



Editorial

Third Euchem Conference on “*Nitrogen ligands in organometallic chemistry and homogeneous catalysis*”, Camerino, Italy, September 2004. Classical organometallic chemistry and beyond

Keywords: N-donor ligands; Catalysis; Bio-organometallics; Supramolecular organometallic chemistry

1. Introduction

In the last 30 years, organometallic chemistry has produced many results of both academic and industrial importance. The development of new methodologies for organic syntheses and the increased catalytic use of metal complexes have given rise to a great deal of research directed towards the synthesis and mass production of multifunctional, complex molecules, such as agrochemicals and pharmaceuticals. However, the main industrial applications of organometallic complexes are associated with catalytic reactions in homogeneous conditions involving relatively simple, high volume chemical intermediates and polymers.

An essential part of the success of homogeneous catalysis is surely the possibility of selecting the proper metal (or oxidation state) and of tailoring the ligands. For example, the majority of homogeneous catalysts employed in industrial applications involve monodentate phosphorus ligands. Indeed, several complexes of this catalytically active class accelerate selective breaking and formation of chemical bonds through the electronic and steric control of the ligands. When such control is optimized, highly reactive intermediate species are formed, which can react in a well defined and productive way. Other common catalytic cycles employing P-ligands include the well known transition metal catalyzed C–C coupling protocols, the palladium-catalyzed (e.g., Heck) and cross-coupling reactions, all of which are useful synthetic tools in the organic chemists' hands. However, it was not until the mid 1990s that special attention was drawn to nitrogen ligands, for example in the Pd-catalyzed coupling reactions. Thus, only recently new ligands, such as bi- (or poly-)dentate nitrogen ligands, together with cyclopentadienyls (as metallo-

enes) groups, have found practical applications. The renewed interest in the C–C coupling reactions, catalyzed by systems containing ligands other than those based on phosphorus donors, has also permitted the formulation of new rules and even the rejection of old paradigms. The careful evaluation of their steric and electronic properties of ligands is important in developing such rules.

Systems based on biologically active ligands typically bind to first row transition metals in relatively high oxidation states; therefore, oxygen-, nitrogen- and sulphur- (rather than phosphorus-) containing ligands are preferred. Thus, the catalytic activity of enzymes, metalloproteins and analogous species under strict homogeneous conditions (i.e., *in vivo*) is based upon different reaction types, and continuously challenges biochemists toward the preparation, or optimization, of tailored biomimetic species.

Sponsored by FECS (the European Federation of Chemical Societies), the Universities of Camerino and Insubria, and the Division of Inorganic Chemistry of the Italian Chemical Society, staged the Third Euchem Conference on “Nitrogen Ligands in Organometallic Chemistry and Catalysis”, in Camerino (Fig. 1) on September, 8–12, 2004, and gathered together about 150 participants from the five continents (Fig. 2). The main objectives of this conference were the following: (a) to bring together chemists active in the field of coordination and organometallic chemistry and interested in the comprehension of the mechanistic effects at the basis of the catalytic activity and in the design of suitably tuned systems, (b) to analyse the structure–property relationships among the different classes of N-ligand-containing coordination compounds, (c) to establish the state-of-the-art in the field by covering both the



Fig. 1. The Rocca di Varano near Camerino and the University of Camerino and Insubria emblems.

experimental and theoretical aspects, (d) to link present applications to future developments with special concern for technological or industrial areas.

During five days of animated scientific presentations and discussions, the highly motivated scientists from 27 different countries have fulfilled most of these goals. The oral sessions comprised 8 invited lectures and about 40 (shorter, but not less important) contributions. In addition, two highly attended poster sessions, featuring more than 80 contributions, facilitated the exchange of ideas and information between experienced or young scientists and students, and between researchers from different areas of interest. Indeed, many of the presenting authors were young scientists at the beginning of their careers and both the quality of the talks and that of the scientific results were of a high standard.

Accordingly, the scientific program included presentations and discussions of many relevant aspects of coordination and organometallic chemistry. Typical subjects extensively discussed in this Conference included:

- Synthesis, structure and spectroscopy of organometallic complexes.
- Reaction mechanisms and catalytic activity.
- Asymmetric catalysis.
- Photochemistry, photophysics and electrochemistry of complexes.
- Nanoporous and mesoporous hybrid materials.
- Supramolecular chemistry.
- Biomimetic chemistry.

The present account will briefly focus on selected N-donor ligands and on selected structural or functional features described at the Conference. Because of the large number of systems presented this short summary cannot truly reflect the whole diversity of the scientific results. The reader is referred to the Conference homepage <http://web.unicam.it/discichi/nligands2004/index.htm> for the detailed program and full list of abstracts.

Although the Journal of Organometallic Chemistry generally restricts contributions to compounds containing metal–carbon bonds, the Editor has kindly agreed



Fig. 2. Group photo of all participants.

to widen the scope of the Journal for this issue, because it is clear from the papers presented there that nitrogen ligands are replacing the traditional phosphorus based ligands in many homogeneous catalytic processes.

2. Scorpionate ligands

Since their discovery in the mid 1960s [1], poly(pyrazolyl)borates (Tp^x) (Fig. 3(a)), often referred to as *scorpionates*, have been considered as some of the most useful ligands in modern coordination chemistry. Their versatility derives from the different steric and electronic effects that can be obtained by varying the nature, number and position of the substituents in the pyrazole rings, to fine-tune the stability, inertness and reactivity of their metal complexes. Their intriguing name derives from the typical structure of these complexes, where, like the pincer of a scorpion, the Tp ligands bind a metal with the nitrogen heteroatoms from two pyrazole rings, the third pyrazole ring being capable to bend forward like a scorpion's tail to "sting the metal". More precisely, the term *scorpionate* has been used to describe the interchange between bidentate and tridentate coordination modes of these ligands, which is at the core of the structural and chemical versatility of many metal complexes of this kind. In a rich lecture, Trofimenko reported that tris(pyrazolyl)borates are now widely used as catalysts, mainly for polyolefin polymerization. For example, yttrium complexes of Tp^x can catalyze the polymerisation of ethylene to PE [2]. Several studies have

indicated that also $\text{Tp}^x\text{TiCl}_n(\text{OR})_{3-n}/\text{MAO}$ catalysts ($n = 1-3$) can polymerize ethylene, ethylene/ α -olefins and styrene, but with poorer activity and with a broad molecular weight distribution [3]. $\text{Tp}^x\text{Rh}(\text{COD})$ derivatives have been employed in the homopolymerization of differently *para*-substituted phenylacetylenes [4].

Copper scorpionate derivatives such as Tp^xCu (ethylene) catalyze the reaction of ethyldiazoacetate with alkenes to form cyclopropanes under mild conditions [5]. Trofimenko's most recent work includes functionalization of aliphatic C–H bonds with a brominated scorpionate copper(I) catalyst, $\text{Tp}^{\text{Br}3}\text{Cu}(\text{MeCN})$. The $\text{Tp}^{\text{Br}3}$ ligand, having nine bromine atoms, three on each pyrazolyl ring, is the only ligand devoid of C–H bonds (*shall we call it an inorganic ligand?*). It was shown that $\text{Tp}^{\text{Br}3}\text{Cu}(\text{MeCN})$ provides good yields and high selectivities, improving the performance of other copper catalysts in inserting ethyl diazoacetate into tertiary C–H bonds of alkanes [6].

Recently, the development of "non classical" scorpionates (such as the bis(pyrazolyl)acetate employed by Burzlaiff and co-workers [7], (Fig. 3(b)), took place, not only as model ligands for metalloenzymes, but also for the synthesis of a variety of carbonyl, carbene, vinylidene and allenylidene complexes.

3. Pincer ligands

Pincer ligands (Fig. 3(c)), so named from their rigid multiple-chelating shape, are tridentate ligands allowing for the insertion of transition metals into the

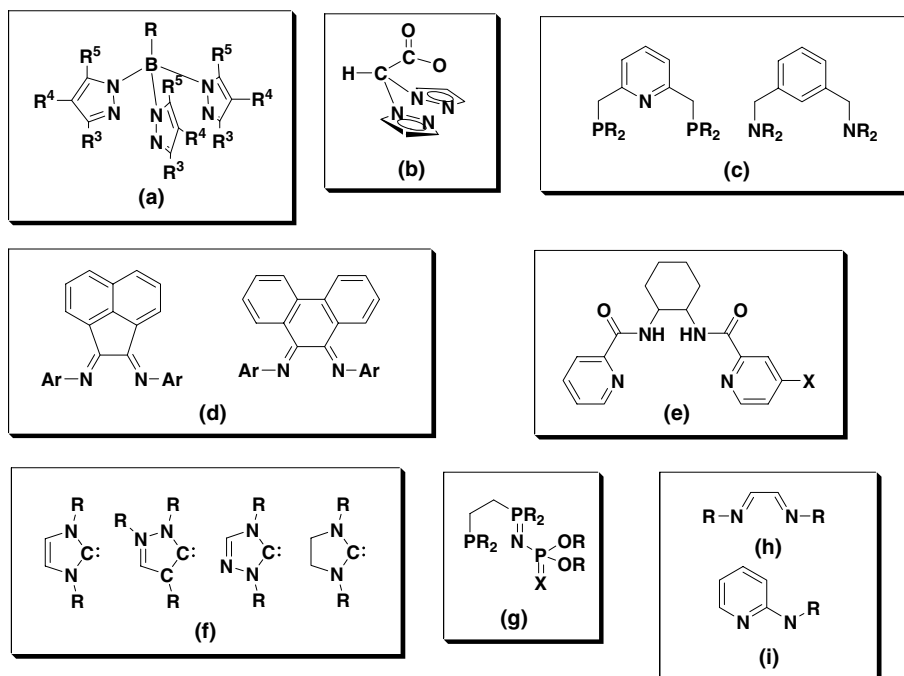


Fig. 3. Schematic drawings of the nitrogen ligands (a–i) cited in the text.

aromatic CH-bond situated between donor atoms such as P, S or N [8]. The aromatic moiety interacts with the metals and can act as an electron reservoir when highly unsaturated systems are involved. Complexes formed from pincer ligands are generally efficient catalysts for a variety of organic reactions. During the last decade, this type of ligands have been found to provide efficient dehydrogenation and Heck type catalysts, and to activate strong C–O and C–C bonds; the reactivity of these pincer-based metal complexes can easily be controlled by systematic ligand modification. Milstein reported a number of electron-rich, asymmetric pincer-type complexes, based on both nitrogen and phosphorus donor functionalities. These systems have been investigated in C–C, C–H and O–H activation processes. Milstein also described a number of PCN “hemi-labile” ligands, useful for the preparation of unusual compounds, such as anionic, electron-rich, highly electrophilic platinum species, which do not require stabilization by π -acceptors.

4. Ar-BIAN and Ar-BIP ligands

In the 1990s, Elsevier and his group [9] developed rigid bidentate N-ligands (Fig. 3(d)) combining suitable σ -donor and π -acceptor properties, and thus acting as efficient ligands for both high(er) and low(er) oxidation states. The rigidity of the chelating acenaphthene moiety forces the iminic N atoms to remain in a fixed *cis*-orientation, thus facilitating reductive coupling of organic groups from this type of complexes. Following this track, Ragaini and coworkers described new asymmetric Ar-BIAN ligands, possessing one strongly electron-withdrawing group and one strongly donating substituent on the two aryl rings.

5. Imido and pyridylamides

Transition metal complexes containing imido ligands $[\text{NR}]^{2-}$ have also raised the interest of the organometallic chemist; the dianionic π -donor terminal imido group can indeed be involved in a large number of reactions: those in which the imido moiety acts a spectator ligand ($[\text{NR}]^{2-}$ being isolobal with C_5H_5^-) and those in which the $\text{M}=\text{NR}$ linkage itself is broken (such as imine synthesis, oxo-imido exchange, C–H activation, reaction with unsaturated C–C or C–X bonds, etc.). Arylamido complexes were introduced by Focante, who discussed several aspects of their coordination chemistry and presented novel applications in olefin polymerization. Moberg and co-workers [10] showed that electronic tuning of bispyridylamides can yield efficient catalyst for Mo-catalyzed allylations and that polymer supported

bispyridylamides (Fig. 3(e)) can be efficiently recovered (and reused) in catalytic processes.

6. N-heterocyclic carbenes

Since the first report by Öfele [11a], N-heterocyclic carbenes (NHCs) (Fig. 3(f)) derived from pyrazole, imidazole and triazole have become an important class of ligands [11], widely employed in inorganic and organometallic chemistry. Although the first transition metal complexes (Cr and Hg) were reported in 1968, research in this area really took off with Arduengo's breakthrough isolation of the free carbenes in 1991. These ligands are similar to tertiary phosphines, both for ligand properties and metal complex syntheses. Both classes are pronounced σ -donor ligands with only little backbonding character. Metal-NHCs complexes continue to assume an important role as catalysts, because of their relevant thermal stability and tolerance to air and moisture. NHCs bind to practically all transition metals, both in low or high oxidation states, and also to a few main group elements (Be, S and I). It is now commonly accepted that a new generation of organometallic catalysts with N-heterocyclic carbenes will replace triorganophosphine complexes because of their activities and wide ranging applications. In particular, ruthenium-based NHC catalysts are likely to be efficiently employed in the olefin metathesis.

7. Iminophosphines and iminophosphoranes

Transition metal complexes with hemilabile heteroditopic ligands are also useful materials for a number of stoichiometric and catalytic processes. Although P-donor ligands were the first type of ligands used in transition metal catalysis, it is now accepted that mixed phosphorus–nitrogen ligands can lead to an increase of the activity of the catalyst. For example, phosphino-oxazoline and pyridylphosphine ligands proved to be very efficient catalysts; however only a limited number of imino- or amino-phosphine ligands have been used in catalysis. Gimeno and co-workers [12] reported a number of ruthenium complexes bearing imino- and amino-phosphines catalytically active in transfer hydrogenation of arylalkyl and dialkyl ketones in propan-2-ol. Novel heterotrifunctional ligands $\text{Ph}_2\text{PCH}_2\text{P}\{\text{=NP(=O)(OR)}_2\}_2\text{Ph}_2$ (Fig. 3(g)) showing a P,N,O-donor framework can be easily prepared via single stage oxidation of bis(diphenylphosphino)methane with phosphoryl azides $(\text{RO})_2\text{P(=O)N}_3$ (R = Et, Ph). These potentially hemilabile ligands show a versatile coordination ability in ruthenium complexes. Some of these complexes have been

proven to be suitable catalyst precursors for the transfer hydrogenation of cyclohexanone by propan-2-ol.

8. Di-imines, di-amines, polyamines and aminopyridinato ligands

Renaud reported new allylic ruthenium complexes, of the $[\text{Cp}^*(\text{allyl})(\text{diimine})\text{Ru}]\text{PF}_6$ type, that can be depicted as trapped transient electrophilic intermediates active in several useful allylic substitution reactions. The solvent and the counterion effects on the aggregation and structure of cationic arene ruthenium complexes bearing α -diimine and diamine ligands (Fig. 3(h)) has been discussed by Zuccaccia, who demonstrated the predominance of ion pairs in propan-2-ol, a solvent frequently used in the transfer hydrogenation of unsaturated functionalities. The cationic fragment $[\text{PtCl}(\text{tetramethylethylenediamine})]^+$ has been reported by Maresca as a powerful olefin activator. In cationic complexes generated by coupling with higher homologues of ethene easy, base promoted, allylic activation is observed. Gd(III) complexes of polyaminopolycarboxylic ligands described by Anelli et al. [13] are now extensively used as Magnetic Resonance Imaging (MRI) extracellular contrast agents: indeed, these species immediately equilibrate between plasma and the interstitial fluids in the body and are quickly eliminated through the renal route. Employing both early- and late-transition metals, Kempe reported aminopyridinato ligands with different steric and electronic properties; moreover, their lanthanoid and group 10 metal complexes have been used as catalysts for ring-opening polymerization, olefin polymerization, catalytic polysilane synthesis and cross-coupling reactions. Interest towards this class of ligands (Fig. 3(i)) stems from the flexibility of their binding geometries.

9. Pyridines, bipyridine, polypyridines and related ligands

Several applications of *chiral* bipyridine derivatives in enantioselective catalysis have been presented. The most successful transformations favoured by these ligands were copper-catalysed cyclopropanation and allylic oxidation, and palladium-catalysed allylic substitution reactions. Enantioselective nucleophilic catalysis is a new emerging area where chiral bipyridine N-oxides have recently made a considerable impact.

Chiral ligands with two or three pyridine units assembled together to yield 2,2'-bipyridine or 1,10-phenanthroline scaffolds have been described by Gladiali and co-workers [14]. The chirality of the ligands is due to the presence of a chiral alkyl substituent on the heterocyclic rings, or to pyridine moieties supported onto a

chiral template featuring either a stereogenic axis or a stereogenic plane. 1,10-phenanthrolines substituted in position 2 with sterically demanding chiral alkyl groups yield also catalysts of outstanding activity.

The synthesis of a new class of phosphine-based ruthenium catalysts bearing 2-aminomethyl-pyridine has been described by Baratta. It has been reported that the presence of P-donor in association with 2-aminomethyl-pyridine at the metal center yields systems exhibiting a remarkable high catalytic activity in transfer hydrogenation.

Square-planar platinum $[\text{PtMe}(\text{2,9-Me}_2\text{-phenanthroline})\text{L}]^+$ complexes, exhibiting a fast fluxional motion between two non-equivalent exchange sites have been presented and discussed by Romeo, who also investigated the dynamic exchange as a function of the nature of the neutral ligands L, of the solvent and of the counterions. The mechanism is switchable between the intramolecular dissociative and bimolecular associative pathways, depending on the inter-ionic structure of the complex and the action of potential nucleophiles.

10. Aziridines

Aziridines have been proposed by Lorenz, who showed that these ligands can react with transition metal complexes in different ways. It is noteworthy that the ring opening reaction of one aziridine ligand is followed by its insertion into the N–H bond of a second one, yielding a *N,N'*- β -aminoaziridine complex.

11. Biomimetic assemblies

Nitrogen ligands are widely present in biological systems, and are also ubiquitous in synthetic metal complexes of relevant pharmacological activity. Thus, the comprehension of the structure and the energetics of simple molecules, mimicking nucleobase-metal interactions and selective molecular recognition, is at the basis of bioinorganic chemistry. In this respect, Navarro and Lippert [15] presented interesting talk about the interplay of coordinative bonds and hydrogen-bonds in forming oligonuclear (Pt-based) assemblies of heteroaromatic ligands. The selective formation of supramolecular entities (rings and ribbons) was extensively discussed and further presented by Navarro, who introduced the host-guest chemistry of metalla-calixarenes based on heteroaromatic ligands and their molecular recognition properties with chiral biologic systems. Preorganized calix[4]arenes with copper and zinc ions, catalytically active in transesterification of phosphodiester and oligonucleotides, were later discussed by Salvio, with particular emphasis on mechanistic and cooperative effects.

12. Extended materials

Polynuclear coordination compounds often display a reactivity which is rather different from that expected from the simple sum of the properties of the building entities. This is largely due to cooperative and synergistic effects and to the rigidity of the metal coordination spheres imposed by the presence of multitopic ligands. Also, the study of their intriguing, poorly predictable, geometrical features represents a research field on its own. With this in mind, Reger et al. [16] presented a number of metal complexes which, in the solid state, display extended polymorphism, cage structures, aromatic π - π interactions, weak(er) C-H...F(O) interactions and low-temperature spin-transition behaviour when co-ordinated to iron(II). Porous metallorganic frameworks, capable of selective gas sensing and ion pair recognition were discussed by Barea, who nicely showed reversible transformation paths of self-assembled copper pyrimidinolates, driven by salt sorption, salt removal and thermal treatments.

13. Functional properties

Among the most relevant functional properties displayed by the species presented during the Conference (apart from the obvious catalytic activities in homogeneous conditions), a few merit specific mention: the *heterogeneous* catalytic activity in the carbon-dioxide reduction displayed by thin films of Os⁰ polypyridyl nanowires (Chardon-Noblat); luminescence (Stagni, Kozhnikov, Haberecht, Lee, Pettinari); enclathration (Casellas); molecular recognition (Galindo Cuesta), second-harmonic generation (Galli), photoreactivity (Thummel) and MRI activity (Gateau, Sisti).

All the above topics are debated in peer-reviewed manuscripts gathered in this special issue of the Journal of Organometallic Chemistry. The Conference has confirmed that nitrogen ligands and their application in homogeneous catalysis is a unique and interdisciplinary field of investigation, which will need a deeper understanding of some fundamental aspects, either by theoretical tools (DFT) or by new powerful structural and spectroscopic techniques, such as diffraction from polycrystalline materials, synchrotron XPS, dynamic NMR, luminescence or electrochemical methods.

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