

# Organometallic Chemistry of the Platinum Metals

## A REVIEW OF PAPERS AT THE DUBLIN SYMPOSIUM

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*At the joint annual meeting of The Chemical Society, The Institute of Chemistry of Ireland and the Royal Institute of Chemistry held in Dublin in April, one of the symposia was on 'Recent Progress in Organometallic Chemistry'. Several of the plenary lectures and contributed papers given at this symposium were concerned with the chemistry of the platinum metals, and these are summarised and reviewed here.*

In recent years there has been enormous interest in organometallic chemistry. One very important interest has been the use of metal complexes, especially of the platinum metals, as homogeneous catalysts. This aspect was hardly touched upon at the recent Dublin meeting, but there is nowadays no shortage of symposia and meetings on homogeneous catalysis and perhaps it was a refreshing change to have a meeting concerned with other aspects of organometallic chemistry.

### Metal Carbonyls

Interest has been particularly keen in the field of metal carbonyls, and in his opening lecture on "Recent Progress in Metal Carbonyl Chemistry", Professor F. G. A. Stone (University of Bristol) described some recent developments in methods of synthesising polynuclear carbonyls of ruthenium, osmium, rhodium and iridium, e.g.  $[\text{Ru}_3(\text{CO})_{12}]$ ,  $[\text{Os}_3(\text{CO})_{12}]$ ,  $[\text{Rh}_4(\text{CO})_{12}]$ ,  $[\text{Rh}_6(\text{CO})_{16}]$  and  $[\text{Ir}_4(\text{CO})_{12}]$ . These carbonyls are readily prepared by reductive carbonylation, i.e. reduction of a metal salt in the presence of carbon monoxide. Their structures have been determined by X-ray diffraction and indicate metal-metal bonds and sometimes bridging carbonyl groups. Carbonyls of the type

$[\text{Pd}_x(\text{CO})_y]$  and  $[\text{Pt}_x(\text{CO})_y]$  are so far unknown. Polynuclear metal carbonyls with two different metals can also be prepared, e.g.  $[\text{Fe}_2\text{Ru}(\text{CO})_{12}]$  and  $[\text{FeRu}_2(\text{CO})_{12}]$ .

$[\text{Ru}_3(\text{CO})_{12}]$  has been used as the starting point for many syntheses. Thus by reduction to  $[\text{Ru}(\text{CO})_4]^{2-}$  and acidification it gives  $[\text{RuH}_2(\text{CO})_4]$  as an unstable volatile liquid.  $[\text{Ru}_3(\text{CO})_{12}]$  reacts with acetylenes to give products similar to those formed from  $[\text{Fe}_3(\text{CO})_{12}]$  and acetylenes. With halides or hydrides of sub-group B elements it reacts to give compounds containing ruthenium-metal (metalloid) bonds, e.g. with  $\text{Me}_3\text{SnH}$  it forms  $[(\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_4]$  but with  $\text{Me}_3\text{SiH}$  the product is  $[\text{Me}_3\text{SiRu}(\text{CO})_4\text{Ru}(\text{CO})_4\text{SiMe}_3]$ . Compounds containing germanium-ruthenium bonds were also described.

Perfluoroalkyl or perfluoroaryl groups form particularly stable and/or inert bonds to transition metals and Professor Stone's lecture concluded with a discussion of the preparation of a large variety of such compounds.

### Allylic and Related Complexes

The lecture by B. L. Shaw was concerned with aspects of the chemistry of allyl derivatives of rhodium, iridium and palladium. An allyl (or allylic) group can of course be

$\sigma$ -bonded to a metal but about 1960 it was recognised that the three carbon systems of an allylic group could be sideways,  $\pi$ - or sandwich bonded to a metal and thereby act as a four electron donor (if regarded as an allyl anion). More recently asymmetrically bonded ( $\pi^l$ ) allylic ligands have been recognised both by NMR and X-ray studies, the first example being  $[\text{PdCl}(\text{2-methylallyl})(\text{PPh}_3)]$ . In this complex the terminal carbon atom of the allylic group opposite to the phosphine is less strongly bonded to the palladium than the one opposite to chlorine. In solution in the presence of ligands which can coordinate to the palladium the more weakly bonded terminal allylic carbon breaks away from the palladium to give a transient  $\sigma$ -allylic complex which can reform the  $\pi^l$ -allylic ligand in a different orientation from before. In the presence of  $[\text{Pd}_2\text{Cl}_2(\text{2-methylallyl})_2]$  or triphenylphosphine such rapid rate processes occur and they can be conveniently studied by  $^1\text{H}$  NMR. In the presence of an excess of triphenylphosphine (i.e.  $\text{PPh}_3:\text{Pd}$  ratios  $> 1$ ) phosphine exchange also occurs. A large number of systems of this type have been studied by NMR with different allylic ligands, different phosphines or arsines etc. and at various temperatures. Interconversions of  $\pi$ - (or  $\pi^l$ -) and  $\sigma$ -allylic systems are thought to be very important in homogeneous catalysis, e.g. in the oligomerisation of butadiene by metal complexes and probably occur by processes such as described in this lecture.

Also discussed were some interconversion reactions of  $\pi$ -,  $\pi^l$ - and  $\sigma$ -allylic complexes of iridium (III) and the acid catalysed conversion of a  $\sigma$ -2-methylallyliridium (III) complex into a  $\sigma$ -isobutenyliridium (III) complex, e.g.  $[\text{IrCl}_2(\sigma\text{-2-methylallyl})(\text{CO})(\text{PMe}_2\text{Ph})_2] \rightarrow [\text{IrCl}_2(\sigma\text{-isobutenyl})(\text{CO})(\text{PMe}_2\text{Ph})_2]$  (a new type of reaction which may be important in some catalytic systems).

A very convenient synthesis of allylic-rhodium complexes was discussed which involves the hydrolysis of coordinated carbon monoxide ligands (to give carbon dioxide) in the presence of an allylic halide. Thus

treatment of  $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$  with an allylic chloride (all-Cl) in methanol/water gives carbon dioxide, a hydrocarbon (all-H) and the allylic-rhodium complex  $[\text{Rh}_2\text{Cl}_2(\text{all})_4]$ . The reaction is promoted by a base and in the presence of acid the major product from 2-methylallyl chloride is  $[\text{Rh}_2\text{Cl}_2(\text{2,5-dimethylhexa-1,5-diene})_2]$ . Mechanisms for these reactions were suggested and supported by deuteration experiments. The reactions now make allylic complexes of the type  $[\text{Rh}_2\text{Cl}_2(\text{all})_4]$  very readily available and these are convenient starting materials for the synthesis of many types of allylic-rhodium complexes, e.g.  $[\text{Rh}(\sigma\text{-allyl})(\pi\text{-allyl})(\text{C}_5\text{H}_5)]$ ,  $[\text{Rh}(\pi\text{-allyl})_3]$ ,  $[\text{Rh}(\pi^l\text{-allyl})_2(\text{dipyridyl})][\text{BPh}_4]$  etc. These conversions and the properties of the products were discussed.

## Fluxional Molecules

Professor F. A. Cotton (Massachusetts Institute of Technology) discussed some fluxional molecules which have two or more equivalent nuclear configurations of lowest energy and pass from one to the other quickly at room temperature. The fluxional motions are slowed down and eventually stopped by lowering the temperature and such systems may be studied by variable temperature NMR. Molecules such as these are now fairly commonplace in organometallic chemistry; allylic-metal complexes of the type  $[\text{M}(\text{all})_x]$  ( $\text{M}$  = metal;  $x = 2, 3$  or  $4$ ) being one example.

Professor Cotton discussed the variable temperature  $^1\text{H}$  NMR spectrum of  $[\text{Fe}(\sigma\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_5)(\text{CO})_2]$ . At room temperature the spectrum consists of two singlets one due to the  $\pi$ -cyclopentadienyl protons and the other due to the  $\sigma$ -cyclopentadienyl protons. On cooling the first singlet remains sharp but the one due to the  $\sigma$ -cyclopentadienyl protons broadens, then splits into broad peaks which gradually sharpen until at or below  $-100^\circ$  a sharp but complex resonance pattern characteristic of an  $\text{ABB}'\text{CC}'$  spin system, i.e. a "frozen"  $\sigma$ -cyclopentadienyl group is obtained. The equivalence of the five protons at room

temperature is caused by the rapid motion of the iron atom around the ring by a 1,2-shift. NMR only "sees" the time arranged environment and if the motion is sufficiently rapid all five protons of the  $\sigma$ -cyclopentadienyl group appear to be equivalent.

A similar situation exists for the cyclo-octatetraene (COT) complexes  $[\text{Fe}(\text{CO})_3(\text{COT})]$  and  $[\text{Ru}(\text{CO})_3(\text{COT})]$ . The X-ray structure of  $[\text{Fe}(\text{CO})_3(\text{COT})]$  shows the iron atom to be bonded to only four of the carbon atoms yet the  $^1\text{H}$  NMR spectrum at room temperature shows only a sharp singlet resonance. As the temperature is lowered the resonance broadens then splits, but even at  $-145^\circ$  is still broad. The ruthenium complex, however, which also shows a singlet resonance at room temperature shows four well-defined resonances at  $-145^\circ$  interpretable in terms of a structure in which the ruthenium is bonded to only four carbon atoms. The computer simulated spectra are only consistent with the ruthenium atom moving around the ring by a 1,2-shift and rule out 1,3; 1,4; 1,5 or random shifts. Professor Cotton went on to discuss some more complex fluxional molecules some of which have been investigated by variable temperature NMR; these include  $[\text{Cr}(\text{CO})_3(1,3,5,7\text{-tetramethylcyclo-octatetraene})]$ ,  $[\text{Fe}_2(\text{CO})_5(1,3,5,7\text{-tetramethylcyclo-octatetraene})]$ ,  $[\text{Ru}_2(\text{CO})_6(\text{COT})]$  and  $[\text{Ru}_3(\text{CO})_4(\text{COT})_2]$ .

### Reactions with Rhodium Chloride

B. R. James, M. Kastner and G. L. Rempel (University of British Columbia) studied the kinetics of reactions between  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and ethylene. In non-aqueous solvents such as dimethylacetamide, the anion  $[\text{Rh}^{\text{I}}\text{Cl}_2(\text{C}_2\text{H}_4)_2]^-$  is formed but in water the production of small amounts of rhodium(I) species catalyses the formation of  $[\text{Rh}^{\text{III}}\text{Cl}_2(\text{H}_2\text{O})_7]^+$ . Acetylenes are catalytically hydrated by chlororhodate(III) complexes. The reaction mechanisms all involve insertion of the unsaturated organic molecule (ethylene or acetylene) into a  $\text{Rh}^{\text{III}}\text{-OH}$  bond.

R. Murray and J. Walker (I.C.I. Petrochemical and Polymer Laboratory) have made a thorough 220 MHz. and 100 MHz.  $^1\text{H}$  NMR study of substituted triphenylphosphine complexes of palladium(II) and platinum(II), and corresponding  $^{19}\text{F}$  studies on  $\text{P}(p\text{-FC}_6\text{H}_4)_3$  and  $\text{P}(m\text{-FC}_6\text{H}_4)_3$  complexes. They interpret their results in terms of  $\sigma$ - and  $\pi$ -electronic effects. Our knowledge and understanding of factors contributing towards chemical shifts and spin-spin coupling constants is still limited and only tentative interpretations can be at present given to such studies.

### An Improved Schottky Diode

The conventional Schottky barrier diode (which does not inject minority carriers) is capable of switching times less than 0.1 nanosecond. An improved version has been developed by M. P. Lepselter and S. M. Sze at the Bell Telephone Semiconductor Device Laboratory (*Bell Laboratories Record* 1967, 45 (Nov.), 340). The introduction of a guard ring eliminates "edge effect", giving a breakdown voltage close to the theoretical limit, while the use of a very clean junction between the n-type silicon semiconductor and a layer of platinum silicide provides an almost ideal forward current-voltage characteristic.

The n-type silicon substrate is cleaned by a glow discharge in which gas ions remove impurities by bombardment. Without removal from the vacuum chamber a smooth layer of platinum is then sputtered on. The result is a layer of uncontaminated platinum silicide with a near-perfect interface to the n-type silicon. Successively, a guard-ring of p-type silicon is formed, a silicon dioxide layer deposited, channels of access etched, and gold beam leads applied.

Platinum silicide is a very stable compound, highly resistant to corrosion and able to form a low-resistance contact. In other related applications the silicide layer receives a deposit of titanium followed by a platinum layer. The titanium layer bonds strongly to the silicon dioxide insulating layer, which it improves by absorbing impurities. The further platinum layer is required to form a strong bond with the gold leads, and also to prevent gold/titanium reactions.

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