

The 4th Cape Organometallic Symposium: Organometallics and Their Applications

THE ORGANOMETALLIC CHEMISTRY OF PLATINUM GROUP METALS

Reviewed by David J. Robinson

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The annual Cape Organometallic Symposia (COS) series was started in 2003 through the combined efforts of researchers at the Universities of Cape Town, Stellenbosch and the Western Cape in South Africa, and the COS 2006 chairman was Professor John R. Moss, Department of Chemistry, University of Cape Town (jrm@science.uct.ac.za). These symposia were designed as informal one-day sessions, bringing together researchers with similar interests from the three institutions, and successfully exposing graduate students to a mixture of invited lectures and student presentations. In particular, all students would have opportunities to network with their peer group and to present their work in oral or poster format for discussion.

In 2006 this event was timed for 10th and 11th of August, to run immediately before the 37th International Conference on Coordination Chemistry (ICCC) (1), affording visitors an opportunity to attend both events, and exposing local graduate students to some of the best researchers in organometallic chemistry from around the world. The format therefore changed to a two-day event, and a greater proportion of presentations than usual were given by these leading invited international researchers. However, the event was limited to around 100 delegates to ensure that the atmosphere remained fairly informal, and the event more intimate than most international gatherings. The theme for the COS 2006 event was "Organometallics and their Applications" (OATA) (2), with a view to emphasising the links between the multiplicity of academic research directions being followed and the potential for practical applications of organometallic chemistry.

The presentations were fairly evenly divided

between the organometallic chemistry of early, late and first row transition metals. However, it is the purpose of this review only to consider those presentations involving the development of the organometallic chemistry of the platinum group metals (pgms), and its potential applications.

Nanotechnology and Catalysis

The systematic development of the field of nanotechnology and catalysis was well illustrated by Professor Brian F. G. Johnson's (University of Cambridge, U.K.) presentation on supported nanoparticle preparations and nanocatalyst activity, entitled: 'Small and Beautiful: Nano-Catalysts by Design or Strategically Designed Single-Site Heterogeneous Catalysts for Clean Technology, Green Chemistry and Sustainable Development'. Starting with a myriad of well characterised mixed-metal clusters, this group has designed and prepared a range of very active catalysts with varying metals, in particular these include platinum and ruthenium in well controlled and varied ratios. When these were supported inside mesoporous materials, an added dimension to their reactivity was described. In the second part of this presentation, the tethering of active metal centres to a 'non-passive' support with a chiral ligand was described as a further advantageous manner in which novel catalysts could be prepared.

Similarly starting with the useful precursors $\text{RuHCl}(\text{CO})\text{L}_3$ and *trans*- $\text{IrCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{PPh}_3$), Professor Anthony Hill's group (Australian National University), have previously prepared and studied the reactivity of a number of mono-, bi- and trimetallic carbene and carbyne complexes. In this talk: 'Tricarbido Complexes: $\text{L}_n\text{M}\equiv\text{C}-\text{C}\equiv\text{C}-\text{M}'\text{L}_n$ ' a fairly general route to

mono-, di- and tricarbido complexes was presented, involving the isolation and characterisation of a range of interesting new compounds containing one or more of the p-gms, gold, mercury, molybdenum, tungsten and other metals.

Professor Anna M. Trzeciak (University of Wrocław, Poland) presented interesting results from her group's study of the methoxycarbonylation of iodobenzene and the Sonogashira coupling of an aryl acetylene and aryl halide both using a palladium catalyst in an ionic liquid, in particular addressing the inhibiting effect of imidazolium halides: 'Palladium Catalysed Methoxycarbonylation in Ionic Liquids, Inhibiting Effect of Imidazolium Halides'. With the methoxycarbonylation reaction, a simple palladium precursor (such as [PdCl(COD)], COD = cycloocta-1,5-diene) and a base were sufficient to achieve good yields in certain ionic liquids. Similarly, good yields could be obtained in the Sonogashira reaction in the presence of a base and a [PdCl₂{P(OPh)₃}₂] catalyst. Systematic variation in the components of the ionic liquid, and the effects of such changes on the reaction yields and on isolation of a number of interesting adducts and intermediates, have helped to throw light on these respective mechanisms.

Mechanistic Studies

Recent developments in our understanding of the mechanism of the asymmetric hydrogenation of olefins using a number of derivatives of the clusters M₃(CO)₁₂ (M = Ru or Os), H₂O₈(CO)₁₀ or H₄Ru₄(CO)₁₂ were presented by Professor Ebbe Nordlander (Lund University, Sweden): 'Cluster-based Catalytic Systems for Asymmetric Reactions'. In particular, a range of catalysts [H₄Ru(CO)₁₀(P-P*)] and [H₄Ru(CO)₈(P-P*)₂] (P-P* = BINAP, MOBIPH, DIOP) were prepared. Their activity and enantioselectivity were studied for the hydrogenation of 2-methyl-2-butenic acid at elevated temperature and pressure. Most interesting were the enhanced reactivity and enantioselectivity obtained when ferrocene-containing diphosphine ligands were used, and the further enhancement in enantioselectivity which was observed when the reaction was performed in the presence of trace amounts of mercury.

As part of a broader presentation on catalytic chemistry, and particularly ethylene oligomerisation/polymerisation, a number of new palladium complexes ligated to one or more derivatised ferrocene units were prepared and used as catalysts in Suzuki coupling reactions. This work, assessing the potential for 'modular design' of efficient catalysts and the isolation of several palladium(0) and palladium(II) intermediates in the proposed mechanism, was presented by Professor T. S. Andy Hor (National University of Singapore): 'Design of Smart Catalysts by the Combinative & Complementary Uses of Hemilability and Metal Unsaturation'.

Synthesis of Metallacycles and Clusters

Two presentations from the group of Professor John Moss extended the range of metallacycles that have been made, typically *via* one of two routes involving either a di-Grignard reagent or the application of the Grubbs catalyst and a ring closing metathesis reaction upon a di-alkenyl complex. Akella Sivaramakrishna presented a talk entitled: 'Synthesis & Structure of Metal-alkenyl Complexes – Novel Precursors to Fascinating Chemistry!'. Starting with [PtCl₂(COD)] or Cp*IrClL₂, a range of di-alkenyl compounds of PtL₂R₂, PtL'R₂ or Cp*IrLR₂, respectively, (R = alkenyl group; L = PPh₃ or P^tBu₃, L' = dppe or dppp), of varying stability were prepared by reaction with appropriate Grignard reagents (and additional phosphine L or L' for platinum). While the thermal decomposition of several of these new compounds was studied, of greater interest was the use of a ring closing metathesis reaction catalysed by first-generation Grubbs catalyst to form platina- and iridacycles with up to 21 ring atoms. Several side reactions and other interesting transformations including dimerisation, internal isomerisation, allyl formation and transmetallation reactions were reported. The insertion of metal carbonyls and small molecules into metal-alkenyl ligand bond and the potential for formation of hetero-bimetallic clusters and other novel complexes were described. Emma Hager presented 'The Synthesis of Novel Rhodacycloalkanes: "Old" and New Methods'. The analogous use of

$\text{Cp}^*\text{RhLCl}_2$ ($\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}$ or PPhMe_2) and appropriate di-Grignard reagents also resulted in a series of compounds of the type: $\text{Cp}^*\text{RhL}\{(\text{CH}_2)_n\}$. These metallacycles are considered to be model compounds for several chain forming catalytic reactions, including ethylene trimerisation. As such, their thermal decomposition is also of interest and was reported. Di-alkenyl rhodium complexes were similarly prepared from $[\text{Cp}^*\text{RhCl}_2]_2$ and excess appropriate Grignard reagent with longer carbon chain groups. The same reaction with short chain Grignard reagents resulted in interesting allylic rhodium complexes.

A student presentation from Cathrin Welker (University of Cape Town, South Africa): 'Fischer-Tropsch Synthesis on Organometallic Ru-Model Catalysts', addressed the systematic preparation of model ruthenium clusters of varying sizes and the study of their thermal decomposition and Fischer-Tropsch activity.

Concluding Remarks

Over 30 excellent posters were also presented during the symposia. Student participation, as desired, was evident throughout the proceedings. The format for 2007 is again to be slightly different to allow the symposium to be incorporated into the South African Chemical Institute, Inorganic Chemistry Conference (3), again chaired by Professor John Moss. It is clear that the series of Cape Organometallic Symposia, and indeed inorganic and organometallic chemistry, are very

much alive and thriving in the Western Cape and more generally in South Africa. The timing of the COS 2006 and the 37th ICC (1) in consecutive weeks afforded an almost unique opportunity for many local students and academics to meet and interact with experts from around the world, while the large amount of pgm chemistry presented at both conferences appropriately highlighted the importance of these metals and their applications in today's world.

References

- 1 D. J. Robinson and M. Arendse, *Platinum Metals Rev.*, 2007, 51, (1), 36
- 2 4th Cape Organometallic Symposium: Organometallics and their Applications; <http://www.wildmice.co.za/chemistry/oata2006.html>
- 3 INORG 007: Inorganic Chemistry Conference 2007, Club Mykonos, Western Cape, South Africa, 8th–12th July, 2007; <http://www.wildmice.co.za/chemistry/inorg007.htm>

The Author



David John Robinson was active in both fundamental and applied pgm chemistry research, and in particular, the development of improved separation technologies over a 15 year career with Anglo Platinum. He was involved directly in their production at the modern precious metals refinery near Rustenburg, South Africa. Since writing this review he has moved to CSIRO Minerals' Parker Cooperative Research Centre for Integrated Hydrometallurgy Solutions, Karawara, Western Australia. His interests include developing improved industry-academia research collaborations and the application of improved fundamental knowledge to the solution of real refining problems. In his new position he will be active in the area of base metal hydrometallurgy and developing advantages for industry through better scientific research, optimising hydrometallurgical processing and efficient technology transfer.