

Platinum Metals in Organometallic Chemistry

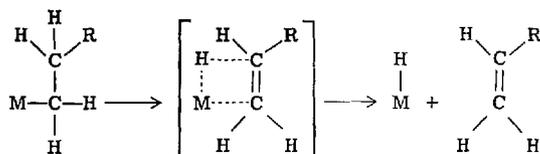
THE INTERNATIONAL CONFERENCE IN MOSCOW

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At the Fifth International Conference on Organometallic Chemistry, held in Moscow in August 1971, no fewer than 463 papers were presented, of which 189 were actually delivered orally, together with 11 section lectures, in three parallel sessions. This review can therefore give only a brief account of such a conference and of the many contributions that concerned the platinum metals.

A highlight of the Conference came on the first day when Professor Geoffrey Wilkinson (Imperial College, London) cast aside many time-honoured ideas about the factors responsible for the formation of strong metal-carbon σ -bonds. Wilkinson emphasised that, before these factors can be meaningfully discussed, it is necessary to have criteria for deciding how to measure bond strength. The ideal source of data, namely thermodynamic measurements, is at present insufficient to be of any value in comparing bonds. In addition, relatively few metal-carbon σ -bond lengths are known with sufficient accuracy for them to be used. One possible way of comparing bond strengths is to compare the thermal stabilities of complexes, although for this to be used it is essential to understand the mode of decomposition of the complex which Wilkinson suggested was by an "alkene-elimination hydride transfer" mechanism:



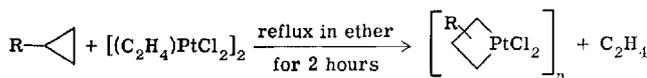
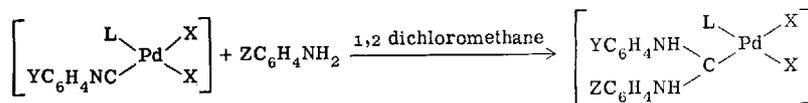
The formation of a stable metal-carbon σ -bond requires the formation of a complex

stabilised against such a reaction. This may be achieved by:

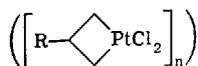
(i) the formation of complexes with alkyl ligands of the type $-\text{CH}_2\text{Y}$ where Y is an atom that cannot form a double-bond to carbon (e.g., $\text{Y}=\text{H}$, CMe_3 , SiMe_3 or Ph),

(ii) blocking all the coordination sites around the metal atom with strong ligands such as triphenylphosphine, pyridine, or even carbon-bonded ligands themselves, thus preventing a second coordination site being available for the hydride to transfer to. This new approach, which satisfactorily explains many of the anomalies that have recently arisen in connection with Chatt's electronic theory of the stabilisation of metal-carbon σ -bonds by tertiary phosphine ligands has enabled Wilkinson to prepare a number of binary alkyl complexes of such species as V^{IV} , Cr^{IV} , Mo^{IV} , W^{IV} , etc., with ligands such as $-\text{CH}_2\text{SiMe}_3$. The stability of these complexes dispels the suggestion that the presence of a tertiary phosphine or other similar ligand is necessary for the formation of stable metal-carbon σ -bonds.

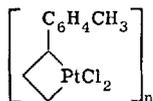
F. J. McQuillin (University of Newcastle upon Tyne) reported on the reaction of substituted cyclopropanes with platinum(II) complexes to form analogues of Tipper's Compound:



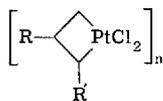
It was found that the reactivity of the cyclopropane increased with increasing electron density in the ring (with electron withdrawing groups such as CN or OCH₃ no reaction occurred). When R was H, *n*-C₆H₁₃, Ph, *o*-NO₂C₆H₄, PhCH₂, the resulting product



indicated that ring opening had occurred at the least substituted bond, probably due to electronic rather than steric effects since the bulky *p*-tolyl group gave

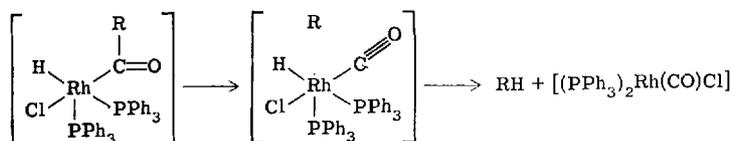


Although with *trans*-1,2-disubstituted cyclopropanes ring opening occurred to give



with *cis*-1,2-disubstituted cyclopropanes, the cyclopropane was isomerised to olefin. No platinocyclopropane ring complex was formed.

H. M. Walborsky (Florida State University) reported a study of the decarbonylation of acyl complexes of the "Wilkinson Catalyst". The reaction was stereoselective but not stereospecific, and consistent with the formation of a radical pair intermediate:



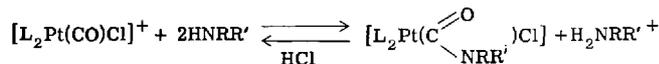
Crociani (CNR, Bologna) reported a study of the kinetics of formation of carbene complexes of palladium(II)

according to the above reaction.

It was found that the rate increased with both increasing σ -donor ability of the amine nitrogen and increasing electron-withdrawing ability of the substituent Y on the isocyanide ligand indicating that the reaction proceeds by nucleophilic attack of the amine on the coordinated isocyanide.

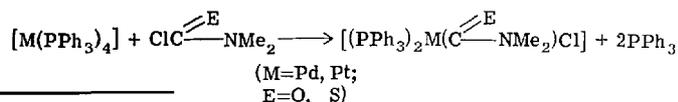
R. J. Angelici and his colleagues (Iowa State University) reported two routes for the preparation of carbene complexes of platinum(II) and palladium(II):

(i) Nucleophilic attack of amines on cationic carbonyl complexes.



This reaction, which can be reversed by addition of hydrochloric acid, is only applicable to cationic carbonyl complexes, since in neutral carbonyls the amine substitutes the carbonyl ligand.

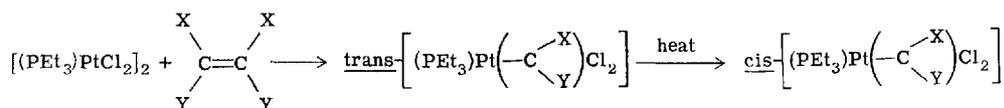
(ii) Oxidative addition of ClC(=O)NMe₂ and ClC(=S)NMe₂ to platinum(0) and palladium(0) complexes.



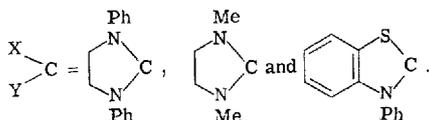
The triphenylphosphine complex shows no rotation about the C-N bond even on heating to 200°C, although with less bulky tertiary phosphine such rotation is observed.

Professor Abel read a paper by M. F. Lappert and his co-workers (University of Sussex) on the use of electron-rich olefins

in the synthesis of carbene complexes in which the published range of olefins that can be used in the reaction



was extended to include



The bis(dibenzylideneacetone) complexes of both platinum and palladium were described by two groups of workers, Professor Maitlis of McMaster University, and Ito and his colleagues from Nagoya University, Japan, as useful air-stable starting materials for the preparation of other complexes of these metals. The complexes are prepared by treating Na_3PdCl_4 or Na_2PtCl_4 with dibenzylideneacetone (DBA) in an alcoholic solvent in the presence of sodium acetate. The structures of the complexes $[\text{M}(\text{DBA})_2]$ are unknown, the Canadian group favouring bonding of the carbonyl group to the metal and the Japanese bonding of the olefin group to the metal.

Professor Maitlis, in a masterly section lecture, reviewed his work on the cyclo-oligomerisation of acetylenes by palladium

salts and emphasised the importance of the oxidation state of the metal on the mechanism of the cyclotrimerisation of acetylenes. This is not unexpected, since acetylene complexes of palladium(0) involve strong π -back donation of electron density from the metal to the acetylene so that the acetylene is susceptible to electrophilic attack whereas, in the acetylene complexes of palladium(II), σ -donation of charge from the acetylene to the metal is more important than the reverse π -back donation so that the acetylene is susceptible to nucleophilic attack. These and other differences in the properties of olefin and acetylene complexes of transition metals were considered by the present author, who suggested that olefin complexes fell into one of two classes, whose similarities and differences are shown in the table.

In other papers on olefin complexes Panunzi (University of Naples) reported extensions of his work on the attack of nucleophiles on olefin complexes to include

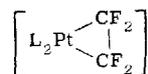
Classification of Olefin Complexes		
	Class S	Class T
Model complex	$\text{K}^+[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2]^-$	$[(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{H}_4)]$
Coordination number of the metal	4 or 6	3 or 5
Rotation of the olefin about metal-olefin bond?	Yes	No
Angle between axis of double-bond and square-plane of metal	$77-90^\circ$	$0-24^\circ$
Multiple bond lengthening on coordination	$\sim 0.02\text{\AA}$	$\sim 0.15\text{\AA}$
Angle at which substituents on multiple bond bent back away from metal	$\sim 15^\circ$	$\sim 35^\circ$
Examples of metal ions giving each class of complex	$\text{Pt}^{\text{II}}, \text{Pd}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Rh}^{\text{I}}, \text{Re}^{\text{I}}, \text{Mn}^{\text{I}}$	$\text{Pt}^{\text{0}}, \text{Pd}^{\text{0}}, \text{Fe}^{\text{0}}, \text{Ir}^{\text{I}}, \text{V}^{\text{I}}, \text{Mo}^{\text{I}}$

both *cis*- and *trans*-[Pt(olefin)LCl₂] and cationic [Pt(olefin)ClLL']⁺ complexes (L is a ligand that enables the initial platinum(II)-alkyl complex to be isolated). It was found that the stereochemical route of the reaction of the *trans*-complexes was less dependent on the nature of L than in the *cis*-complexes.

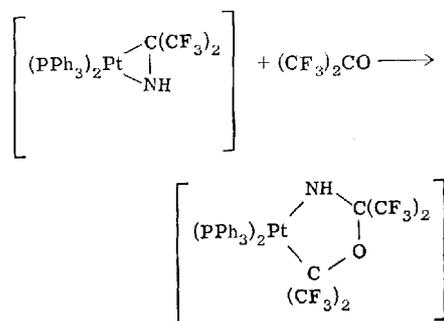
H. Thyret of Munich described evidence which suggested that an earlier report of a vinyl alcohol complex of platinum(II), [(CH₂=CHOH)PtCl₂]₂, was incorrect and described the preparation of complexes of Fe(CO)₄ with vinyl alcohol and vinyl alcohol derivatives. H. A. Tayim (American University of Beirut) has prepared complexes of 1,4-cyclooctadiene (1,4-COD) with Pt^{II}, Pd^{II}, Rh^I, Ag^I, and Cu^I and found that the properties of 1,4-COD are intermediate between 1,3-COD and 1,5-COD.

Y. Fujiwara of Osaka University reported a detailed study of the reaction of styrene and benzene in the presence of palladium(II) acetate to give *trans*-stilbene. The electronic effects of substituents in the aromatic rings (electron-donating substituents in the benzene give *ortho*, *para*-substitution; electron-withdrawing give *meta*-substitution; electron-withdrawing substituents on the styrene make it more reactive), the steric effect of groups on the olefin, which lead to the aryl group being introduced on to the least substituted carbon atom of the olefin, and the fact that no hydride shift occurs during the reaction are consistent with the mechanism shown here:

Professor Stone of Bristol discussed the ability of unsaturated fluorocompounds to form 3- and 5-membered rings with zero-valent platinum, palladium, and nickel. Thus, for example, while most unsaturated fluoro-compounds such as CF₂=CF₂, (CF₃)₂C=O, (CF₃)₂C=NCH₃ form 3-membered ring compounds of the type

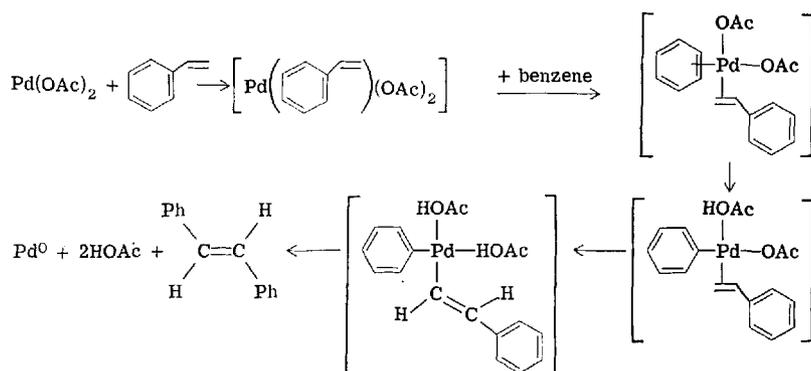


some of these compounds can react further to give 5-membered ring compounds:



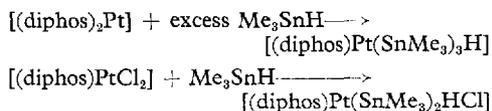
Stone showed that such ring expansion depended in a complex way on the electronic properties of the phosphine ligand, which should be a strong, but not too powerful, σ-donor. Nickel(O) appears to give ring expansion more readily than platinum(O).

A. P. Belov (Kurnakov Institute, Moscow) described the chemical oxidation of π-allyl palladium halides in aqueous solution and showed that the redox potential decreases as

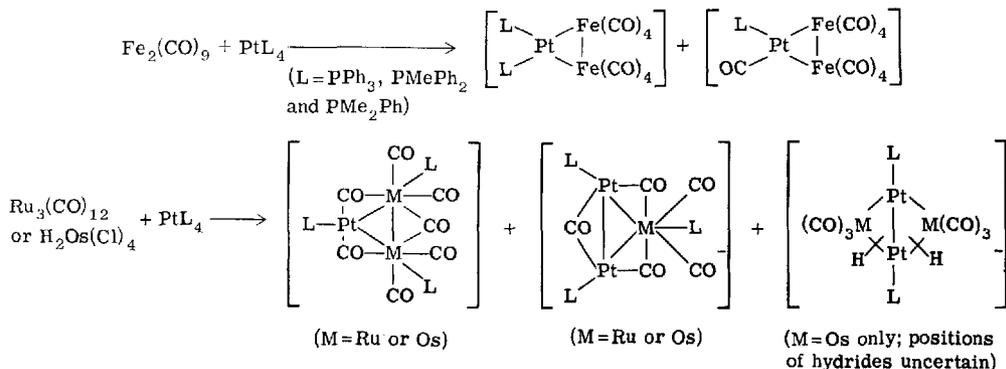


the halide is altered in the order chloride > bromide > iodide.

F. Glockling (Queen's University, Belfast) reported the preparation of platinum(IV) complexes of trimethylstannane which, although widely implicated as intermediates



M. I. Bruce (Bristol University), described a number of interesting complexes in which iron, ruthenium, or osmium were co-ordinated directly to platinum(II).



in the reactions of platinum(II) complexes of trimethylstannane, had not been isolated until recently. Two main routes both involving oxidative-addition reactions were reported for the preparation of these complexes:

J. Dehand (Institute of Chemistry, Strasbourg) discussed the vibrational spectra of the related compounds $[(\text{pyr})_2\text{M}(\text{M}'(\text{CO})_n)_2]$, where M = Pd or Pt, $\text{M}'(\text{CO})_n = \text{Mn}(\text{CO})_5$, $\text{Co}(\text{CO})_4$ or $\text{Mo}(\text{CO})_3(\pi\text{-C}_5\text{H}_5)$ and pyr = pyridine, 3-methylpyridine or 4-methylpyridine.

Rhodium Coating on Plastics

RADIO FREQUENCY SPUTTERING TECHNIQUE

Techniques developed by Precision Instrument Company of Palo Alto, California, have made it possible to coat heat-sensitive substrates with a variety of metals by sputtering. This work grew out of the need to coat strips of polyester with thin films of rhodium. The rhodium-coated strips form part of a mass memory computer core but any distortion renders them useless for this purpose. The sputtering technique used by the company ensures that substrate temperatures do not exceed 50°C, thus avoiding thermal distortion. This enables pin hole-free metal coatings 200Å thick or less to be deposited uniformly over the whole surface of the substrate to ±10 per cent accuracy.

The apparatus was developed from work carried out at Argonne National Laboratory.

It consists of a supported glow discharge system. The rhodium or other metal to be coated is fixed to a cathode connected to a radio frequency or d.c. power supply and is enclosed in a vessel capable of withstanding a high vacuum. The substrate is supported some 10 cm below the cathode. Between the cathode and the substrate is a double coil of wire connected to a 1.2 kW, 13.5 MHz R.F. power source. After evacuation to 10⁻⁶ torr and backfilling to 10⁻³ torr with argon, power in the double coil stimulates a glow discharge in the argon, so that argon ions strike the cathode metal target and displace metal atoms, which are deposited on the substrate. The substrate temperature remains low because it is not connected to the electrical system.