

Organometallics in Organic Synthesis: Introduction

“Organometallic Chemistry directed towards Organic Synthesis” (OMCOS) is the topic of a flourishing series of international conferences under the auspices of IUPAC. The last one (OMCOS 10) was held in Versailles, France, in 1999, and the next (OMCOS 11) will take place in July of 2001 in Taipei, Taiwan, as detailed in an announcement on the inside of the front cover of this issue. The steadily increasing number of participants from 230 at the first OMCOS conference in Fort Collins, CO, in 1981 to well over 1000 in Versailles in 1999 impressively reflects the ever growing importance that organometallics play in organic synthesis. In fact, many organometallic processes are unsurpassed in elegance and efficiency and have intruded into many related areas of research, making this field truly interdisciplinary. Moreover, with increasing societal attention to environmental concerns, organometallics continue to be viewed as catalytic agents par excellence for many chemical processes which have passed the barrier from research to industrial applications. Another important trend of the last decade is the steadily growing complexity of organometallic transformations which make multistep processes proceed in a single operation. All these developments undoubtedly are not yet at their peak, and they will continue to grow for the foreseeable future. In recognition of the expanding field of organometallic research, several topics of current and future interest are addressed and summarized in this thematic issue of *Chemical Reviews*.

The pole position is held by the article by Piet van Leeuwen with co-authors P. Kamer, J. Reek, and P. Dierkes. They present the concept of “ligand bite angles” and review the recognized effects in metal-catalyzed C–C bond formations. It significantly relates to most of the other contributions in this issue, as ligands make up a major part of a catalyst in any homogeneously catalyzed process.

Titanium plays the dominant role in the succeeding three articles. Andreas Gansäuer and co-author H. Bluhm review reagent-controlled transition-metal-catalyzed radical reactions in view of the latest developments of titanium-catalyzed diastereoselective pinacol reductions. Low-valent titanium species, generated by reduction of titanium(IV) derivatives, can act as precursors to reagents which are either

1,1-, 1,2-, 1,3-, or even 1,4-dicarbonyl synthesis equivalents as discussed by Oleg Kulinkovich and Armin de Meijere. The most extensive progress has undoubtedly been made in recent years with the synthetic applications of 1,2-dicarbonyl titanium intermediates generated from titanium tetraalkoxides and Grignard reagents, opening up new and easy accesses to cyclopropanols and cyclopropylamines both in inter- as well as intramolecular reactions. The same type of low-valent titanium intermediates generated by ligand exchange with alkenes and their reactions with esters and amides significantly broaden the scope of possible applications, as summarized by Fumie Sato and co-authors H. Urabe and S. Okamoto. The review by Ilan Marek highlights the synthesis and reactivity of sp^2 geminal bis(metallic) systems $=CMM'$. M and M' include various combinations of lithium, magnesium, aluminum, indium, gallium, zinc, zirconium, and titanium, with the ultimate achievement being a 1,1,2-trititanioalkene reagent generated from a 1-haloalkyne and a low-valent titanium intermediate.

Yoshinori Yamamoto with co-author S. Saito then discuss transition-metal-catalyzed regioselective approaches to polysubstituted benzene derivatives from three alkyne molecules or two alkynes and one alkene, the latter with subsequent elimination or oxidation. The metals utilized include nickel, rhodium, cobalt, ruthenium, and, in particular, palladium. The succeeding article by Peter Kündig with A. Pape and K. Kaliappan presents an overview over transition-metal-mediated dearomatization reactions, i.e., reactions leading from substituted aromatic compounds to synthetically useful cyclohexadienes in a regioselective way. Hans-Joachim Knölker's article deals with the synthesis of cyclohexadiene tricarbonyliron complexes and the asymmetric catalytic complexation of prochiral ligands. Thus, these two reviews nicely complement each other.

The focus of the succeeding article by Larry Yet is on the synthesis of medium-sized rings. The reviewed methodology includes ring-closing metathesis, free-radical, reductive, as well as nucleophilic cyclizations promoted by metals, palladium-catalyzed cyclizations, metal-catalyzed cycloadditions, and metal-promoted carbenoid cyclizations. Palladium catalysis dominates the next two reviews, the first of which

by Irina Beletskaya with co-author A. Cheprakov concentrates on the now widely used coupling of alkynyl and aryl halides or analogues with alkenes, the so-called Heck reaction, in particular the steadily advancing improvement of the catalysts. Reinhold Zimmer's contribution with co-authors C. Dinesh, E. Nandan, and F. Khan deals with palladium-catalyzed reactions of allenes, many of which are cascade reactions consisting of two or more steps and lead to impressive increases of molecular complexity in simple one-pot operations.

Stoichiometric reactions of transition-metal complexes are often the discovery stage of new catalytic reactions which are developed with great efforts when the stoichiometric variants open up novel and interesting transformations of organic molecules. Thus, the overview of Rai-Shung Liu with co-author Chien-Le Li on the synthesis of heterocyclic and carbocyclic compounds via alkynyl, allyl, and propargyl organometallics of cyclopentadienyl iron, molybdenum, and tungsten complexes describes such exploratory work which may well be as valuable for organic synthesis in the long run as fully developed catalytic processes. The next article by James Marshall on the synthesis of allylic, propargylic, vinylic, and arylmetal compounds from halides and esters via transient organopalladium intermediates can be seen in a similar context, while the contribution by Tien-Yau Luh with co-authors M. Leung and K. Wong concentrates on the metal-catalyzed activation of aliphatic C–X bonds in C–C bond formations.

For a long time, sulfur in any form had been considered as a poison for transition-metal catalysts.

However, recent developments have demonstrated that under appropriate conditions, metal-catalyzed substitutions with thiolates and additions of thiols as well as disulfides to multiple bonds, all forming new carbon–sulfur bonds, can be brought about very efficiently, as extensively discussed by Take-aki Mitsudo with co-author T. Kondo. Transition-metal-catalyzed additions of silicon–silicon and silicon–heteroatom bonds to carbon–carbon multiple bonds are summarized in the succeeding article by Yoshihiko Ito with co-author M. Suginome. Finally, Mark Lautens with co-authors N. Smith and J. Mancuso review metal-catalyzed hydrostannations of unsaturated organic molecules. All three articles in this concluding set emphasize the importance of metal catalysis in the preparation of valuable intermediates for the synthesis of complex natural and nonnatural organic molecules.

Considering the importance and scope of applications that organometallic chemistry has achieved in the second half of the past century, this thematic issue naturally can only present an exemplary part of the whole story. However, each of the articles presents a “state of the art report” on an important concept, reaction type, or transformation that nowadays plays a major role in organic synthesis.

Armin de Meijere
Institut für Organische Chemie,
Georg-August-Universität Göttingen

CR000424B