Coordination Compounds of the Platinum Group Metals

A REVIEW OF THEIR PREPARATIVE METHODS AND APPLICATIONS

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Strictly speaking, most compounds of the platinum group metals can be classified as coordination compounds. For our purposes they will be divided into three main groups:

(a) The common commercially available starting materials such as oxides and chlorides.

(b) Organometallic complexes — which usually contain at least one metal-carbon bond, are soluble in organic solvents and are generally hydrophobic in nature. (This includes phosphine complexes.)

(c) Purely inorganic complexes—which are usually soluble in aqueous systems and are generally hydrophilic in nature.

The compounds in group (a) account for the greatest proportion of the production of platinum group metal chemicals. However, the other coordination complexes in groups (b) and (c) are starting to find increasing applications in various fields. This article discusses the methods of manufacture and uses of these compounds. Those in group (c) can often be produced relatively easily by modification and scale-up of laboratory preparations but group (b) contains many compounds which involve new technology if multiple small batches are to be avoided. Volatile and odorous solvents, inert atmospheres and high pressure syntheses are sometimes involved.

Homogeneous Catalysis

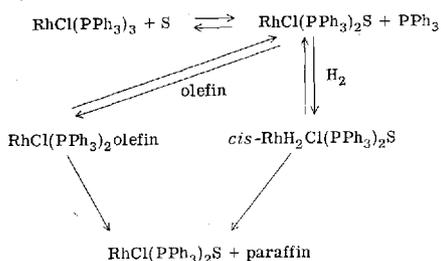Over the last decade interest and expansion in the field of homogeneous catalysis have been phenomenal. Many of the systems employed have involved noble metal coordination compounds, particularly those with d^8 electronic configurations that tend to perform oxidative addition reactions. A majority of these complexes fall into group (b) and require relatively sophisticated preparative and recovery techniques. Hydrogenation and hydroformylation reactions have attracted most attention but oxidation, olefin isomerisation and hydrosilation have also been investigated.

Effective catalysts for hydrogenation of olefins and acetylenes include the d^8 complexes $[Rh(H)CO(PPh_3)_3]$, $[RhCl(PPh_3)_3]$, $[Rh(CO)Cl(PPh_3)_2]$, $[Ir(H)CO(PPh_3)_3]$, and $[Ir(CO)Cl(PPh_3)_2]$ with trans-$[Pt(H)Cl(PEt_3)_2]$ and $[PtCl(SnCl_3)(PEt_3)_2]$ somewhat less potent. Also, Ru(II) and Os(II) d^6 species such as $[RuCl_2(PPh_3)_3]$ and $[Os(H)Cl(CO)(PPh_3)_3]$ have been extensively studied (1).

The complex $[RhCl(PPh_3)_3]$ (often known as Wilkinson's catalyst) is probably the most important hydrogenation compound. It has been shown to hydrogenate successfully —C=C— bonds in a wide variety of substrates (e.g. olefins, cyclic monoenes and dienes, terpenes, and exocyclic methylene groups) with the great advantage that under mild conditions it does not reduce other functional groups (1) (e.g. keto, hydroxy, cyano, nitro, chloro, azo, ether, ester, carboxylic acid). A cyclic mechanism has been proposed and this is probably typical (2). (See opposite, where S=solvent.)
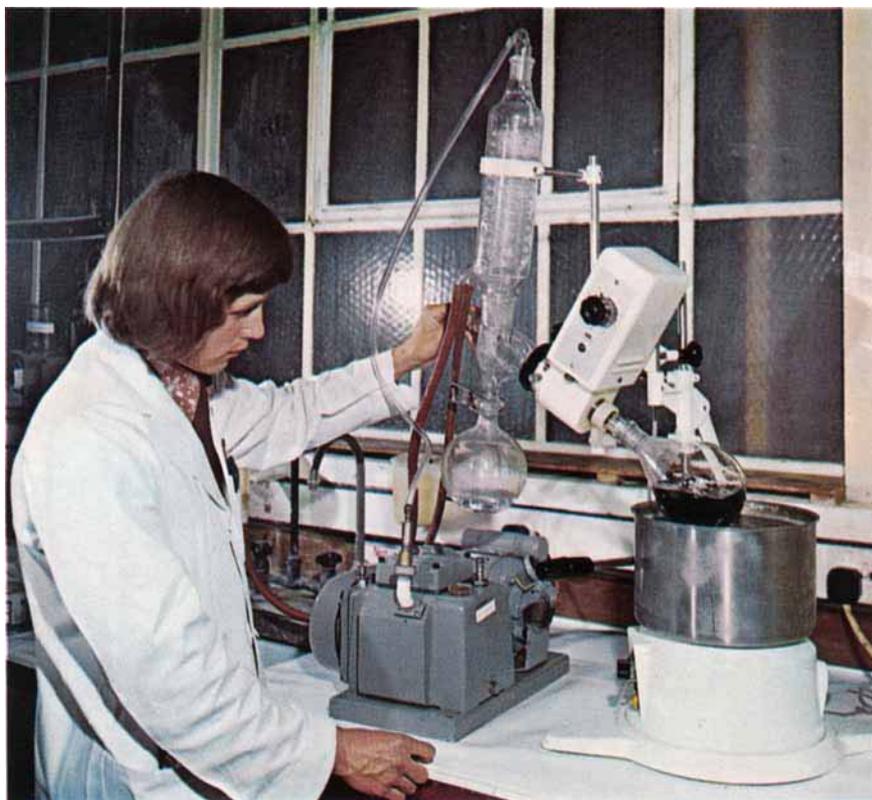
In the preparation of organometallic compounds of the platinum metals the removal of solvents may be achieved rapidly by rotary evaporation. Here dimethyl formamide is being removed from a rhodium carbonyl complex

$$RhCl(PPh_3)_3 + S \rightleftarrows RhCl(PPh_3)_2S + PPh_3$$

$$RhCl(PPh_3)_2\,olefin \qquad cis\text{-}RhH_2Cl(PPh_3)_2S$$

$$RhCl(PPh_3)_2S + paraffin$$

These phosphine compounds can be prepared by reduction of the halide starting materials from group (*a*). The reaction can often be achieved in one step, particularly where the reducing agent can also act as a carbonyl donor. For example, the action of formic acid or formaldehyde on rhodium trichloride gives a pale yellow solution containing $[Rh(CO)_2Cl_2]^-$ which yields $[Rh(CO)Cl(PPh_3)_2]$ on the addition of triphenylphosphine (2, 3). In the preparation of
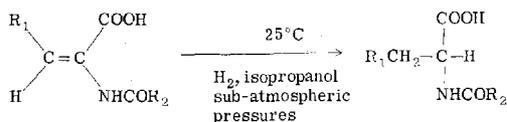
$[RhCl(PPh_3)_3]$ from rhodium trichloride, reduction occurs with triphenylphosphine and ethanol (2).

Similarly, $[Os(H)Cl(CO)(PPh_3)_3]$ can be prepared directly from $(NH_4)_2[OsCl_6]$ and triphenylphosphine in 2-(β-methoxyethoxy)-ethanol with the hydride and carbonyl ligands arising from decomposition of the solvent. However, the rate of heating is critical if a high yield and good quality product are to be obtained. The above preparations are generally carried out in a single vessel and are relatively easy to scale up.

In general, heterogeneous techniques are well established for hydrogenations and widespread industrial usage of coordination compounds is unlikely. However, the specific case of asymmetric hydrogenation is more promising (4). In this case a complex con-

taining asymmetric phosphine ligands cataly-
ses a hydrogenation reaction to give an excess
of a particular optical isomer. The chirality
of the phosphine ligand can be centred either
on the phosphorus atom or on a hydrocarbon
side chain. A pertinent example is
found in the pharmaceutical industry in
the manufacture of α amino acid deriva-
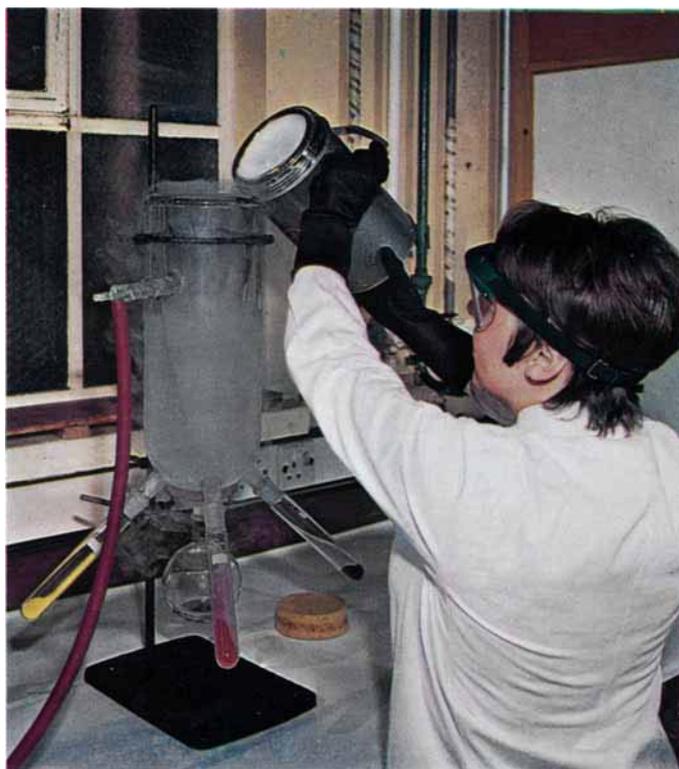tives of both the natural (L) and
unnatural (D) series.

However, the preparation of these asym-
metric complexes is a complicated procedure
involving several steps. For example, o-ani-
sylmethylcyclohexylphosphine requires six
stages (4):

o-Anisylmethyl-
cyclohexylphosphine
(A) (5): when com-
plexed with rhodium
in the form [RhA$_2$
(diene)]BF$_4$, (diene =
1,5-hexadiene), can
catalyse the hydrogenation of α-acyl-
aminoacrylic acids to give L or D amino

Rhodium complexes are beginning to
replace the traditional cobalt carbonyls
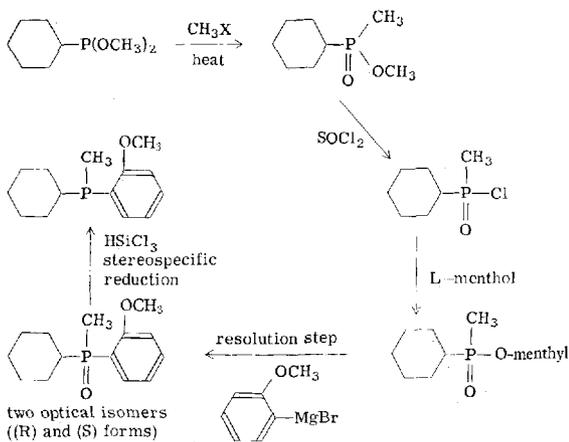in hydroformylation (OXO) reactions:

acids with optical yields
of 80 to 90 per cent, as
shown here.
The (+)-phosphine gives
the L acid and the (—)-
phosphine yields an excess
of the unnatural D series.
Effectively one is resolving
a few kilograms of catalyst
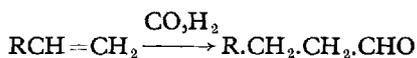to save resolving thousands
of kilograms of product.

*Freeze drying is used to remove
water from heat-sensitive
compounds. This technique is
being employed here to dry
three platinum group metal
compounds simultaneously*

$$RCH = CH_2 \xrightarrow{CO, H_2} R.CH_2.CH_2.CHO$$

The major advantages of the rhodium system are the higher straight chain:branched chain ratio of the product and the use of a much lower reaction pressure which still gives an activity that may be orders of magnitude higher than for the cobalt catalyst (1). The active species is generally considered to be [Rh(H)CO(PPh$_3$)$_2$] (6). These reactions are generally performed in the presence of excess triphenylphosphine and, consequently, many Rh(I) complexes that are soluble in the reaction system are active catalysts since they are converted to the above species in the presence of H$_2$ and CO. Suitable compounds include [Rh(H)CO (PPh$_3$)$_3$], [Rh(CO)Cl(PPh$_3$)$_2$] and [Rh(CO)$_2$ acac] (acac = acetylacetonate anion).
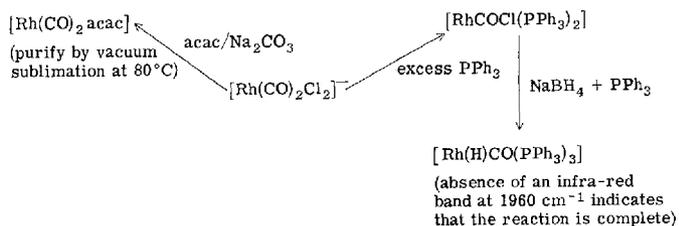
The preparative intermediate for these species is a solution containing [Rh(CO)$_2$Cl$_2$]$^-$ (which yields the important starting material [Rh(CO)$_2$Cl]$_2$ on evaporation to dryness), which can be produced from hydrated rhodium trichloride by the action of several reducing carbonylating agents such as formic acid or carbon monoxide (3). The relevant reactions are indicated here (7, 8).

The large excess of triphenylphosphine is thought to suppress dissociation but it gives rise to much more complex rhodium recovery procedures.

Other potential homogeneous catalytic applications include olefin isomerisation, which usually occurs to some extent during hydrogenation, but this has found little industrial application compared to the heterogeneous type. The dioxygen complex [Pt(PPh$_3$)$_2$O$_2$] is very reactive and can catalyse the oxidation of triphenylphosphine to its oxide (10), isocyanides to isocyanates (10), hydrocarbons to hydrocarbon hydroperoxides (11), and cyclohexene to cyclohex-3-one and cyclohexene oxide (12). This complex may find industrial application and it is fairly readily prepared from K$_2$[PtCl$_4$] by reaction with excess triphenylphosphine in ethanol. The initial product is [Pt(PPh$_3$)$_4$], which is converted to the catalyst by the passage of oxygen. Hydrosilation of olefins

[Rh(CO)$_2$ acac] ↖ (purify by vacuum sublimation at 80°C) — acac/Na$_2$CO$_3$ ↗ [Rh(CO)$_2$Cl$_2$]$^-$ → excess PPh$_3$ ↗ [RhCOCl(PPh$_3$)$_2$] | NaBH$_4$ + PPh$_3$ ↓ [Rh(H)CO(PPh$_3$)$_3$] (absence of an infra-red band at 1960 cm^{-1} indicates that the reaction is complete)

A possible mechanism has been suggested by Wilkinson et al. and this corresponds closely with that proposed for the cobalt system (6, 9). Starting with [Rh(H)CO(PPh$_3$)$_3$] we have:

[Rh(H)CO(PPh$_3$)$_3$] ⇌ dissociation [Rh(H)CO(PPh$_3$)$_2$] + PPh$_3$

↕ CO addition

[Rh(H)(CO)$_2$(PPh$_3$)$_2$(R.CH = CH$_2$)] ⇌ olefin / fast [Rh(H)(CO)$_2$(PPh$_3$)$_2$]

hydride transfer ↕ fast

[Rh(CO)$_2$(PPh$_3$)$_2$(R.CH$_2$.CH$_2$)] ⇌ carbonyl transfer [Rh(CO)(PPh$_3$)$_2$(R.CH$_2$.CH$_2$.CO)]

dihydride formation ↕ slow H$_2$

[Rh(H)CO(PPh$_3$)$_2$] ← [Rh(H)$_2$(CO)(PPh$_3$)$_2$(R.CH$_2$.CH$_2$.CO)]
+
R.CH$_2$.CH$_2$.CHO

has been achieved using Rh(I) and, particularly, Pt(II) complexes. One such patented process uses considerable quantities of trans-[Pt(Et$_2$S)$_2$Cl$_2$] (13). This is prepared by the action of the ligand on K$_2$[PtCl$_4$] but the crude product needs careful recrystallisation and characterisation (infrared spectrum and melting point) to separate and identify the isomers.

Plating Electrolytes

Most platinum metal plating solutions are based on specific coordination complexes which fall into group (c). Indeed, some of the most successful baths have been discovered via the routine screening of ionic complexes. The preparative methods are generally quite simple and the compounds are produced on a relatively large scale. Ammine and nitro ligands figure prominently. A successful platinum bath is based on the acid form of [Pt(NO$_2$)$_2$SO$_4$]$^{2-}$, which is prepared from [Pt(NO$_2$)$_4$]$^{2-}$ by the action of sulphuric acid. Semi-bright palladium baths are based on [Pd(NH$_3$)$_4$](NO$_3$)$_2$, which is prepared by dissolving palladium in dilute nitric acid, followed by warming with excess ammonia. Thin bright palladium deposits are produced from trans-[Pd(NH$_3$)$_2$(NO$_2$)$_2$], which is made up to pH 8–9 with ammonia before use and thus must exist in solution largely as [Pd(NH$_3$)$_4$](NO$_2$)$_2$. The mechanism by which ionic (particularly anionic) complexes electroplate is not well understood and does not appear to have been studied extensively. Small changes in the complex structure can cause large differences in plating ability and quality. A particularly interesting example is the successful ruthenium plating salt K$_3$[Ru$_2$NCl$_8$(H$_2$O)$_2$], which contains a bridging nitrido ligand and was prepared during investigations into nitrosyl complexes (14). Without routine screening it would have been difficult to predict that this very stable complex would be the best ruthenium plating salt yet discovered. It performs best with the addition of ammonium formate—a mild reducing agent. It is prepared by the action of SnCl$_2$ on K$_2$[Ru(NO)Cl$_5$], followed by careful recrystallisation to remove any traces of impurities containing coordinated (SnCl$_3$)$^-$.

Special additives to electroplating baths are usually required to give brighter and less stressed deposits, and these can be as important as the complex itself to the final result. Chelating agents such as EDTA or EDTA complexes often perform this function.

The other class of coordination complexes —referred to as group (b) earlier in this article—has found limited application in the area of vapour deposition techniques. Some organometallics, particularly acetylacetonates and other β-diketone complexes, have sufficiently low decomposition temperatures to enable plating to be done on plastics, rubber and even paper (15, 16).

Biological Applications

It has been demonstrated recently that certain Pt(II) amine complexes have potent anti-tumour activity against a wide range of transplantable animal tumours. These studies have been covered previously in this journal (17). A number of compounds are at present undergoing extensive animal trials, while cis-[Pt(NH$_3$)$_2$Cl$_2$] is entering the second stage of human clinical trial. Although it has some toxicity problems, this compound has shown genuine activity against human neoplasms, particularly those arising in the testicles or ovaries. Active complexes (against transplantable animal tumours) have been of the general type cis-[PtA$_2$X$_2$] and are all neutral with cis leaving (reactive) groups X of intermediate lability, e.g. Cl$^-$, Br$^-$. However, some dicarboxylate groups, which are relatively non-labile in vitro, e.g. oxalate and malonate, can give rise to active compounds. The amine ligands A also play an important role and should be relatively inert and neutral. They have a pronounced effect on the activity, and this has not yet been related to any physical parameter, such as kinetic or solubility effects.

These anti-tumour amine complexes, *cis*-$[PtA_2X_2]$ and $[Pt(A)X_2]$, may be prepared by several routes (18). The most generally applicable method involves the initial precipitation of the corresponding iodo complex by the reaction of the amine and $K_2[PtI_4]$.

$$K_2[PtI_4] + 2A \rightarrow cis\text{-}[PtA_2I_2] \downarrow + 2KI$$
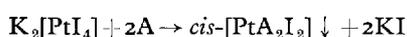
The iodide can be converted to complexes containing other anionic ligands via the aquo species produced using silver nitrate.

$$cis\text{-}[PtA_2I_2] + 2AgNO_3 + 2H_2O \rightarrow$$
$$cis\text{-}[PtA_2(H_2O)_2](NO_3)_2 + 2AgI$$
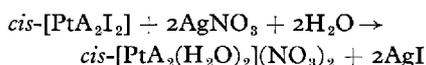
The discovery of anti-tumour activity was preceded by the finding that certain platinum complexes were strong bacteriocides and at certain concentrations below a lethal dose could cause filamentous growth in Escherichia coli (19). This property of affecting cell division but not growth led to the anti-cancer investigations. As yet all complexes which show anti-tumour activity also cause some filamentous growth but the reverse is not true. Anti-bacterial applications are obviously limited, not only due to the wide spectrum of relatively non-toxic (to humans) antibiotics but also because silver, with its powerful "oligodynamic" effect at 0.5 p.p.m. or less, is already in considerable use and has fewer toxic effects.

Certain complexes of ruthenium and rhodium have also shown the ability to cause filamentous growth in bacteria. Again this is mainly limited to chloro and chloroamine species. *Trans*-$[Rh(py)_4Cl_2]Cl$ and $[Ru(NH_3)_3 Cl_3]$ are particularly potent in this respect but neither has shown any appreciable anti-tumour activity (20). However, *mer*-$[Rh(NH_3)_3Cl_3]$ and some of its derivatives have shown activity against the ADJ/PC6A

A wide range (4000 to 200 cm^{-1}) infra-red spectrophotometer used to characterise platinum group metal coordination complexes. The low frequency region (600 to 200cm^{-1}) is particularly useful for this type of compound

and Walker carcinosarcoma tumours (21). These amine and ammine complexes are usually prepared by direct reaction with the corresponding chloro species, although controlled ammination agents, such as ammonium acetate or carbonate or a buffered system, are often preferred.

Other Applications

An interesting new application for β-diketonatobis(carbonyl)-rhodium complexes is in gas chromatography columns for the separation of olefins (22). The 3-trifluoroacetylcamphorate is particularly good and is marketed for this purpose. The complexes are prepared by the action of the corresponding β-diketone on $[Rh(CO)_2Cl]_2$. The columns contain approximately 0.02 per cent of the rhodium complex and the separation is due to the different degrees of interaction of the olefins with the square planar Rh(I) system.

Other uses for compounds in group (*b*) include additives for industrial purposes

(solubility in heavy organic solvents is a necessary requirement) and both groups (*b*) and (*c*) are occasionally involved as starting materials for the preparation of certain heterogeneous catalysts.

Characterisation

The characterisation of industrially produced coordination compounds is generally achieved by elemental analysis and comparison of spectral data with that available in the literature. In this respect infrared spectroscopy is the major technique and a wide range instrument is essential in order to study the interesting metal-ligand modes below 650 cm^{-1}. These often allow isomeric variations (both structural and linkage) to be detected. The degree of characterisation depends on the eventual use. For example, the anti-tumour complex *cis*-$[Pt(NH_3)_2Cl_2]$ is subjected to a variety of techniques, including ultra-violet/visible spectroscopy and paper chromatography, while criteria for plating salts are not usually as severe. The

presence of cis-[Pt(Et₂S)₂Cl₂] in the *trans* isomer causes a lowering in melting point, making this a sensitive criterion in this case, more so than the far infra-red spectrum. In catalysis applications chloride is often undesirable and strict limits are placed on its presence.

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Ruthenium as a Binder for Cemented Carbides

A potential means of improving the performance of cemented carbides is to raise the melting point of the binder constituent, thereby increasing the hardness and reducing the amount of wear at the high temperatures involved in machining operations. Whereas conventional binder phases are based on nickel, cobalt or iron, which form eutectics with the carbides at melting points between 1300 and 1400°C, suitable binders for higher melting points must be chosen from refractory transition or platinum metals. Most platinum metals, however, decompose transition metal carbides but ruthenium has been shown to form an eutectic with titanium carbide at 1840°C.

Two papers giving a deeper insight into the TiC-Ru system were presented recently at the 8th International Plansee Seminar on "Refractory and Wear Resistant Materials". J. S. Jackson of Production Tool Alloys Ltd., Sharpenhoe, Bedford and R. Warren and Professor M. B. Waldron of the University of Surrey studied the sintering behaviour, microstructure, hardness, and resistance to cracking over the whole TiC-Ru composition range. They found that titanium carbide did not decompose to form graphite during sintering and that after sufficient milling alloys of almost full density were produced below the 1840°C eutectic temperature. Good sinterability is partly the effect of good adhesion between the carbide and ruthenium. These alloys are harder than cemented carbides incorporating a nickel binder but ruthenium is less effective than either cobalt or nickel in preventing cracking of TiC.

The studies also showed that TiC-Ru is particularly promising as a potential cutting tool material. Small amounts of nickel, cobalt or iron picked up during milling assist full densification of TiC-Ru at 1500°C, which is a convenient sintering temperature. Nickel, for example, does not seriously affect the properties of TiC-Ru and the melting point of a binder phase containing both ruthenium and nickel remains higher than that of conventional cemented carbides.