

Platinum Metal Salts and Complexes as Homogeneous Catalysts

SCOPE FOR NOVEL CHEMICAL PROCESSES

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Olefin complexes of the platinum group metals have recently been recognised as intermediates in a number of homogeneous catalytic processes. Among the reactions undergone by co-ordinated olefins are oxidation, isomerisation, hydrogenation and polymerisation. The oxidation of olefins to aldehydes or ketones catalysed by palladium chloride is already an important commercial process, and it seems likely that many other similar reactions will achieve prominence in the future.

The first olefin complex of a platinum group metal to be discovered was Zeise's salt, $K[C_2H_4PtCl_3]$. For over a hundred years after its discovery in 1827 there was little further progress in this field, until the work of Kharasch and of Anderson in the 1930s (1). These olefin complexes have, however, been the subject of intensive study during the past decade (2, 3), with the result that not only are large numbers of these compounds known but the structures of many are also understood and applications for them are now being discovered.

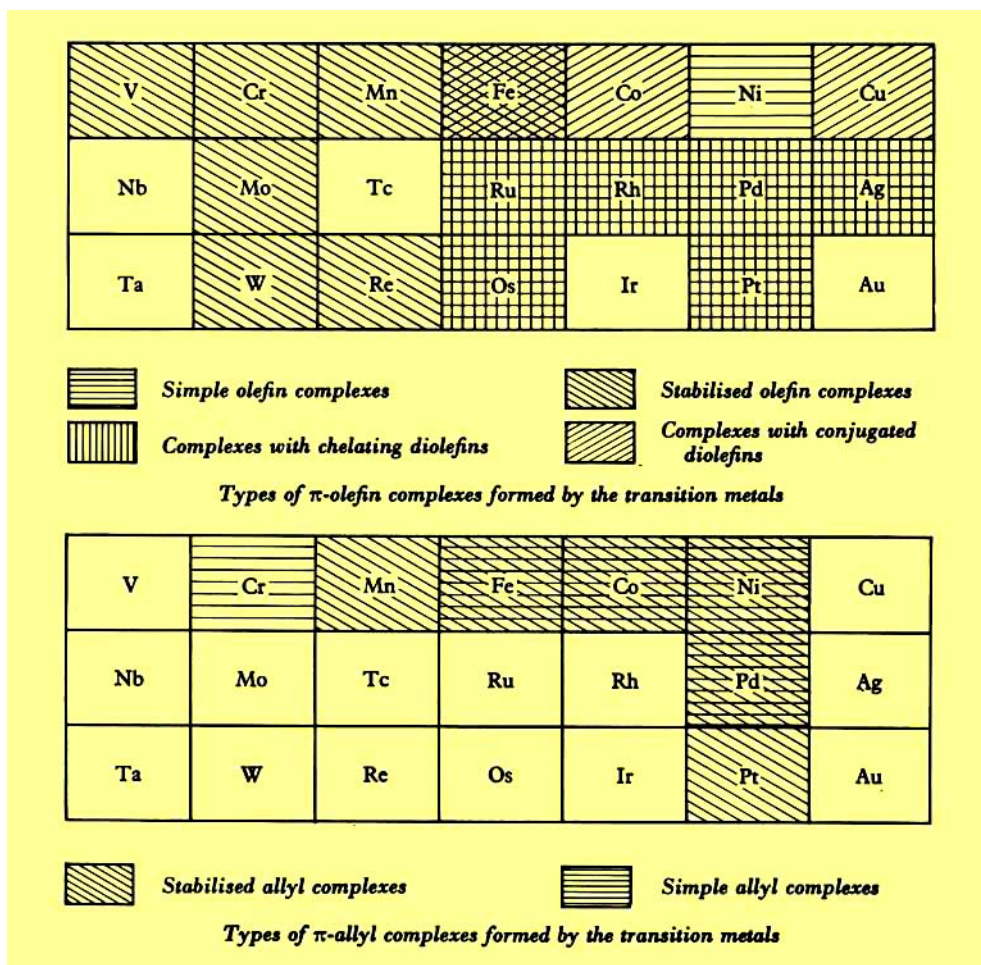
Classification of Olefin Complexes

For the purpose of classification we may divide olefins into three groups: (i) mono-olefins, (ii) conjugated diolefins (e.g. butadiene) and (iii) non-conjugated or chelating diolefins (e.g. cyclo-1,5-octadiene). With **mono-olefins**, the elements ruthenium, rhodium, palladium and platinum form "simple" complexes which contain additionally only halogen atoms (3). Examples of these are the 1:1 Ru^{II} chloride-olefin complexes formed with ethylene and propylene, but not isolated (4); $[(C_2H_4)_2RhCl]_2$; $[C_2H_4PdCl_2]_2$; and $[C_2H_4PtCl_2]_2$ and Zeise's salt. Mono-olefins also form some-

what unstable compounds with silver salts (3). **Conjugated olefins** do not form simple complexes with palladium salts; they do, however, form stable compounds on reaction with iron and cobalt carbonyls (2). They also form stable compounds with cuprous chloride. **Chelating diolefins** form stable and simple compounds with the halides of ruthenium, rhodium, palladium and platinum, although the ruthenium compound is probably polymeric: they also form yellow compounds with silver nitrate. No simple stable olefin complexes of iron, cobalt, nickel or copper are known: simple olefin complexes of iridium have been reported but not thoroughly examined (1).

The elements vanadium, chromium, molybdenum, tungsten and manganese only form stable olefin complexes when other strongly π -bonding ligands, such as the π -cyclopentadienyl radical or carbon monoxide are present in the molecule (2). These compounds are termed "stabilised olefin complexes".

Another recently discovered class of complexes involves the π -allyl ($\pi-C_3H_5$) group or its analogues (2). The compound $[(\pi-C_3H_5)PdCl]_2$ results on heating palladous chloride with allyl alcohol, and many other related



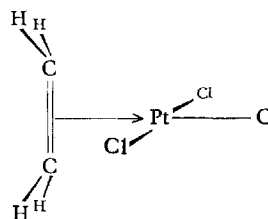
compounds can be obtained directly from olefins. The reaction of butadiene with a palladous chloride-nitrile complex gives a π -allyl compound. Compounds of the general formula $(\pi\text{-C}_3\text{H}_5)_x\text{M}$ are known where $x=2$ when M is nickel or palladium, and $x=3$ when M is chromium, iron or cobalt. "Stabilised" π -allyl complexes of iron cobalt and manganese are also known.

The diagram summarises the types of olefin complexes formed by the metals of the transition series.

The Structure of Olefin Complexes

A variety of modern physical methods has been applied to the elucidation of the structure of olefin-metal complexes. The

techniques of infra-red, X-ray and nuclear magnetic resonance spectroscopy have all been fruitfully applied. It is now established that in Zeise's salt and in the related simple ethylene complexes of platinum and palladium the axis of the carbon-carbon multiple bond is normal to the plane in which the metal atom and halogens lie (2, 5) as shown here.



Structure of the $[\text{C}_2\text{H}_4\text{PtCl}_3]^-$ ion in Zeise's salt

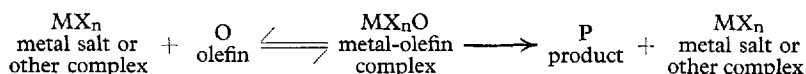
The carbon-carbon bond is weakened by the co-ordination : it becomes longer and the C=C vibration frequency in the infra-red ($\sim 1500 \text{ cm}^{-1}$) is lowered. The hydrogen atoms, while still coplanar, are displaced away from the central metal atom.

The structure of π -allyl palladous chloride is also known (6): the planes of the three carbon atoms comprising the allyl groups are normal to the axis of the metal-metal bond, and the carbon-carbon bond lengths are all equal ($\sim 1.3 \text{ \AA}$).

There have been several theoretical discussions of the nature of the bonding of olefins to metal atoms. It is now generally agreed that the bonding involves a π -bond, formed by overlap of the filled bonding $\pi_z 2p$ molecular orbital of the olefin with a vacant s or dsp^2 hybrid orbital of the metal atom, and also a π -bond, by overlap of the vacant antibonding $\pi_z^* 2p$ molecular orbital of the olefin with a filled d or dp hybrid orbital of the metal atom. This bonding adequately accounts for all the known properties of metal-olefin complexes.

The Reactivity of Olefin Complexes

In a homogeneous catalytic reaction where the net process is the conversion of an olefin to some other species, the original platinum metal salt or complex may be regarded as the catalyst and the olefin-metal complex as the catalyst-substrate combination. Thus:



Thus for a successful overall reaction, the metal-olefin complex must (i) be formed sufficiently quickly from its components, (ii) be sufficiently stable (i.e. must not decompose rapidly back to its components), and (iii) yet not be so stable as to be incapable of reacting to form the product. A proper balance between these three factors will ensure maximum reaction velocity.

The reactivity of the metal-olefin complex is often of first importance. The ability of a metal salt to form reasonably stable but not too stable olefin complexes is of itself no guarantee that those complexes will be reactive.

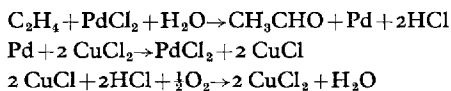
Thus for example the silver ion forms a large number of moderately stable olefin complexes, but as yet no method has been found of causing them to react to form any other product. The reason for this may be that the complexed silver ion has insufficient residual bonding capability towards any further reagents, so that the necessary transition state cannot be formed.

There is much evidence to suggest that an olefin molecule co-ordinated to a metal atom has a reactivity which is different in kind from the normal reactivity of olefins. The act of co-ordination decreases the electron density between the olefinic carbon atoms, and hence renders the olefin liable to attack by nucleophilic reagents such as hydroxyl or acetate ions, or indeed any electron-rich species which is seeking an electron deficient site. It is not possible to judge at the present how far this hypothesis accounts for the reactions undergone by co-ordinated olefins, although it almost certainly explains the occurrence of oxidation and hydrogenation processes. To what extent it explains the occurrence of isomerisation and polymerisation remains to be seen.

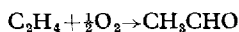
(a) Oxidation and other nucleophilic attacks

Olefin oxidation is the most important, most investigated and best understood of the reactions of co-ordinated olefins. The Wacker process (7) for the oxidation of olefins to aldehydes and ketones (e.g. ethylene to acetaldehyde) is accomplished by means of palladous chloride in an acidic aqueous

medium. Unfortunately the palladous chloride is reduced to metallic palladium during the reaction, and it is necessary to have an excess of cupric chloride present to re-oxidise it. The cupric chloride is thereby reduced to cuprous chloride and is re-oxidised by air. These processes are represented by the equations

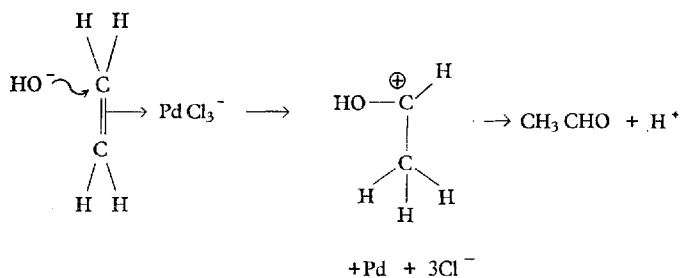


the net reaction being



The process of olefin oxidation is thus not truly catalytic, although the presence of the copper salts makes possible a continuous "catalytic cycle". Higher olefins react more slowly than ethylene, and temperatures of about 70°C are required; propylene yields chiefly acetone, but the yield of ketone decreases as the molecular weight of the olefin increases (7).

Although there have been several kinetic studies of the reaction (8), the mechanism is still not definitely established. However, most of the observations are accommodated by a reaction scheme in which an hydroxyl ion attacks the olefin in the complex ion $[\text{C}_2\text{H}_4 \text{ PdCl}_3]^-$ the remaining steps in the process are shown below.



Schematic representation of ethylene oxidation by the Wacker process

There are a number of other homogeneous catalytic processes which may be interpreted as nucleophilic attack on a co-ordinated olefin molecule. If the acetate ion is used as the nucleophilic in a non-aqueous medium, reaction with ethylene palladous chloride

yields vinyl acetate (9). Amines and amides can also act as nucleophiles: thus the reaction of acetamide with ethylene palladous chloride yields N-ethylacetamide (10). The reaction of carbon monoxide with this complex gives β -chloropropionyl chloride (11):



Transesterification of vinyl esters can be accomplished without reduction of the palladous salt (7).

It is worth noting that in all these instances it is a palladium salt which has been used as catalyst. Although oxidation of ethylene-platinum complexes does give acetaldehyde, the rate is too slow to be useful, probably because of the greater stability of the complex. However, aqueous sodium hexafluoroplatinate is rapidly attacked by ethylene with the formation *inter alia* of acetaldehyde: other olefins diolefins and alkynes behave analogously (12).

(b) Isomerisation

In the course of a study of olefin oxidation, it was observed that if the reaction was stopped before completion the olefin had isomerised and that an equilibrium mixture of isomers was present (13). This led to the discovery that palladous chloride and its olefin and nitrile complexes catalysed olefin

isomerisation under mild conditions, e.g. at atmospheric pressure and the normal boiling point of the olefin. Neither π -allyl palladium chloride nor platinum-olefin complexes were nearly as efficient. Rhodium salts are said to isomerise the butenes at 50°C, but no details

are available (14). Little is known of the mechanisms of olefin isomerisation by metal salts.

(c) Polymerisation

A third important class of reactions homogeneously catalysed by platinum metal salts is polymerisation. Mono-olefins, particularly ethylene and propylene, have been oligomerised (converted to low polymers, mainly dimers and trimers) by palladium and platinum salts in a variety of solvents at about 100°C and at 1–50 atm. pressure (15): under such conditions acetylene sometimes gives quite high yields of vinyl acetylene. Rhodium salts in polar solvents catalyse the polymerisation of butadiene to almost pure *trans*-polybuta-1,4-diene (14, 16), as does also iridium chloride (16), although less rapidly. Rhodium chloride in alcohol gives mainly oligomerisation, and butenes and many other products have been recognised (14). Mechanisms have not been discussed.

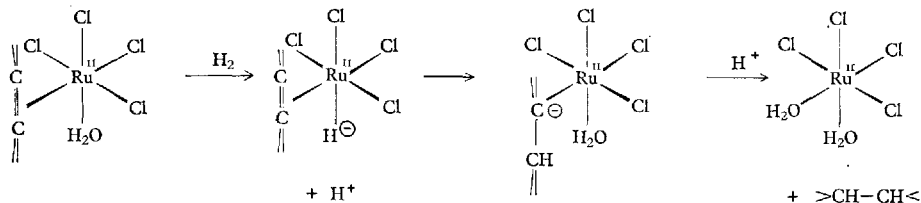
Palladium chloride catalyses the dimerisation of acetylenic hydrocarbons such as diphenylacetylene, and the complex tetraphenylcyclobutadiene-palladous chloride results (17): on decomposition of the complex, a hydrocarbon whose formula is $C_{56}H_{40}$ obtained (m.p. 430°), but its structure is not yet definitely established (18). The chlorides of palladium, ruthenium, platinum (IV) and osmium in the presence of an hydridic reducing agent such as lithium hydride catalyse the oligomerisation of 1-heptyne (19).

(d) Hydrogenation

We come finally to the last major class of reaction capable of being homogeneously

catalysed by platinum group metal salts and complexes: this is the hydrogenation of multiple carbon-carbon bonds, especially the olefinic bond. The first observation in this field was that ethylene platinumous chloride could act as the catalyst-substrate complex in the hydrogenation of ethylene at low temperatures (20). This work has twice been repeated (21, 22), and it appears that the process may be truly homogeneous if great care is taken, but if the temperature is permitted to rise colloidal platinum is deposited and the reaction becomes heterogeneous (21). In extension of this, it has recently been reported that a stannous chloride-platinum chloride complex is a more efficient and a more stable catalyst: it is also effective for acetylene hydrogenation (23).

Divalent ruthenium in an anionic form in hydrochloric acid catalyses the hydrogenation of olefinic acids such as maleic and fumaric acids at about 80° (4): other compounds containing a conjugated keto-group are also readily reduced (24). The kinetics of some of these reactions have been studied, and it appears that the rate of complex formation is not rate-determining. A mechanism has been suggested: this supposes the ruthenium (II) chloride species has the formula $[RuCl_4(H_2O)_2]^-$ and that the olefin can easily displace one water molecule to give $[(olefin) RuCl_4(H_2O)]^-$. A hydrogen molecule is then heterolytically split by this complex, and the hydride ion attacks the complex. If this is so, this is a further example of a nucleophilic attack on a co-ordinated olefin. The mechanism is represented here schematically.



Proposed schematic mechanism for the hydrogenation of olefins by Ru^{II} chloride

The chlorides of ruthenium, rhodium and especially palladium in dimethylformamide catalyse the hydrogenation of dicyclopentadiene (21). The use of other olefins and diolefins resulted in the immediate precipitation of metal. That the reactions were homogeneous was shown by adding thiophene, which would poison any colloidal metal, but in the case of palladium chloride the rate *increased* by a factor of four, perhaps as a result of the formation of a more active palladium-thiophene complex.

Other Applications of the Co-ordination of Olefins

Two other applications of olefin complexes, in which no net chemical transformation occurs, are worthy of mention. Very extensive use of the interaction of olefins and diolefins with silver ion has been made in the gas-liquid chromatographic (GLC) analysis of hydrocarbon mixtures (25). The use of silver nitrate dissolved in for example benzyl cyanide or ethylene glycol as a stationary phase permits the rapid passage of saturated hydrocarbons and separation of olefins which are otherwise difficult to separate (e.g. cis-trans isomer pairs). The use of salicylaldimines and glyoximes of nickel, palladium and platinum for this purpose has also been described (26); a triethylphosphite-palladium chloride complex is also effective, but the corresponding platinum compound is not. The gas-chromatographic method is a most attractive procedure for obtaining both qualitative and quantitative information on the interaction of olefins with metal salts and complexes.

A second but less widely applicable use of olefin complexes is in the resolution of optically-active olefins such as trans-cyclooctene (27). Use is made of the complex [(olefin) PtCl₂ am] where am represents an optically-active amine.

Summary and Conclusions

Two broad conclusions emerge from this survey of platinum metal salts as homogeneous catalysts. First, we sense the enormous scope for the development of novel chemical processes which is offered by the metal-olefin system: there are without doubt many more applications awaiting discovery and exploitation. It is significant and important that homogeneous catalytic processes are often more selective and specific than the corresponding heterogeneous processes would be.

Secondly, there is a pattern of behaviour which may have implications in wider fields. The types of complex formed depend in a way not yet clearly formulated on the structure of the metal atom (see the diagram on page 93). The reactivity of metal-olefin complexes has resemblances to the reactivity of olefins adsorbed on metal surfaces. Thus it is probably no coincidence that palladium salts feature largely as homogeneous catalysts for reactions of olefins, while olefins are known to be more weakly adsorbed by palladium than by platinum (28). Many details of this correlation remain to be explored, but it is certain that we shall witness in the coming years a fruitful interplay between the studies of homogeneous and of heterogeneous catalysis. It is also likely that homogeneous catalytic processes will have an important commercial future.

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Electrical Resistivity of Refractories

DETERMINATION AT HIGH TEMPERATURES

In selecting suitable refractories for electric melting furnaces it is necessary to know how their resistivity varies with temperature, but data on this subject are not always available. To measure the resistivity of such materials at temperatures up to 1500°C an apparatus has been designed and built at the Pilkington Brothers Research Laboratories by J. Fenerty and C. E. Smith and is described in a recent paper (*Glass Technology*, 1964, 5, (2), 78-81).

The sample, in the form of a one-centimetre cube, is heated in a vertical muffle furnace, wound with 20 per cent rhodium-platinum wire on a fused alumina tube. This furnace is fitted with two synthetic mullite tubes, each containing a platinum:rhodium-platinum thermocouple and a platinum lead to an electrode. To ensure good electrical contact with the electrodes, two opposite faces of the sample are coated with a thin film of platinum, either by cathodic sputtering or by means of a paste consisting of metallic platinum in suspension in an organic medium.

The furnace is heated to the maximum temperature required with the test sample

held between the two electrodes and resistance readings are taken, by means of a modified Tinsley electrolytic conductivity bridge, at intervals during controlled cooling.

