

Preface

We have long stopped wondering at the fantastic achievements of chemistry spanning from materials to the life sciences. The organometallic chemistry is undoubtedly amongst the most useful keys to new materials and technologies. Organometallic chemistry has successfully served as a bridge between organic and inorganic chemistry; it influenced a lot the coordination and physical chemistry, and resulted in a major breakthroughs in catalysis. New structures and new bond types, new reagents and catalysts, new mechanistic concepts, new possibilities for enantioselective transformations have been forthcoming from this bountiful source. Homogeneous catalysis by transition metal complexes enabled effective transformations, which could not be realized using traditional organic chemistry methods. Simple and versatile approaches to C–C and C–heteroatom bond formation, assembly of complex carbocyclic and heterocyclic systems have been discovered and implemented in the state-of-the-art organic syntheses. Enantioselective catalysis by chiral complexes opened routes to the synthesis of many important naturally occurring molecules, as well as new generation pharmaceuticals with high enantiomeric purities. These findings were recognized by the award of a Nobel Prize in chemistry in 2001.

The other breakthrough of the recent years is the development of catalytic systems employing very low concentrations of catalysts, thus being characterized by huge turnover numbers exceeding millions or even billions. Often very simple catalyst precursors can be used, with additional activation being achieved by advanced techniques, such as microwave heating, allowing for dramatic reductions of the reaction times from minutes to seconds.

One of the most serious drawbacks of homogeneous catalysis are the low stabilities of catalysts under reaction conditions, their high cost, and the sophisticated procedures required for post-reaction separation of catalyst from products. These problems can be effectively eliminated by the application of new catalytic systems combining the characteristics of homogeneous and heterogeneous catalysts, such as various biphasic systems, supported catalysts, encapsulated and other nano-sized particles, etc. The so-called smart or thermomorphic polymeric supports help chemists address

the known problems of common supported catalysts associated with ineffective functioning of catalytic centers located at solid support surfaces.

A few comments need to be made concerning the use of the term *atom efficiency*. Originally introduced by R. Sheldon, this term has since enjoyed considerable popularity. Briefly, this notion implies that a good reaction should transform as many atoms of the starting reagents into the products as possible. Absolute atom efficiency is thus achieved in addition or rearrangement reactions, while in substitution (metathesis) reactions, which inevitably give rise to a by-product, often a salt, cannot be *atom efficient*. Thus, it is evident that in order to fulfill this principle, substitution reactions should be replaced by addition reactions in as many cases as possible. This is unfortunately impossible in many practically important cases. The principle's major role is to attract attention to the development of new addition reactions involving the classical petrochemical raw materials – alkenes, dienes, acetylenes, as well as carbonyl compounds, etc. The emphasis on the no-waste procedures makes the atom efficiency principle the basis for the development of environmentally benign *green* technologies, which, in their turn, imply the use of catalysts.

This issue includes the contributions of many leading scholars in organometallic chemistry and catalysis. In spite of rather broad scope of chemistry involved all contributions share a common idea – the development of new methods allowing for improvement of efficiency of organometallic and catalytic reactions. Particularly amazing is the scope of metals involved – Pd, Cu, Ti, Cr, Rh, Ir, Re, Ni, etc. A broad geography of contributors including the teams from China, EC, Japan, Russia, and USA clearly shows the world-wide expansion of organometallic chemistry.

References

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