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## Introduction to the *Ennobling a Base Metal: Presenting Copper in Organometallic Chemistry Issue*

Copper is the cheapest and most abundant member of the coinage metal series: Cu, Ag, and Au. In its metallic form it has been a marvel for engineers and artists for centuries. Copper metal melts at a relatively low temperature; its alloys find application in fields as diverse as the construction industry, in the transport of electricity, and in making sculptures. Its salt forms are used as biocides: e.g., as antifouling agents.

The first uses of copper in academic chemistry and the chemical industry started with the pioneering work of Ullmann and, independently, Goldberg in the early 1900s, on biaryl synthesis, copper-mediated aromatic nucleophilic substitution reactions, etc. Interestingly, many of these early reactions centered on C–C and C–X cross-coupling reactions and the various industrial applications involved in the production of intermediates for pharmaceuticals, agrochemicals, and polymers. Copper's "base" origins allowed it to be used economically even in stoichiometric applications, while more recently its attributes have been "ennobled" for uses where catalytic transformations are essential.

Over the previous three decades C–C and C–X cross-coupling reactions gradually became the domain of the precious or noble metals. However, the recent quest for sustainable approaches in organic synthesis spurred renewed interest in copper-mediated and -catalyzed reactions. Interestingly, the palladium- and copper-catalyzed versions of C–C and C–X coupling reactions show different but complementary scope (see Beletskaya and Cheprakov, within).

Phenyl- and methylcopper(I) (highly explosive as a dry solid) were the first organometallic copper compounds (synthesized by Reich (1923) and Gilman (1952), respectively). The importance of organocopper materials as intermediates in organic synthesis was obvious early on from observations by Ullmann in the copper(0)-catalyzed synthesis of biaryls from aryl chlorides and later by Grignard, who showed that by addition of copper salts the reactivity of a Grignard reagent could be selectively turned from its common 1,2-addition reactivity into a 1,4-addition in its reaction with  $\alpha,\beta$ -unsaturated ketones. It appeared that these reactions involved the in situ generation of highly reactive organocuprates as the key intermediates.

During the past 40 years, organocuprates have gained the position of privileged reagents in organic synthesis. Numerous important reactions have been discovered, starting with the C–C cross-coupling reactions between organocoppers and organic halides in the 1930s. Since then numerous other reactions were developed, ranging from the early discovery of 1,4-addition reactions of cuprate type reagents derived from Grignard reagents, to  $\alpha,\beta$ -unsaturated ketones, up to the directed ortho-cupration reactions that have become the subject of recent studies.

The understanding of the structural features of organocopper(I) materials is rapidly growing and comprises all aspects of supramolecular chemistry, including the self-assembly of the organocopper(I) unit to homo or hetero (with

other salt or organometallic groupings) aggregated species involving electron-deficient C–anion bonding to two coppers or one copper and one other metal, e.g. Li in the case of a cuprate, as well as formation of contact ion or solvent separated ion pairs, depending on the solvent used.

This special issue contains a series of nearly 40 research articles, reviews, and perspectives spanning modern organo-copper chemistry with interests in structure, mechanism, catalysis, synthesis, computation, and materials. From a quantitative point of view, it is remarkable that half of these articles correspond to catalysis induced by copper compounds, in what some consider the current most interesting feature of this metal. Structure and characterization follow in this ranking. In spite of decades (maybe a century) of progress in these areas, we continue to expand our knowledge of the chemical properties of copper compounds.

Some contributions based on catalysis refer to cross-coupling reactions, for which our know-how continues to increase now more than 100 years after the aforementioned work by Ullmann and Goldberg. New insights into the catalytic formation of C–X bonds by this methodology have been provided by contributions from the groups of Hartwig, Evano, and Ribas, with reviews by Beletskaya and Jutand. The copper azide–alkyne cycloaddition reaction (CuAAC), one of the typical examples of "click chemistry", also appears in this issue, described in the work developed by the groups of Cazin and Gautier. The nitrene transfer reaction has been thoroughly reviewed by Warren for C–H bond amidation and applied by Pérez in the synthesis of hydropyridines from furans. The role of the copper-based atom transfer radical polymerization is presented from Matyjaszewski's laboratories. Boron-based reagents serve nicely for the catalytic formation of allenyl silanes or for borylated dicarbonylic compounds, as shown by Sawamura and Fernández, respectively. Silyl conjugate additions to dienones have been well developed in Hoveyda's lab. Mechanistic studies of the methoxylation of arylboronic esters are described by Stahl. To complete this catalytic part of the issue, from an experimental point of view, enantioselective hydroaminations, aromatic functionalizations, and dimerization of nitronates and enolates are presented by Chemler, Nicholas, and Daugulis, respectively.

Whereas some of the above contributions contain theoretical calculations in part, others are completely devoted to such issues. This is the case for work from Krause's lab, regarding the Cu–H catalytic synthesis of hydroxyallenes, or the studies with azomethine ylides by Zhenyang Li. Liebeskind and Musaev have also contributed with theoretical mechanistic studies on the aerobic cross-coupling reaction of thiol esters and boronic acids.

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The classic and fundamental topic of the synthesis and characterization of novel copper complexes also finds room in this issue. Thus, Dias and Xiong describe a series of ethylene complexes, in separate contributions. Hofmann reports on compounds bearing NHC-P ligands, a topic related to that by Kunz's lab, presenting bis(NHC)-containing copper complexes. NHC-Cu compounds have also been developed by M. Thompson in order to study their photochemical properties. The López laboratory has investigated interesting three-coordinate Cu-carbene complexes not involving NHC ligands. Mixed-valence Cu(I)/Cu(II) species have been prepared by the group of Pombeiro with a variety of ligands, including 1,3,5-triaza-7-phosphaadamantane (PTA). Vicic has focused on oxygen-bound trifluoromethoxide compounds in his contribution. This area is fulfilled with two reviews focusing on alkyne and alkynide complexes by Lang and on carbonyl and cyanide compounds by Pike. The use of  $\beta$ -diketimine complexes as precursors for chemical vapor deposition has been described by J. Thompson.

As already mentioned, aryl- or alkylcopper (organocopper) reagents were discovered in the first quarter of the last century. And yet, this still constitutes a quite active area of research. A personal view of organocopper chemistry is provided by van Koten in a review/perspective article. In addition, Meyer has reviewed the use of mesitylcopper from a synthetic point of view. From here, a series of contributions regarding such compounds complete this issue. Thus, dimethylcuprate chemistry is provided by Bertz, with two papers related to  $\pi$  complexes generated from that reagent. Casey's lab presents an experimental/theoretical study on the reaction of enones with lithium dimethylcuprate. The latter species as catalysts for decarboxylative coupling reactions have been studied by O'Hair. Finally, a series of lithium and magnesium organocuprates have been prepared and characterized in the solid state by Davies.

When organizing a task such as this issue, it is obvious that there are always some missing authors; however, the idea of presenting a current overall picture of the importance of copper in organometallic chemistry at the beginning of this century seems to be accomplished on the basis of the list of contributors. We are indebted to their efforts and enthusiasm to participate in this project. We hope that the organometallic community will find these contributions of interest not only for those working with this "noble" coinage metal but also to those that could be now at the beginning of their careers and are searching for a place to make an impact in the chemistry "arena".

Finally, the cover art for this issue intends to convey the strong excitement for copper chemistry found throughout the organometallic community, with the enthusiasm resident in the science showcased by the many compelling contributions contained within this issue. It also features the more subtle message that future generations invite present researchers to continue to make novel inventions and discoveries using abundant, recyclable metals, such as copper.

**Gerard van Koten**, Guest Editor

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### Biographies



Prof. Dr. Gerard van Koten (born 1942) is a Distinguished University Professor at Utrecht University and Honorary Distinguished Professor (2011–) at Cardiff University U.K. He is well-known for his fundamental and applied organometallic research comprising organocopper and XCX-pincer metal complexes. The preparation and use of the first examples of homogeneous metallodendrimer catalysts demonstrate his interest for supramolecular systems with (organometallic) catalytically active functionalities. He is a member of the Royal Netherlands Academy of Arts and Sciences and the governmental Foresight Group Chemistry that is responsible for the coordination and initiation of innovation in Industry and Academia in The Netherlands. During the period 2002–2012 he was Chairman of the Governmental committee that is responsible for the renewal of the Chemistry Educational Program at the preuniversity level.



Pedro J. Pérez (Aroche, Spain, 1965) graduated in Chemistry in 1987 and received his Ph.D. degree in Chemistry (1991) at the Universidad de Sevilla, under the supervision of Prof. Ernesto Carmona. As a Fulbright Scholar, he then joined Prof. Brookhart's group at UNC-Chapel Hill (USA), where he started research related to the use of copper-based catalysts for diazo decomposition. In 1993 he moved to a new University founded in Huelva, as an Assistant Professor (1993–1995), later becoming Lecturer (1995) and finally Professor of Inorganic Chemistry (2005). The general research interest of his group is related to the development of late-transition-metal complexes for their use as catalysts in transformations with low-reactivity substrates such as plain alkanes. He is the current director of the Center for Research for Sustainable Chemistry (CIQSO, <http://www.uhu.es/ciqso>) and group leader of the Homogeneous Catalysis Laboratory, an Associate Unit to the Spanish National Council of Research (CSIC). In 2007 he was honored by the Royal Society of Chemistry of Spain with the Inorganic Chemistry Award.



Lanny S. Liebeskind, Samuel Candler Dobbs Professor of Chemistry at Emory University, graduated from the State University of New York at Buffalo in 1972 with a B.S. degree in chemistry. A Ph.D. in 1976 from the University of Rochester, where he worked with Andrew S. Kende, was followed by a year at the Massachusetts Institute of Technology as a National Science Foundation Postdoctoral Fellow and a year at Stanford as a National Institutes of Health Postdoctoral Fellow, both in the laboratories of Nobel Laureate K. Barry Sharpless. In 1978 he was appointed Assistant Professor of Chemistry at Florida State University, was promoted to Associate Professor in 1983, and then moved to Emory University at the beginning of 1985. He was promoted to Professor in 1988 and at the same time was awarded a Samuel Candler Dobbs Chair in Chemistry. Professor Liebeskind has served since 1990 as an Associate Editor of the journal *Organometallics*, published by the American Chemical Society. Professor Liebeskind's research interests have centered on the discovery of new reactions and the application of transition-metal chemistry to challenging problems in organic synthesis. Professional international travel and the many positive experiences that come with it have helped Professor Liebeskind avoid the myopia that can sometimes result from never leaving the borders of the continental United States.