



DOW CHEMICAL

FULL-STEAM AHEAD FOR ORGANOMETALLICS

ACS MEETING NEWS: Chemists pay tribute to a respected editor and look to the future of the field

STEPHEN K. RITTER, C&EN WASHINGTON

IT'S OFTEN REFRESHING to stop what you are doing, take a moment to acknowledge your successes, and then reflect on what you plan to do next. A cross-section of organometallic chemists followed that course of action at the American Chemical Society's national meeting in Boston last month during a symposium organized by associate editors of the ACS journal *Organometallics* and sponsored by the Division of Inorganic Chemistry.

The symposium was held in part as a forum for chemists to pay tribute to the journal's founding editor, Massachusetts Institute of Technology emeritus professor Dietmar Seyferth, who stepped down earlier this year after 28 years at the helm. Scientists speaking at the three-day event shared stories of their interactions with Seyferth and showcased their latest research results, which highlighted continuing and emerging areas in which the field is expected to shine in the coming years.

Themes that stood out in Boston included the ongoing need for new catalysts and catalytic reactions for synthetic organic chemistry, new catalysts and materials for energy and fuel production, and innovative industrial chemical processes.

Seyferth, who graduated with a Ph.D. from Harvard in 1955, spent his career at MIT. In 1963, he became a regional editor for Elsevier's then-new publication, the *Journal of Organometallic Chemistry*. It turns out his region covered a big chunk of the world—North America and Asia—he recalled in an interview.

In 1980, ACS began developing a journal devoted to organometallic chemistry. Seyferth was initially alarmed by the prospect of a competitor, and he opposed the idea. "I thought I would lose most of my authors to the new journal," Seyferth said. But in the end, he fretted over nothing, because he was unexpectedly asked to be the inaugural editor of the ACS journal. Seyferth accepted the offer and began soliciting manuscripts, and the first issue of *Organometallics*, a name he selected, appeared in January 1982.

He was right about losing most of his old authors to the new journal: "They started sending their manuscripts to *Organometallics*," Seyferth said. "We had an instant journal without any of the growing pains that new journals often have."

Seyferth, who is now 81, retired from teaching and research in 1999. But he continued to shepherd *Organometallics* and,

RISING STARS These molded olefin block copolymers, tailored to have different photonic properties, were made possible by organometallic catalysts.

"for my own amusement," indulged his interest in history by writing essays on organometallic chemistry, which have been published in the journal with much acclaim.

"Dietmar started from square one, and with his hard work and

love of chemistry, *Organometallics* has become known for its expeditious handling of quality manuscripts," commented Northwestern University's Tobin J. Marks, one of the journal's associate editors.

BY DEFINITION, organometallic chemistry centers on the design, synthesis, and reaction chemistry of compounds with at least one metal-carbon bond, Seyferth pointed out. Until 1950, the focus was mostly on main-group metal compounds; only a few isolated examples of transition-metal compounds had been described, he said. The field got its true start in 1951 with the discovery of ferrocene, at the time a revolutionary molecule consisting of an iron atom sandwiched between two cyclopentadienyl rings.

Organometallic chemistry quickly took off from there with the synthesis of a multitude of organotransition-metal compounds and the development of polymerization catalysts, followed more recently by olefin metathesis and C-H activation chemistry. Also notable have been the syntheses of transition-metal and main-group compounds containing multiple bonds. "It's a venerable field that hasn't run out of steam," Seyferth said.

For example, MIT's Richard R. Schrock spoke about his "third-generation" molybdenum and tungsten olefin metathesis catalysts developed in collaboration with Amir H. Hovedya of Boston College. Schrock shared the 2005 Nobel Prize in Chemistry for developing catalysts for olefin metathesis, a versatile class of reactions that cleave double bonds and redistribute the pieces to form new molecules. Although many advances have been accomplished via metathesis during the past 30 years, Schrock said, there are still areas for improvement.

One goal is developing methods to selectively furnish Z (cis) alkenes, he noted. Nearly all ring-opening and cross-metathesis reactions catalyzed by his molybdenum catalysts or by ruthenium catalysts such as those developed by his fellow Nobel Laure-

ate Robert H. Grubbs of California Institute of Technology almost exclusively yield E (trans) alkenes.

Building on earlier versions of his catalysts, Schrock's third-generation catalysts, rolled out over the past three years, incorporate a modified ligand system that includes a monoalkoxide-pyrrolide (MAP) ligand combination. This system provides longer lived catalysts with improved activity—and with selectivity for Z products. The design could lead to “thousands of new

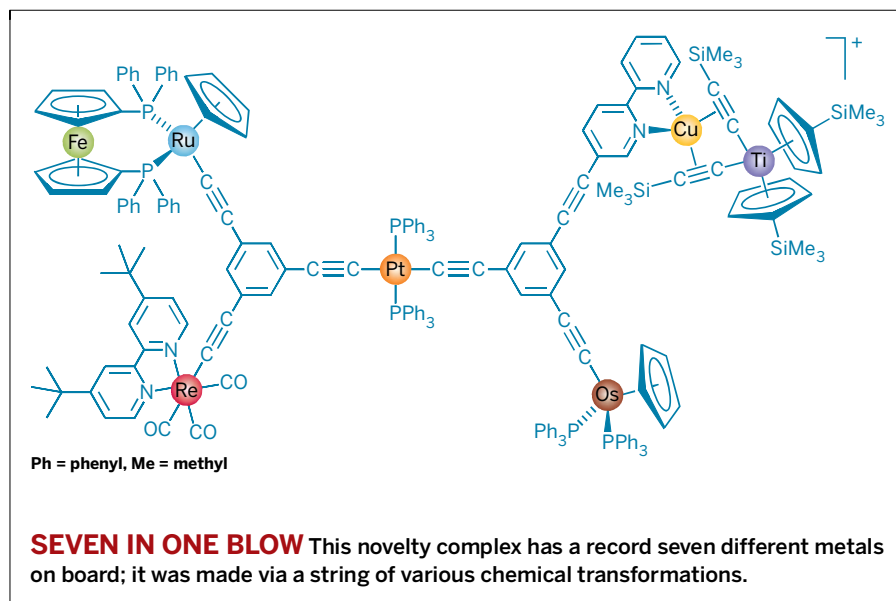
reactant by migrating to and inserting in a metal-ligand bond, which in Hartwig's case is a palladium-amide bond.

These studies are increasing chemists' understanding of the stereochemical control possible in alkene functionalizations, Hartwig said. “We are now getting close to synthetically useful hydroamination reactions,” he remarked.

Another major theme driving organometallic chemistry is energy research, noted Caltech's John E. Bercaw. For ex-

sis studies to refine Fischer-Tropsch reactions to help move in that direction.

One thrust of the Bercaw group's research is the reductive coupling of CO with H₂ using rhenium carbonyl complexes with pendant Lewis acid ligands. In these systems, one metal atom cleaves H₂ and another coordinates to and activates CO, Bercaw explained. The Lewis acid then encourages hydride delivery from one metal to the other and migratory insertion of the reduced carbonyl into another carbonyl, thereby selectively building hydrocarbon chains.



catalysts,” Schrock suggested, and access to more complex functionalized substrates for pharmaceuticals and other chemicals.

In one example, he showed that a MAP catalyst is efficient at coupling terminal olefins to give a product with exclusive Z internal double bond configuration or at splitting unsaturated hydrocarbons into two terminal olefins (*J. Am. Chem. Soc.* 2009, 131, 16630).

John F. Hartwig of the University of Illinois, Urbana-Champaign, known for using rhodium and palladium catalysts to carry out C–H activation and functionalization chemistry, also discussed his group's efforts to develop new types of catalytic reactions. Fundamental to this work is conducting mechanistic studies on individual reaction steps, he said.

For example, Hartwig described experiments to define the reactivity of palladium amido complexes in catalytic aminations of alkenes (*C&EN*, June 7, page 41). During migratory alkene insertions, the alkene ligand on the metal complex serves as a

ample, as petroleum resources decline there is a growing need for catalysts that improve upon Fischer-Tropsch chemistry to convert syngas (carbon monoxide and hydrogen) derived from coal and natural gas into hydrocarbon fuels and chemical feedstocks, he said. “There is still plenty of coal and natural gas,” Bercaw added, “but we need to figure out better ways to use them besides burning them.”

Fischer-Tropsch chemistry is still the best way to upgrade syngas into fuels and chemical feedstocks, he pointed out, but processes need to be more energy efficient and greener. One idea is to switch from traditional heterogeneous iron, cobalt, and ruthenium catalysts that require high temperatures and pressures to homogeneous catalysts that can operate at lower temperatures and pressures. Homogeneous catalysts also could offer improved selectivities for making specific alkanes or alcohols, rather than producing a complex mixture of products. Bercaw and colleagues have been conducting some fundamental cataly-

DEVELOPING INDUSTRIAL processing methods to take advantage of new catalysts and synthetic reactions is also a wide-open area for organometallic chemistry, said James C. Stevens, a Dow Chemical research fellow based in Midland, Mich. Stevens related how a Dow Chemical team used high-throughput screening to identify a zirconium bis(phenoxyimine) catalyst selective for ethylene polymerization and a hafnium pyridylamide catalyst selective for 1-octene polymerization that work in combination to build olefin block copolymers.

The polymerization process takes advantage of diethylzinc as a transfer reagent to shuttle the growing polymer chains back and forth between the two catalysts in a continuous, single-reactor process. This “chain-shuttling polymerization” alternates blocks of ethylene and ethylene/1-octene copolymer with precise control, resulting in olefin block polymers with the useful combination of high-melting-point “hard” crystalline segments that have low octene content and low-glass-transition-temperature “soft” amorphous segments with higher octene content.

Dow chemists have also developed a continuous process that uses only the hafnium catalyst and two reactors containing different monomers in succession, Stevens noted. Rather than producing a multiblock polymer chain architecture, the polymerization results in chains containing just two long blocks. Stevens reported that the different types of copolymers, now becoming commercially available under the Infuse brand, have advantages over random copolymers or two polymers that are physically blended.

The olefin block copolymers can self-assemble into materials with ordered phases that give rise to colorful optical properties, he added. Compared with colloidal crystals and other photonic materials,

these copolymers present an opportunity to implement photonic polymers for many low-cost applications, he said, including energy-efficient building materials that reflect sunlight.

“Computer modeling and high-throughput techniques are revolutionizing the way we identify catalysts,” Stevens told C&EN. “We can sort through thousands of candidates to find the one catalyst we want that will work well with the polymer processes we have developed. Even with something as simple as polyethylene, we are still discovering new ways to make functional materials. This is an approach that is going to continue.”

Pure research, which may not have obvious application, is also important in organometallic chemistry. One example is the record-breaking synthesis by Heinrich Lang’s group at Chemnitz University of Technology, in Germany, of a complex that contains an unprecedented seven different transition metals.

Heteromultimetallic molecules are potentially useful in homogeneous catalysis and as electronic materials, Lang noted.

His group is interested in finding out “how much stress you can put on a molecule with different redox-active metal centers before it falls apart.”

The out-of-the-box design of the hepta complex includes a framework structure of the seven metal centers—Fe, Ru, Re, Pt, Os, Cu, and Ti—connected via triethylbenzene and bipyridyl linker groups, the kind of linkages chemists use to make molecular wires. The researchers built the complex by using a string of metathesis, dehydrohalogenation, and carbon-carbon cross-coupling reactions.

Seyferth described Lang’s work as “fun chemistry” that involves “clever application of the entire armamentarium of organometallic chemistry.”

AS A FOLLOW-UP to the Boston symposium, a special issue of *Organometallics* dedicated to Seyferth is slated for November, and a special issue with essays on the future of organometallics will be published in January, noted John A. Gladysz of Texas A&M University, who is the journal’s new editor-in-chief.

Gladysz plans to continue Seyferth’s high standards as editor, but he also recognizes the need to be innovative and plans to roll out some new features. “We want to remain the go-to journal in the field,” he told C&EN.

At the top of Gladysz’s to-do list are changing the cover graphic each issue, possibly sponsoring a young investigators’ symposium at future ACS meetings, and introducing an “organometallics roundtable” section to the journal. Gladysz envisions this section as a forum where elder statesmen, younger chemists, and international members can discuss topics of the moment, such as imminent chemical breakthroughs, research that exceeded expectations, or ideas that didn’t pan out.

“Organometallic chemistry has a well-defined core involving transition- and main-group metals, but this extends out in many directions and dimensions to other disciplines,” Gladysz observed. “We want to implement outreach measures to tie the organometallics community together, building upon the spirit established and nurtured by Dietmar.” ■

The Dreyfus Prize in the Chemical Sciences



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