

Introduction to Frontiers in Transition Metal Catalyzed Reactions (and a Brief Adieu)

1. INTRODUCTION TO THIS THEMATIC ISSUE

The subject of this issue of *Chemical Reviews*, “Transition Metal Catalyzed Reactions”, represents an established area of endeavor, but one in which important new and often unexpected developments continue unabated. Notably, three Nobel Prizes in Chemistry have been shared among nine individuals for their seminal contributions to this field during the past decade (2001, 2005, and 2010). In the following pages, a new generation of experts present 30 in-depth reviews dealing with transition metal catalyzed reactions and/or ligand platforms that are experiencing rapidly increasing application. Some of these will undoubtedly earn their discoverers awards in the future, and it would not be surprising if another Nobel Prize were among them.

Transition metal catalysts can now be bought to bear on just about any type of bond-forming or bond-breaking reaction involving carbon. One current focus involves the replacement of aryl halides and pseudohalides used in coupling reactions by the parent arenes themselves. This theme is represented in several articles, the first being by Le Bras and Muzart, who describe recent progress on intermolecular dehydrogenative Heck reactions. The following treatise, by Yeung and Dong, focuses on a mechanistically broader spectrum of processes in which carbon–carbon bonds are formed from two carbon–hydrogen bonds. Sun, Li, and Shi then survey the use of iron catalysts for numerous types of carbon–hydrogen bond functionalizations. Finally, Ackermann examines the special mechanistic role of catalyst carboxylate ligands in facilitating sp^2 and sp^3 carbon–hydrogen bond activations, especially direct arylations and alkylations.

Next up is a series of articles dealing with carbon–carbon bond-forming reactions in which one coupling partner features a carbon–heteroatom bond. In the first, Rosen, Quasdorf, Wilson, Zhang, Resmerita, Garg, and Percec organize the rapidly growing number of nickel-catalyzed cross-coupling reactions that utilize arenes with carbon–oxygen bonds, helping to decrease reliance upon aryl halides. Jana, Pathak, and Sigman then review advances in palladium-, nickel-, and iron-catalyzed cross-coupling reactions that employ main group metal alkyls (boron, magnesium, indium, silicon). Metal-catalyzed reactions are now major players in materials science, and Carsten, He, Son, Xu, and Yu highlight the applicability of multiple Stille reactions (polycondensations) for assembling functional oligomers and macromolecules. Finally, Partyka examines the transmetalation of unsaturated boron-based carbon nucleophiles to d-block metals that participate in coupling reactions.

Transition metal catalysts offer many avenues for the introduction of heteroatoms. The first article in this section, by Beletskaya and Ananikov, provides an overview of carbon–sulfur, –selenium, and –tellurium bond formation via cross-coupling and atom economical addition reactions. Smith and Hii then systematize the rapidly growing area of enantioselective α -heterofunctionalization of carbonyl compounds. In one of two articles dealing with gold catalysts, Corma, Leyva-Pérez, and

Sabater critically analyze the diverse types of carbon–heteroatom bond-forming reactions established to date.

Two articles that examine opposite sides of conceptually related processes are then paired. In the first, Xie, Zhu, and Zhou present the latest on metal-catalyzed enantioselective hydrogenations of enamines and imines. In the reverse direction, Choi, MacArthur, Brookhart, and Goldman relate the potential of alkane dehydrogenations and related reactions promoted by iridium pincer complexes. Another contribution that incorporates oxidative carbon–carbon and carbon–heteroatom bond formation is provided by Liu, Zhang, Shi, and Lei, who examine couplings between two nucleophiles. Suzuki reports on the growing number of iridium-catalyzed oxidations of oxygen and nitrogen containing molecules, including tandem reactions.

Additional types of carbon–carbon bond-forming reactions are represented. Weaver, Recio, Grenning, and Tunge describe the catalytic extrusion of CO_2 from easily introduced allyl- and benzylcarboxylate moieties, affording new allyl- and benzyl–carbon bonds. A complementary article by Ding and Hou details the most efficient methods for metal catalyzed enantioselective propargylations. In a different direction, Kuninobu and Takai detail the growing and diverse body of carbon–carbon and carbon–heteroatom bond-forming reactions catalyzed by rhenium(I) carbonyl compounds.

Carbocycle and heterocycle syntheses are the major focus of two articles. In the first, Aubert, Fensterbank, Garcia, Malacria, and Simonneau detail a wealth of metal-catalyzed cycloisomerizations of 1,*n*-allenynes and -allenes. Gold-catalyzed nucleophilic cyclizations of functionalized allenes are then described by Krause and Winter. Another review is organized around a type of cyclic reactive intermediate, metallaoxetanes. The authors, Dauth and Love, emphasize their potential role in reaction development.

For three articles, the supporting ligand takes center stage. In the first, Selander and Szabó inventory the diverse types of reactions—Heck, Suzuki–Miyura, Sonogashira, Aldol, allylations, etc.—that are efficiently catalyzed by palladium pincer complexes. van Leeuwen, Kamer, Claver, Pàmies, and Diéguez then highlight the use of chiral phosphite-containing ligands in metal-catalyzed enantioselective transformations. The preparation and application of other types of chiral phosphorus donor ligands—phosphine–phosphinite and phosphine–phosphite systems—is subsequently treated by Fernández-Pérez, Etayo, Panossian, and Vidal-Ferran.

Two contributions will be of special interest to the process chemistry community. To lead off, Magano and Dunetz describe and evaluate large-scale applications of transition metal catalyzed coupling reactions to pharmaceutical syntheses. Molnár then

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critically analyzes the recyclability of palladium catalysts for carbon–carbon coupling reactions.

The final four articles deal with the oligomerization and polymerization of olefins, which are topics of considerable commercial importance. The first, by McGuinness, treats the development of catalysts that can selectively di-, tri-, or tetramerize α -olefins, with a special emphasis on the role of metallocyclic intermediates. Nomura and Zhang then describe the design of precision vanadium catalysts for several types olefin polymerization. This is followed by Makio, Terao, Iwashita, and Fujita's account of a tour-de-force from Japanese industry, the discovery and application of bis(phenoxy–imine) early transition metal catalysts ("FI" catalysts) for olefin polymerization. The issue is crowned by an article by Delferro and Marks that outlines the opportunities offered by multinuclear olefin polymerization catalysts where active sites are held together by one or more covalent linkages. Such catalysts give rise to distinctive polymer chain branching, enhanced α -olefin comonomer enchainment selectivities, and significant molecular weight enhancements compared to their mononuclear counterparts.

2. FROM "TRANSITION METAL CATALYZED REACTIONS" TO ORGANOMETALLICS

I have mentored many colleagues that introductions, be they to seminars, addresses, or written bodies of work, should call attention to the speakers and/or authors, and not the moderator or Editor. However, this issue holds much personal meaning for me, and it is impossible to let this occasion pass without some comments that violate these guidelines.

About the time that the first manuscripts for this issue were submitted, I was asked to become the Editor in Chief of *Organometallics*, succeeding the Founding Editor, Dietmar Seyferth. Thus, I stepped down as Associate Editor of *Chemical Reviews* last July, after more than 26 years in office. The most logical course with respect to this issue was to assume the role of Guest Editor, with my friend and most able successor Guy Bertrand taking over the role of Associate Editor. I warmly thank Guy and his staff for their assistance, and it is with considerable sadness that I now put the finishing touches on what is likely my last editorial effort for this journal.

Looking back, I learned an incredible amount of chemistry from the many authors with whom I interacted, and I would like to express my deep appreciation for this opportunity. My duties required that I read and evaluate manuscripts that were often considerably outside of my own research field, and this brought me into realms of inquiry where I would never have ventured myself. For those authors who publish organometallic chemistry, which includes all of those represented in this issue, I look forward to a continuing relationship in the context of my new responsibilities.

I would also like to thank the many reviewers who helped in the evaluation of these manuscripts. The selfless engagement of our referees, who often provide multipage critiques, has never ceased to amaze all of the Editors. The combined reviewing and production process has been shepherded by a number of dedicated secretaries over the years, without whom nothing would have been possible. And it terms of general advice and guidance, the many outstanding scientists who served on the Editorial Board opened my eyes as to everything an advisory group could be.

Particular appreciation is due to my editorial colleagues. Josef Michl has been an inspiring Editor in Chief to work with, as well as a long-time friend and colleague. I deeply thank him for all the opportunities he has given me. There has never been a dull moment since we began our duties in July of 1984. During a substantial fraction of this period, Robert Kuchta served as an Associate Editor, and the creative sparks that flowed between the three of us—generated in part by our complementary backgrounds—made our many special projects a joy.

In conclusion, this thematic issue underscores the ongoing importance and relevance of organometallic and transition metal based catalysis in the service of organic and materials synthesis. By pure coincidence, the subject matter is especially befitting of my transition from an Associate Editor of *Chemical Reviews* to the Editor in Chief of *Organometallics*. May *Chemical Reviews* and its author and reader community continue to grow and prosper, and I hope to welcome many of you to my new home journal, *Organometallics*.

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BIOGRAPHICAL SKETCH



John A. Gladysz is a native of the Kalamazoo, Michigan, area and obtained his B.S. degree from the University of Michigan (1971). He was hooked on chemistry via undergraduate research projects involving cyclophane and sulfur chemistry with D. T. Longone. He then obtained his Ph.D degree from Stanford University (1974) with E. E. van Tamelen, working on nitrogen fixation.

Gladysz subsequently held appointments at UCLA (Assistant Professor, 1974–1982) and the University of Utah (Associate Professor and Professor, 1982–1998). He then accepted the Chair of Organic Chemistry at the University of Erlangen-Nuremberg in Germany, where he succeeded Paul von Rague Schleyer. Since 2007, he has held the Dow Chair in Chemical Invention at Texas A&M University, where he is Distinguished Professor of Chemistry.

Gladysz has been a fellow of the Alfred P. Sloan Foundation (1980–1984) and a Camille and Henry Dreyfus Teacher–Scholar Grant recipient (1980–1985). He received an Arthur C. Cope Scholar Award in 1988, the University of Utah Distinguished Research Award in 1992, the ACS Award in Organometallic Chemistry in 1994, a von Humboldt Foundation

Research Award for Senior Scientists in 1995, and the International Fluorous Technologies Award in 2007. He was elected as a Fellow of the American Chemical Society in the inaugural year, 2009.

From June 1984 through July 2010, he served as the Associate Editor of *Chemical Reviews*. In June of 2010, he succeeded the Founding Editor Dietmar Seyferth as Editor in Chief of *Organometallics*.

Gladysz has authored over 400 papers and patents, and his research spans a wide range of problems in the general areas of synthetic and mechanistic organometallic chemistry, and catalysis.

On the personal side, he enjoys running, all types of literature, a hearty Bavarian Hefeweizen beer, and a good red wine. He is married to Janet Blümel, a Professor of Chemistry at Texas A&M University who specializes in inorganic chemistry, supported catalysts, and solid-state NMR spectroscopy. Together they manage the Crow's Nest Ranch, located 15 minutes from the University.