Polymer-Immobilised Clusters of the Platinum Group Metals

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In this review major developments associated with the synthesis, properties, structure and applications of polymer-immobilised clusters of platinum, palladium, iridium, rhodium, osmium and ruthenium, are presented. Special attention is paid to polymer analogous reactions with metal clusters and new directions involving the polymerisation and copolymerisation of cluster-containing monomers. Some specific features of fixing heterometallic clusters on polymers are examined and the more interesting application of PCNM in catalysis, and future developments in this direction, are discussed.

Polymer-immobilised clusters of the noble metals (PCNM) are of great interest for at least two reasons; first, they are a new type of catalyst which can be used in many organic syntheses* and second they can be widely used as a basis for the production of different polymeric materials with unusual properties. In addition polymer-immobilised clusters can act as a convenient model of metal catalyst surfaces (3). Studying immobilised clusters can provide information about the structure of the catalyst surface, such as metal-substrate bond energies, the stereochemistry of the active centre and structural transformations occurring during catalytic reactions, and also about the mechanism of the catalytic reaction.

At least three fields of chemistry are linked by PCNM: cluster co-ordination chemistry, polymer chemistry and catalysis. There are three major methods for the preparation of PCNM; these are the physical insertion of small metal particles into a polymer, chemical insertion and (co)polymerisation of cluster-containing monomers, see Table I.

Preparation of PCNM Clusters of Unidentified Structure

The methods of preparing platinum metals clusters immobilised on polymers having unidentified structure are based on forming small metal particles from fine powders, salts and mononuclear complexes in the presence of polymers, which act as protective covers. The specific features of these methods are the direct route and the relative simplicity of preparation of the products. PCNM prepared in this way have a wide size distribution, typically 10 to 700 Å, which can change during use. By comparison with typical mechanical mixtures of polymer and large metal particles of micron size, the polymer immobilised clusters additionally have a relatively high dispersion, a uniform size distribution of metal particles within the bulk of the polymer, and a substantial irreversible sorption of macromolecules on the surface of the metallic particles. Such PCNM have a tendency to encompass metal particles within the natural hollows of the polymer matrix, and their formation is often accompanied by chemical reactions. However, the PCNM produced by these methods may be of single-phase metallopolymeric compositions due to the high dispersion of the metal particles. Various methods for preparing polymer immobilised noble metal clusters are shown in Table I.

Another method for preparing clusters with unidentified structures is by the reduction of mononuclear complexes. This method uses carbon chain polymers or polymers produced by polycondensation as the organic medium for

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*Immobilised catalysts based on noble metals mononuclear complexes were first mentioned here (1, 2).

Table I

Methods of Preparing Polymer-Immobilised Noble Metal Clusters (PCNM)

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1		PCNMs with Unidentified Structure
	a	Decomposition of volatile metal salts, metal carbonyls, organometallic derivatives in polymer matrixes as well as in melts followed by cluster formation
	b	Chemical, photochemical and electrochemical reduction of mononuclear complex in active medium in the presence of polymers
	c	Spraying of metal atoms (at low temperatures and pressures) on thin polymer films
	d	Mixing clusters with polymer (microencapsulation)
	e	Mechanochemical insertion of highly dispersed metal particles, metal salts or met oxides into polymer matrix
2		Polymer analogous reactions with cluster participation
	a	"Assembly" of polynuclear complexes from mononuclear ones including reduction of polymer-immobilised complexes
	b	Cluster immobilisation by functionalised polymers
	c	Immobilisation of heterometallic clusters
	d	Cluster immobilisation by polymer compounds
3		(Co)polymerisation reactions in PCNM synthesis
	a	Vibrational milling or other dispersive methods (decomposition of metal salts or oxides, metal dissolution, etc.) in a vinyl monomer medium followed by polymerisation reactions
	b	(Co)polymerisation of cluster-containing monomers
	c	Polycondensation of metal cluster complexes

the process. For example, the reduction of palladium chloride, absorbed on polyheteroarylenes, by $NaBH_4$ or hydrogen leads to the formation of Pd^0 clusters of size 1 to 3.5 nm (4). Such small particles interact so strongly with the polymer matrix that positive charge, Pd^+, appears on the palladium atoms as a result of electron transfer. The p-electron system of the polymer chain promotes this process and subsequently transforms into an ion-radical state.

Similar interactions between formed clusters and the polymer matrix are characteristic of many other metallopolymeric systems (5, 6), including clusters produced by spraying solvated metal atoms *in vacuo* at 77 K (7). The polymer matrix in such cases acts to stabilise the highly dispersed metal particles and prevents the subsequent enlargement of the clusters.

Metal particle growth prevention by the polymer matrix can be shown by examples from the formation of cluster-, or colloidal particles of palladium, ruthenium, rhodium, osmium, iridium, silver or gold, in protective polymer coverings (8, 9).

The following transformation sequence occurs on boiling $RhCl_3$ with polyvinyl alcohol (PVA) or polyvinylpyrrolidone solutions: in the first stage $RhCl_3$ is co-ordinated by the polymer, then oxoniene $RhCl_3$ complex is formed followed by fixing the hydride complexes as the alkoxide form; alkoxide groups being precursors of hydride forms. This sequence is necessary to form homogeneous colloids and is accompanied by consecutive growth of the particles, see Scheme I.

The clusters formed with thirteen rhodium nuclei have a face centred cubic lattice, and the
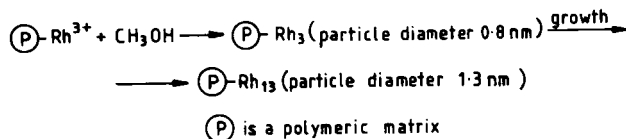
co-ordination number of rhodium is 12. They are attached to the protective colloid by electrostatic attraction or physical absorption and possibly by co-ordination bonds. The dimensions of the cluster particles may be changed by using a different polymer as well as by the reaction conditions.

The same method was used to prepare palladium particles of diameter 1.8 nm within the protective colloid, polyvinylpyrrolidone. Natural polymers, such as β-cyclodextrine (10), different functionalised cellulose derivatives, oligo- and polysacharides (11), indian silk (12), chitin and chitosane (13), may also be used as stabilising agents for colloidal particles of rhodium, platinum and palladium of diameter 1 to 100 nm.
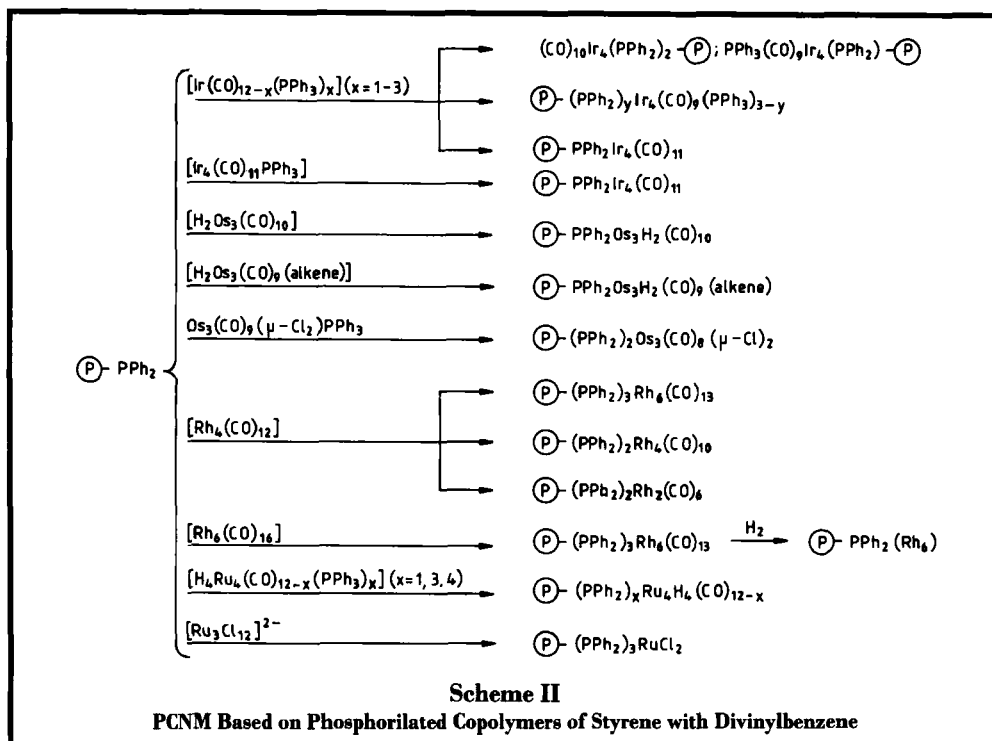
Synthesis by Polymer Analogous Reactions

The development of new methods is needed to create materials composed of individual clusters or metal atom assemblies of diameters 1.5 to 5 nm with a narrow size distribution. In one method the assembly of polynuclear complexes from mononuclear complexes often occurs during the immobilisation or mononuclear complexes, by functionalised polymers, from highly concentrated solutions, as well as by fixation by unfunctionalised polymers. However, published data show that the nuclearity of the initial complexes can be preserved by fixing binuclear or trinuclear ruthenium complexes on ion-exchange resins, such as Amberlite IR-20 or Dianion CR-10, which contain iminodiacetate groups (14).

More elaborate methods of producing PCNM are based on fixing individual clusters of known structure by polymer macroligands. Macroligands, such as "popcorn" polymers (phosphorilated copolymers of styrene and divinylbenzene

(P)-PPh₂, or sometimes variations (triple block-copolymer styrene-divinylbenzene-vinyldiphenylphosphine) in the form of thin membranes or grains with size dimensions of 200 to 400 mesh are usually employed. Fixing the clusters can be performed by ligand- or ion exchange, oxidative addition, decarbonylation, ligand addition, and so on. Some of the more interesting PCNM prepared by these methods, grouped according to similarities in their preparations, are listed in Scheme II (15–20).

Polymer-immobilised clusters with a one-centre bonded cluster, for example iridium, are formed at low concentrations of phosphine groups, where less than two per cent of the benzene rings are functionalised, or at a statistical distribution of PPh₂-groups. A convenient method of showing the structure of immobilised clusters is by comparison of the infrared spectra of the initial substances and the products formed. However, for macroligands with rather high concentrations of PPh₂-groups, where more then three per cent of the benzene rings are functionalised, a mixture of clusters connected to the polymer by one and two PPh₂ groups is formed. Clusters connected to the polymer by two PPh₂ groups are produced as the sole product when the block-copolymer styrene-divinylbenzene-divinylphenylphosphine, containing 8 to 15 per cent of PPh₂-groups, is used. Clusters connected to three PPh₂-groups, are prepared in this way (for instance (P)-(PPh₂)₃RuCl₂, see Scheme II).

It is important that immobilised complexes of Ir₄ are synthesised by assembly from Ir(CO)₂Cl-(p-toluidine) or from Ir₂Cl₂(C₈H₁₂)₂ *in situ* in the presence of zinc and carbon monoxide. Attempts to fix Ir₄(CO)₁₂, dissolved in toluene, permenently with (P)-PPh₂ were unsuccessful; a mix-

$(CO)_{10}Ir_4(PPh_2)_2$-(P); $PPh_3(CO)_9Ir_4(PPh_2)$-(P)

(P)-$(PPh_2)_y Ir_4(CO)_9(PPh_3)_{3-y}$

(P)-$PPh_2 Ir_4(CO)_{11}$

(P)-$PPh_2 Ir_4(CO)_{11}$

(P)-$PPh_2 Os_3 H_2(CO)_{10}$

(P)-$PPh_2 Os_3 H_2(CO)_9$ (alkene)

(P)-$(PPh_2)_2 Os_3(CO)_8 (\mu-Cl)_2$

(P)-$(PPh_2)_3 Rh_6(CO)_{13}$

(P)-$(PPh_2)_2 Rh_4(CO)_{10}$

(P)-$(PPh_2)_2 Rh_2(CO)_6$

(P)-$(PPh_2)_3 Rh_6(CO)_{13}$ $\xrightarrow{H_2}$ (P)-$PPh_2(Rh_6)$

(P)-$(PPh_2)_x Ru_4 H_4(CO)_{12-x}$

(P)-$(PPh_2)_3 RuCl_2$

$[Ir(CO)_{12-x}(PPh_3)_x](x=1-3)$

$[Ir_4(CO)_{11}PPh_3]$

$[H_2Os_3(CO)_{10}]$

$[H_2Os_3(CO)_9$ (alkene)]

$Os_3(CO)_9(\mu-Cl_2)PPh_3$

$[Rh_4(CO)_{12}]$

$[Rh_6(CO)_{16}]$

$[H_4Ru_4(CO)_{12-x}(PPh_3)_x]$ (x=1, 3, 4)

$[Ru_3Cl_{12}]^{2-}$

(P)- PPh_2

Scheme II
PCNM Based on Phosphorilated Copolymers of Styrene with Divinylbenzene

ture of mono-, bi- and trisubstituted forms was obtained.

More complicated cluster transformations have been observed; for example, when $Rh_4(CO)_{12}$ was reacted with (P)-PPh_2 in hexane at 50°C binuclear clusters were formed (19). However, when this procedure was carried out with $Rh_6(CO)_{16}$ in benzene, a precipitation of black spots of metallic rhodium was observed on the walls of the reactor (20). The black spots were of size 25 to 40 Å, and each spot contained about 100 rhodium atoms. The same effect has also been observed for anionic ruthenium clusters. At higher temperatures of 100 to 150°C the immobilised clusters dissociate to form metal crystallites in the polymers.
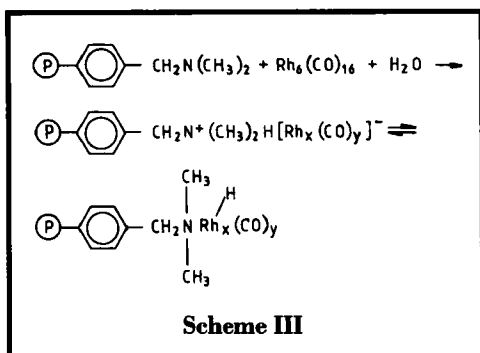
Cluster fragments of $Ir_4(CO)_{10}$ can be fixed by other phosphorus containing macroligands on polymers which have been modified with the optically active groups 2,3-(o-isopropylidene-2,3-dioxi)-1,4-bis(diphenylphoshino)-butane (21).

The processes for immobilising noble metal clusters by other polymers have been studied less. In particular, the immobilisation of cluster $Os_3(CO)_{12}$ on poly(4-vinylpyridine) (P4VPy) in dimethylformamide at 110°C in an atmosphere of carbon monoxide occurs by means of two pyridine rings, one of which is chelated (22):
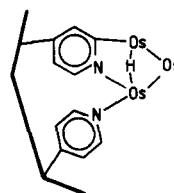
The mechanism for bonding $Rh_4(CO)_{12}$ with poly(4-vinylpyridine), as well as the structures of the products formed by the interaction of $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ with NH_2-groups of the polymer (aminated polystyrene), requires further study (23). This also applies to the immobilisation of $Ru_3(CO)_{12}$ on cross-linking macroporous chelating polymers, functionalised with the following: bipyridine,

$$\text{(P)}-\langle\bigcirc\rangle- CH_2N(CH_3)_2 + Rh_6(CO)_{16} + H_2O \longrightarrow$$

$$\text{(P)}-\langle\bigcirc\rangle- CH_2N^+(CH_3)_2 H[Rh_x(CO)_y]^- \rightleftharpoons$$

$$\text{(P)}-\langle\bigcirc\rangle- \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{CH_2N}} \overset{\displaystyle /H}{Rh_x(CO)_y}$$

Scheme III

2-aminopyridine, 2-aminophenol, 2-iminopyridine and sodium anthranilate (24), for example; and to products formed by the interaction of $Rh_2(CO)_4Cl_2$ with copolymers of styrene and divinylbenzene, modified by N,O-chelating nodes (25).

The interaction of $Rh_6(CO)_{16}$ (the first cluster to be immobilised (16)) with resin Amberlyst A-21 proceeds in a more complicated manner and leads to the formation of immobilised rhodium clusters of different nuclearity, see Scheme III (26).

The formation of $HOs_3(CO)_{11}N^+Et_3CH_2P$ from $Os_3(CO)_{12}$ has been identified (27). Sulphur- and oxygen-containing matrixes are rarely used to immobilise clusters; polymeric alcohols and acids are the more often used macroligands. Thus, the addition of triosmium clusters to polymeric alcohols proceeds, as in the case of inorganic oxide, by oxidative addition, see Scheme IV (28).

Very stable compounds, for example the bi- and trinuclear complexes Ru^{III}-O-Ru^{IV}-ORu^{III}, can be fairly easily fixed on the ion-exchange resin Diaion CR-10 (14). It is important to note that the preservation or dissociation of their polynuclear structure depends on the nature of the ligands. Thus, during the heterogenisation of the binuclear acetate complex $Rh_4(OOCCH_3)_4$
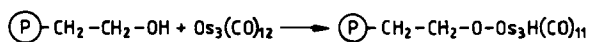
on a polymer which contains ligands of 3(5)-methylpyrazole or imidazole groups (29), the binuclear structure and the degree of oxidation of the rhodium (+2) remain on the polymer. In contrast, for rhodium binuclear complexes of sulphate, acetonitrile and hexafluoroacetylacetonate the rhodium-rhodium bond breaks and the degree of oxidation on the central atom increases. An analogous result has been obtained during fixing the cluster anion $Ru_5Cl_{12}^{2-}$ on (P)-PPh_2 (30): the cluster anion can not penetrate into the polymeric matrix and so, for steric reasons, dissociates forming fixed mononuclear and dimer complexes.

There is no data available at present about bonding noble metal clusters by polymer-polymer compositions, unlike mononuclear complexes for which data which is available.
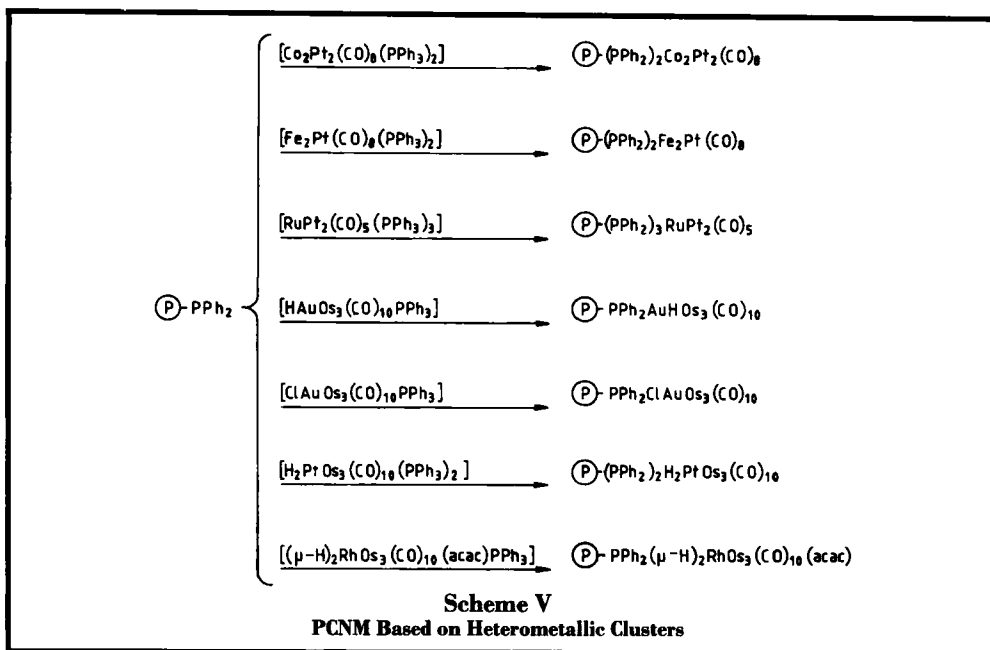
Polymer-Immobilised Bimetallic Clusters

A heterometallic polynuclear centre is preferable to a mononuclear one for many catalytic processes. Such systems can be considered as models of bimetallic catalysts, for example as the contact crystallites on the surface of catalysts used for refining oil distillates industrially. However, PCNM, in contrast to fused catalyst are of uniform structure. As a rule the same methods that are used to immobilise mononuclear complexes are used both to immobilise heterometallic clusters and to identify the structure of the products. The most widely used method is the assembly synthesis of clusters from monometallic complexes. A co-operative dissociation of H_2PtCl_6-$Fe(NO_3)_2$ and/or $Rh_4(CO)_{12}$-$CoCl_2.6H_2O$ in polymeric matrixes has been carried out.

Bimetallic clusters can be formed in a colloidal dispersion of platinum and palladium stabilised by polyvinylpyrrolidone, if the ratio of palladium:platinum is 41; the dispersion being pre-

$$\text{(P)}- CH_2-CH_2-OH + Os_3(CO)_{12} \longrightarrow \text{(P)}- CH_2-CH_2-O-Os_3H(CO)_{11}$$

Scheme IV

$(P)\text{-PPh}_2$:

Precursor	Product
$[Co_2Pt_2(CO)_8(PPh_3)_2]$	$(P)\text{-}(PPh_2)_2Co_2Pt_2(CO)_8$
$[Fe_2Pt(CO)_8(PPh_3)_2]$	$(P)\text{-}(PPh_2)_2Fe_2Pt(CO)_8$
$[RuPt_2(CO)_5(PPh_3)_3]$	$(P)\text{-}(PPh_2)_3RuPt_2(CO)_5$
$[HAuOs_3(CO)_{10}PPh_3]$	$(P)\text{-}PPh_2AuHOs_3(CO)_{10}$
$[ClAuOs_3(CO)_{10}PPh_3]$	$(P)\text{-}PPh_2ClAuOs_3(CO)_{10}$
$[H_2PtOs_3(CO)_{10}(PPh_3)_2]$	$(P)\text{-}(PPh_2)_2H_2PtOs_3(CO)_{10}$
$[(\mu\text{-H})_2RhOs_3(CO)_{10}(acac)PPh_3]$	$(P)\text{-}PPh_2(\mu\text{-H})_2RhOs_3(CO)_{10}(acac)$

Scheme V
PCNM Based on Heterometallic Clusters

pared by the combined reduction of $PdCl_2$ and H_2PtCl_6 in a water-ethanol solution in the presence of polyvinylpyrrolidone (10). Clusters of different metals, for example, a mixture of the clusters $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ in molar ratios from 1:1 to 3:1, can be fixed on amino-containing ion-exchange resins to use as a model of a bimetallic catalyst (31).

Heterometallic clusters of known structure are of greater use in the same way that immobilised monometallic clusters of known structure are. Phosphorilated polystyrenes are polymer matrixes of optimal structure, and ligand exchange or sometimes ionic exchange is widely used to immobilise clusters on them. The structure of the products is always determined by analysis of the infrared spectra of the carbonyl group clusters and by a comparison of the spectra of individual molecular compounds. Typical examples of immobilised heterometallic clusters are summarised in Scheme V (3, 17, 32–34). Other examples show the immobilisation of $H_2FeOs_3(CO)_{13}$ on cross-linking macroporous chelating polymers (24). There is also data about the immobilisation of $Co_2Rh_2(CO)_{12}$ on the ion-exchange resin Dawex-1 (35), as well as for

$H_2FeRu_3(CO)_{13}$, $[FeRh_4(CO)_{15}][NMe_4]_2$ and $Rh_{4-x}Co_x(CO)_{12}$, where x = 2 or 3, on macroligands. The mechanism of these processes has not yet been studied, and it is very possible that there are no examples of immobilisation of trimetallic type clusters.

PCNM Formation in the Course of Polymerisation

The formation of polymer-immobilised noble metal complexes during the preparation of the polymeric matrix has advantages both in simplifying the synthesis of the complexes and in determining their structure. The methods for preparing PCNM which were considered earlier are generally accompanied by numerous processes, the most important of which is an increase or decrease in their nuclearity.

The polymerisation of vinyl monomers in the presence of formed small dispersive particles of the platinum metals is not a commonly used method at present. However, in recent years methods for the polymerisation of cluster-containing monomers (as for other types of metal-containing monomers (36)) have aroused great interest. As this area of study is presently

Scheme VI
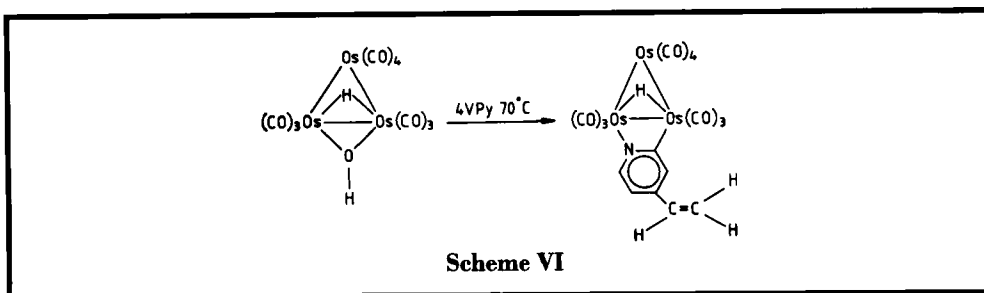
undergoing development, we shall demonstrate its possibilities with some examples.

The cluster monomers listed below were synthesised by the interaction of trinuclear clusters $M_3(CO)_{12}$ (where M is osmium or ruthenium), $Os_3(CO)_{11}(CH_3CN)$, $Os_3(CO)_{10}(CH_3CN)_2$ and $(m\text{-}H)Os_3(m\text{-}OR)(CO)_{10}$ (where R is hydrogen or phenyl) with conventional monomers, such as 4-vinylpyridine, (4VPy) acrylic acid and allylsulphide, see Scheme VI (37).

It is interesting to note that in such monomers the pyridine ring is chelated as in the case for the product of the interaction of $Os_3(CO)_{12}$ with poly(4-vinylpyridine) (P4VPy) (see above). At the same time the interaction of $Rh_6(CO)_{16}$ with P4VPy in the presence of (N-oxide of trimethylamine) proceeds under mild conditions and is accompanied by the formation of the basic product, the monosubstituted derivative $Rh_6(CO)_{15}.(4VPy)$, and small amounts of di-substituted compounds $Rh_6(CO)_{14}.(4VPy)_2$ (38). These are easy separated by chromatography and may be isolated individually. In contrast to the Os_3-derivatives the monomer $Rh_6(CO)_{15}.(4VPy)$ is an octahedron cluster with 11-end and 4-μ-bridge carbonyl ligands, and 4-vinylpyridine is connected to the rhodium atom only through the nitrogen atom, and occupies the co-ordination position of the twelfth terminal carbonyl group. The average length of the rhodium-rhodium bond is 2.762 Å and is similar to that of other rhodium clusters.

Polymer-immobilised noble metal clusters may also be produced by polymerisation and more often by copolymerisation of cluster-containing monomers, for example according to Scheme VII (39).

The composition of the polymers and their molecular weights are controlled by the usual methods, such as the composition of the monomer mixture and the polymerisation conditions. It is important that in such PCNM mutual thermal stabilisation of the polymer and the cluster in its chain, is observed. For example, the temperature of dissociation of clusters in copolymers containing the Os_3 complex and 4-vinylpyridine increases from 295 to 450°C, but the temperature for the thermal destruction of the polystyrene framework increases by 50 to 100°C (the cluster units are 0.5 to 1.0 mol per cent of the contents). The effect of the polymer chain is such that it can dissipate the diffusion of energy from the free rotary-oscillatory movement of the cluster into translation in the polymer segments, which therefore increases the thermal stability of the polymer.
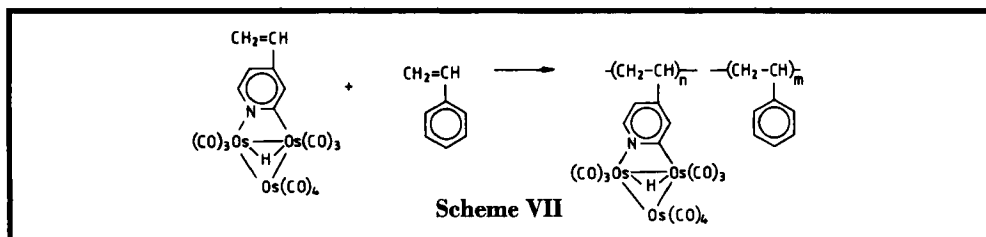

Scheme VII

Table II
Some Catalytic Reactions Which Use PCNM

Catalysed reactions	PCNM
Reduction of nitrobenzene to aniline	$Rh_6(CO)_{16}$ on Amberlyst A-21
Ethylene hydrogenation	$P-PPh_2Ir_4(CO)_{11}$
Hexene-1 hydrogenation	Rh/PVA (particle size 4 nm)
Selective hydrogenation of cyclopentadiene	Colloid particles of Pd on P4VPy (particles size 1.8–5.6 nm)
Isomerisation of alkenes	Os_3 clusters on polymers with OH groups
Electrochemical oxidation of CH_3OH	Pd on solid polymer electrodes
H_2-D_2 exchange	Rh, Pd, Pt on P4VPy
Photoelimination of H_2 from H_2O	Colloidal particles protected by polymers (particle size 1–100 nm)
H_2O oxidation with elimination of O_2	Polynuclear Ru complexes on Dianion CR-10
Fischer-Tropsch reactions	$Ru_3(CO)_{12}$, $H_2FeOs_3(CO)_{13}$ on polymers with chelate units
Di-isobutylene hydroformylation	$Rh_2(CO)_4Cl_2$ on copolymers with N,O-chelate units
Hexene-1 hydroformylation	$Rh_6(CO)_{16}$ on polymers
	$Co_2Rh_2(CO)_{12}$, $RuOs_3$ on polymers
Oxidation of 2-olefins to alcohols	A mixture of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ on amino-containing resins
The water-gas shift reaction	$Os_3(CO)_{12}$ on P4VPy, clusters of Rh_2, Rh_4, Rh_6 on aminated polystyrene
Hydrogen transfer	$Rh_2(OCOCH_3)_4$ on polymers with imidazole groups

It may be that such an approach will soon become wide spread and that new classes of polymer-immobilised noble metal clusters can be prepared with its help. This also applies to polymer-immobilised clusters of noble metals prepared by polycondensation of cluster-containing compounds, which is not as yet known.

PCNM in Catalysis

Although a role for polymer-immobilised clusters of noble metals in catalysis has only just begun to develop, some publications and reviews have appeared (3, 40). The most important applications of PCNM in catalysis, in our opinion, are summarised in Table II.

Such catalysts can be used as powders, beads, balls, thin membranes (of thickness up to 7 nm), swelling gels, and sometimes in solutions. Kinetic parameters have many features in common with catalysis using immobilised mononuclear complexes. For instance, the rate for ethylene hydrogenation using polymer-immobilised noble metal clusters is ten times higher than for cyclohexene hydrogenation, and the ratio between the rates for cyclohexene and benzene hydrogenation is 25 to 50. The rate of reaction decreases with the accumulation of phosphine ligands in the cluster. The M^0 particles, where M is the noble metal, formed by reduction of the polymer-immobilised noble metal clusters, for example by hydrogen, differ in their sizes and activities in olefin hydrogenation and isomerisation. This isomerisation is promoted by hydrogen and occurs on the co-ordinated unsaturated active centres. The enlargement of the produced metal particles depends on both the method

of preparing the catalysts and the conditions of catalysis.

By comparison with homogeneous systems the polymeric carrier substantially suppresses the integration of particles, and the small dimensions, 1 to 2 nm, of the particles produced do not allow them to act as metallic objects. There are probably multinuclear associations, and the dynamics of their formation is very complex. It is important that such processes will be accompanied by saving the co-ordination vacancies after the activation of the catalysts. In many cases the centres, arranged on borders of clusters and stabilised by their electronic systems, are responsible for the catalyst activity. Such co-operative interactions increase the stability and activity of the PCNM and allow them to carry out repeated reactivation and regeneration as well as preventing the precipitation of catalyst from solution, including that on the reactor walls.

The conditions for immobilisation of the clusters and subsequent processes determine the evolutionary transformations of the clusters from being fixed mononuclear complexes to cluster-type structures with a polymeric carrier as macroligand. However it is very difficult to find correlations between the catalytic activity of the PCNM and their nuclearity. We note only that the rate of the water-gas shift reaction increases for complexes immobilised on polymeric amines (23) as: $Rh_2(CO)_4Cl_2 < Rh_6(CO)_{16} < Ru_4(CO)_{12} < RhCl(PPh_3)_3$. Additional possibilities for controlling the catalytic properties by changing the nuclearity of the immobilised complex could be created.

There is a series of processes which are catalysed by clusters, including immobilised clusters. For example, polynuclear clusters are the active elements of transport chains in enzyme photo systems (photo systems II of natural photosynthesis) and/or the catalytic centres responsible for redox transformations; natural polymer peptides are their carriers. Immobilised metalloclusters in heterogenised catalysts are used as catalysts for the water-gas shift reaction, see Table II; here the processes proceed under milder conditions.

The immobilisation of metalloclusters is very useful for investigating the mechanism of catalytic reactions, since in many cases it permits the isolation and thus identification of the intermediates. Immobilised $Ru_3O(OCCH_3)_6L_3^+$ particles, for example, have been identified during the hydrogenation of cyclooctene by ruthenium complexes fixed on carboxylate matrixes (41). Some researchers (23) think that the two cluster anions $Rh_{14}(CO)_{25}^{4-}$ and $Rh_{14}H(CO)_{25}^{3-}$ are active forms in the water-gas shift reaction when catalysed by $Rh_2(CO)_4Cl_2$ on aminated polystyrene.

There are numerous examples of the higher catalytic activity achieved when using polymer-immobilised bimetallic clusters than when using monometallic clusters; in particular the use of cobalt-rhodium and cobalt-ruthenium in hydroformylation reactions. The observed synergism is probably connected with a matrix effect due to the second metal, which isolates the rhodium or ruthenium atoms, respectively, as well as stabilises the intermediates and improves the introduction of carbonyl into the metal-alkyl bond. Other reasons can be linked to a decrease in the charge density on the atom in the active centre of the heterometallic clusters, for example cobalt-rhodium or iron-rhodium, as well as cobalt and iron acting as a ligand for rhodium since the formation of direct bonds rhodium-cobalt-oxygen and possibly rhodium-iron-oxygen prevents caking of the rhodium and of the catalyst (42).

Several examples of the occurrence of segregation of immobilised heterometallic clusters during the catalytic reaction are known. Thus, $(\mu-H)_2RhOs_3(CO)_{10}(acac)PPh_3$ on Ⓟ-PPh$_2$ fractures during ethylene hydrogenation at 100°C and butene isomerisation, to form a cluster with an osmium-osmium bond (which explains the isomerisation activity) and a mononuclear rhodium complex, which is transformed into rhodium particles of diameter 1 nm, which is active in the hydrogenation (43).

Conclusions

The examples listed above testify to the intensive development which is going on for PCNM in catalysis; including effective methods for

immobilising homo- and heterometallic clusters of the noble metals and identifying their structure. Approaches based on the polymerisation and copolymerisation of cluster-containing monomers are just being developed. However, data on non-carbonyl polymer-immobilised noble metal clusters, such as halides and sulphides are not yet available. This is also true for data on the immobilisation of trimetallic-type clusters and giant clusters.

The quest for effective methods to construct such PCNM is one of the important directions in catalysis. Reviews have recently been published containing data on the immobilisation of noble metal clusters by natural polymers, for example Rh_6 (44), Os_3 and Ru_3 (45) by biopolymers.

In ending it should be noted that the search for methods of improving the properties of polymers may be at the expense of immobilising the metalloclusters. However, increasing the stability of polystyrene, is a possible way to create metallopolymers of uniform structure as new types of construction materials.

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Platinum Assists in Coal Flue Gas Desulphurisation

The flue gas from coal-fired power stations contains particulates, nitrogen oxides and sulphur dioxide. The latter is generally held to be a major contributor to acid rain, a cause of much environmental damage, and thus its elimination from such flue gas is highly desirable. Various ways to achieve this are under development in a number of countries, including the U.S.A. where the 1991 Clean Air Act requires there to be a substantial reduction in the sulphur dioxide emissions, from the levels of 1980. Most existing processes require expensive reagents, involve reheating the flue gas and might require a landfill site where the captured sulphur can be dumped. The currently most frequently used method removes sulphur dioxide by a limestone scrubbing process.

However, researchers from the Georgia Institute of Technology in the U.S.A. have proposed the use of an electrochemical membrane desulphurisation process which is similar to other membrane separation processes except that it uses an applied electric field to achieve the separation, instead of the conventional pressure or concentration gradients (D. J. McHenry and J. Winnick, "Electrochemical Membrane Process for Flue Gas Desulfurization", *AIChE J.*, 1994, **40**, (1), 143–150).

Their process utilises the fact that sulphur oxides are the most acidic species present in the corrosive emissions from coal-fired power stations, and since they are therefore the strongest electron acceptors in the flue gas they can be electrochemically separated by a membrane. This consists of an inert chemically stable ceramic containing an electrolyte of $K_2S_2O_7$ with V_2O_5 which is held between two porous gas diffusion electrodes, made of lithiated nickel oxide. The structure is positioned inside a ceramic housing containing a baffled gas-flow channel, the baffles being treated with platinum to distribute the electric current. Simulated flue gas enters this cell through a heated glass tube containing a preoxidation catalyst of platinised silica gel which converts the sulphur dioxide to sulphur trioxide, after which the treated gas leaves the cell via a platinised alumina tube.

Platinum is additionally used to achieve good electrical contact to the electrodes, and a platinum wire reference electrode is positioned within the housing. The platinum wire and the platinised alumina tube serve to oxidise the sulphur dioxide completely. When current densities of between 0.5 and 500 A/m^2 are applied to the lithiated nickel oxide electrodes, a reduction in sulphur dioxide content of 90 per cent is achieved with almost a 100 per cent electric current efficiency.

The advantages of this method are that the electrodes remain stable during operation, no reagents are necessary, other than 1 to 2 per cent of the electric power output from the plant, the process occurs at flue gas temperatures so that reheating is not required, and the operation is continuous and totally enclosed. In addition there is no emitted waste, no liquids are pumped and oleum is produced.

While commercial and economic evaluations are still required, a full-scale design has been planned using a single set of stacks operating at 500 A/m^2 to achieve a 90 per cent reduction in sulphur dioxide. Savings are predicted when compared with conventional limestone scrubbing and using the new electrode material has led to an increase in cell lifetime.

Ruthenium Oxide Anode Coatings

Coatings containing platinum metals oxides have replaced many of the anode materials previously used by the electrochemical industry. The addition of various non-noble metal oxides to ruthenium oxide coatings is known to improve their selectivity and stability, and hence their performance. Now researchers at the Central Electrochemical Research Institute Karaikudi, India, have reported the effects of gradually replacing the titanium oxide in ruthenium-titanium oxide coatings with tin oxide (S. Pushpavanam and K. C. Narasimham, *J. Mater. Sci.*,1994, **29**, (4), 939–942). With constant ruthenium content, the morphology and porosity are determined largely by the ratio of titanium oxide to tin oxide.