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Smart use of metal reagents unlocks greener organic synthesis

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Main group and transition metal compounds are ubiquitous in modern organic synthesis either as reagents or as catalysts for various chemical transformations. Through the 20th century, the application of organometallic compounds progressively evolved from the use of simple Grignard and organolithium derivatives as carbon-based nucleophiles to the design of sophisticated transition metal catalysts capable to perform a myriad of reactions with high atom economy and functional group tolerance, eventually in a highly enantioselective manner. Noteworthy, many of such transformations, considered as impossible for a long time from the point of view of classic organic chemistry, now account for new efficient instruments for the preparation of elaborated organic molecules *via* unorthodox retrosynthetic connections.

Despite tremendous progress in this area, it should be noted that the majority of homogeneous catalytic processes still require complexes of noble transition metals. Yet, beyond the continuously increasing price and elevated toxicity of these elements [1], the later point being of particular importance for the pharmaceutical industry, the main forthcoming challenge to deal with is their limited stock in the Earth's crust [2], which will unavoidably lead to potential resource problems in a long-term perspective. Possible solutions to overcome such vital importance issues in the context of sustainable development include drastic optimization of the reaction conditions allowing to decrease the catalyst loading and/or facilitate precious metals recovery, or ideally their replacement with analogues based on abundant, cheaper and less toxic 3d or main group metals. Such alternative chemical processes would be even more attractive from practical point of view whenever the minimization of harmful organic solvents waste and/or the use of renewable sources of energy such as electricity and solar irradiation is also considered. The contributions gathered in this issue highlight the recent achievements in selected emerging topics directly relevant to the tackling these important challenges in the domain of green chemistry.

Though it has long been considered that organolithium and organomagnesium derivatives should be handled under strictly inert conditions **Vito Capriati and coll.** show in their contribution that a variety of main group species incorporating C-, N- or P-anionic moieties can be successfully used for organic synthesis in deep eutectic solvents or neat water under air. Importantly, it is demonstrated that such polar synthons are not only compatible with these counterintuitive reaction conditions, but also often afford better product yields in shorter reaction times than the procedures carried out in conventional ethereal solvents.

The quest for the decrease of precious metal content and organic solvent removal in transition metal catalyzed synthesis of amines was addressed by **Bruce Lipshutz and coll.** Here they show that both objectives could be simultaneously achieved *via* micellar catalysis in water using specifically designed surfactants and molecular- or nanoparticle-based palladium catalysts. Remarkably, this protocol permitted to reduce the amount of palladium by 1-2 orders of magnitude compared to standard reaction setup with possible catalyst recycling as well as to facilitate the final product isolation with low residual Pd contamination. In the same vein, **Valentine P. Ananikov and coll.** outline the peculiarities of cocktail-type systems in Pd-catalyzed cross-coupling processes. The most

salient feature of this approach resides in its self-tunable character due to the existence of the dynamic interplay between monometallic species, small clusters, and nanoparticles in solution thus leaving the nature to choose the most active metal form for each particular substrate and reaction type. Recent advances in metal-catalyzed reactions under mechanochemical conditions limiting to minimum the amount of any organic solvents is presented in the review by **Xavier Ottenwaelder, Tomislav Friščić and coll.** In addition to significantly reduced E-factor, such processes look optimal for the substrates having low solubility, allow the use of bulk metals or minerals as catalysts and sometimes lead to a different chemoselectivity relative to the one observed in solution.

The second group of mini-review articles of this issue nicely illustrate the advances and potential future impact of noble metal replacement in many important chemical processes. In particular, **Shaozhong Ge and coll.** show that rhodium complexes could be in some cases readily replaced for cobalt complexes in asymmetric alkene hydrogenation and hydroboration retaining excellent level of enantioselectivity. Though the catalytic activity and substrate scope for Co-catalyzed reactions still have to be improved, recent results clearly suggest that the ultimate goal to limit the consumption of this rarest platinum group metal in pharmaceutical industry may be achievable in the future. Similarly, **Jennifer M. Schomaker and coll.** present some convincing evidences that silver could be a viable alternative to gold for some enantioselective transformations of alkynes and alkenes. Taking into account that the development of efficient asymmetric gold-catalyzed processes remains highly challenging [3], the use of silver, beyond the economic benefits, can also lead to unusual reactivity modes due to the combination of a strong Lewis acidity with a unique redox behavior of this metal. The rapidly emerging application of manganese complexes in transfer hydrogenation of multiple carbon-carbon and carbon-heteroatom bonds is highlighted in the contribution of **Stéphanie Bastin, Jean-Baptiste Sortais and coll.** While this area still is in its infancy, the existence of numerous mechanistic parallels with ruthenium-based complexes, the emblematic catalytic systems in transfer hydrogenation, permit to forecast a bright future for the organometallic derivatives of this abundant metal in reduction catalysis. Since the beginning of the 21th century, photocatalytic transformations enabled by Ru- and Ir-based photosensitizers revolutionized many aspects of organic chemistry [4]. **Olivier Baslé** presents the current attempts to find sustainable alternatives to these classic systems derived from 3d metals for the application in valuable C–H bond activation processes. Several interesting results combined with an apparent simplicity of the metallic species engaged in these photocatalytic transformations demonstrate that such approach could be of interest from a practical point of view. Finally, the contribution of **Marc Magre, Magnus Rueping and coll.** shows that the replacement of precious transition metal catalysts does not necessarily requires the use their 3d analogues as magnesium compounds containing properly designed auxiliary ligands can do the same job. This statement was illustrated by the excellent performance of Mg-based catalysts in hydroelementation of various classes of organic compounds including the recent development of highly enantioselective ketone hydroboration, this reaction class being traditionally a pure prerogative of transition metal catalysts.

The final part of the issue illustrates the role of metal catalysis for addressing urgent societal challenges, namely the improvement of anthropogenic CO₂ balance [5] and the management of environmental pollution with end-of-life plastics [6]. One evident solution for the first problem deals with a larger use of carbon dioxide as cheap C1 synthon. **Carlo Nervi and coll.** outline the progress in the development of 3d transition metal catalysts for the electrocatalytic CO₂ reduction. In the case of a favorable evolution of such catalytic systems, the transformation of carbon dioxide into valuable simple molecules such as CO or formic acid using green electricity sources could be amenable to industrial production. Alternatively, **Yong-Yuan Gui, Da-Gang Yu and coll.** illustrate the outstanding potential of metal-catalyzed carboxylation of various types of organic molecules directly

with CO₂ to form selectively carboxylic acids being essential building blocks in organic chemistry. It is notable that the combination of metal catalysts with photo- and electrochemical activation in these reactions was particularly interesting in terms of chemoselectivity and substrate scope. Metal catalysis can influence environmental problems related to plastic materials either by facilitating the access to easily degradable polymers or through the chemical recycling of macromolecules to valuable products. The first point is addressed in the contribution of **Tarun K. Panda and coll.** describing the application of alkali-metal complexes for the *iso*-selective ring opening polymerization of *rac*-lactide. The second aspect reviewed by **Osama El-Sepelgy and coll.** is focused on the metal-catalyzed reductive depolymerization of polyesters, polycarbonates and polyamides to the corresponding alcohols and amine derivatives. Though this option remains highly challenging, the perspective to produce monomers directly from plastic waste without the use fossil-based resources looks extremely attractive in terms of circular economy.

I hope that you will enjoy reading this collection of mini-reviews from recognized scientists in each particular discipline, eventually providing some inspirations for your own research work.

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Conflict of interest

The author declares no competing financial interest.

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Biographical details

Dr. Dmitry A. Valyaev obtained his PhD in 2007 at the INEOS RAS (Moscow) and then spent there several years as Researcher. Since 2009, he performed three consecutive postdoctoral stays in France terminated by its recruitment in the Laboratory of Coordination Chemistry of CNRS in 2013. In 2018, he got the Habilitation from the University of Toulouse. His scientific interests mainly concern the

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