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Editorial

NHC Ligands in Organometallic Chemistry and Catalysis

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Abstract

Thanks to their appealing properties, N-Heterocyclic Carbene (NHC) ligands have gained considerable significance as powerful ligands in organometallic chemistry and catalysis. Twenty-two excellent research articles are gathered in this Special Collection, showcasing the different application domains and current trends in the organometallic chemistry of NHCs.

Manuscript

N-Heterocyclic Carbenes (NHCs) are undoubtedly among the most powerful tools in modern chemical sciences, and they are attracting ever-growing interest as organocatalysts, as stabilizing entities for radical species, or as outstanding ligands in main-group, transition-metal, nano- and surface chemistries.

This Special Collection of the European Journal of Inorganic Chemistry (EurJIC) focuses on the applications of NHC ligands in organometallic chemistry and catalysis and aims to highlight the effervescence of the field. Their extraordinary stereoelectronic properties, facile accessibility and synthetic flexibility are key features that have stimulated their application as ligands in functional organometallics. NHC-metal complexes have indeed shown excellent performances in

homogeneous catalysis, supramolecular, medicinal chemistry, and material science. Noteworthy, they have received the qualification of SMART ligands for catalysis, as they are Switchable, Multifunctional, Adaptable, or Tunable, and therefore able to directly interact with the substrate or modify their steric or electronic properties to fulfill the requirements of a defined catalytic transformation. This Special Collection gathers twenty-two contributions, written by some of the international leading researchers in this field, and covering various aspects of NHC-complexes.

An important part of these articles deals with the synthesis, the study of the structural features and reactivity of novel complexes bearing NHCs. In the last decade, the synthesis of NHC-metal complexes has been greatly facilitated by the advent of the “weak-base route”, based on the use of a mild base under practical conditions. Cazin and Nolan reported a mechanistic investigation into the synthesis of Rh(acac)(CO)(NHC) complexes based on this synthetic route, while Bertrand and Jassar implemented the latter for the synthesis of Cyclic (Alkyl)(Amino)Carbene copper(I) complexes. Noteworthy, the last publication deserved the distinction of very important paper.

Organometallic catalysis continues to be an important field of study and constituted the main part of contributions: Rhodium(I) complexes bearing a hydroxyl-functionalized 1,2,3-triazolylidene ligand catalyzed the hydrosilylation of terminal alkynes and the 1,4-addition of arylboronic acids onto α,β -unsaturated ketones as found by Mendoza-Espinosa. Likewise, non-chelating bis-NHC ligands led to more efficient Pt-based catalysts than their monodentate counterparts in hydrosilylation of internal alkynes, as defined by Žak. Ru-catalyzed dehydrogenative β -alkylation of secondary alcohols with primary alcohols and dimerization of terminal alkynes were investigated by Bellemin-Lapponnaz and Achard and by Song, respectively. NHC-Ir complexes were evaluated in formic acid dehydrogenation and water oxidation by Iglesias and Albrecht, respectively. Noteworthy, Buchmeiser disclosed new molybdenum silyloxy alkylidene complexes supported by NHC ligands, which are stable in air and highly active in alkyne metathesis. In the same approach towards earth-abundant metal catalysts, NHC-Mn complexes were developed and studied in hydrogenation of heteroaromatics by Choudhury and in hydrosilylation by Lugan and Valyaev.

Biological effects of NHC-metal complexes are also a relevant research field. In this special collection, two contributions were focused on this aspect. Pd(II) indenyl complexes with monodentate NHC were evaluated as antiproliferative agents against various ovarian cancer cell lines by Scattolin and Visentin, and cationic NHC-gold complexes bearing a pendant phosphonium groups were tested against MCF7 cancer cell lines by Bellemin-Lapponnaz and Tubaro.

Cyclometallation of NHC ligands in ruthenium complexes was investigated by Mahon and Whittlesey upon mixing $\text{RuHCl}(\text{PPh}_3)_3$, IMes, and ZnMe_2 , and by Kajetanowicz, Bastin, Grela, and César in order to generate Z-selective olefin metathesis catalysts.

Coordination of bis-phenolate NHC pincer ligands was investigated with scandium(III) by Trifonov and with vanadium by Hohloch. In the latter case, these ligands allowed the access to twenty-one complexes in three oxidation states [V(III), V(IV), V(V)]. The redox properties of NHC-metal complexes were also studied by Smith et al. on square-planar Co(I/II) complexes supported by bulky, strongly donating bis(NHC)borate ligands and by Radius et al. on linear nickel complexes of type $[\text{Ni}(\text{NHC})_2]^{0/+}$. These reports confirmed the ability of NHC to stabilize transition metals in various oxidation states.

Last but not least, while a novel four-membered NHC based on 1,3-diazetidene was disclosed by Ganter, Plenio reported extremely bulky NHC ligands based on the incorporation of triptycene groups as N-substituents. The beneficial impact of the ring-expansion of the carbenic heterocycle was exemplified by Mahon and Liptrot through the stabilization of linear dicoordinate NHC copper(I) boryl complexes by a six-membered NHC ligand. Of note, the latter article was selected as a very important paper.

A special thank goes to the many authors and reviewers for their invaluable contributions, as well as to the highly professional Editorial Team of *EurJIC*. This Special Collection aims at giving a flavor of this highly active and flourishing research field, we sincerely hope that readers will find the contributions interesting and inspiring.

Bios



Macarena Poyatos received her Ph.D. Degree (2005) at Jaume I University, under the supervision of Prof. Eduardo Peris. She then moved to Strasbourg as a postdoctoral fellow under the supervision of Prof. Lutz H. Gade and Dr. Stéphane Bellemin-Lapponnaz. In 2006, she joined Prof. Robert H. Crabtree's group at Yale University, where she stayed for two years. In 2010, she was awarded a 'Ramón y Cajal' contract and in 2019 she was appointed 'Profesora Titular' at Jaume I University. She is focused in the design and preparation of organometallic complexes bearing switchable NHC ligands.



Vincent César obtained his Ph.D. from the University of Strasbourg (France) in 2004 under the supervision of Prof. Lutz H. Gade and Dr. Stéphane Bellemin-Lapponnaz. He then joined the group of Prof. Dr. Alois Fürstner at the Max Planck Institut für Kohlenforschung in Mülheim (Germany) as an Alexander-von-Humboldt fellow. In 2006, he was appointed CNRS researcher at the Laboratoire de Chimie de Coordination (LCC) in Toulouse, France, where he is now CNRS senior researcher. His research interests include diverse aspects of organometallic synthesis, reactivity and homogeneous catalysis around N-Heterocyclic Carbenes.