
CONFERENCE REPORT

Chimia 59 (2005) 756–759
© Schweizerische Chemische Gesellschaft
ISSN 0009–4293

OMCOS 13 – 13th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis Geneva, Switzerland, 17–21 July 2005

Graham R. Cumming*

Keywords: Asymmetric catalysis · Geneva · IUPAC · OMCOS · Organometallic chemistry

The OMCOS series of biannual conferences has run since 1981 and this, the 13th edition and the first in Switzerland, saw the conference return to Europe following visits to Toronto (2003) and Taipei (2001). Held under the auspices of the International Union of Pure and Applied Chemistry (IUPAC), the conferences cover the full spectrum of the applications of organometallic chemistry in organic synthesis, from mechanistic elucidation to natural product synthesis and all points between.

OMCOS 13 took place at a lakeside venue in Geneva, running over five days. The hard work and ability of the joint chairs, *Alexandre Alexakis* and *E. Peter Kündig* (both University of Geneva) to attract ex-

tensive sponsorship meant that conference fees were kept low for young researchers. Bringing together almost 1200 participants from industrial, academic and student backgrounds, and from a total of 42 nations, this was the largest and most diverse OMCOS yet.

The format of the conference ensured a lively mix of chemistry from both established and up-and-coming names. A total of 46 oral presentations was made up of an OMCOS Award Lecture, 13 ‘long’ and 10 ‘short’ invited lectures and 22 communications, with the theatre venue accommodating the large number of participants without the need for parallel sessions. In addition, more than half of those participants became presenters themselves, with over 600 posters displayed for the duration of the conference.

The conference began with a demonstration by *Alois Fürstner* (Max Planck Institute, Mülheim) that cross-coupling does not start and end with Pd, Cu, and Ni. Although couplings under iron catalysis actually predate those with palladium, they have received very little attention. This could be changing, however, as we were shown the wide range of C–C bond formations between Grignard reagents and electrophiles that may be catalysed by inexpensive iron salts. Aryl, allylic and alkyl halides, enol triflates, propargylic epoxides, α -bromo esters and acid chlorides are all amenable to such catalysis. We were given a foretaste of

the synthetic potential of this in the synthesis of the actin binder Latrunculin A, which also included the selective ring closing alkyne metathesis (RCAM) of an enyne-yne precursor.

The second speaker of the morning, *Carsten Bolm* (RWTH Aachen), showed the application of sulfoximine-based ligands in asymmetric catalysis. Both C_2 and C_1 -symmetric examples were shown and also mixed sulfoximine-phosphine ligands; new syntheses of the sulfoximine portion were also disclosed. Applications range from hetero-Diels Alder reactions to Mukaiyama aldols, the carbonyl-ene reaction and imine hydrogenations.

After such elaborate molecules, the next talk turned to more fundamental chemistry. *Masahiro Murakami* (Kyoto University) served up a blend of theoretical calculations and precise experimental observations to delineate the subtle effects of silicon substitution in the electrocyclic ring opening of cyclobutenes. Within the confines of the conrotatory opening, there are two possible modes in which the substituents move either ‘inwards’ or ‘outwards’; a simple analysis of product distribution gives the figures, but to interpret and explain is a more challenging task.

Citing an absence of organometallics in his current research, *Louis S. Hegedus* (Colorado State University) presented anecdotes and photos of many of the present luminaries in their earlier days at the first

*Correspondence: Dr. G.R. Cumming
Department of Organic Chemistry
University of Geneva
30, Quai Ernest-Ansermet
1211 Geneva 4
Tel.: +41 22 379 6083
E-Mail: graham.cumming@chiorg.unige.ch

OMCOS (Colorado, 1981) at which he was secretary. He then gave the lie to his earlier statement by presenting a serendipitous tale of optically active propargyl and allenyl organometallics in synthesis, alluding to their unpredictable nature in his view of methodology; "if you can't get what you love, you can learn to love what you get."

Following a lunch held amongst the poster boards, **Jacques Maddaluno** (IR-COF and University of Rouen) discussed how the formation of mixed aggregates between alkyl lithiums and chiral lithium amides may be used to induce asymmetry, while the complexes themselves were characterised by both NMR and DFT methods.

The second speaker of the afternoon, **Hisashi Yamamoto** (University of Chicago), began by offering to roll up his sleeves and help when an unseasonable lightning storm fused the giant projector and caused temporary panic amongst the IT team. As calm returned, a variety of catalytic asymmetric processes were presented under the umbrella of 'combined acid catalysis.' The concept involves a catalyst containing multiple Brønsted and/or Lewis acidic sites working in tandem to increase reactivity, provide a more organised asymmetric environment or allow fine-tuning.



Hisashi Yamamoto

Geneviève Balme (Claude Bernard University, Lyon) focussed on the application of palladium and copper catalysis in cascade and multicomponent carbo- and heterocyclic ring syntheses. Examples included a flexible, one pot synthesis of hitherto unknown furo[2,3-*b*]pyridones in which the palladium catalyst performs three distinct transformations.

The final slot of the afternoon was reserved for the **OMCOS Award** (previously known as the Springer Award), given to a

scientist under the age of 40 who has made significant contributions in the field of organometallic chemistry. **Shengming Ma** (Shanghai Institute of Organic Chemistry and Zhejiang University, Hangzhou) joined previous award winners Kyoko Nozaki, Gregory C. Fu, Erick M. Carreira, and Shu Kobayashi, giving a lecture on transition metal-catalysed reactions of allenes. After dispelling myths about the instability of allenes, Prof. Ma began a *tour-de-force* encompassing heterocycle synthesis by both intramolecular and multicomponent reactions and the first Heck-type allenylations. The utility of allenes in synthesis was amply demonstrated in the single step synthesis of new tetracyclic steroid scaffolds from readily available bis-allene precursors.



Shengming Ma

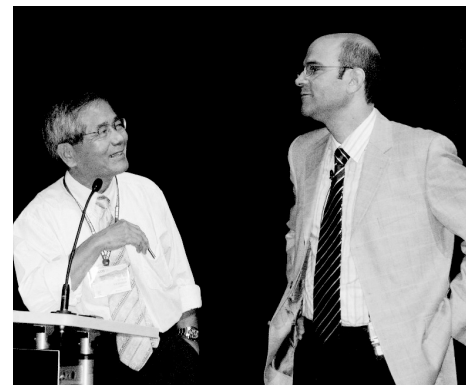
Despite the successful poster party held the night before (the success due, in equal measures, to the excellent quality of the posters and the excellent quality of the locally-produced beer and wine), the conference hall was full on the second morning to hear **Stephen L. Buchwald** (Massachusetts Institute of Technology) describe progress made in the rapidly-evolving field of carbon-carbon and carbon-heteroatom cross-coupling. Practical chemistry was at the forefront, with new-generation ligands (some commercially available) showing excellent generality and functional group tolerance. In a nod towards those of more industrial leanings, sulfonate-substituted ligands enable Suzuki-Miyaura couplings of aryl chlorides under aqueous conditions, while cheap diamine/copper salt combinations were shown to promote the amidation of aryl halides.

Cross-coupling then moved into 'radically' different territory with the lecture of **Koichiro Oshima** (Kyoto University). Cobalt catalysis promotes the coupling of

Grignard reagents and alkyl halides at temperatures as low as -40°C , while cyclic and acyclic alkyl-Heck-type products are also accessible *via* a radical mechanism.

Carbon-carbon bond formation was also the theme chosen by **Eric N. Jacobsen** (Harvard University), who spoke on the application of the versatile salen scaffold in ring-openings and conjugate addition (and onwards to quinine). A Cr-Schiff base complex came under close scrutiny, with the workup employed in synthesis determining the finer details of catalyst composition and its suitability for either quinone or hetero-Diels-Alder chemistry, leading to a unified strategy towards several natural products.

While the second afternoon was kept free for excursions and visits to the picturesque old town, the conference began again in earnest the following morning. **Erick M. Carreira** (ETH Zürich) showed the creative flair that made him the 1999 Springer (OMCOS) Award winner. Terpenes provide ready access to a library of chiral diene ligands for iridium and rhodium, and the resulting complexes are interesting catalysts that show particular promise in conjugate addition to cyclopentenones and other enones. Not one, but two cheaper alternatives to Quinap were also reported, whose syntheses do not require resolution by stoichiometric diastereomeric palladium complexes.



Ei-ichi Negishi and Erick M. Carreira

Simon Woodward (University of Nottingham) told us of his quest for an air-stable, organometallic methyl carbanion equivalent. The versatile reagent that resulted, known as 'DABAL', has been employed so far in enantioselective additions to aldehydes and in cross-coupling.

Ease of use was also a major driver for **Dean F. Toste** (University of California), who spoke on the rapidly expanding field of gold catalysis. The remarkable ability of gold(I) to activate alkynes, often under 'open flask' conditions, brings a variety of

carbocyclisations and a propargyl-Claisen rearrangement reaction into reach.

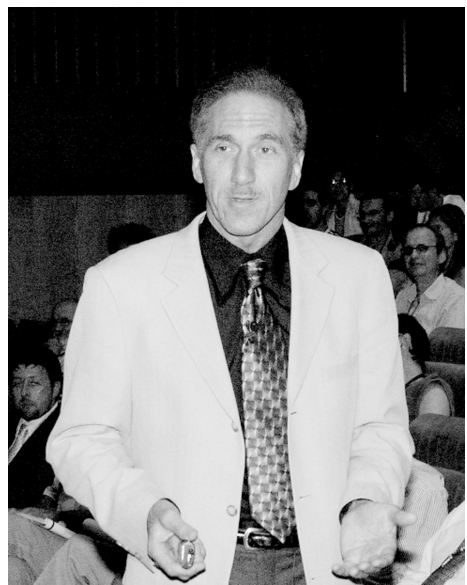
Mikiko Sodeoka (Tohoku University) was the recipient of the ChemComm 40th Anniversary lecture award and spoke of her elegant work on the use of palladium complexes outside their familiar role as cross-coupling promoters. Instead, mono- and binuclear complexes with chiral phosphine backbones were shown to be highly effective acid-base catalysts in enantioselective Michael additions, Mannich-type reactions, fluorination and protonation.



E. Peter Kündig and Mikiko Sodeoka

Old chemistry received a fresh twist in the hands of **Hélène Lebel** (University of Montreal). The Curtius rearrangement can be carried out in one pot – avoiding isolation of acyl azides – under mild, zinc-catalysed conditions that avoid racemisation in the case of α -chiral acids.

Bruce H. Lipshutz (University of California at Santa Barbara) performed a modern alchemy with base metals, impregnating nickel and copper salts into charcoal and graphite to create simple and yet highly



Bruce H. Lipshutz

efficient heterogeneous catalysts. With a showman's ability to work the audience, Prof. Lipshutz paced the theatre while explaining the wide variety of cross-coupling reactions that proceed in minutes under microwave conditions with the 'cost-free' nickel catalysts. Reduction was also explored, with the copper-impregnated catalysts giving excellent preliminary results in hydrosilylation and conjugate reduction.

Unlike the Josiphos family of ligands, the P,S-bidentate ferrocene-based ligands of which **Juan Carlos Carretero** (Universidad Autónoma de Madrid) spoke have only axial chirality. However, on coordination to a metal the sulfur becomes stereogenic, creating a unique asymmetric environment for catalysis. Allylic substitutions, Mannich-type condensations and cycloadditions were discussed, to name but a few.

The third day closed with a lecture by **Albert S.C. Chan** (Hong Kong Polytechnic University). Continuing a sub-theme of accessible, practical chemistry that ran throughout the conference, a single step synthesis of a family of aminonaphthol catalysts was described, in which the products are simply crystallised from the reaction mixture. The catalysts show excellent results in asymmetric alkenylation and arylation of aldehydes.

A successful gala dinner was held on the penultimate evening, with a reception held overlooking the lake. Food and company aside, the evening was notable for an impromptu rendition of 'Edelweiss' by an eminent member of the party, and for the troupe of performance artists shadowing unsuspecting guests and 'looking for dogs' under the tables.

The final morning began with **Mark Lautens** (University of Toronto), who spoke on the making and breaking of rings with metal complexes. Both inter- and intramolecular reactions featured, and also the direct C–H functionalisation of arenes. A notable example of the chemistry was a modular indole synthesis by a domino amination/Suzuki-Miyaura coupling.

The focus of **Masaharu Nakamura's** (University of Tokyo) lecture was one of the great challenges in synthesis, the selective functionalisation of unactivated carbon-carbon multiple bonds. Attacking the topic from two angles, we first saw asymmetric addition of zinc aza-enolates and electrophiles across an alkene, then moved on to indium-catalysed addition of active methylene compounds to alkynes.

Kuiling Ding (Shanghai Institute of Organic Chemistry) proved to have two strings to his bow, with the common driver being the development of practical asymmetric catalysis. The first 'string' covered the syn-

thesis of new modular ligands amenable to a combinatorial approach, while the second dealt with the novel concept of 'self-supporting' catalysts. In this latter approach, self-assembly of multitopic chiral ligands with metal ions creates a heterogeneous catalyst. This strategy combines many of the advantages of traditional heterogeneous catalysts and a simple 'mix-and-match' synthetic approach without the need for a separate solid support.

The penultimate speaker, **Cesare Genari** (University of Milan) carried the 'ligand library' concept further. Tropos P-bound biphenol units combined with chiral alcohols or amines gave a bank of ligands which were paired and screened as catalysts in asymmetric hydrogenation; interestingly, some phosphoramidite/phosphite pairings performed markedly better than the single ligands.

Although postponed from the first morning as a result of illness, **Varinder K. Aggarwal** (University of Bristol) was as engaging as ever as he gave the closing talk. Billed a 'cornucopia of chiral chemistry', the lecture more than lived up to its name as chiral sulfur ylides turned catalytic (drawing upon carbene chemistry) in the synthesis of epoxides. Recent results included reactions of sulfur ylides with boranes, resulting in an innovative asymmetric synthesis of diaryl methanols and other benzylic alcohols.



Varinder K. Aggarwal

Interspersed between the lectures described above, 22 short communications gave a flavour of the chemistry we may be seeing over the next few editions of OM-COS. Although there is not space to mention them here, the quality of these 'snippets' served to remind us of the breadth of chemistry and wealth of ideas present in the organometallic community.

So, after 4 days, 22 hours of varied lectures and 8 hours eating and drinking amongst the posters, what can we say about the current position of organometallics in organic synthesis? Looking back, there were few talks that did not involve catalytic metals in one form or another, with asymmetric catalysis forming the greater part. Although palladium, the 'giant' of metal catalysis, featured in many talks, results with gold, nickel and other transition or main group metals show that there is still great scope in the quest for new reactivity. For many of the speakers, total synthesis was the 'proving ground' for new or enhanced reactions that demonstrate new levels of selectivity and functional group tolerance. At the other end of the scale, the wealth of practical methods for the flexible synthesis of important building blocks continued to grow. In short, organometallic methods

rest at the heart of the 'toolbox' of organic synthesis.

Perhaps the best way to sum up the achievements and aims of those involved in the OMCOS story is by quoting Hisashi Yamamoto, who defined his own goals as, "more reactive, more versatile, more selective." The next instalment in the OMCOS series will take place in August 2007 in Nara, Japan, under the chairmanship of Koichiro Oshima. We look forward to seeing more progress towards these goals, and hope to see you there.

The OMCOS 13 website remains up and running (omcos13.unige.ch) and contains links to the homepages of all invited lecturers, in addition to the names of our many and generous sponsors to whom we are greatly indebted. We also wish to thank Alvaro Enriquez for photography.

Received: August 29, 2005