

# XXV International Conference on Organometallic Chemistry

Vital role of platinum group metals highlighted at 'Jubilee' conference

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The XXV International Conference on Organometallic Chemistry (XXV ICOMC) (1), was held for the first time in Portugal, taking place in Lisbon from 2nd to 7th September 2012. This highly successful series of biennial conferences was launched in 1963 in Cincinnati, USA. This was the 'silver event' (25th) and the 'golden year' (the 50th year since the series began) of this chain of conferences, and provided an opportunity for a 'Silver/Gold Jubilee' celebration. A celebratory book (2) will be published, and a special celebratory medal was coined (**Figure 1**) featuring on its reverse a representation of a platinum centre interacting with a carbon–carbon double bond (the Chatt-Dewar-Duncanson model). The medal was received by all the invited speakers and the members of the ICOMC International Advisory Board.

The conference was attended by 1218 delegates from 54 countries (**Figure 2**). Over 1100 were from outside Portugal, with a good quota (38%) of students. The countries most represented were Germany (*ca.* 160 delegates), Japan (*ca.* 135 delegates, the second largest representation), Portugal (*ca.* 115), Spain, UK, France, Russia, Switzerland, Italy and Poland, in this order. Japan, the country that will organise the next ICOMC in 2014, was strongly represented; other more distant countries included mainland China (*ca.* 40); South Africa, Australia, USA and Canada (*ca.* 20 each); Taiwan, Singapore and Hong Kong (between 10 and 20 each). The participation of China (mainland



Fig. 1. Silver/Gold Jubilee ICOMC celebratory medal

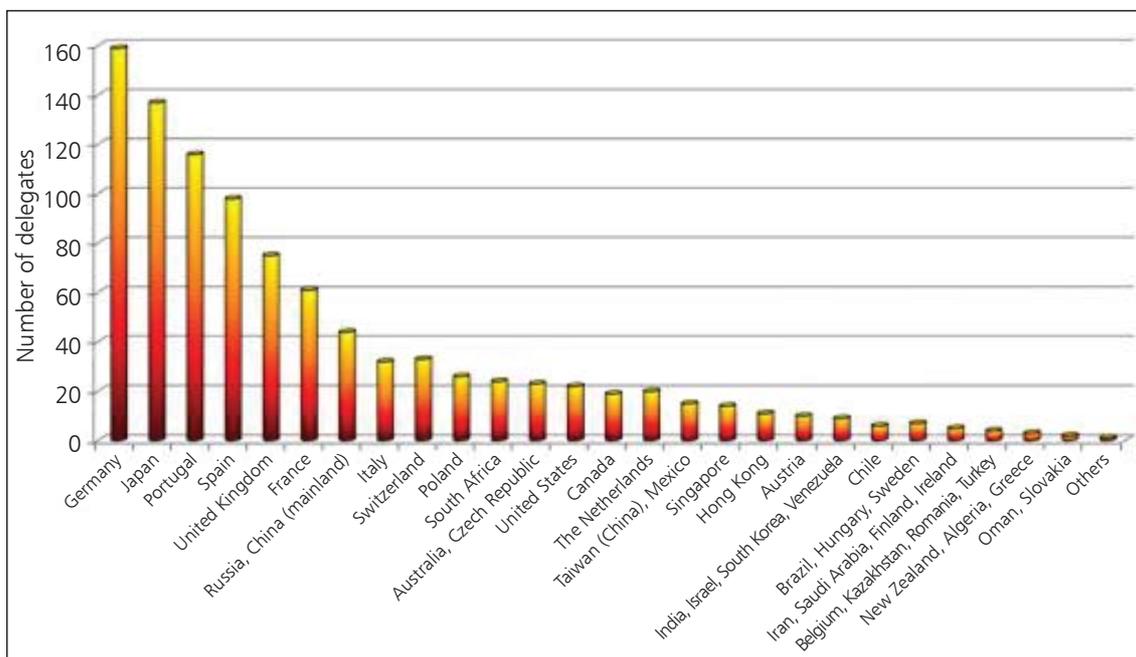


Fig. 2. Distribution of delegates (numbers) from different countries, grouped by number of delegates

plus Taiwan) was identical to that of France at *ca.* 60 delegates each.

The scientific programme included a total of 1265 contributions of different types, i.e. 1.03 per participant. There were 5 Plenary and 17 Keynote Lectures, 195 normal oral and 794 poster contributions, and the programme also included, for the first time in this series of conferences, 165 Flash oral presentations (to allow mainly young researchers to briefly advertise their posters) and 77 Satellite Sessions (invited lectures) spread throughout the conference to promote cooperation between younger and senior researchers of various countries.

The inclusion of the *Journal of Organometallic Chemistry (JOM)* symposium (11 invited Lectures) in the programme, following a proposal by the Editor Richard D. Adams (University of South Carolina, USA), was also noteworthy.

The scientific programme covered all fields of organometallic chemistry, from fundamental to applied, and related areas of other sciences, eliminating artificial boundaries and promoting interdisciplinary collaboration (Figure 3). Catalysis was the most represented field (261 contributions), followed by Fundamental Organometallic Chemistry (156 contributions); Activation of Small Molecules, C–H and C–C Bond Activation and Functionalization,

and Metal-Mediated Synthesis (each with *ca.* 80 contributions); Organometallic and Green Chemistry, Bioorganometallic and Bioinorganic Chemistry, and Organometallics Related Chemistry (*ca.* 75 each). They were followed by Organometallics for Materials (*ca.* 65); Polynuclear and Supramolecular Assemblies, Polymers, and Reaction Mechanisms (*ca.* 50 each).

Quite a good number of contributions included platinum group metals (pgms), and a representative selection (which is intended to be merely illustrative rather than comprehensive) is briefly outlined herein, concerning the main areas of the conference. Many of the sections include contributions of relevance to other areas in accordance with the interdisciplinary nature of the conference.

### Catalysis

Three decades of Noyori's 2,2'-bis (diphenylphosphino)-1,1'-binaphthyl (BINAP) chemistry were reviewed by their inventor, Ryoji Noyori (RIKEN and Nagoya University, Japan), with emphasis on asymmetric hydrogenation with rhodium- and ruthenium-BINAP catalysts, nowadays practiced worldwide and with broad application in stereoselective organic synthesis, both in the laboratory and in industry.

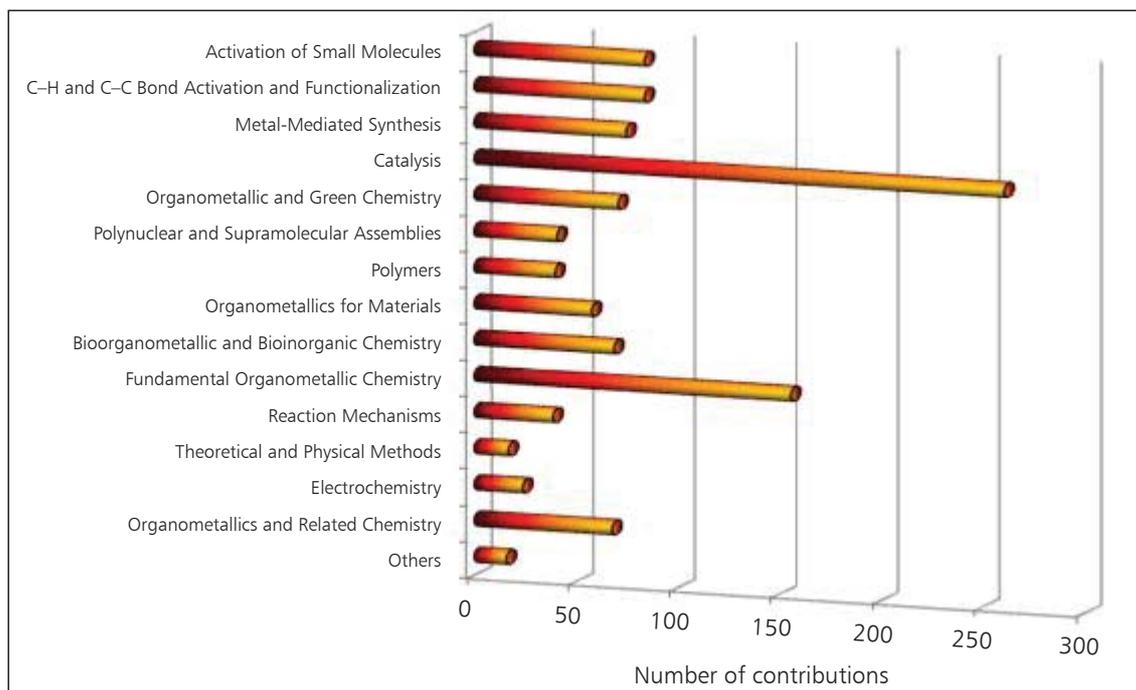


Fig. 3. Distribution of abstracts (numbers) from each of the scientific areas covered by the conference, in order of appearance

Ferenc Joó (University of Debrecen, Hungary) described various hydrido-Ru complexes which form in aqueous solutions at different pHs and hydrogen pressures; these include a rare *trans*-dihydride, *trans*-[RuH<sub>2</sub>(*m* tppms)<sub>4</sub>], and one of the very few dihydrogen complexes ever observed in aqueous solution, [RuH<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>)(*m* tppms)<sub>3</sub>] (*m* tppms = monosulfonated triphenylphosphine). The concentration distribution of the hydrido-Ru(II) phosphine complexes explains the rate and selectivity changes in aqueous biphasic hydrogenation of α,β-unsaturated aldehydes as a function of pH.

Maurizio Peruzzini (Consiglio Nazionale delle Ricerche (CNR), Florence, Italy) pointed out several neutral mono- and bidentate P-N donor ligands derived from the C-6 ('upper rim') functionalisation of the hydrosoluble triazaphosphine 1,3,5-triaza-7-phosphaadamantane (PTA), together with the analysis of catalytic data related to the activity of Ru(II) complexes in hydrogenation reactions under very mild conditions (3).

Anna Trzeciak (University of Wrocław, Poland), seeking for alternative palladium catalysts for the Suzuki-Miyaura reaction, presented Pd(II) carbene complexes of the types [Pd(μ-IL)<sub>2</sub>Cl<sub>2</sub>] (IL = *N*-substituted imidazole) and [IL]<sub>2</sub>[PdCl<sub>4</sub>], the former with a high activity in ethylene glycol.

Lanny Liebeskind (Emory University, USA) explored the chemoselective metal-catalysed desulfurative coupling of thioorganics with boronic acids (involving carbon-sulfur bond cleavage and carbon-carbon bond formation) at neutral pH, and its biological significance. He discussed a strategy based on a dual thiophilic-borophilic activation for thiol ester-boronic acid coupling under non-basic conditions, catalysed by tetrakis(triphenylphosphine)palladium(0) in the presence of a copper(I) carboxylate as cofactor (Figure 4) (4).

Yong-Gui Zhou (Dalian Institute of Chemical Physics, China) discussed three kinds of activation

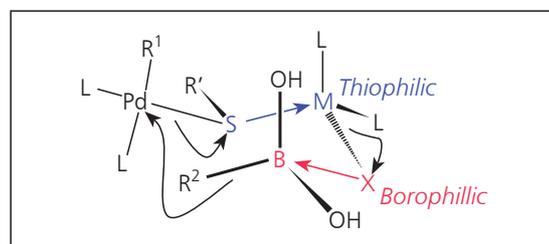


Fig. 4. Turning on transmetalation at palladium thiolates. The M-X cofactor enhances kinetics and thermodynamics (dual activation). L are ligands; R<sup>1</sup> and R<sup>2</sup> are functional groups; M is copper or a thiophilic metal; and X is a borophilic group

strategies for the successful asymmetric hydrogenation of heteroaromatics (substrate activation, catalyst activation and relay catalysis) indicating several rhodium, ruthenium, iridium and palladium catalysts which can be used for this purpose (5).

Hong Yan (Nanjing University, China) presented several electronically unsaturated 16-electron cobalt, rhodium, iridium, ruthenium and osmium half-sandwich complexes containing a carborane-1,2-dichalcogenolate ligand, their involvement in catalysis towards alkyne trimerisation, and their biological activity.

Jwu-Ting Chen (National Taiwan University) showed that cationic methylpalladium(II) complexes of the type  $[\text{Pd}(\text{Me})(\text{NCMe})(\text{L})]$  (L = chelating substituted pyridinyl aminates) can act as catalysts for the formation of alternating cyclic olefin copolymerisation.

Dalmo Mandelli (Federal University of ABC, Brazil) presented the Os carbonyl complex  $[\text{Os}_3(\text{CO})_{12}]$  as a rare example of a homogeneous metal catalyst for the oxidation of glycerol with  $\text{H}_2\text{O}_2$  to produce dihydroxyacetone, glycolic acid and hydroxypyruvic acid.

Pedro Góis (University of Lisbon, Portugal) described the possibility of combining, in a cooperative manner, metal and organic catalysts, giving a dirhodium carboxylate system as an example.

### Activation of Small Molecules

Jitendra Bera (Indian Institute of Technology, Kampur) discussed an organometallic approach towards water activation. A naphthyridine group suitably placed on a ligand scaffold (**Figure 5**) enhances the hydration activity of a Rh(I) catalyst, and bifunctional water

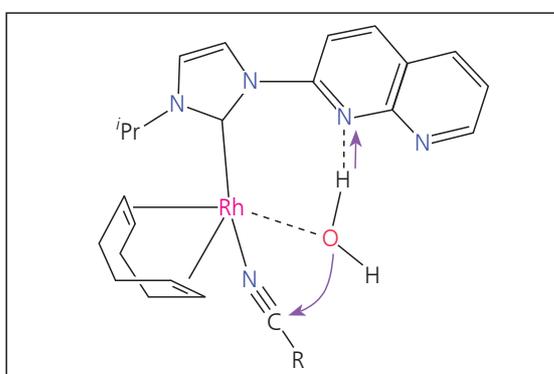


Fig. 5. Water activation by a rhodium catalyst

activation for the catalytic hydration of organonitriles was demonstrated (6).

Erwin Reisner (University of Cambridge, UK) addressed the subject of bio-inspired solar water splitting with metalloenzymes and synthetic catalysts integrated in nanostructured materials, recalled that direct solar fuel generation needs a finely tuned combination of light absorption, charge separation and redox catalysis, and referred to Ru-dye sensitised titania nanoparticles modified with hydrogenases as suitable catalysts for proton reduction to molecular hydrogen (7).

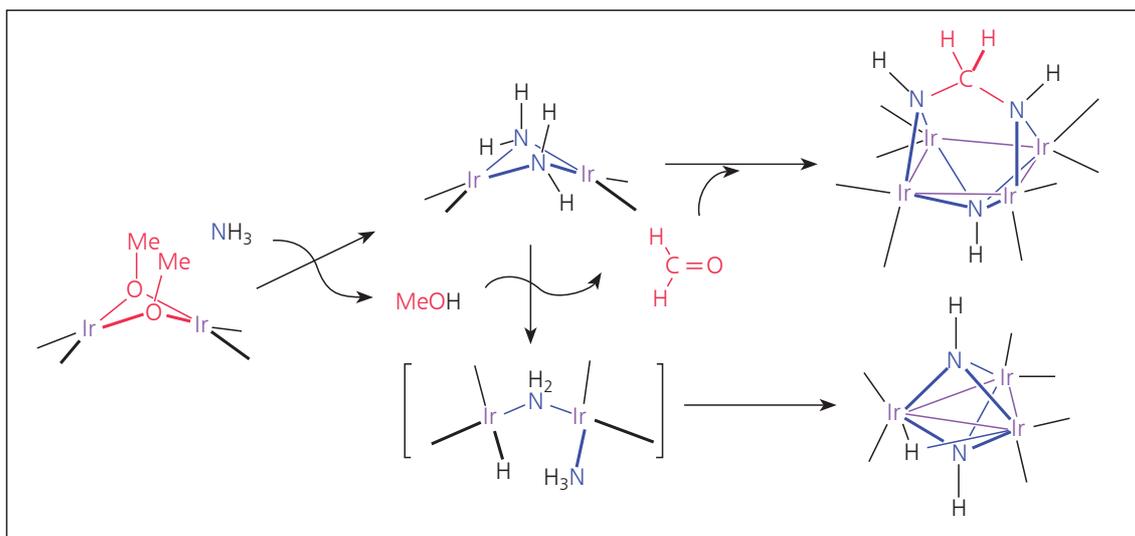
Sylviane Sabo-Etienne (University of Toulouse, France) focused on dihydrogen and  $\sigma$ -borane Ru complexes and presented recent results on hydrogenation/dehydrogenation, hydrogen/deuterium exchange and carbon dioxide functionalisation.

Luis Oro (University of Zaragoza, Spain) reported a direct entry to amido  $\text{Ir}_2$  and  $\text{Rh}_2$  complexes, by interaction of ammonia with alkoxo-bridged precursors under mild conditions (**Scheme 1**). In particular, the dinuclear amido-bridged complex promotes dehydrogenation of alcohols, affording unusual mixed amido/imido  $\text{Ir}_4$  and bis(imido)  $\text{Ir}_3$  clusters. Theoretical calculations suggest that  $\mu\text{-NH}_2$  linkages are crucial to the formation of hydrido ammine  $\text{Ir}_2$  species, active in H-transfer reactions.

Claudio Pettinari (University of Camerino, Italy) described the chemistry of Rh and Ir derivatives containing scorpionate ligands and detailed the reactions between  $[\text{M}(\eta\text{-diene})(\mu\text{-Cl})_2]$  dimers,  $[\text{M}(\text{Cp})\text{Cl}_2]_2$  (Cp = cyclopentadienyl) and also  $[\text{Ru}(\eta^6\text{-arene})\text{Cl}_2]_2$  with bis- and tris-(pyrazolyl)borates. Their catalytic applications were also addressed.

Eric Clot (Institute Charles Gerhardt, Montpellier, France) showed features of the chemistry of Ru-borane complexes such as  $[\text{RuH}(\text{X})(\eta^2\text{-H}_2\text{BR})(\text{PR}_3)_2]$ . With R = mesityl and X = H, the bis  $\sigma(\text{BH})$  coordination of borane was observed, whereas changing X = H to X = Cl afforded the reversible formation of a borylene complex. Density functional theory (DFT) calculations described the nature of the coordination of the borane to the Ru centre as a function of X and R.

Sanshiro Komiya (Tokyo UAT, Japan) presented a study on the synergy of two different transition metals (platinum and manganese) in catalysis and showed that regio- and stereo-selective C–S bond cleavage at dimethylthiiranes by heterodinuclear R-Pt-Mn complexes, e.g.  $[\text{Pt}(\text{Me})(\text{dppe})\{\text{Mn}(\text{CO})_5\}]$  (dppe = 1,2-bis(diphenylphosphino)ethane), lead to (thiamanganacycle)platinum compounds (8).



Scheme 1. Formation of amido and imido Ir<sub>2</sub>, Ir<sub>3</sub> and Ir<sub>4</sub> iridium cluster complexes

### C–H and C–C Bond Activation and Functionalization

Alan Goldman (Rutgers University, USA) focused on pincer-ligated Ir complexes as catalysts for alkane dehydrogenation, and discussed the mechanism, the scope of dehydrogenations and coupling with secondary reactions (tandem catalysis).

William Jones (University of Rochester, USA) compared the reactivities of the nickel or rhodium metal fragments [Ni(dippe)], [Tp'RhL], [Cp\*RhL] and [Rh(dippe)]<sup>−</sup> (dippe = 1,2-bis(diisopropylphosphino)ethane; Tp' = tris(3,5-dimethylpyrazolyl)borate; Cp\* = pentamethylcyclopentadienyl; L = PR<sub>3</sub> or CNR) towards the cleavage of C–H, C–C and C–S bonds.

Georgiy Shul'pin (Semenov Institute of Chemical Physics, Moscow, Russia) discussed the functionalisation of C–H compounds with peroxides catalysed by organometallic complexes of Os and Rh. For example, [Os<sub>3</sub>(CO)<sub>12</sub>] (9) and [Cp\*<sub>2</sub>Os] (10) efficiently catalyse the oxygenation of hydrocarbons with hydrogen peroxide, while Rh carbonyl complexes catalyse the oxygenation of benzene.

Maurice Brookhart (University of North Carolina, USA) focused on useful hydrocarbon conversions employing Ir pincer complexes capable of efficient transfer dehydrogenation and their application in alkane metathesis, synthesis of aromatic molecules from linear alkanes and synthesis of *p*-xylene from ethylene as the sole feedstock (Scheme II).

Todd Marder (Würzburg University, Germany) addressed the Ir-catalysed borylation of aromatic C–H bonds, covering applications and issues affecting selectivity. With Patrick Steel (Durham University, UK) (11), they developed the microwave assisted borylation of aromatic C–H bonds and one-pot, single solvent processes for combined aromatic borylation (Suzuki-Miyaura cross-coupling and aromatic borylation) conjugate addition sequences. Marder described the application of selective C–H borylation to the synthesis of substituted 2-phenylpyridines and functionalised pyrenes (Figure 6) (12). These processes rely on the formation of pgm boryl complexes, and their unusual properties.

David Davies (University of Leicester, UK) described a Rh-catalysed ambiphilic metal ligand activation (AMLA) of C–H bonds (Scheme III) and determined, through DFT calculations, the relative ease of this activation, similarly to other recently reported work (13).

Robert Crabtree (Yale University, USA) clarified that with primary oxidants Ce(IV) and NaIO<sub>4</sub>, precatalysts of the types [Cp\*Ir(chel)Cl] (chel = 2,2'-dipyridyl, 2-pyridylphenyl and related groups) mediate oxidation of alkyl C–H to C–OH with retention of configuration at carbon. These oxidants (also, anodic oxidation) lead to water being converted to dioxygen by [Cp\*Ir(chel)Cl] and [Cp\*Ir(OH<sub>2</sub>)<sub>3</sub>]SO<sub>4</sub>. In some cases the catalysis is homogeneous, in others heterogeneous, a distinction

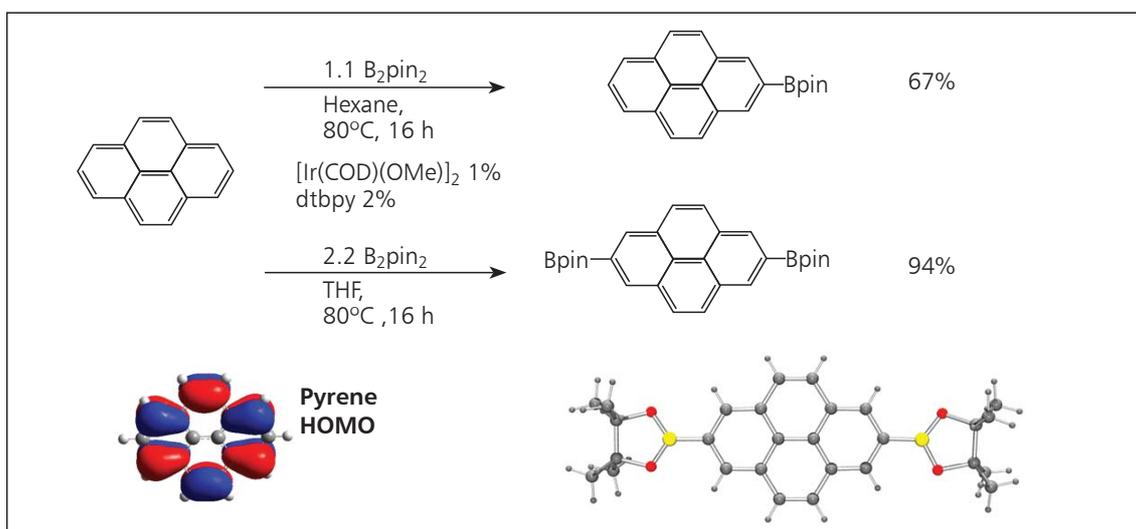
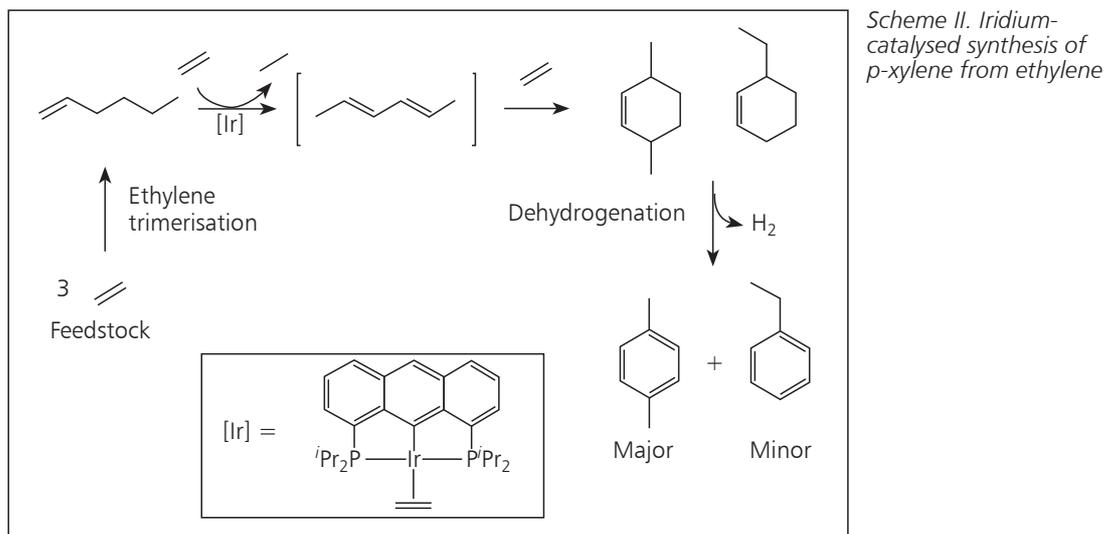


Fig. 6. Borylation of pyrene exclusively at the 2- and 2,7-positions using an iridium catalyst. *B*<sub>2</sub>*pin*<sub>2</sub> and *dtbpy* stand for diboron pinacol ester and 4,4'-di-*tert*-butyl bipyridine, respectively (HOMO = highest occupied molecular orbital)

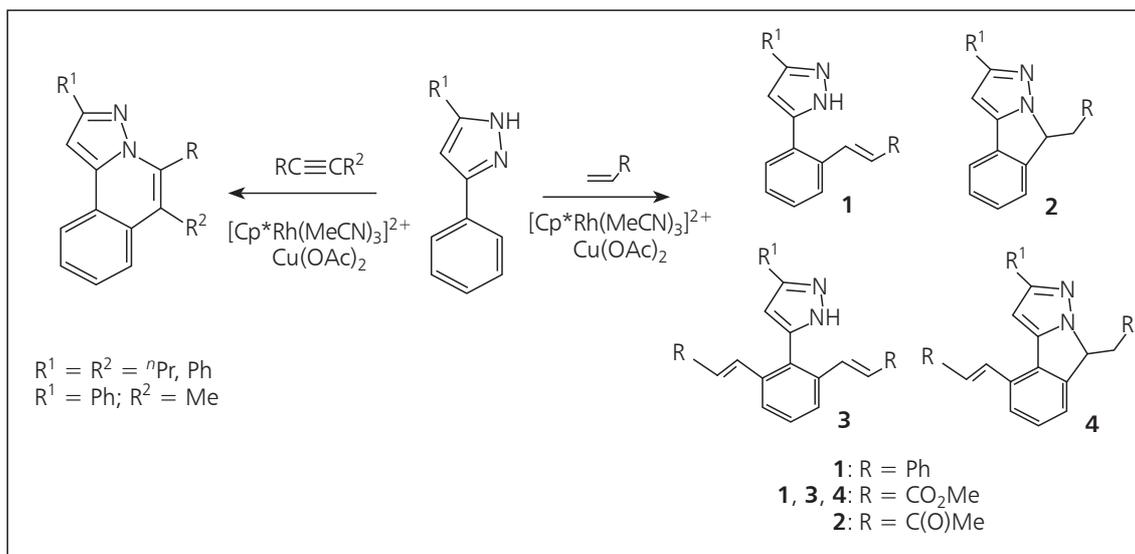
that is made from dynamic light scattering and quartz crystal nanobalance measurements (Figure 7) (14).

Pierre Dixneuf (University of Rennes, France) discussed the use of Ru(II)-cymene complexes, assisted by coordinated or external bases, as catalysts for a variety of arylation reactions from cheap and available aryl and heteroaryl chlorides (15).

Andrew Weller (University of Oxford, UK) outlined his recent studies on whether similar organometallic structures, transformations and catalysis can occur in the solid state, when compared to the analogous solution-phase chemistry, using Rh and Ir phosphine

complexes. He demonstrated that C–H activation (16), C–C bond formation and activation (17) and B–H activation can all occur in the solid state. He also discussed the characterisation of intermediates that invoke sigma interactions.

Salvador Conejero (University of Seville, Spain) showed that coordinatively unsaturated Pt(II) 14-electron complexes can intermolecularly activate the C–H bonds of aromatic compounds, depending on the electronic and steric properties of bulky *N*-heterocyclic carbene (NHC) ligands, leading to unsaturated Pt(II)-aryl complexes (18). A mononuclear



Scheme III. Rhodium-catalysed activation of carbon–hydrogen bonds

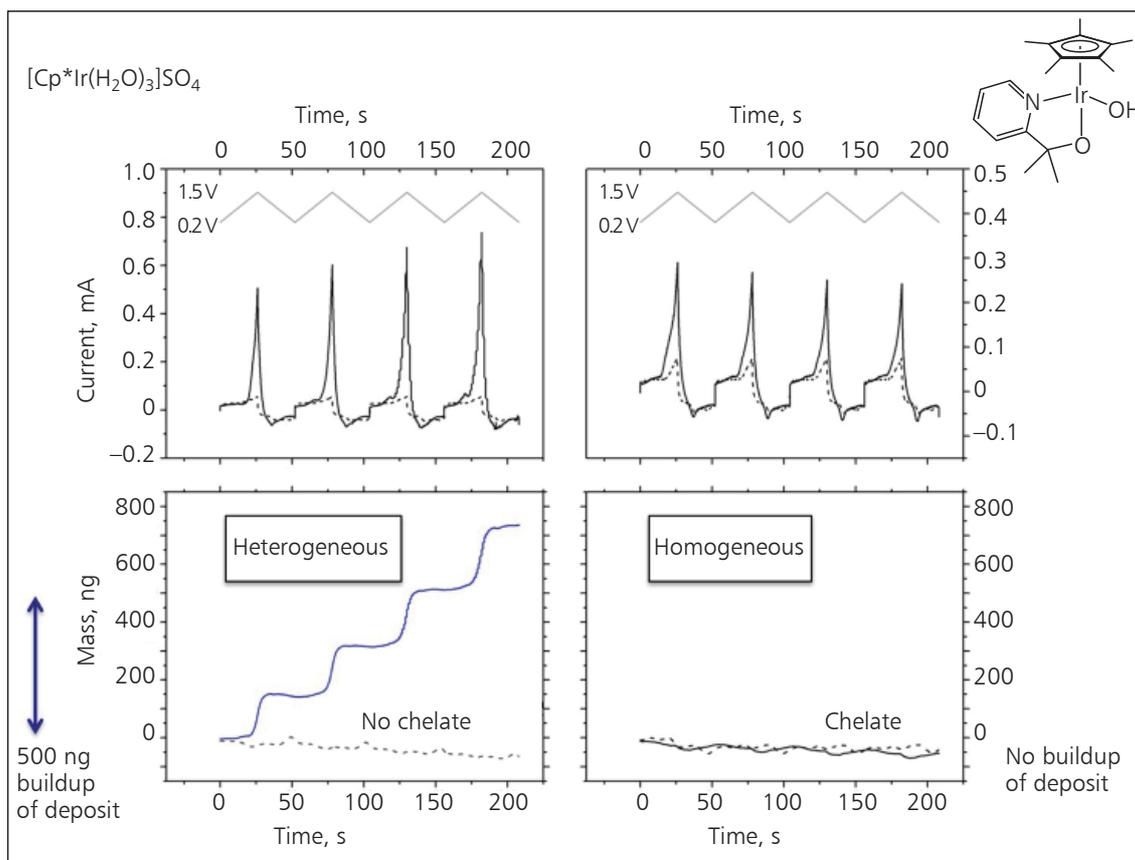


Fig. 7. Distinguishing the homogeneity of electrocatalyst by quartz crystal electrochemical nanobalance data

Pt(III)-alkyl complex is an intermediate in carbon-halogen coupling reactions.

Richard Adams (University of South Carolina, USA) reported examples of oxidative addition of gold-carbon bonds to Os cluster compounds (**Scheme IV**). Because the H atom and the Au(PPh<sub>3</sub>) group are both isoelectronic and isolobal, studies of the reactivity of Au-C bonds may have important implications for understanding the activation and cleavage of C-H bonds.

### Organometallic and Green Chemistry

Munetaka Akita (Tokyo Institute of Technology, Japan) described the use of clean and inexhaustible solar energy to drive organic transformations *via* two different catalytic tactics, i.e. bimetallic photocatalysis and photo-redox catalysis, based on the unique photochemical properties of the excited species of [Ru(bipy)<sub>3</sub>]<sup>2+</sup> (bipy = 2,2'-bipyridine) and its organo-Ir analogues. Their photo-excited states contain singly occupied molecular orbitals of high and low energies, which can work as reductant (electron donor) and oxidant (electron acceptor), respectively. Sequential redox processes led to efficient generation of organic radicals from enamines, organoborates and trifluoromethylating reagents. Sunlight efficiently induces Giese-type coupling and solvolytic olefin trifluoromethylation.

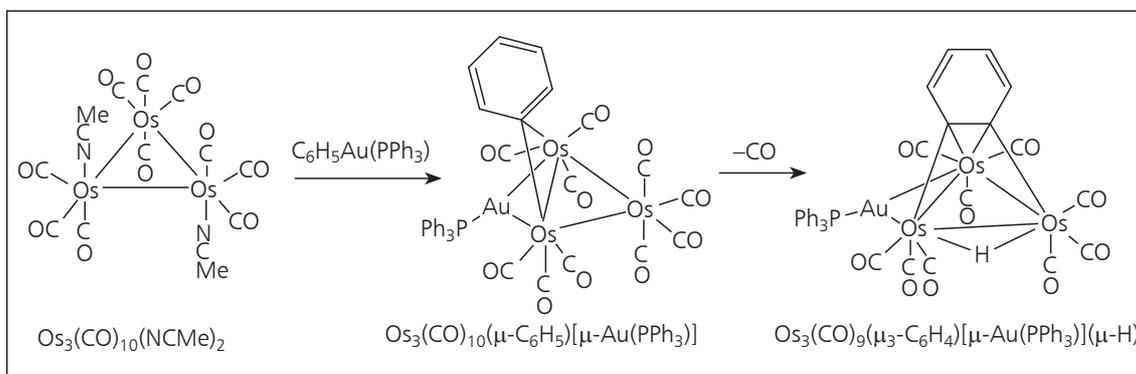
Antonio Romerosa (University of Almería, Spain), pursuing his work on water soluble, air stable heteropolymetallic polymers (19), presented several examples of a family of compounds with formula {{{(PTA)<sub>2</sub>(Cp)Ru-μ-CN-Ru(Cp)(PTA)<sub>2</sub>-μ-MCl<sub>3</sub>}}<sub>n</sub> (M = Co, Cd, Ni, Cu, Pt and Pd) and their catalytic, biological, optical and gel properties in water.

### Polynuclear and Supramolecular Assemblies

Hani Amouri (Pierre and Marie Curie University, Paris, France) reported a class of *o*- and *p*-quinonoid metal complexes of the type [Cp<sup>\*</sup>M(η<sup>4</sup>-C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)]<sup>n</sup> (M = Ru, *n* = -1; M = Rh or Ir, *n* = 0) (20). These compounds were used as organometallic linkers in the synthesis of supramolecular coordination assemblies with luminescent properties. Such compounds show panchromatic absorbance as well as red and near infrared emission properties (**Figure 8**), and are promising for optoelectronic and photovoltaic applications (21).

Matti Haukka (University of Eastern Finland) addressed the complexes [Rh(L)(CO)<sub>2</sub>]<sup>+</sup> (L = 2,2'-biimidazole, 2,2'-bipyridine or 1,10-phenanthroline) which form cationic one-dimensional chains in the solid state. The Rh-Rh distances and the absorption properties of the stacks can be effectively modified by varying the counter anions and solvents of crystallisation. The neutral dinuclear [Rh<sub>2</sub>(R<sub>2</sub>bim)Cl<sub>2</sub>(CO)<sub>4</sub>] units (R<sub>2</sub>bim = N,N'-dialkyl-2,2'-biimidazole) form neutral chains with strongly anisotropic optical properties. Another type of neutral chain structures consisting of alternating cationic and anionic square planar complexes is commonly found with Pt and Pd but not with Rh.

Guo-Xin Jin (Fudan University, China) reported an efficient method for synthesising molecular macrocycles of half-sandwich Ir and Rh complexes *via* C-H and B-H activation with terephthalate and dicarboxylate carborane, in order to construct organometallic macrocycles with interesting structural features and technologically useful functions.



Scheme IV. Oxidative addition of gold-carbon bonds to osmium cluster compounds

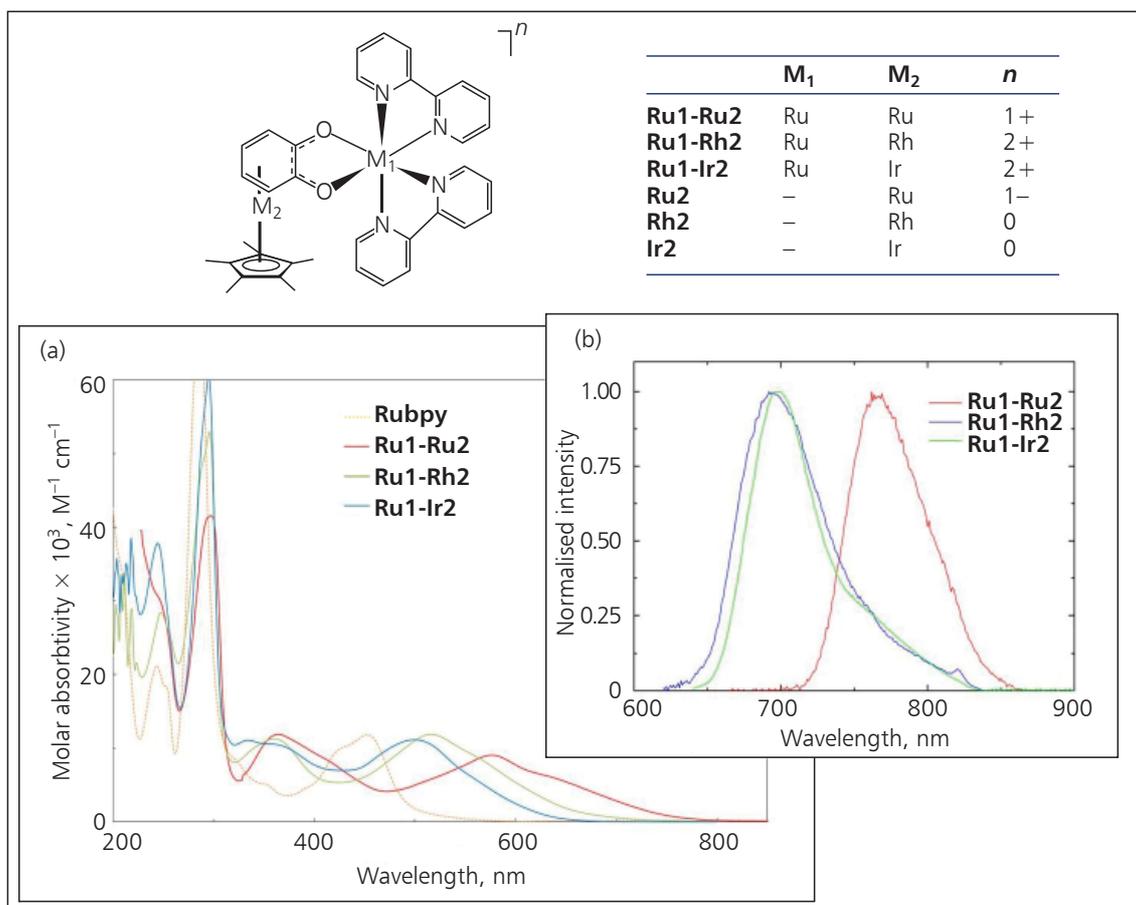


Fig. 8. Octahedral ruthenium, rhodium and iridium complexes with organometallic linkers: (a) panchromatic; and (b) red and near-infrared phosphorescence (77 K) of the complexes

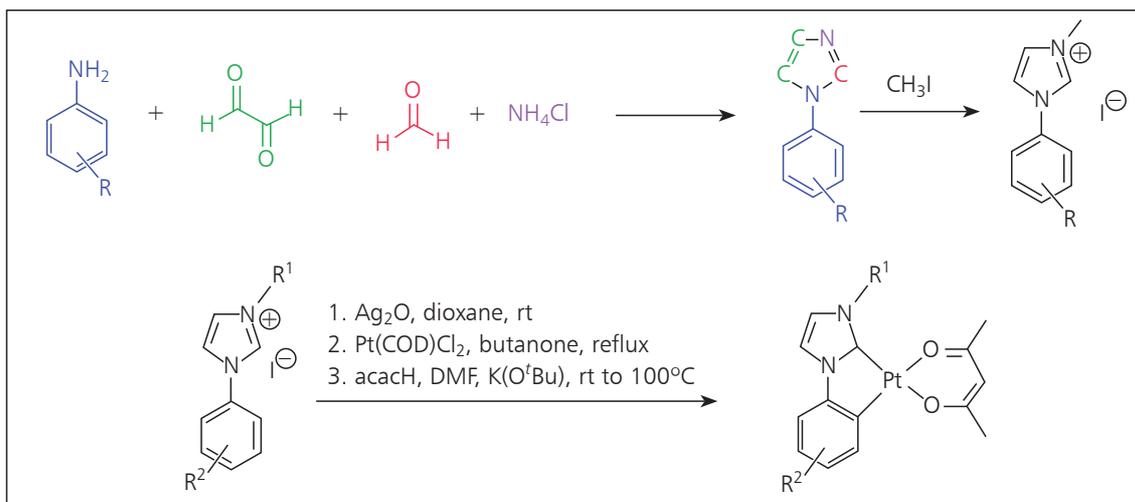
### Organometallics for Materials

Bruno Chaudret (Institut National des Sciences Appliqués (INSA), Toulouse, France) focused on the synthesis and characterisation of Ru nanoparticles stabilised by phosphines, phosphites and NHC ligands, the characterisation of such particles, their surface reactivity towards carbon monoxide and alkenes and the influence of the ligands on styrene hydrogenation, CO oxidation and CO hydrogenation.

Thomas Strassner (Technical University of Dresden, Germany) discussed bis- and tetracarbene Pt(II) complexes bearing bis(triazoline-5-ylidene) and/or bis(imidazoline-2-ylidene) ligands, and cyclometallated Pt(II) complexes with donating NHC ligands (Scheme V). Such complexes show high potential for application as triplet emitters in organic light-emitting devices (OLEDs) (22–24).

### Bioorganometallic and Bioinorganic Chemistry

Fabio Marchetti (University of Camerino, Italy) reported potentially important anticancer Ru complexes, obtained through conjugation of an (arene)Ru(II) moiety with ligands that show biological activity: acylpyrazolones, Schiff bases of acylpyrazolones, curcumin and bis(pyrazolyl)methanes. The (arene)Ru(II) curcuminates induce apoptosis by inhibiting tumour cell proteasomes, bind DNA and activate caspase-3 in cells and DNA fragmentation. Cationic (arene)Ru(II) complexes with bis(pyrazolyl)methanes show a high *in vivo* activity against an A17 model cell line (able to generate metastases on various parts of the body) and their antimetastatic activity is similar to or even higher than that of the Ru(III) imidazolium *trans*-imidazole-dimethylsulfoxidetetrachlororuthenate (NAMI-A)

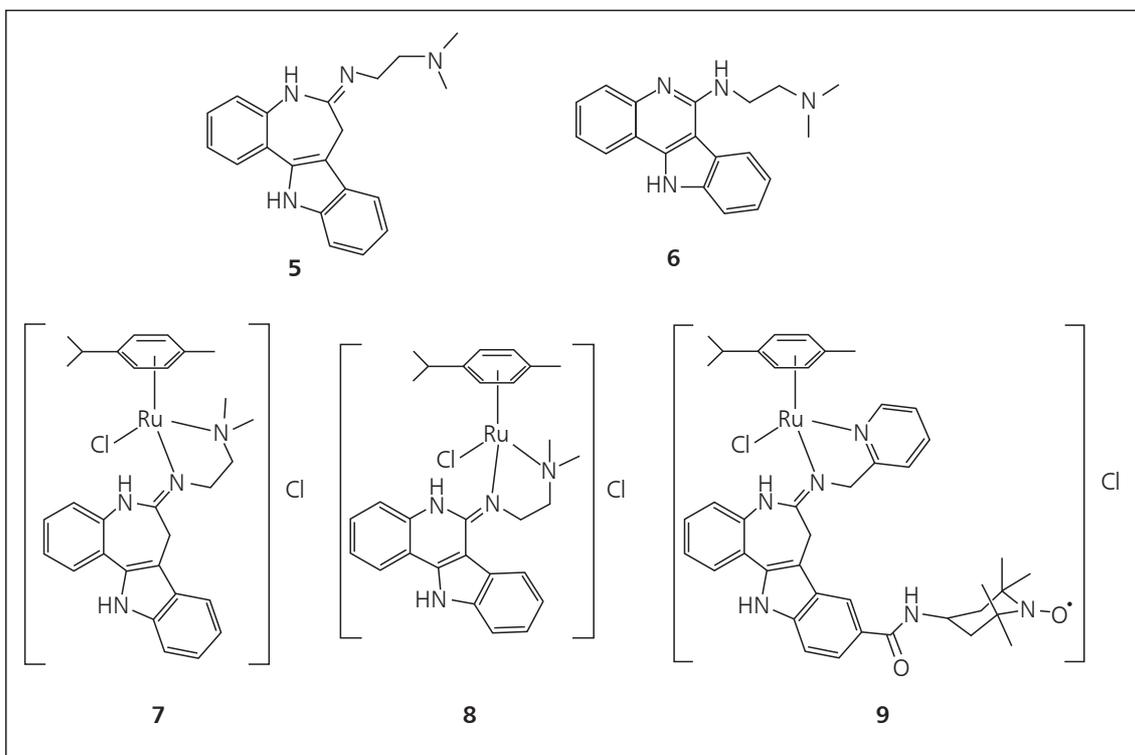


Scheme V. Preparation of cyclometallated platinum(II) complexes with donating *N*-heterocyclic carbene ligands

complex, which recently entered phase II clinical trials as one of the few active compounds against metastases.

Vladimir Arion (University of Vienna, Austria) focused on arene Ru(II) and Os(II) complexes with

indolobenzazepines (**5** and **7**, Scheme VI), also referred to as paullones, with high antiproliferative activity in human cancer cell lines. Searching for structure-activity relationships, he replaced the 7-membered folded azepine ring with a flat pyridine,



Scheme VI. Indolobenzazepines (**5**) and indoloquinolines (**6**) and their arene ruthenium(II) complexes (**7–9**)

via a two-step procedure leading to another class of biologically active compounds, indoloquinolines (**6**, **Scheme VI**). Arene Ru(II) and Os(II) complexes with indoloquinolines (**8**, **Scheme VI**) show 6- to 9-fold higher antiproliferative activity than related systems based on indolobenzazepines (25). In addition, arene Ru(II) and Os(II) complexes with indolobenzazepines bearing a stable 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical unit (**9**, **Scheme VI**) have been developed as potential anticancer drugs (26). The attached electron paramagnetic resonance (EPR) label should be explored for monitoring the intracellular distribution.

João Rodrigues (Madeira University, Portugal) addressed Ru containing dendrimers as important alternatives to the clinically used Pt chemotherapeutic agents; the preparation of poly(alkylideneamine)-nitrile metallodendrimers functionalised with the Ru moieties  $[\text{Ru}(\text{dppe})_2\text{Cl}]^+$  or  $[\text{Ru}(\text{Cp})(\text{PPh}_3)_2]^+$  was described, as well as their stability/degradation in solution.

Maria Helena Garcia (University of Lisbon, Portugal) described the family of compounds  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PP})\text{L}]^+$  (L = mono- or bidentate *N* heteroaromatic  $\sigma$ -bonded ligand, PP = diphosphine), and their interaction with serum, nuclear proteins and DNA. In respect to the latter, the planarity of L enables intercalation, as well as other types of interaction (27).

Debbie Crans (Colorado State University, USA) addressed the use of microemulsion solubilisation as an alternative cancer treatment capable of application in locations with limited facilities, and described the development of an intracavitary administration vehicle that delays administration of carboplatin, eventually providing treatment of metastasis after removal of a tumour, especially in developing countries (**Figure 9**) (28).

Gerard Van Koten (Utrecht University, The Netherlands) referred to the synthesis and properties of pincer organometallics, their stability and versatile catalytic properties, in particular the directed inhibition of cutinase with a pincer-Pt catalytic site (29).

### Fundamental Organometallic Chemistry

Pierre Braunstein (Strasbourg University, France), dealing with metallaligands and phosphoryl migration reactions, illustrated the bonding versatility of a functional 1,1-bis(diphenylphosphino)methane (dppm)-type ligand bearing an oxazoline substituent on the PCP carbon atom towards Pd(II) and Pt(II) complexes, for both its neutral and monoanionic forms. Whereas a chelating *gem*-diphosphine resulted from migration of one of the  $\text{PPh}_2$  groups from a phosphino-oxazoline nitrogen atom to carbon, the reverse migration is triggered by metal coordination and various H/phosphoryl tautomeric forms have been stabilised (**Figure 10**).

Andy Hor (National University of Singapore) devoted his talk to Pt hybrid NHC compounds. The ligands (hybrid carbenes) have at least one heterofunctional entity besides the carbene carbon and may confer to their complexes structural diversity, additional reactivity and functional applications in photoluminescence, catalysis, electrochemistry, etc.

Michael Bruce (University of Adelaide, South Australia) described the types of complexes obtained through the reactions of polycyanoalkenes, particularly tetracyanoethene (TCNE) and tetracyanoquinodimethane (TCNQ) with  $[\text{Ru}(\text{C}\equiv\text{C}-\text{R})(\text{PPh}_3)_2\text{Cp}]$  (R = H, Ph) or  $[\text{Ru}(\text{C}\equiv\text{C}-\text{R})(\text{dppe})\text{Cp}^*]$ , among others.

Anthony Hill (Australian National University) reviewed the synthesis of a variety of bi- and

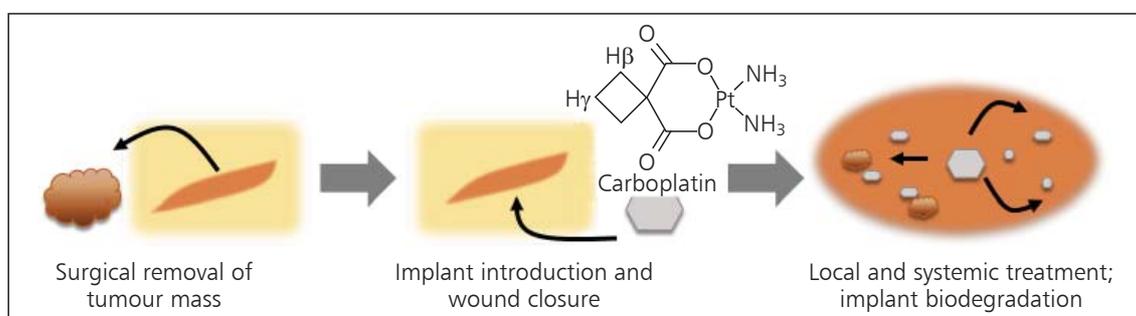


Fig. 9. Implantable formulation containing anticancer agent carboplatin for post-surgical treatment

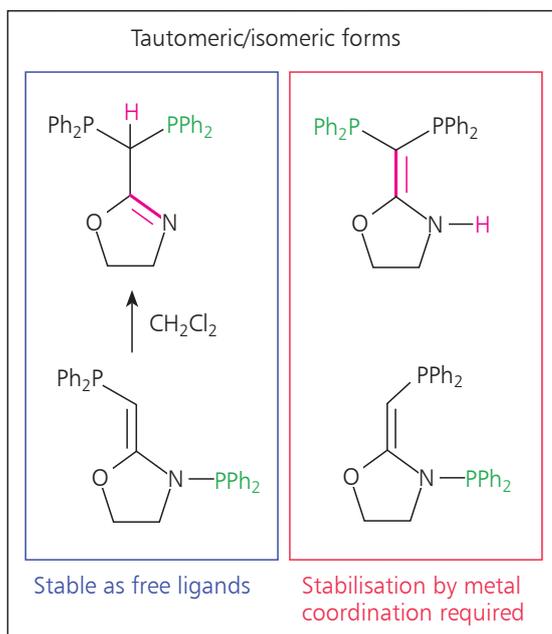


Fig. 10. Illustration of the versatility of an oxazoline functionalised dppm ligand

polymetallic molecular carbido complexes resulting either from condensation of metal halides and lithiocarbynes, selenocarbonyl ligand cleavage (30), oxidative addition of halocarbynes, or carbon disulfide activation.

Pierre Le Gendre (University of Burgundy, France) described the synthesis of the mixed P-olefin ligand (3,5-cycloheptadienyl)diphenylphosphine, whose conformational flexibility and the relative position of the two double bonds in regard to the phosphorus atom promoted coordination diversity (31).

Mark Gandelman (Israel Institute of Technology) presented the first examples of nitrenium ions as ligands for pgms (32), and discussed their preparation, structures, unique properties and reactivity.

Elena Shubina (A. N. Nesmeyanov Institute of Organoelement Compounds (INEOS), Moscow, Russia) discussed the role of hydrogen bonds in the chemistry of transition metal hydrides (namely of Ru and Os) which can act either as proton donors or proton acceptors. The proton transfer between two transition metal hydrides with opposite polarities may lead to the formation of  $M-H^{\delta-}\cdots^{\delta+}H-M'$  dihydrogen bonds (33), which precedes the proton transfer and the development of  $\mu, \eta^{1:1}-H_2$  species featuring an end-on coordination mode between the two transition metals.

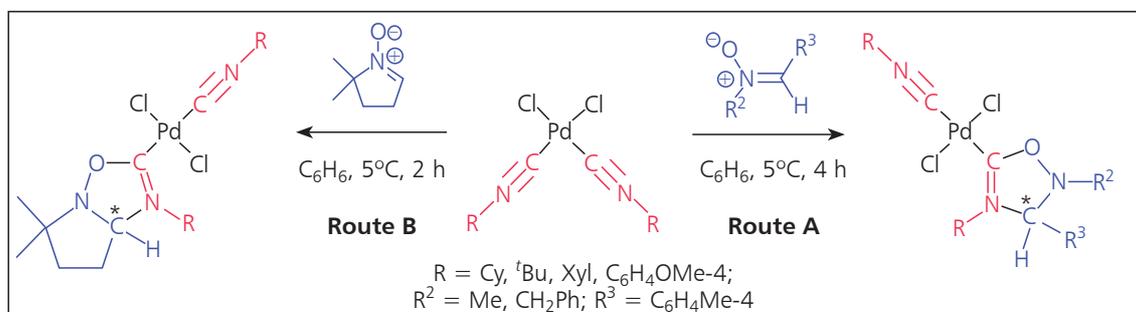
### Reaction Mechanisms

Konstantin Luzyanin (Technical University of Lisbon, Portugal) showed that Pd-mediated dipolar cycloaddition of nitrones (Scheme VII) to isocyanides opened a route to complexes with new types of NHC ligands. The mechanism of this reaction was studied by theoretical (DFT) methods. The structures of the cycloaddition products, the transition states, the kinetic and thermodynamic parameters of the reactions and solvent effects were rationalised.

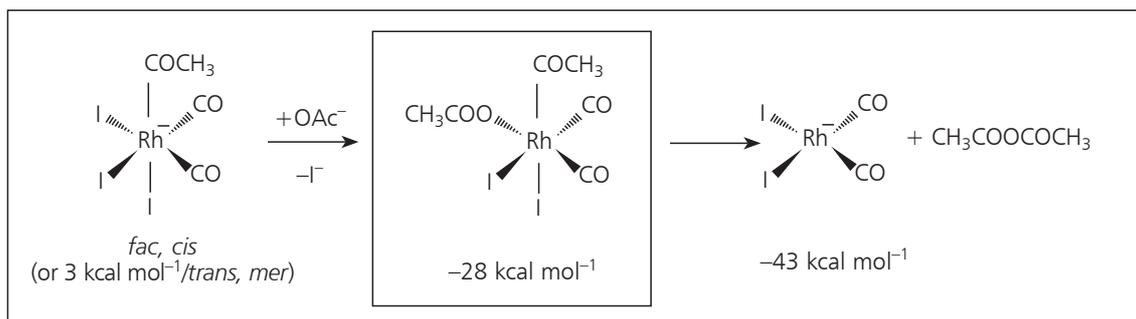
Philippe Kalck (University of Toulouse, France) proposed a role of the acetato ligand within the reductive elimination step in the industrially important Rh-catalysed methanol carbonylation reaction (Scheme VIII). At low water content, the rate-determining step was demonstrated by high pressure nuclear magnetic resonance (HP-NMR) observations, kinetic measurements and DFT calculations to be the reductive elimination of acetic anhydride from the intermediate  $[RhI_2(COCH_3)(COOCH_3)(CO)_2]^-$ . This reaction pathway is largely exergonic.

### Electrochemistry

Wolfgang Kaim (University of Stuttgart, Germany) showed how the ligand redox system  $Q^{n-}$  [ $Q = 4,6$ -di-*tert*-butyl-(2-methylthiophenyl)imino]-



Scheme VII. Dipolar cycloaddition of nitrones mediated by palladium complexes



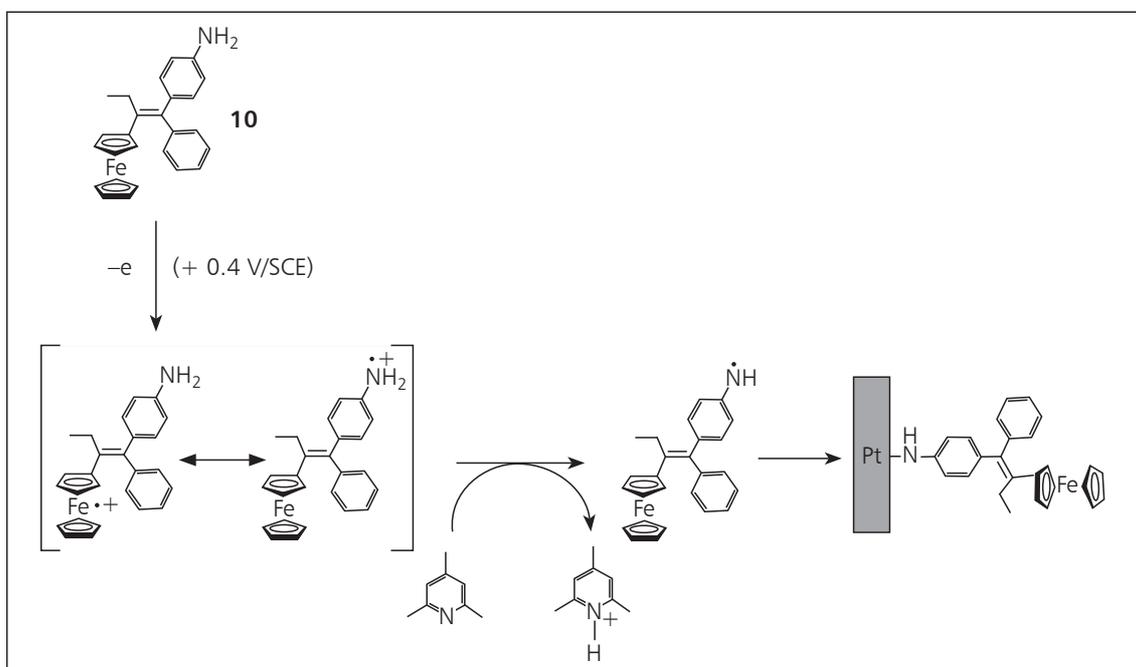
Scheme VIII. The role of acetato ligand in rhodium-catalysed methanol carbonylation

*o*-benzoquinone;  $n = 0, 1, 2$ ] provided options for transition metal coordination, involving changes of charge state and binding mode, and, by using  $[\text{Ir}(\text{C}_5\text{Me}_5)(\text{Q})]^{0/+2+}$ ,  $[\text{M}(\text{C}_6\text{R}_6)(\text{Q})]^{0/+2+}$  ( $\text{M} = \text{Ru}, \text{Os}$ ) and  $[\text{M}(\text{Q})_2]^{2-/-0/+2+}$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{Ru}, \text{Os}$ ) as examples, he demonstrated how redox activity ('non-innocence') and preferred coordination number are related.

Fabrizia Fabrizi de Biani (University of Siena, Italy) addressed the topic of molecular metal clusters for molecular electronics by reviewing the electron transfer properties of a heterogeneous collection of metallic clusters including low- to high-nuclear Pt

clusters. In this respect, Pt<sub>6</sub> clusters were found to have a transistor-like behaviour (34).

Olivier Buriez (École Normale Supérieure, Paris, France) electrochemically grafted at a Pt surface, by oxidation of the ferrocene moiety, a  $\pi$ -conjugated ferrocene-aniline (**10**, Scheme IX) possessing anticancer properties. The mechanism relies on an intra-molecular electron transfer between the amino and the electrogenerated ferricenium moiety which allows the indirect oxidation of the amino group. The radical cation thus formed is then prone to react with a base (collidine) to produce the corresponding aminyl radical that may add onto the Pt surface (35).



Scheme IX. Electrochemical grafting of a ferrocenyl aniline anticancer drug onto a platinum surface (SCE = saturated calomel electrode)

## Conclusions

The success of the XXV International Conference on Organometallic Chemistry and the important role played by the pgms in so many of the contributions, as illustrated in this review, demonstrate conclusively that organometallic chemistry as a whole, and in particular that involving pgms, is crucial to developing both fundamental and applied chemistry in many significant areas.

The XXV ICOMC succeeded in achieving its main aims: to contribute to the promotion of excellence in science, of international research collaboration and of the universal character of science, which also constitute main objectives of the International Council for Science (ICSU Strategic Plan, 2012–2017). The next conference in the series is to be held in Japan in 2014.

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