, EPR spectroscopy, catalysis, light-switchable redox bistable molecules, DFT calculations, and (catalytic) synthesis of new materials. September 2005, Bas de Bruin obtained an *NWO-VIDI grant* to uncover new catalytic reactions. November 2005 he moved to the University of Amsterdam (UvA, group Reek, Homogeneous and Supramolecular Catalysis), where he was promoted to Associate Professor (UHD, October 2008). January 2013 he was promoted to Full

Professor (chair) at the same university.

Bas de Bruin presently focuses at the development of new tools in homogeneous catalysis, using metals in unconventional oxidation states and unconventional ligands, specifically aiming at the development of new catalytic reactions. In 2008 he obtained a prestigious ***ERC Starting Grant*** (first round of the EU 7^{th} framework Ideas Program; ERC = European Research Council). In 2012 he obtained a prestigious ***NWO-VICI grant*** to investigate new controlled (catalytic) radical-type transformations. Bas de Bruin is involved in teaching Inorganic Chemistry, Thermodynamics, Organometallic Chemistry, Bioinorganic Chemistry, Homogeneous Catalysis and (Catalytic) Reaction Mechanisms.