

The Platinum Metals in Catalysis

PAPERS AT THE ANNUAL CHEMICAL CONGRESS

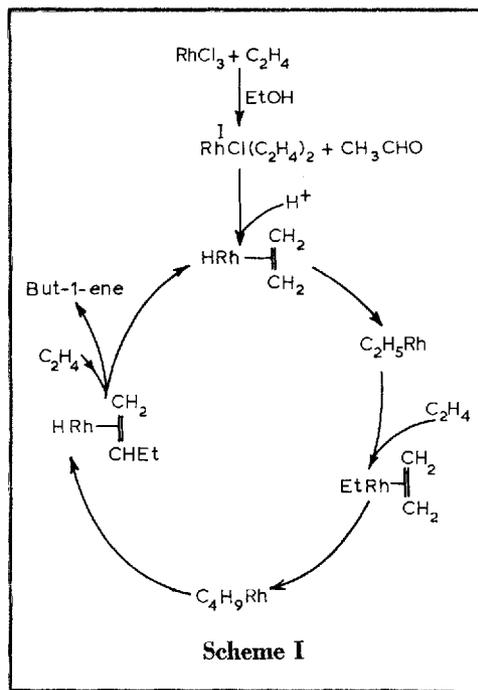
Among the papers presented at the Dalton Symposium held during the Annual Congress of the Chemical Society in Glasgow were contributions concerned with the use of the platinum group metals as heterogeneous and homogeneous catalysts and with recent developments concerning the molecular structure of some osmium and ruthenium complexes.

The use of the platinum metals as heterogeneous hydrogenation catalysts was reviewed by Professor S. J. Thomson and Dr G. Webb of the University of Glasgow. These authors demonstrated that, in spite of the vast number of papers which have been published concerning hydrogenation reactions on metal catalysts, the subject still has no basic unifying theory. The controversy over reaction mechanisms and the underlying properties of metals which account for their behaviour as catalysts was demonstrated by considering typical results relating to the basic features of many aspects of hydrogenation. Examining each of these aspects in turn, the problems and inconsistencies of interpretations were emphasised. These included the inability of kinetics to yield unequivocal results; the importance of catalyst pretreatments to determinations of activity; the insensitivity of activation energy to the metal and of reaction rates, on an atom for atom basis, to the nature of the surface; the insensitivity of hydrogenation to catalyst structure, when compared with the "demanding" reactions of skeletal isomerisation and hydrocarbon cracking; the occurrence of self-hydrogenation and the retention of "carbide" residues on the catalyst surface and the lack of correlation between the electronic, magnetic and geometrical factors with activity. This last point is well demonstrated in alloy catalysis, where neither the rates of hydrogenation nor the activation energy shows the expected change at the point corresponding to the filling of the d-band of the alloy.

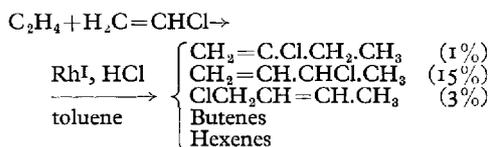
From these considerations it was concluded

that the metal was only of secondary importance in hydrogenation. It was suggested that all of the various aspects, outlined here, can be satisfactorily interpreted by considering a general mechanism in which hydrogenation involves a hydrogen transfer between an adsorbed carbonaceous residue $M-C_2H_x$ and adsorbed olefin, rather than by direct addition of adsorbed hydrogen to adsorbed olefin. Hydrogenation thus becomes an extension of self-hydrogenation; the latter reaction is self-poisoning, but in the presence of added hydrogen (hydrogenation) becomes a continuous process.

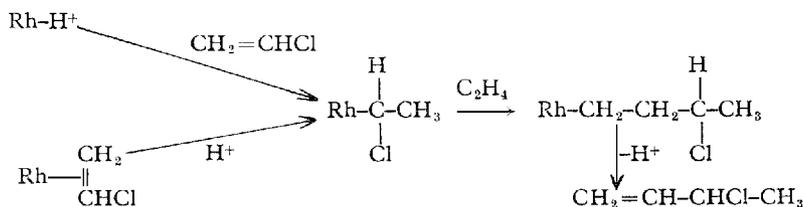
Dr G. W. Parshall of E.I. du Pont de



Nemours, U.S.A., outlined the role of transition metal complexes to some catalytic and synthetic processes. Among the examples cited was the rhodium(I)-catalysed dimerisation of ethylene to but-1-ene (see Scheme I) and the commercial synthesis of hexa-1 : 4-diene (see Scheme II). In the latter example one of the major advantages of using rhodium as catalyst, compared with iron or cobalt, is its ability to catalyse the isomerisation of the thermodynamically more favoured anti-1-methyl- π -allyl complex to the syn complex and hence to produce the desired trans-hexa-1 : 4-diene product. The stereochemical aspects of the mechanism of the co-dimerisation of ethylene and vinyl chloride in the presence of rhodium(I) as catalyst were discussed:

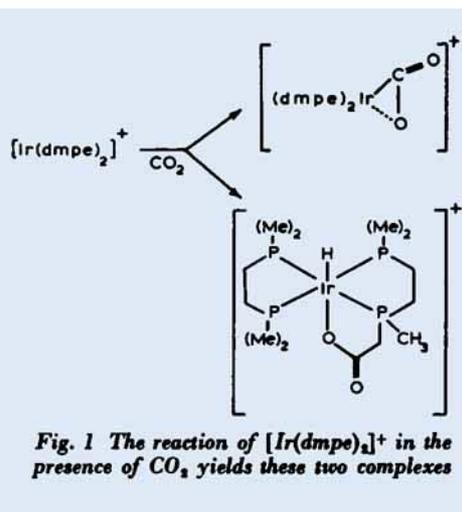
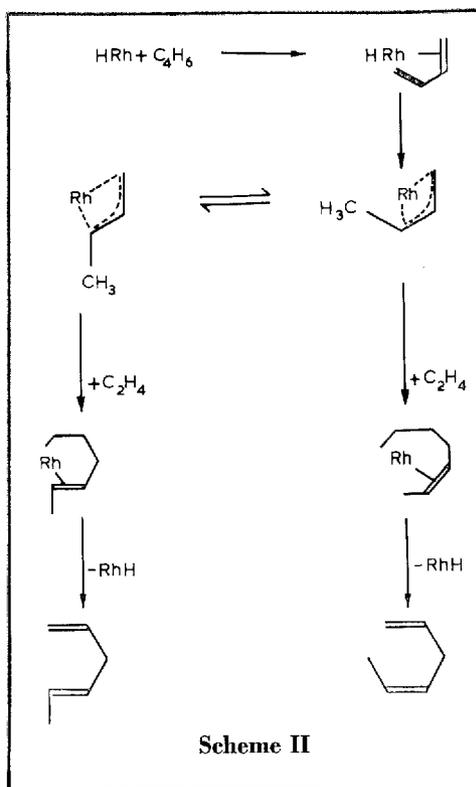


The major reaction pathway postulated is:



Dr Parshall concluded by describing some recent work on the reactions of carbon dioxide with some iridium(I) complexes. $[\text{Ir}(\text{dmpe})_2]^+$ in the presence of CO_2 yields two complexes as shown in Fig. 1, while the action of CO_2 on the complex $\text{IrCl}(\text{C}_8\text{H}_{14})(\text{PMe}_3)_3$ produces the novel complex [A] shown in Fig. 2, which has been characterised crystallographically. Slow heating of [A] results in the reversible loss of CO_2 whereas rapid heating leads to the carbonyl complex and CO_3^{2-} .

Dr A. C. Skapski of Imperial College, London, described recent developments relating to the structures of some osmium and ruthenium complexes in the crystalline state. Whereas derivations of OsO_4 , formed in *cis*-



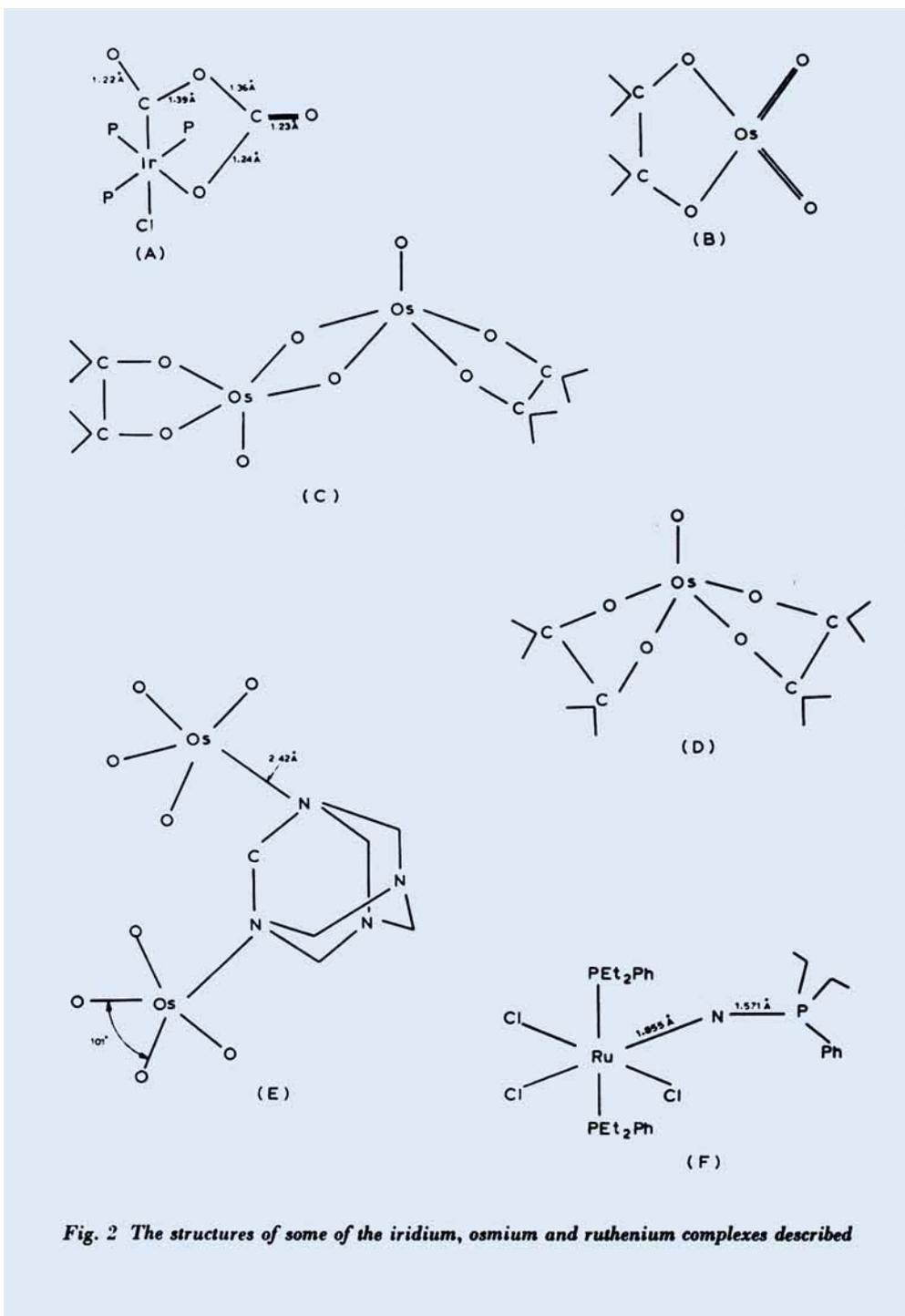


Fig. 2 The structures of some of the iridium, osmium and ruthenium complexes described

hydroxylation of olefins and in biological staining, are usually considered to have a structure [B], a more likely structure is that found with $[\text{OsO}_2(\text{O}_2\text{C}_2\text{H}_4)_2]_2$, structure [C],

involving 5-coordinate osmium. A similar structure [D] has been found for the monomeric complex $(C_2H_4O_2)_2OsO_4$, showing that osmium can bridge two C-C linkages in both monomer and dimer. It was suggested that OsO_4 could also attack -SH and -NH₂ groups in proteins; a complex of hexamethylene tetramine with OsO_4 has the structure [E]. The Os-N bond length is very large (2.42Å) explaining why the OsO_4 can be readily vaporised from the complex.

Using the large cation $[Ph_4As]^+$ to minimise packing effects on the anion, it has been found that in the tetraphenyl arsine complexes, the anions $[OsNCl_4]^-$, $[OsNI_4]^-$ and $[RuNCl_4]^-$ are isostructural having C_{4v} symmetry and a short $M \equiv N$ and large M-halogen bond lengths.

In contrast to this, in the complex

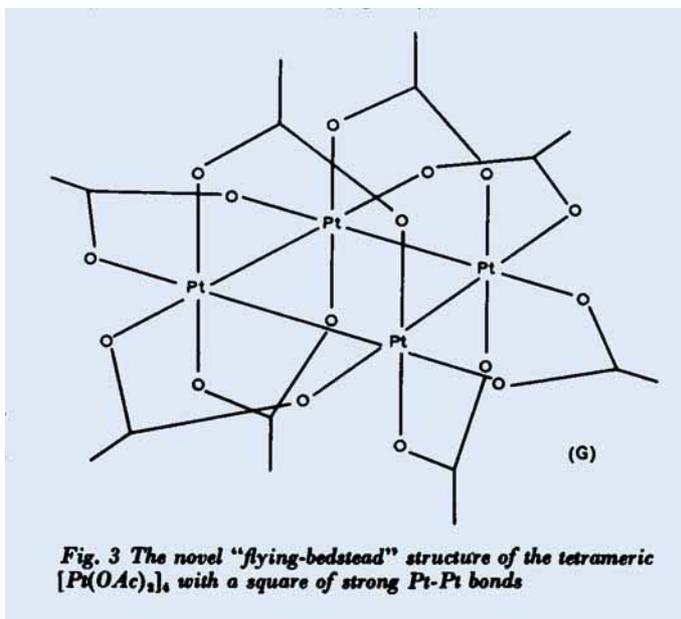


Fig. 3 The novel "flying-bedstead" structure of the tetrameric $[Pt(OAc)_2]_4$ with a square of strong Pt-Pt bonds

$Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2$ (structure [F]) the Ru-N bond is longer than expected for a single bond while the P-N bond is somewhat shorter than in a P=N double bond.

Finally Dr Skapski referred to the novel "flying-bedstead" structure of the tetrameric $[Pt(OAc)_2]_4$ involving a square of strong Pt-Pt bonds (Fig. 3, [G]).

G. W.

Advances in Platinum Metallurgy in Russia

Physical Metallurgy of the Platinum Metals BY E. M. SAVITSKII, V. P. POLYAKOVA, N. B. GORINA AND N. R. ROSHAN, Metallurgiya, Moscow, 1975, 242 pages

Over the past ten years or so a great deal of original work on the platinum metals has been carried out in the Metallurgical Institute of the U.S.S.R. Academy of Sciences in Moscow and this volume, contributed by four of the leading workers in the Institute's laboratories, brings up to date the whole subject of their physical metallurgy and metal physics.

The background knowledge on the structure and properties of the platinum metals and their many alloys is, of course, adequately covered, but much newer material has to do with their work on single crystals of the pure metals and with the interaction of the platinum metals with almost every other element and the nature and structure of the resulting intermetallic compounds.

There are sections on metallography—including field ion emission—and a full range of equilibrium diagrams of the alloy systems.

The book is described as being written for workers in the Russian noble metals industry to familiarise them with developments in the physical metallurgy of the platinum metals since the publications of V. A. Nemilov and A. A. Rudnickii which appeared some thirty and twenty years ago respectively, and a great deal of valuable information has indeed been compressed into a relatively small volume.

There are in all 499 references, the great majority of them to Russian work, although some of the leading British, German, American and Japanese workers in this field receive honourable if brief mention.

L. B. H.