

CONFERENCE

International Symposium on Homogeneous Catalysis ISHC-XVI

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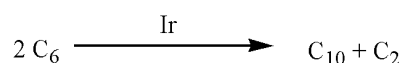
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The regular International Symposium on Homogeneous Catalysis took place in Florence from 6th to 11th July 2008. The conference was attended by 750 participants and was honored by a star choice of lecturer. The schedule included 8 key lectures (KL), 17 invited lectures (IL), 22 oral presentations and 484 posters. The chairman of the symposium was a renown Italian specialist in catalysis Claudio Bianchini.

Taking into consideration that in many studies the catalyst was used on a carrier it is evident that the boarder between the homogeneous and heterogeneous catalysis becomes more and more arbitrary. Obviously the catalytic processes play increasingly important role both in the industry and in laboratory syntheses. It is known that over 80% of the industrual production of chemical products is underlain by the application of catalysis. A special part belongs to the catalysis in the production of pharmaceuticals, in the preparation of enantiomerically pure drugs. The homogeneous catalysis is mighty versatile, but on the conference catalysis with the transition metal complexes traditionally prevailed. The continuing triumphal parade of this catalysis is astonishing, it leads to discoveries of more and more new reactions due first of all to its capability to activate bonds of versatile types: $C_{sp^2}-H$, $C_{sp^3}-H$, $C-C$, $C=C$, $C\equiv C$, $Si-H$, and even $N-N$. The activation of ordinary $C-H$ and $C-C$ bonds led to the creation of a new field of research, the study of alkane metathesis. This theme was a strong point in the lectures of Brookhart, Basset, and Milstein. The alkane metathesis is the process where a linear alkane is scrambled into lower and higher linear homologs. These processes were discussed by M.Brookhart (KL) (USA) with the use of catalysts based on the complexes of Rh, Co, and Ir. The following reaction can serve an example:

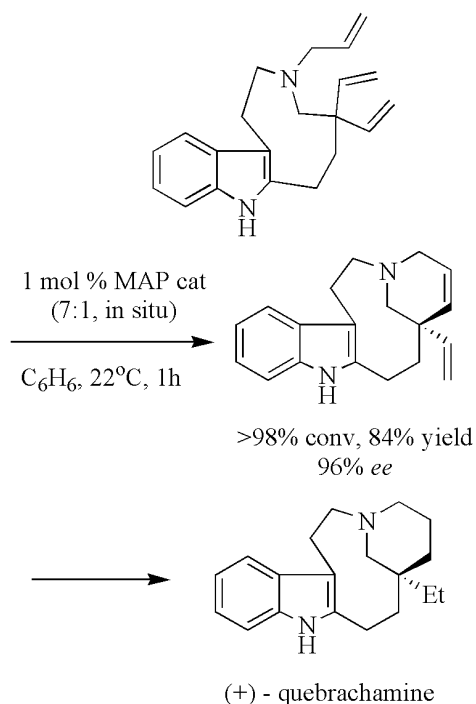


It is evident that the reaction proceeds through a stage of dehydrogenation and of the formation of iridium hydride complex. Besides the reduction was considered of carbon–halogen and carbon–oxygen bonds effected by silanes.

J.-M.Basset (KL) (France), whose contribution to the problem of the ordinary $C-C$ bonds activation is especially great, has demonstrated the possibility to create a “single site” on a heterogeneous surface of an oxide or a metal thus making a hybride catalyst. The new catalytic systems with Mo, Ta, etc. as metals were employed in versatile reactions including depolymerization, alkane and alkene metathesis, methane dimerization to give ethylene and hydrogen, cleavage of alkanes under the action of methane, and even nitrogen dissociation.

Numerous new reactions, including the activation of the $C-H$ bond and hydrogen with pincer iridium complexes with a pyridine ligand were displayed in the lecture of D.Milstein (Israel) (IL). In the demonstrated unusual reactions the key role belonged to the cooperative interaction metal–ligand that caused aromatization and dearomatization of the pyridine ring ensuring the activation of H_2 and the $C-H$ bond. On ruthenium complexes the transformation of alcohol was performed into an ester and hydrogen, an amide was synthesized from an alcohol and amine with hydrogen liberation. In these reactions the activation of the $C-H$ bond occurred with uncommon regioselectivity.

Nobelist R.Schrock (KL) (USA) presented in his lecture numerous new complexes based on molybdenum

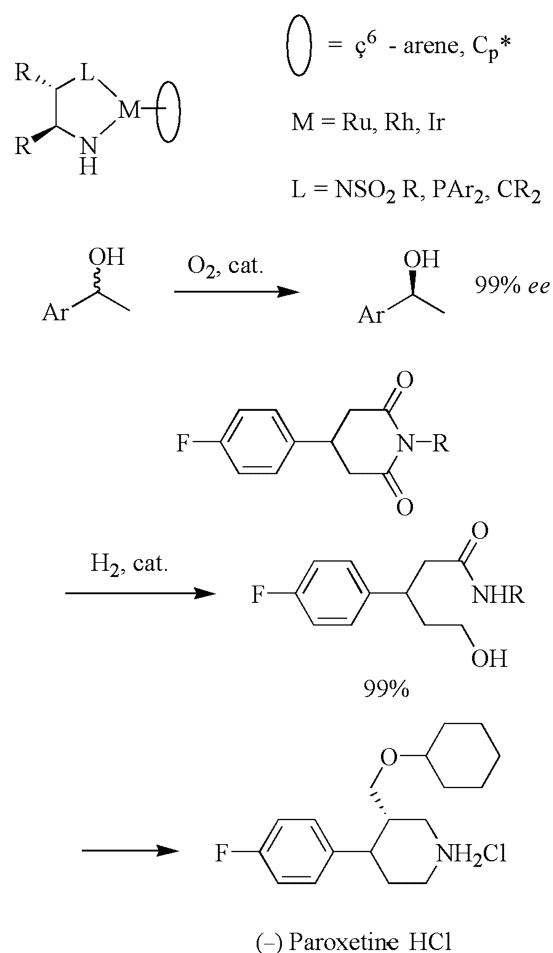


with a chirality both in the ligand and on the metal permitting performance of the metathesis of multiple bonds in complex molecules with a high turnover number (TON) and enantioselectivity leading to the formation of important natural products.

The great role of the ligand nature in the metal complex catalysis is well known, and the mechanism of its action is frequently obscure. Therefore the wide screening of ligands is necessary, and it is understandable, why versatile ligand libraries were presented on the conference, and also the ways of their synthesis and testing. A significant progress was reached owing to the new approaches to the simultaneous synthesis and screening of ligands, what was especially important for the industry. These methods are named High Throughput experiments (THE), in particular, High Throughput computation (HTC). The application of these methods to the polymerization processes was covered in the lecture of V. Busico (KL) (Netherlands).

A new approach to preparation of efficient bifunctional catalysts based on transition metals for asymmetrical reactions (concerto molecular catalysis) taking into consideration the synergistic effect was developed by T. Ikariya (KL) (Japan). It was shown on numerous reduction and oxidation reactions that the replacement of ligand NSO₂R in the complex by PAR₂ dramatically changed the result of the reaction.

Scheme 1.



The lecture of C. Gennari (IL) (Italy) presented a library of new monodentate ligands, and an idea was formulated of the application in a rhodium catalysis of heterocombination of two types monodentate ligands. This approach provided a possibility to reach high enantioselectivity of hydrogenation (up to 99% ee), similar values were obtained in the addition of arylboric acids to cyclic enones.

It should be stressed that exclusive results were obtained in the enantioselective hydrogenation of versatile olefins. We owe this success mainly to the research teams of Germany and Switzerland. One of the leaders in this field is M. Reetz (KL) (Germany). However the most interesting was the second part of his lecture dedicated to a new type of combinatorial catalyst that he called "Darwinism in the test-tube". It concerned a new methodology on directional changing the enantioselectivity of enzymes (hydrolases, oxidases) based on gene mutagenesis and on a simultaneous highly efficient screening.

Further development of this idea aiming at application of the catalysts obtained to new reactions was the creation of hybrid catalysts where the protein (the binding pocket) was linked to a synthetic ligand. The optimization of the catalytic quality was attained after several mutagenesis cycles, and this resembled the course of evolution.

In the lecture of J.Reek (IL) (Netherlands) supramolecular ligands and their linear analogs were demonstrated. It was shown that at parallel screening on 9 catalysts of 32 was obtained a value *ee* >90%, and on 7 catalysts of 55 was obtained a conversion of 100% and >95% *ee*.

The skilled selection of efficient ligands in the asymmetrical synthesis of complex systems by the domino type reactions was revealed in the lecture of G. Poli (IL) (France). The example of an enantioselective Pauson-Khand reaction at the catalysis with chiral cobalt complexes was demonstrated by S.Gibson (IL) (Great Britain).

However not only new but also the known ligands could show excellent results as confirmed by the lecture of A.Togni (KL) (Switzerland) where an application of nickel catalyst was reported in asymmetrical reactions

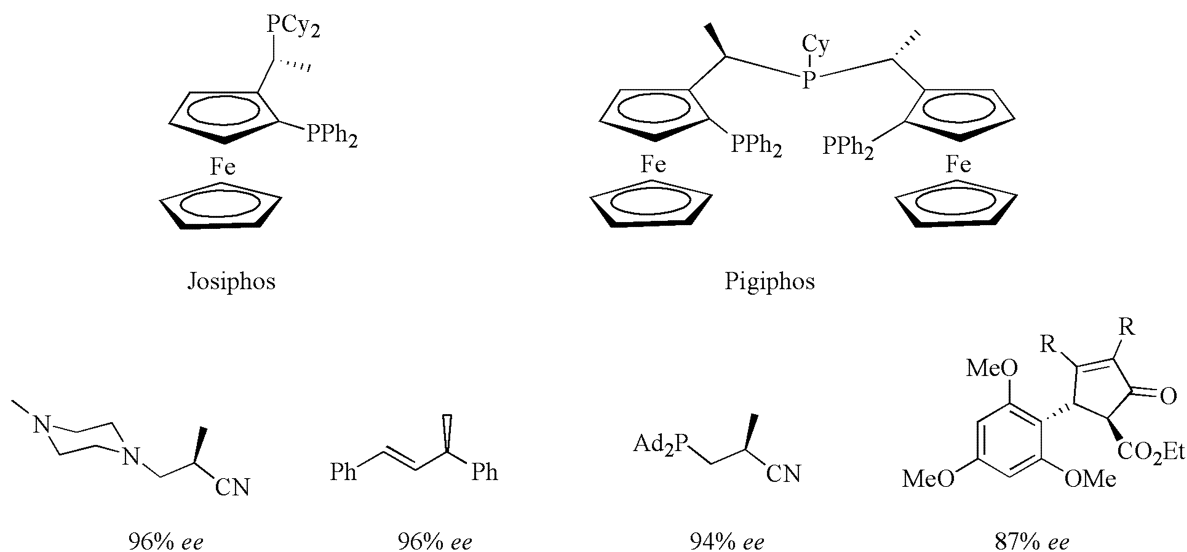
of hydroamination and hydrophosphination of methacrylonitrile, in allyl phosphination, Nazarov cyclization with Josiphos and Pigiphos as ligands. The reaction products were mentioned and the obtained *ee* (Scheme 2).

The lecture of M.Beller (IL) (Germany), interesting both by the form and the content, indicated the importance of going over from the catalysis by the complexes of noble metals to the catalysts based on the complexes of copper and iron. Examples were shown of application of these complexes in oxidation, reduction, and most interestingly, in cyanation of aryl halides.

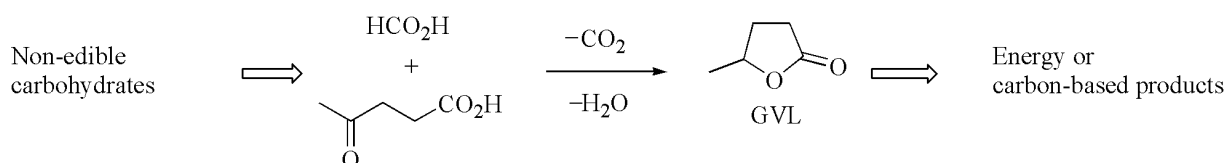
In a bright lecture of I.Horvath (Hungary) a problem was treated of energy and chemicals production from the recycled raw material. The application of a well chosen ruthenium catalyst made it possible to reprocess the biomass (inedible carbohydrates) into levulinic and formic acids, 1,4-pentanediol, γ -valerolactone, 2-methyl-tetrahydrofuran, and alkanes. The formic acid was used as reducer for converting the levulinic acid into GVL (Scheme 3).

The preparation of new nickel and palladium complexes with ligands of PyNox type and their application in

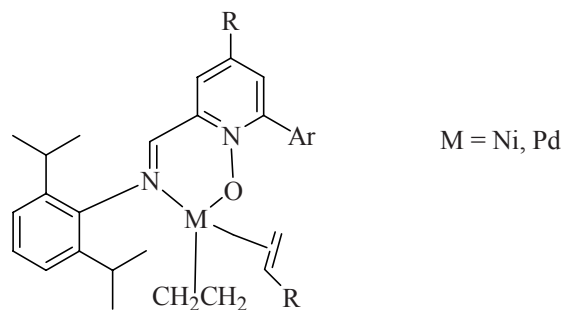
Scheme 2.



Scheme 3.



polymerization processes was the theme of the lecture of J. Campora (IL) (Spain).



The alkoxy carbonylation of olefins applied to the synthesis of medicinals of ibuprofen type and the refinement of the catalytic system by addition of certain ions was considered in the lecture of R. Chaudhari (IL) (USA).

The immobilization of the catalyst was performed and the kinetic aspects of the reaction were established.

In the lecture of I. Beletskaya (Russia) the catalysis for the formation of carbon–carbon bonds was described of palladium nanoparticles in the micelles of water-soluble polymer or applied on a polymer soluble in organic solvents. It was shown for the first time that although the catalyst activity was retained at the recyclization, it changed the morphology.

M. Tanaka (IL) (Japan) in the lecture showed that acid chlorides $XCH_2C(O)Cl$, $Cl_3CC(O)Cl$, $RC(O)C(O)Cl$ added to alkynes retaining the CO group.

In the lecture of B. Marciniak (IL) (Poland) reactions of vinylmetalloids were treated resulting in interesting products.

The catalysis with Brønsted acids was covered in two lectures. In the lecture of M. Green (IL) (South Africa)

was suggested a new Lewis acid catalyst: aluminum triflate. J. Michl (IL) (USA) demonstrated outstanding ability of free lithium cation, in particular, in the radical polymerization.

P. Jessop (IL) (Canada) regarded in his lecture various, among them some unusual, versions of employing CO_2 in catalysis. The conversion of ketones into β -hydroxycarboxylic acid occurring with high enantioselectivity by catalysis with ruthenium complexes was reported. The opportunity of reversible alteration of the medium polarity on addition and removal of CO_2 was demonstrated; this possibility is favorable at separation of the catalyst from the reaction products. And finally a compound was named that is capable under the action of CO_2 to turn into surfactant, and on CO_2 removal to become a demulsifier.

In an outstanding lecture of the youngest member of the Chinese Academy of C.-M. Che (IL) (Hong Kong, China) were presented new types of ruthenium complexes capable under mild conditions to catalyze a selective oxidation of alkenes with H_2O_2 into *cis*-diols or with the cleavage of the double bond into carboxylic acids. A porphyrin ruthenium complex was synthesized suitable for recyclization, catalyzing the oxidation of terminal olefins with a singlet oxygen into aldehydes/ketones.

The oral communications and posters also contained many new and useful information. The only reproach to the organizers can be the lack among the key and invited lectures a report on the present-day enantioselective organic catalysis, but this topic is outside the traditional schedule of these symposia.

The goal of these notes is to call the attention of the organic chemists to all the scope of the homogeneous catalysis.