

Co-ordination Chemistry of the Platinum Metals

A REVIEW OF THE SEVENTH INTERNATIONAL CONFERENCE

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The Seventh International Conference on Co-ordination Chemistry, held at Stockholm and Uppsala during June 1962, was attended by six hundred participants from more than thirty countries. About two hundred and fifty papers were presented, some thirty of which dealt wholly or partly with the chemistry of the platinum metals.

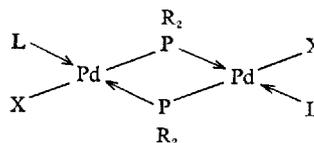
While many of these papers describe work that has at present no obvious application, some of the complexes described have potentialities as homogeneous catalysts. There is a rapidly growing interest in the co-ordination compounds formed from platinum and palladium complexes with olefinic or acetylenic ligands; the subsequent reactions of these complexes will undoubtedly assume importance in synthetic organic chemistry.

M. R. Truter, Leeds University, discussed the structure of the monomeric complex trimethyl (acetylacetonyl) 2,2'-bipyridyl platinum and of the related dimeric complex $\text{Me}_3\text{Pt}.\text{PrCOCHCOPr}$, both of which showed the interesting feature of some form of a co-ordination bond from the central carbon atom of the β -diketone to the platinum group metal.

A. J. Edwards, J. H. Holloway, R. D. Peacock and R. W. H. Small, of Birmingham University, showed that tetrameric units exist in the solid state of a number of transition metal pentafluorides. The refinement of the ruthenium pentafluoride structure had not been completed, but it appears that the metal itself possesses a distorted octahedral co-ordination. Osmium pentafluoride was found to be the isostructural with the ruthenium compound.

C. Berecki-Biedermann, of the Royal Technical High School, Stockholm, mentioned experimental problems in the preparation of solutions of pure rhodium(III) and palladium(II) perchlorates.

R. G. Hayter, Mellon Institute, Pittsburgh, presented his findings on some palladium(III) complexes. He reported a series of compounds $[\text{PdX}(\text{PR}_2)_2\text{L}]_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{SCN}$; $\text{R}=\text{Et}, \text{Ph}$; $\text{L}=\text{R}_2\text{PH}$ or R_3P), and produced evidence in favour of a phosphorus-bridged structure.



Measurements of a number of physical properties including infra-red spectra, molecular weight, colour and melting points were presented. These compounds were non-electrolytes and were shown to be dimeric in a number of solvents. A halogen-bridged structure is discarded in favour of a phosphorus-bridged one, in view of the nature of the reaction products with reagents such as amines or thiocyanate ion.

Preliminary X-ray data suggested that the *trans* structure indicated in the diagram is correct. A number of related ionic compounds were also reported.

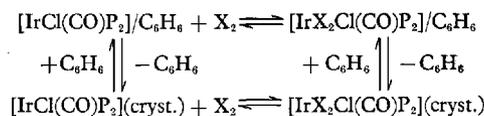
G. B. Kauffman, J. H. Tsai, R. M. Kallo, R. C. Fay and C. K. Jørgensen, of Fresno State College, University of Illinois and Cyanamid Research Institute, Geneva, investigated the iridium complexes of composition $[\text{Ir}(\text{Et}_2\text{S})_3\text{Cl}_3]$. They suggested that the yellow

non-electrolytic isomer possesses the *cis* structure and that the red isomer was a 1:1 electrolyte and could be formulated as an electrolytic polymerisation isomer of the yellow form. The latter formed in benzene under the influence of ultra-violet light a brownish-orange compound formulated as $[\text{Ir}(\text{Et}_2\text{S})_2\text{Cl}_3]_2$.

Allyl alcohol, under conditions of homogeneous catalysis by means of Pt(II) ions and acid, was shown by J. Milgrom and W. H. Urry, American Oil Co., Whitney, Indiana, and University of Chicago, to give in suitable circumstances either diallyl ether or a mixture of this with allyl alkyl ether. The overall process can be written as $\text{CH}_2=\text{CHCH}_2\text{OH} + \text{ROH} \rightarrow \text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CHCH}_2\text{OR} + \text{H}_2\text{O}$ (R=saturated alkyl). If allyl alcohol was the only one present diallyl ether was the sole product, but when a saturated alcohol was added the proportion of the symmetrical to the unsymmetrical ether depended on the nature of the saturated alkyl group.

No saturated dialkyl ethers were detected, indicating the essential nature of the complex of allyl alcohol with the platinum metal ion. The mechanism of the above reactions was discussed in some detail.

A most interesting quadrico-ordinate iridium(I) complex, $[\text{IrCl}(\text{CO})\text{P}_2]$ (P= Ph_3P), was reported by L. Vaska, of the Mellon Institute, Pittsburgh. This can react reversibly under moderate conditions with molecular hydrogen and oxygen. The crystalline adducts were isolated and their properties investigated. The reactions of these adducts in the solid state, as well as in benzene solution, are summarised in the scheme below:

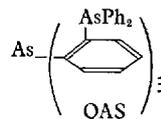


When X_2 is the hydrogen molecule, the monomeric non-electrolytic, diamagnetic adduct was formulated as $[\text{Ir}(\text{III})\text{H}_2\text{Cl}(\text{CO})\text{P}_2]$.

The two hydrogens were considered to occupy *cis* positions. The analogous reactions with oxygen were found to be slower, but the overall properties of the resultant oxygen adduct were rather similar. It was suggested that the compound was peroxidic in nature, with both oxygens attached to the same central atom.

Other reactions with hydrogen chloride, or chlorine, and the interconversion of some of these compounds were also reported.

R. J. Mawby and L. M. Venanzi, of the University of Oxford, described complexes of platinum and palladium with tetradentate arsenic ligands, QAS, and compared these with analogous tridentate ligands.



A series of complexes such as $[\text{MX}(\text{QAS})]\text{X}$ (M=Pt, Pd; X=Cl, Br, I, SCN) and $\text{RhX}(\text{QAS})$ (X=Cl, Br, I) were reported. The platinum(II), and probably also the palladium(II) and the rhodium(I) compounds possess a trigonal bipyramidal structure. On the other hand, ruthenium(II) and osmium(II) compounds form complexes of the type $\text{MX}_2(\text{QAS})$, which are six-co-ordinate. These complexes possess very high thermal stability, as well as considerable resistance to oxidation, which is believed to have a mechanistic origin.

Complex hydrides of iridium and ruthenium were reported by B. L. Shaw and J. Chatt, Leeds University and I.C.I. Limited, Welwyn.

Hydride transfer reactions were described using the iridium(III) complex $[\text{IrCl}_3(\text{PEt}_2\text{Ph})_3]$ as an example. This gave in alcohols, with one,

two or three moles of potassium hydroxide, several crystalline stable hydrides $[\text{IrH}_y\text{Cl}_{3-y}(\text{PEt}_2\text{Ph})_3]$, whose stereo-chemistry was discussed.

A number of other similar iridium complexes were also reported. In the "reversed carbonylation" reaction, a ruthenium(II) complex $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ gave under similar treatment with potassium hydroxide in ethanol, methane and the hydrocarbonyl complex $[\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$.

A. D. Allen and C. D. Cook, of the University of Toronto, reported kinetic and equilibrium measurement for the displacement of some aryl acetylenes by others in platinum complexes $[\text{Pt}(\text{PPh}_3)_2\text{L}]$ (L = aryl acetylene).

F. Zingales, University of Milan, gave a paper on the reactions of palladium (II) chloride with phenyl-ethyl-acetylene (L) from which he obtained three products, 1,2,4-triphenyl-3,5,6-trimethyl-benzene, and two

complex palladium compounds. These were crystalline, diamagnetic, non-electrolytic solids of formulation PdClL_4 and $\text{Pd}_2\text{Cl}_2\text{L}_4$. By reduction of either of the latter two compounds with sodium borohydride, a cyclooctatetraene derivative was obtained. The first of the two palladium complexes could be converted by thiocyanate or iodide ion to $\text{Pd}(\text{SCN})\text{L}_4$ and PdIL_4 respectively.

W. D. Jacobs, J. T. Pyle and R. B. Wilson, of the University of Georgia, described a large number of substituted dithio-oxamides, some symmetric, some unsymmetric, and investigated these as reagents for palladium, platinum, osmium, rhodium and ruthenium. The complexes are formed in very strong hydrochloric acid solutions. With some, maximum colour is developed almost instantaneously at room temperature, while for others considerable time is required and heating is sometimes necessary.

Production of Hydrogen from Coal

PALLADIUM CATALYSTS IN DEHYDROGENATION OF VITRAIN

The possibility of the economic production of molecular hydrogen by the catalytic dehydrogenation of coal is suggested by the results of work reported recently by R. Raymond, I. Wender and L. Reggel, of the Pittsburgh Coal Research Center, U.S. Bureau of Mines (*Science*, 1962, **137**, (August 31st), 681-682). Surprisingly large yields of hydrogen were obtained in attempts to determine the hydroaromaticity of coal by the dehydrogenation of vitrains and other related materials with the use of polycyclic aromatic solvents and supported palladium catalysts.

In the laboratory-scale process, 0.5 g finely-divided coal (-200 mesh), the solvent and 0.55 g palladium-on-calcium carbonate catalyst were refluxed together for five hours in a helium atmosphere. Generally the major part of the gases, consisting of hydrogen with small amounts of carbon monoxide, carbon dioxide and methane, was evolved in the first hour. With phenanthridine as solvent and a 30 per cent palladium-on-calcium carbonate catalyst, 30 per cent of the hydrogen

contained in Pittsburgh vitrain was evolved. Other coals, under the same conditions, gave lower but appreciable yields of hydrogen, depending on their rank. About 50 per cent of the total hydrogen content of Pittsburgh vitrain was evolved when 2-azafluoranthene was used as solvent, but it is thought that some of this hydrogen was due to side reactions.

Yields of about 30 per cent of the total hydrogen in Pittsburgh vitrain were also obtained when other platinum metal catalysts were used with phenanthridine as solvent. Such catalysts included 1 and 5 per cent palladium-on-calcium carbonate, 5 per cent palladium-on-alumina, 5 per cent ruthenium-on-alumina, and 5 per cent rhodium-on-alumina. A commercial chromia-on-alumina catalyst was totally ineffective in these conditions.

This catalytic dehydrogenation process, demonstrated so far only on a small scale, has indicated a possible new use for certain coals as a source of hydrogen gas.

B.M.G.