

# Industrial Platinum Metals Chemistry Towards the Year 2000

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*The First Anglo-Dutch Symposium, sponsored by the Royal Society of Chemistry and including the Ludwig Mond Lecture, was hosted on the 18th September 1996 by the University of Sheffield. This symposium covered a wide range of platinum group metals chemistry, illustrating in particular its continuing importance in catalysis and describing some future industrial uses, thus demonstrating the strength of the work being undertaken in both The Netherlands and the U.K.*

The Ludwig Mond lectureship was established by ICI to award excellence in the field of inorganic chemistry. The present recipient, Professor Peter M. Maitlis of Sheffield University, gave this year's lecture entitled "New Explorations in Metal Catalysed Reactions" at the First Anglo-Dutch Symposium to an audience in Sheffield of over 150 academics and industrialists.

## The Ludwig Mond Lecture

Ludwig Mond was born in Germany, in 1839. After studying chemistry he came to England at the age of 23, and in 1873 with John Brunner founded the firm Brunner, Mond and Company to make sodium carbonate on a large scale using the Solvay process, which Mond improved. By the early 1880s he and Langer had discovered a process for the purification of nickel, whereby nickel was heated with carbon monoxide to form nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , which then decomposed at  $180^\circ\text{C}$  to give pure nickel, free from carbon. In 1900 he founded the Mond Nickel company, a forerunner of ICI.

Professor Maitlis discussed three areas of his current research: methanol carbonylation, hydrodesulfurisation and Fischer-Tropsch reactions.

## Methanol Carbonylation

The work of the University of Sheffield and BP Chemicals on the rhodium and iridium catalysed carbonylation of methanol to acetic acid was described. The reaction steps for both catalytic cycles are similar, but there is a difference

in the reaction rates for the steps between the metals.

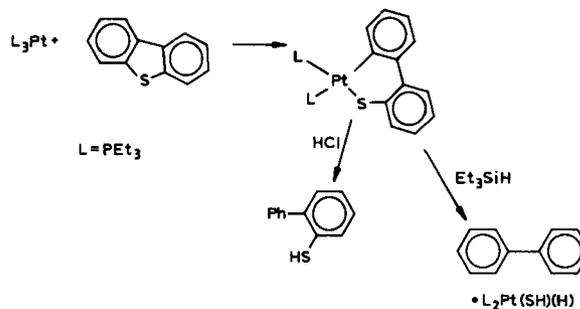
For rhodium, the rate determining step of the reaction is the slow oxidative addition of methyl iodide (made from HI, the co-catalyst and methanol) to the catalytically active species  $[\text{Rh}(\text{CO})_2(\text{I})_2]^-$ . The previously uncharacterised reaction intermediate,  $[\text{MeRh}(\text{CO})_2(\text{I})_3]^-$ , where Me is methyl, has been detected and characterised spectroscopically for the first time. The methyl rapidly migrates to form the acyl species,  $[(\text{MeCO})\text{Rh}(\text{CO})(\text{I})_3]^-$ , which then gains a CO molecule before reductive elimination of acyl iodide occurs and  $[\text{Rh}(\text{CO})_2(\text{I})_2]^-$  is regenerated. The acyl iodide is then hydrolysed to acetic acid, regenerating HI and completing the catalytic cycle.

In contrast, the oxidative addition of methyl iodide to  $[\text{Ir}(\text{CO})_2(\text{I})_2]^-$  is fast, but the methyl migration is slow. However, this step, which requires temperatures over  $80^\circ\text{C}$  in chlorobenzene, can be dramatically accelerated by a factor of ten thousand when methanol is added. This may be due to activation of an Ir-I bond.

## Hydrodesulfurisation

The hydrodesulfurisation of crude oil to remove sulfur is a massive global business. Usually a molybdenum/cobalt, Mo/Co, catalyst is used to remove aliphatic sulfur compounds, such as thiols, thioethers and dithioethers. However, the Mo/Co system has difficulty removing the sulfur contained in aromatics, whereas platinum compounds could potentially

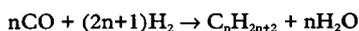
**Fig. 1** A platinum complex,  $L_3Pt$ , removing aromatic sulfur from dibenzothiophene goes via a sulfur-containing platinum intermediate complex which then reacts with  $Et_3SiH$  to yield biphenyl



be very active here. A zero valent platinum complex, for example, can insert into a sulfur-aromatic carbon bond and react further, as shown in Figure 1. The Sheffield group are aiming to make this process catalytic.

### Fischer-Tropsch Reaction

The Sheffield research into the Fischer-Tropsch reaction, where syngas from coal is converted into other chemical feedstocks, was discussed:

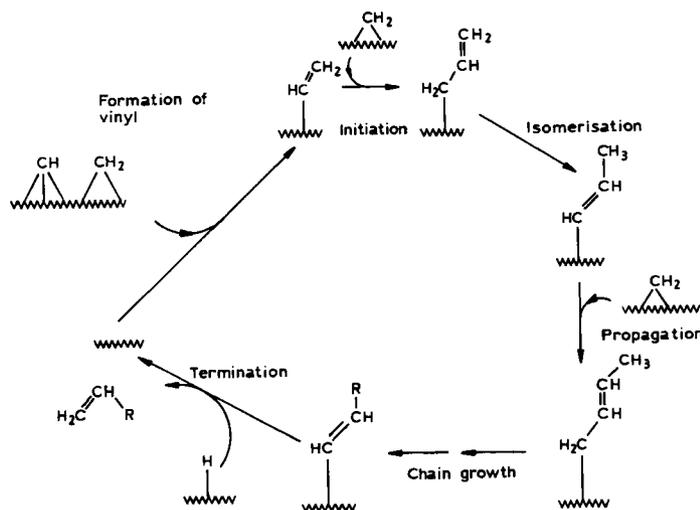


A new catalytic cycle, involving alkenyl intermediates was described by Professor Maitlis.

When  $^{13}C_2$  labelled molecules are used as probes, it can be seen that alkenyl/vinyl species are directly involved in polymerisation on catalytic rhodium and ruthenium surfaces, see Figure 2.

### Industrial Applications of Catalysis

The application of the Sheffield work to the new BP *Cativa* process, was discussed by M. J. Howard of BP Chemicals, Hull. In this process iridium – with advantages over the existing rhodium process – is used to catalyse the carbonylation of methanol. The iridium system has higher catalyst solubility and stability, and can tolerate a wide range of process compositions



**Fig. 2** Scheme of the alkenyl mechanism for the Fischer-Tropsch reaction shows that initiation occurs when a surface methyne and methylene combine to give a surface vinyl. This reacts with another surface methylene to form a surface allyl. The allyl isomerises to the alkenyl, which reacts with more methylene thus increasing the chain length

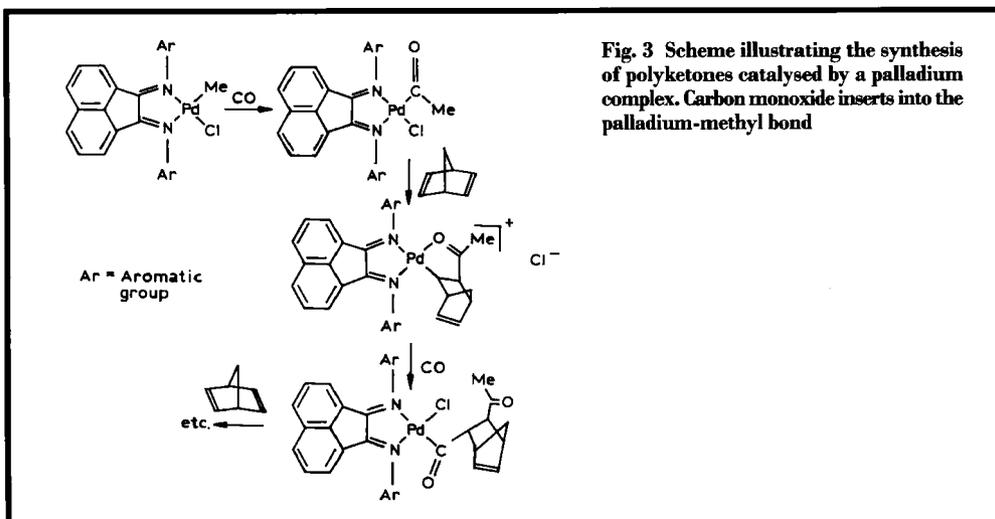
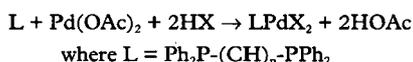


Fig. 3 Scheme illustrating the synthesis of polyketones catalysed by a palladium complex. Carbon monoxide inserts into the palladium-methyl bond

and allows higher rates of reaction than rhodium. The *Cativa* process can be fitted into existing plant, thus increasing capacity by over 30 per cent by “debottlenecking” – speeding up the slowest step of the process. The *Cativa* process is running successfully at a plant in Texas.

A new palladium catalysed polyketone synthesis was discussed by Professor E. Drent of Shell International Chemicals Ltd., Amsterdam. The catalyst is made from palladium acetate and the reaction proceeds as follows:



Professor Drent demonstrated that the reaction is much faster if  $n = 3$  than if  $n = 2$ . The

palladium complex is forced into a *cis* geometry by the bidentate phosphorus ligand, thus restricting its activity. When the palladium complex  $(\text{PPh}_3)_2\text{Pd}(\text{OAc})_2$  is used *cis/trans* isomerisation can occur resulting in rapid product elimination and consequently there is no opportunity to build up a polymer. These polymers are attracting interest as a new type of high performance plastic.

The effectiveness of studying catalytic steps by model systems was illustrated by Professor K. Vrieze of the University of Amsterdam. He showed how a polyketone oligomer is built up by inserting carbon monoxide into a palladium-methyl bond. The alkene co-ordinates to the metal and a new C-C bond is formed. Carbon

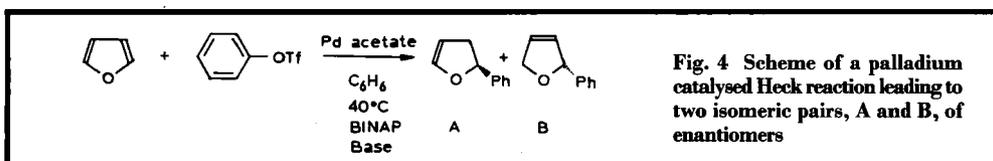


Fig. 4 Scheme of a palladium catalysed Heck reaction leading to two isomeric pairs, A and B, of enantiomers

Base	Product A		Product B	
	Yield, per cent	e.e., per cent	Yield, per cent	e.e., per cent
1,8 $\text{C}_{10}\text{H}_8(\text{NMe})_2$	46	96	17	24
$\text{Cy}_2\text{NH}$	59	82	4	43

Cy is cyclohexyl

monoxide inserts again into the Pd-C bond and forms another C-C bond, which increases the length of the polyketone, see Figure 3.

### Palladium in Chiral Catalysis

Chiral catalysis is a rapidly advancing field and the advent of chiral C-C bond formation is at the leading edge of this research. J. M. Brown, of Oxford University, described the palladium catalysed Heck reaction. He showed that for this reaction the yields and enantiomeric excess of the products depended on the base, see Figure 4.

The conference was very informative on new

developments and progress in the use of the platinum group metals for catalysis. It is proposed that the second Anglo-Dutch Symposium will be held on 25 and 26 September 1997 in the conference hall of the Royal Academy of Arts and Science in Amsterdam. The organisers are Professors C. J. Elsevier, G. van Koten and K. Vrieze.

Information can be obtained from Professor Gerard van Koten, Utrecht University, Department of Metal Mediated Synthesis, Debye Institute, Padualaan 8, 3584 CH Utrecht, The Netherlands, Fax: +31 30 2523615 or E-mail: vankoten@xray.chem.ruu.nl.

### Iridium Microelectrode Array for Trace Metal Detection

The accurate detection of pollutants in natural waters is of continuing importance to the authorities who police water quality and to the water user. There are a variety of laboratory-based methods for detecting and measuring the amounts of toxic pollutants, including heavy metals, in water. Now, an improvement to an iridium microelectrode (*Platinum Metals Rev.*, 1995, 39, (3), 132) is reported, which was developed to detect lead and cadmium in river water.

The earlier microelectrode could detect trace amounts of free cadmium and lead in concentrations as low as 0.5 nM and 0.1 nM, respectively. The group that developed this iridium microelectrode now reports an improved design, with lower detection limits (C. Belmont, M.-L. Tercier and J. Buffle, the Department of Inorganic, Analytical and Applied Chemistry, Sciences II, Geneva, and G. C. Fiaccabrino and M. Koudelka-Hep, Institute of Microtechnology, University of Neuchâtel, Switzerland, *Anal.*

*Chim. Acta*, 1996, 329, (3), 203-214).

The new amperometric microsensor is constructed by successively evaporating iridium and silicon nitride both to a thickness of 2000 Å onto a silicon wafer, followed by photolithographic patterning. The microdisc iridium electrodes of size 5 µm diameter, separated by 150 µm to avoid overlapping of diffusion layers, in 10 × 10 arrays were then bonded to printed circuit board and encapsulated by epoxy resin. Mercury was electroplated onto the iridium microarray. After assessing the reproducibility and reliability of the array, trace metal analyses were performed by the square wave anodic stripping voltammetry technique.

The array had good stability over long periods of time and there was good reproducibility between different arrays. In river water containing lead and cadmium a detection limit of 50 pM was established, which is an improvement upon the earlier, simpler sensor design.

### The Fifth Grove Fuel Cell Symposium

Like the earlier highly successful symposia, this fifth meeting will be held at the Commonwealth Institute, London, England, from 22nd to 25th September 1997, and is again being run under the aegis of Elsevier Advanced Technology.

The Grove Fuel Cell Symposium is one of the major events where scientists from academia and industry can discuss fuel cell technology. World authorities will provide an up-to-date review of fuel cells and their use in clean stationary power and transport applications, focusing on business development and investment opportunities, key technological advances, and leading edge research results. In addition to the oral presentations on

these themes, keynote speakers will focus on the environment as a business and investment opportunity. A question-and-answer led session, with a panel of internationally recognised experts from the fuel cell industry and the business world will provide the opportunity for debate. The symposium will once again feature a technical poster session to which contributions are invited.

Anyone wishing to obtain further information should contact Sharron Emsley, Fifth Grove Fuel Cell Symposium, Elsevier Advanced Technology, The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, U.K. Fax: +44 (0)1865 843958; E-mail: s.emsley@elsevier.co.uk.