

## Organometallic chemistry\*

More than 1200 chemists from 47 countries participated in the 23rd International Conference on Organometallic Chemistry (ICOMC 2008) and reported the latest findings in the field in the form of five plenary lectures, 25 invited lectures, 26 invited communications, 123 oral communications and 920 poster presentations.

ICOMC 2008 is the second such conference in France after the first one at Dijon in 1979. The overwhelming interest shown by more number of participants from all over the world did reveal the state-of-the-art. The co-chairmen of the conference were Pierre H. Dixneuf and Christian Bruneau. In addition, there are 28 members in the international advisory board and 20 in the national advisory board.

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal. It combines aspects of inorganic chemistry and organic chemistry. It remains one of the primary components of chemistry owing to its vital role in the industry, ranging from catalysts to antiknocking agents to medicine. The diversity of modern organometallic chemistry and the role of organometallic chemistry as a link between many branches of chemistry were well demonstrated in the conference by the lectures arranged under different themes. These included homogeneous catalysis, heterogeneous catalysis, molecular catalysts for *concerto* catalysis, biocatalysis, supramolecular chemistry, metal complexes and nanoparticles, molecular electronics, anticancer complexes, etc.

The scientific session began with the lecture by Robert H. Grubbs (USA) on 'The synthesis of large and small molecules using olefin metathesis catalysts'. He elaborated the methods for construction of olefins of various structures using olefin metathesis catalysts. In contrast to other olefin metathesis catalysts, Grubbs' catalysts tolerate other functional groups

in the alkene and are compatible with a wide range of solvents. First-generation catalyst is often used in organic synthesis to achieve olefin cross-metathesis, ring-opening metathesis polymerization, acyclic diene metathesis polymerization, and ring-closing metathesis. It is easily synthesized from  $\text{RuCl}_2(\text{PPh}_3)_3$ , phenyldiazomethane and tricyclohexylphosphine in a one-pot synthesis. Grubbs' catalyst is a relatively stable compound in air, which makes handling easy. Olefin metathesis is a reaction between two molecules containing double bonds. The groups bonded to the carbon atoms of the double bond are exchanged between molecules, to produce two new molecules containing double bonds with swapped groups. Whether a *cis* isomer or *trans* isomer is formed in this type of reaction is determined by the orientation that the molecules assume when they coordinate to the catalyst, as well as the steric nature of the substituents on the double bond of the newly forming molecule. The second-generation catalyst has the same uses in organic synthesis as the first-generation catalyst, but has a higher activity. It is easily synthesized from a combination of the first-generation catalyst and alkoxy-protected 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene. This ligand is an *N*-heterocyclic carbene and in this case, ruthenium is coordinated to two carbene groups.

The different ways for  $\pi$ -bond activation was explained by Alois Fürstner (Germany) in his plenary lecture. The activation of  $\pi$ -bonds upon binding to a transition metal template is one of the most fundamental principles of organometallic catalysis. His presentation summarized efforts to translate this basic process into preparatively useful transformations and catalyst design. Starting from early work on alkene and alkyne metathesis, recent studies on noble metal-catalysed skeletal rearrangements of polyunsaturated substrates were outlined. This included a generalized mechanistic scheme, insights into structure and bonding of relevant organometallic intermediates, as well as efforts towards the design of new ligands. Fürstner also summarized a complemen-

tary approach toward cycloaddition and cycloisomerization chemistry using cheaper and benign metal catalysts. His findings included an unprecedented copper-based [4 + 2] cycloaddition/alkylation cascade, as well as iron-catalysed [5 + 2] cycloisomerization and Alder-ene reactions. The latter reaction utilized low-valent bimetallic lithium ferrate complexes.

P. P. Power (USA) gave a presentation on various aspects of multiple-bonded dimetal complexes. The stabilization of multiple-bonded dimetal complexes by various terphenyl ligands was discussed. These complexes include quintuple bonded chromium(I) species of the type  $\text{ACrCrAr}$ , as well as their iron and cobalt analogues. Power has observed large changes in the nature of metal-metal interactions in the latter complexes. In addition, the synthesis of related mononuclear species, where dimerization and consequent metal-metal bond formation are prevented by the steric effects of larger terphenyl ligands was described. The reactivity of these compounds with various small molecules such as  $\text{CO}$ ,  $\text{CNBu}^t$ ,  $\text{O}_2$ ,  $\text{N}_2\text{O}$ , azides, imines and diazomethanes as well as the implications were discussed in detail.

Chiral bifunctional transition metal catalysts promoted asymmetric reactions, the *concerto* molecular catalysis, offer a great opportunity to open up fundamental aspects for stereoselective molecular transformations and are now realized to be a practical tool to access chiral compounds in organic synthesis. Takao Ikariya (Japan) elucidated in his plenary lecture, how the ligand modification in the bifunctional catalyst causes a drastic change in the catalyst performance. He focused on the recent advances in asymmetric catalytic reactions with newly developed Ru, Rh and Ir bifunctional molecular catalysts, including stereoselective C-H, C-C and C-N bond formation. Generation of multicomponent multinuclear metallosupramolecular architectures in a spontaneous but controlled fashion from specially designed ligand molecules and specific metal ions, was amply demonstrated by Jean-Marie Lehn (France). The structural and inter-

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actional information stored in the ligand molecules is read out and processed by the binding of metal ions through the corresponding coordination algorithm. The process also allows the selection of the binding subunits required for the build-up of the ligand itself from a set of components.

All the invited lectures showed clearly that research in the field of organometallic chemistry leads to new insights to novel applications. These include metal catalysed copolymerization of olefins with polar vinyl monomers by R. F. Jordan (USA). He reported the Pd-catalysed copolymerization of olefins with vinyl ethers and vinyl fluoride. (diimine)  $\text{PdMe}^+$  (diimine =  $(2,6\text{-}^1\text{Pr}_2\text{-C}_6\text{H}_3)\text{N}=\text{CMeCMe}=\text{N}(2,6\text{-}^1\text{Pr}_2\text{-C}_6\text{H}_3)$ ) copolymerizes 1-hexene and  $\text{CH}_2=\text{CHOSiPh}_3$  in  $\text{CH}_2\text{Cl}_2$  at  $20^\circ\text{C}$  to copolymers that contain up to 20 mol% silyl vinyl ether. The copolymers are chain-straightened polyhexenes and are similar to homopoly(1-hexene) generated under the same conditions. The major comonomer units are  $\text{CH}_3\text{CH}(\text{OSiPh}_3)\text{CH}_2-$ ,  $\text{CH}_2(\text{OSiPh}_3)\text{CH}_2-$  and  $-\text{CH}_2\text{CH}(\text{OSiPh}_3)\text{CH}_2-$ . (diimine)  $\text{PdMe}^+$  does not copolymerize olefins with alkyl vinyl ethers due to competing cationic homopolymerization of the vinyl ether or with aryl-vinyl ethers due to fast  $\beta$ -OAr elimination. Another interesting lecture was on environmentally benign homogeneous catalytic processes for the synthesis of fine chemicals and pharmaceuticals by Matthias Beller (Germany). He showed that molecular-defined catalysts enabled chemists to perform their organic syntheses more selectively and with improved economics. Using examples such as Fe-catalysed oxidation

reactions and Pd-catalysed coupling reactions, he demonstrated the superiority of the catalytic processes compared to more traditional stoichiometric reactions. In addition, the importance of the development of new catalysts for the improvement of bulk chemical processes was shown by taking an example of the synthesis of monomers of bulk polymers via palladium catalysis.

Carbon dioxide chemistry in catalysis and separation by P. G. Jessop (Canada) was among the invited lectures in ICOMC 2008. Jessop explained the utility of  $\text{CO}_2$  in asymmetric synthesis and to make switchable solvents and surfactants. Peter J. Sadler (UK) reported work on organometallic anticancer complexes. Sadler and his group have studied structure-activity relationships for ruthenium(II) complexes of the type  $[(\text{arene})\text{Ru}(\text{XY})\text{Z}]$  (where XY is the NN, NO or OO chelating ligand and Z the monodentate leaving group). Organometallic chemistry on the surface of nanoparticles was presented by Bruno Chaudret (France). This concentrated on (i) synthesis of ruthenium nanoparticles and spectroscopic studies aiming at the identification of the surface species, in particular hydrides, and study of their reactivity, and (ii) synthesis and growth process of magnetic nanoparticles leading to the formation of controlled objects for biomedical or micro-electronics applications.

Qi-Lin Zhou (China) explained the development of a new class of chiral ligands with a spirobiindane backbone, including monodentate phosphorus ligands, diphosphines, phosphine-oxazolines and bisoxazolines. These are highly

efficient for a number of asymmetric transformations. He discussed investigations on the applications of these novel chiral, spiro ligands in transition-metal-catalysed asymmetric hydrogenation of unsaturated bonds, carbon-carbon bond forming reactions and metal carbenoid insertions into hetero atom-hydrogen bonds. Photo-switching in coordination and main group chemistry was the theme of the lecture delivered by Neil Branda (Canada). Molecular switching is an area of research lying at the crossroads of chemistry and materials science, and will be key to the successful miniaturization of the components of nanoscale machinery. Branda presented several examples of photoresponsive coordination compounds based on 1,2-dithienylethene ligands.

A large number of oral communications were arranged, which provided the opportunity for many chemists to present their latest findings in their areas of research. Besides, two poster sessions constituted an integral part of the conference, where the participants discussed all the aspects of organometallic chemistry. At the end of the conference, a presentation was given about the next ICOMC to be held at Taiwan in 2010.

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