

# Organometallic Compounds of the Platinum Metals

## A SURVEY OF THE TYPES OF COMPOUNDS, THEIR STRUCTURES AND REACTIONS

By G. Wilkinson, Ph.D., A.R.C.S.

Professor of Inorganic Chemistry, Imperial College, London

*Although platinum provided the first known example of an organometallic complex of a transition metal, intensive studies of compounds of the platinum metals with metal to carbon bonds have come mainly during the past decade. The main classes of stable organo-complexes such as those having olefins, acetylenes, alkyl or cyclopentadienyl groups as ligands are discussed. The study of such stable complexes should assist in the elucidation of the mechanism of various reactions which are catalysed by platinum metal salts or complexes.*

Although a platinum ethylene complex, Zeise's salt,  $K[C_2H_4PtCl_3]$ , was the first platinum metal—indeed, the first transition metal—organometallic compound to be prepared (1), and although the methyl platinum compounds such as  $(CH_3PtI)_4$  were among the first metal alkyls to be prepared, it is generally true to say that only during the past twelve or so years when the organometallic chemistry of the transition elements has been intensively studied have the organo compounds of the platinum metals been examined in detail as part of this general research effort.

The organometallic compounds of the platinum metals are of particular interest since they have provided considerable insight

into the ways in which carbon compounds or radicals can be attached to transition metal atoms—especially regarding the unusual types of chemical bonds not found in the chemistry of non-transition metals and non-metals. However, the chemical utility of these complexes, as chemical compounds, is virtually zero at the present time. Despite this fact, such organometallic species are of considerably more than purely academic interest since their structures and the nature of the bonding in the compounds may throw light on the mechanisms involved in the use of platinum metal catalysts, especially in homogeneous media, and may allow the design of new useful processes. Some of the necessary information may already be at hand and we need only consider that the facts of the hydrolysis of  $[C_2H_4PtCl_3]^-$  to acetaldehyde and of the reduction of palladous salts by ethylene were known for many years (2) before the development of the Wacker olefin oxidation process. Other reactions which doubtless involve labile organometallic intermediates are the stereospecific polymerisation of butadiene using emulsions containing rhodium salts, polymerisations of acetylenes, olefin isomerisations and hydrogenation and carbon monoxide insertion reactions of olefins using ruthenium, rhodium or platinum species. It is not the purpose of this brief review to discuss such matters but only to consider the isolable organo compounds of the platinum metals.

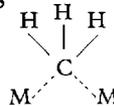
Some Representative Platinum Metal Organometallic Compounds			
Complex	Form	Structure type	Comment
$\pi\text{-C}_5\text{H}_5\text{Ru}(\text{CO})_2\text{C}_2\text{H}_5$	Colourless oil m.p. $-5^\circ$	$\pi$ -cyclopentadienyl alkyl	Volatile. Stable in air Petroleum soluble
$(\text{Et}_3\text{P})_2\text{PdCl}(\text{COCH}_3)$	Yellow crystals m.p. $50^\circ$	Alkyl	Formed by CO insertion into $\text{PdClCH}_3(\text{PEt}_3)_2$
$\text{K}[\text{C}_2\text{H}_4\text{PtCl}_3]$	Pale yellow crystals	Olefin	Water-soluble
$[\text{C}_7\text{H}_8\text{RhCl}]_2$	Yellow crystals m.p. $\sim 240^\circ$ (dec.)	Olefin (norbornadiene)	Soluble organic solvents. Air-stable. Halogen bridged
$\text{Pt}(\text{PPh}_3)_2(\text{C}_4\text{F}_6)$	White crystals m.p. $215^\circ$	Acetylene	Stable. Soluble in organic solvents
$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{C}_5\text{F}_6\text{O})$	Orange crystals m.p. $150^\circ$	Acetylene-derived cyclopentadienone	Extremely chemically inert
$(\pi\text{-C}_5\text{H}_5)_2\text{Ru}$	White crystals	Sandwich	Undergoes aromatic substi- tution reactions. Oxidisable $(\pi\text{-C}_5\text{H}_5)_2\text{Ru}^+$
$\text{C}_6\text{H}_9\text{OPdCl}(\text{C}_6\text{H}_7\text{N})$	Yellow needles	Allylic	Has mesityl oxide bound as allyl group with free ketone group

As part of the main *d*-block transition elements, the six platinum metals have certain similarities in common with the rest of the group, and many of the classes of compounds discussed below are found also for other metals. For a specific metal, not all types of compound may be known—or indeed be capable of existence. In some cases, explanations of special behaviour may be possible on an *ad hoc* basis. However, the reasons for stability or criteria for bonding in certain types of complex are not well known and quantitative data such as bond energies and other thermodynamic data, bond distances, etc., are often lacking. Nevertheless there is already an appallingly extensive literature, which is growing rapidly, covering especially preparations of compounds and their reactions and of recent years details of infra-red and high-resolution nuclear magnetic resonance spectra. The latter technique has been of especial importance in the study and characterisation of organometallic compounds. In the following sections we survey, with examples chosen from the platinum metal complexes, all of the major types of organo compounds known at present. References are

to recent review articles. The table gives the properties of a few representative compounds.

### Alkyls

These are compounds of the type usual among non-transition and non-metallic elements but less common among transition metals, in which aliphatic or aromatic radicals are bound to a metal atom (3). There are two classes: (a) normal alkyls, where the  $\text{M}-\text{C}\equiv$  bond is of the normal  $\sigma$ -bond type, (b) those compounds where the hydrocarbon radical, usually a methyl group, acts as a bridge,



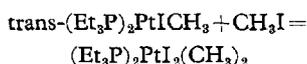
and where the bonding must be regarded as of the multicentre type as in the polymeric alkyls of Li, Be or Al; this type of bonding is not found for transition metals.

Although no simple binary alkyls, i.e.  $\text{M}(\text{CR}_3)_n$ , are known for the platinum group of metals, many complex alkyls where other ligands are also bound to the metal atom are well characterised. The criteria for obtaining

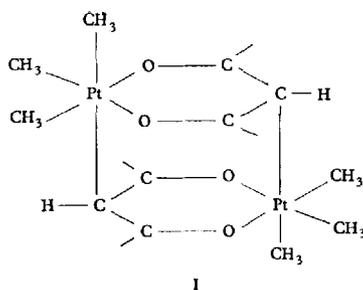
alkyls stable enough to isolate under normal conditions and various factors, whose effects are not well understood, are complicated. Some of these factors are (i) the oxidation state of the metal, (ii) the nature of the attached ligands, (iii) the electronegativity of the metal-ligand system—this involves both (i) and (ii), (iv) the electronegativity of the attached  $-\text{CR}_3$  group, (v) steric factors such as large bulky groups around the metal which can inhibit the approach of attacking molecules, so stabilising the  $\text{M}-\text{C}$  bonds. Concerning the ligands, it appears that  $\pi$ -bonding ligands, which, in effect, remove electron density from the metal, tend to stabilise  $\text{M}-\text{CR}_3$  bonds; however, though carbon monoxide is doubtless the best  $\pi$ -bonding ligand, platinum metal carbonyl alkyls have not been isolated. For compounds of analogous structure, the greater the electronegativity of the  $-\text{CR}_3$  group, generally the more stable the  $\text{M}-\text{C}$  bond and fluorinated derivatives are especially stable. In the absence of any data on  $\text{M}-\text{C}$  bond energies, however, explanations of relative stabilities of complex systems are not necessarily of much significance.

Among the alkyls, there are a few points of special interest. Platinum, especially  $\text{Pt}^{\text{IV}}$ , of all the metals appears most readily to form stable  $\text{Pt}-\text{C}$  bonds. This is illustrated by the fact that whereas  $\beta$ -diketones form chelate complexes normally, with  $\text{Pt}^{\text{IV}}$  the ligand forms an  $\text{M}-\text{C}$  bond as in (I) and this is so stable that in reactions, e.g., with 2,2'-dipyridyl it is the  $\text{Pt}-\text{O}$  bond and not the  $\text{Pt}-\text{C}$  bond which breaks, to give (II).

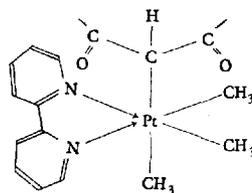
The square planar complexes of  $\text{Pd}^{\text{II}}$ ,  $\text{Pt}^{\text{II}}$  and  $\text{Ir}^{\text{I}}$ , chiefly with phosphine ligands, can undergo two unusual reactions. They can add alkyl halides, halogens or hydrogen halides to give octahedral species of formally oxidation state two higher, e.g.



and they can, like complexes of metal carbonyls such as  $\text{CH}_3\text{Mn}(\text{CO})_5$ , undergo

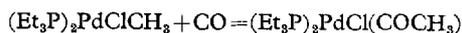


I



II

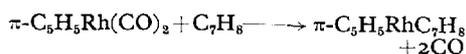
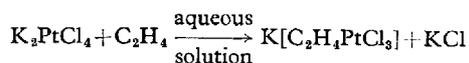
carbonylation reactions to give acyl derivatives, e.g.



Such carbon monoxide insertion reactions are believed to be involved in hydroformylation reactions of olefins.

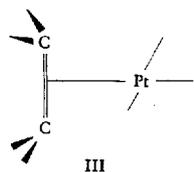
## Olefin Complexes

Compounds containing  $>\text{C}=\text{C}<$  groups can generally be bound to transition metals (4a,b,c). In addition to mono-olefins, cyclic conjugated and non-conjugated olefins can be bound and in this class can also be included such unsaturated compounds as quinones or cyclopentadienones although the latter are usually obtained in metal complexes indirectly through the interactions of acetylenes with carbon monoxide containing metal complexes (see below). Olefin complexes were the first and are the most numerous of organo compounds of platinum metals. They are commonly obtained by direct interaction of platinum metal salts or complexes with olefins, e.g.



Apart from the salts, the complexes are usually air-stable crystalline solids, soluble in organic solvents.

The nature of the binding of an olefin to a metal is fairly well understood. X-ray diffraction on several compounds has shown that the orientation is generally as in (III)



with the olefin group "side-on" to the metal. The C=C bond length is not precisely known but it appears to be longer than the unco-ordinated bond. There is also infra-red evidence which indicates C-C bond weakening on co-ordination. It is not essential that the metal atom lies on a line perpendicular to the C-C axis—indeed in many cyclic olefin complexes it is not possible for this to be so. Regarding the bonding, it is generally accepted that the bond is rather similar to that in the metal-carbon monoxide bond in metal carbonyls with donation of electron density from the  $\pi$ -electrons of the C=C bond into acceptor orbitals on the metal together with a type of  $\pi$ -bond resulting from "back-donation" of electron density from filled metal orbitals to the empty anti-bonding orbitals on the carbon atoms. Estimates of the relative

contributions of these two components are difficult to make but nuclear magnetic evidence suggests that the amount of "double bond" character in the metal-olefin bond is rather small—insufficient in fact to prevent free rotation of ethylene about the bond axis in simple ethylene complexes.

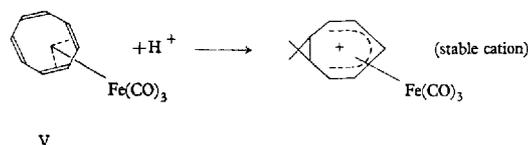
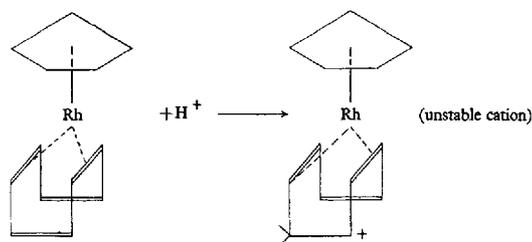
There has been relatively little work on the reactions of the hydrocarbon when bound to metals. Attack by many reagents leads to oxidation of the metal and disruption of the complex or, where

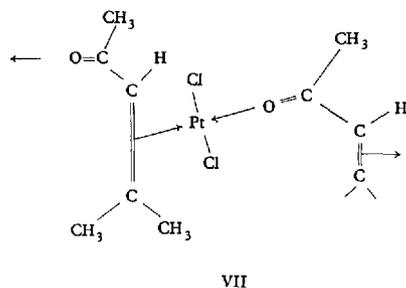
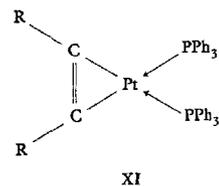
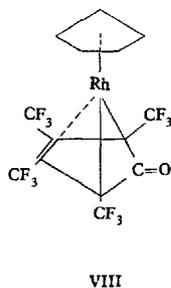
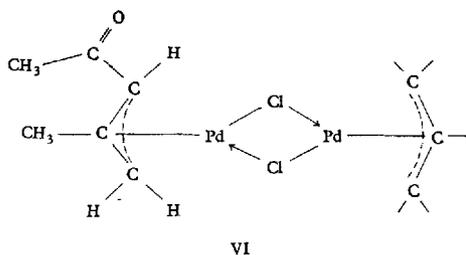
stronger donors are used, to displacement of the olefin. Where not all of the olefinic groups in a polyolefin are bound to the metal, the "loose" double bonds may be protonated by acids to give cationic species. These are not usually stable unless it is possible for the hydro-carbon entity to rearrange to give a partially delocalised allylic type system (see below) in which case the resulting cations may be quite stable. For example in cyclo-octatetraene complexes,  $\pi$ -C<sub>8</sub>H<sub>8</sub>RhC<sub>8</sub>H<sub>8</sub>, where the olefin is bound in the form shown in (IV), gives an unstable species on protonation since a delocalised system cannot be formed, whereas C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> (V) can give such a system.

The inter-relationships of olefin complexes and allylic species are still in the process of development. It is noteworthy that in some instances the metal appears to be the dominant factor. Thus palladium has given allylic complexes whereas, with the same ligands, platinum forms the olefin complex. Thus with mesityl oxide we have the species (VI) and (VII).

### Acetylenic and Acetylene-derived Complexes

Acetylene and acetylenic compounds can interact with platinum metal species in a number of ways depending on the nature of the reacting species and on the reaction conditions. In addition to forming complexes,





compounds some of which may be allylic in nature in addition to other reactions. Thus in alcohol, hexaphenylbenzene is formed together with (IX); this complex with hydrochloric acid gives (X). The formation of hexaphenylbenzene is an example of the polymerisations that can occur; similarly hexafluorobut-2-yne can give  $C_6(CF_3)_6$ ,  $C_4(CF_3)_4CO$  or  $(C_4F_6)_n$ , the latter being an infusible white powder.

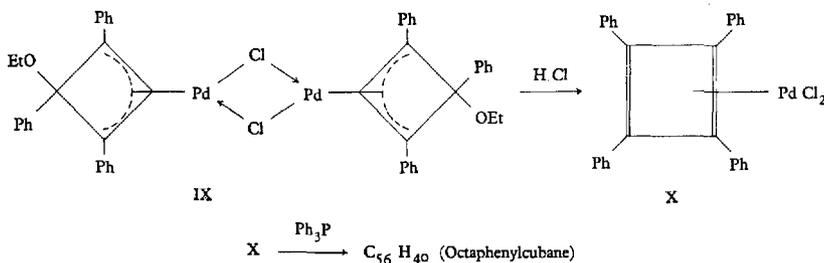
the acetylenes may be polymerised catalytically. There are two main classes of compound: (4 a, b) (a) those in which the acetylenic group is still recognisable—and sometimes recoverable—as such; (b) those in which the identity of the acetylene has been lost by polymerisation and complexation of the polymer; in presence of carbon monoxide or metal carbonyl compounds, the polymerisation can occur with incorporation of CO to give a cyclopentadienone. Although extensive studies have already been made in this area, mostly on Pd, Pt and Rh, we can quote only a few illustrative examples.

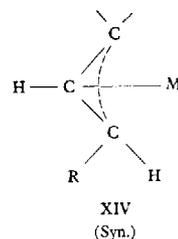
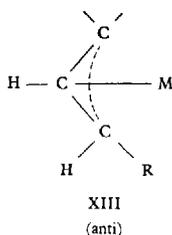
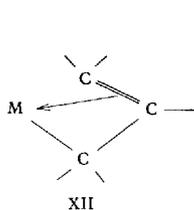
Another class of complex is that which appears to have the acetylene bound by  $\sigma$ -bonds as in (XI) which can be made by treating  $PtCl_2(PPh_3)_2$  with hydrazine in presence of the acetylene. Acetylenes can displace each other in such complexes, the one with most electronegative groups being bound most strongly.

Hexafluorobut-2-yne reacts with  $\pi-C_5H_5Rh(CO)_2$  to give a cyclopentadienone complex (VIII). Diphenylacetylene reacts with palladium halides to give a series of

### Sandwich Compounds

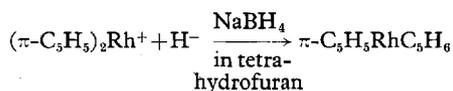
This class of compound, whose name derives from the structure of  $(\pi-C_5H_5)_2Fe$ , ferrocene, is that in which a completely symmetrically delocalised carboxylic system with six  $\pi$ -electrons is bound to a metal (5 a, b). The most extensive class is that of the  $\pi$ -cyclopentadienyls, but arene and cycloheptatrienyl complexes are known, although the



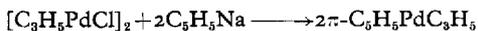


latter not for the platinum metals. In some cases, two rings can be bound to the metal but in others one ring with other ligands occupying the remaining co-ordination positions. A  $\pi\text{-C}_5\text{H}_5$  ring can crudely be regarded as occupying three co-ordination sites on a metal.

After the recognition of the sandwich structure, the ruthenium analogue was the first other complex of this type to be made; it is one of the few organo complexes of platinum metals which are commercially available. The osmium analogue also exists and cationic species, e.g.  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}^+$ , for Ru, Os, Rh and Ir. The ability to form sandwich compounds appears to be related to the stability of a particular oxidation state of the metal and to its ability to give the pseudo-octahedral bonding orbitals necessary to provide overlap with the rings. There are no stable neutral  $(\pi\text{-C}_5\text{H}_5)_2\text{M}$  compounds of Rh, Ir, Pd and Pt since these metals have either an unstable II state or give normally square planar complexes. Attempts to reduce  $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}^+$  lead to a cyclopentadiene olefin complex of  $\text{Rh}^{\text{I}}$



All cyclopentadienyl complexes are made by essentially standard procedure, namely the interaction of a metal halide or complex halide with the sodium salt  $\text{C}_5\text{H}_5\text{-Na}^+$  in tetrahydrofuran solution. Mono  $\pi$ -cyclopentadienyls result when a complex halide with other suitable ligands are used, e.g. for allyl palladium chloride

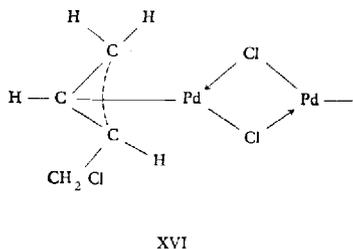
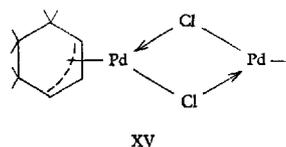


Arene complexes are of little importance for platinum metals although a few benzene and substituted benzene species of Ru, Os and Rh are known; they are not especially stable.

### Allylic and Related Complexes

These complexes have been noted in passing above. They are in a sense intermediate between olefin and sandwich compounds in having a partially delocalised "open-ended",  $\pi$ -electron system bound to a metal (4 a, b). The allyls can be written as involving canonical variants of (XII) but nuclear magnetic resonance spectra have shown that a more realistic and correct formulation is (XIII) or (XIV). Two isomers, *anti* and *syn* with respect to the hydrogen atom on the "central" carbon atom not only exist theoretically but have been separated in some cases.

The first allyls—which are of quite recent recognition—were obtained from the



interaction of palladous chloride with allyl alcohol. They can be obtained in a variety of ways. The recognition of allylic binding also led to the reformulation of a number of known complexes, previously held to be olefin complexes. Typical examples are the 1:3-cyclohexadiene palladium complex which is unequivocally now known to be (XV) and the butadiene palladium halide complex now shown to be (XVI). It is now recognised that allylic species may be most important intermediates in a variety of reactions involving olefins and platinum metal salts. It seems probable, for example, that the polymerisation of butadiene by rhodium salts is of this type and doubtless other olefin reactions will be interpreted in this way in future, although considerably

more experimental work will be required to ascertain the reaction mechanisms in detail.

### References

- 1 H. Zeise, *Pogg. Annalen*, 1827, 9, 632
- 2 See N. V. Sidgwick, *The Chemical Elements and their Compounds*, Vol. II, pp. 1560, 1588. Oxford
- 3 For comprehensive reviews see F. A. Cotton, *Chem. Rev.*, 1955, 55, 551; see also for discussion J. Chatt, *Proc. Chem. Soc.*, 1962, 318
- 4 For reviews see: (a) M. A. Bennett, *Chem. Rev.*, 1962, 62, 11; (b) R. G. Guy and B. L. Shaw, *Advances in Inorganic and Radiochemistry*; 1962, 4, 77; (c) E. O. Fischer and H. Werner, *Angew. Chem. International*, 1963, 2, 80
- 5 For reviews see: (a) G. Wilkinson and F. A. Cotton, *Progress in Inorganic Chemistry*, 1959, 1, 1; (b) E. O. Fischer and H. P. Fritz, *Advances in Inorganic and Radiochemistry*, 1958, 1, 56

## Precision Glaze Resistors

### PALLADIUM IN NEW SCREEN PRINTING COMPOSITIONS

For use in printed circuits there is a demand for resistors with a wide range of values and good electrical properties and capable of being produced by the simple method of screen printing and firing the resistor film on to a ceramic substrate. In a paper given to the Electronics Division of the American Ceramic Society in October 1962, and now published in the *A.C.S. Bulletin* (1963, 42, (9), 490), L. C. Hoffman, of the Electrochemicals Department of du Pont, describes the development of resistors of this type in which the elements consist of conducting glazes containing palladium and silver.

The disadvantages are briefly discussed of resistors produced by screen printing carbon-resin dispersions, and of those made by deposition and attenuation of metal films. The failure of early attempts to produce glaze resistors containing particulate oxide and oxide-metal mixtures is attributed mainly to poor resistance-temperature relationships and critical dependence of resistance values on the concentration of powder conductors in the glaze.

These difficulties, and the current noise which is characteristic of conduction between particles, are claimed to have been overcome by using glazes containing finely divided

(0.1 to 0.5 $\mu$ ) palladium and silver as conductors. The oxidation-reduction behaviour of palladium heated in air is thought to promote sintering of the palladium and silver particles into chain-like aggregates. These are claimed to give continuous rather than particulate conduction, thereby reducing the dependence of resistance on metal concentration in the glaze, promoting heat dissipation and reducing current noise.

The resistor glazes are made by ball-milling the glassy component or frit to an average particle size of 5 $\mu$ , and mixing this with the metal powders. Screen printing preparations are made by milling two-thirds of the inorganic powder with one-third of organic vehicle and controlling the viscosity of the pastes between 170 and 230 poises. The glazes are fired on ceramic substrates at 760°C.

A range of resistance values can be obtained by varying the ratio of palladium to silver and the concentration of metal powder in the glaze, and by attenuating the current path by selection of the screen printed design. The author gives data on the resistivity, temperature coefficients and current noise of various palladium-silver compositions.

F. E. K.