

## SUPPORTED TRANSITION METAL COMPLEXES

### I. ORGANIC POLYMERS AS THE SUPPORT

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#### Summary

Trivalent phosphorus ligand groups have been bonded to a wide range of organic polymers, including polyvinyl chloride, polystyrene, polybutadiene and polyvinyl alcohol. The ligand-polymers complex with a variety of transition metal compounds, and the complexes obtained have been shown to catalyse hydrocarbon reactions such as the hydrogenation of 1-hexene and cyclohexene, the hydroformylation of 1-hexene and the cyclodimerisation of butadiene to 4-vinylcyclohexene and 1,5-cyclooctadiene. Macroreticular high surface area cross-linked polystyrene is the most satisfactory organic polymer support.

Rhodium complexes of acetylacetonate ligand-polymers have also been prepared.

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#### Introduction

Over the past decade, many highly active and selective catalysts for hydrocarbon reactions have been derived from transition metal complexes. These homogeneous complex catalysts have several advantages over conventional heterogeneous catalysts in that the active centres are all accessible to the reagents and the properties can be controlled in a systematic manner by variations in the ligand groups attached to the transition metal [1]. However, the use of homogeneous catalysts on an industrial scale can lead to a number of practical problems, including corrosion, deposition of the catalyst on the walls of the reactor, and recovery of the catalyst from the reaction products. One way of overcoming these problems while retaining the advantages of the transition metal complex catalysts is to attach the complex to the surface of a solid support, and this technique is currently attracting widespread interest [2].

The most satisfactory way of supporting transition metal complex catalysts involves the formation of a chemical bond between the surface of the support

and a ligand group involved in the metal complex. In this way, transition metal complexes may be attached to the surface of both organic and inorganic solids and used as heterogeneous catalysts.

Trivalent phosphorus ligands, present in many transition metal complex catalysts, can readily be bonded to organic polymers. The present paper describes the preparation of these ligand-polymers and complexes derived from them. These materials have been used as catalysts for several reactions, including hydrogenation and hydroformylation of olefins, and oligomerization of dienes. Polymers containing acetylacetonate groups and rhodium complexes derived from them are also described.

A preliminary report of this work has already appeared [3].

## Results and discussion

There are essentially two general methods of preparing ligand-polymers. These involve either chemically bonding ligand groups to a preformed polymer, or polymerization of a ligand-monomer. The first of these two methods has been the more widely used.

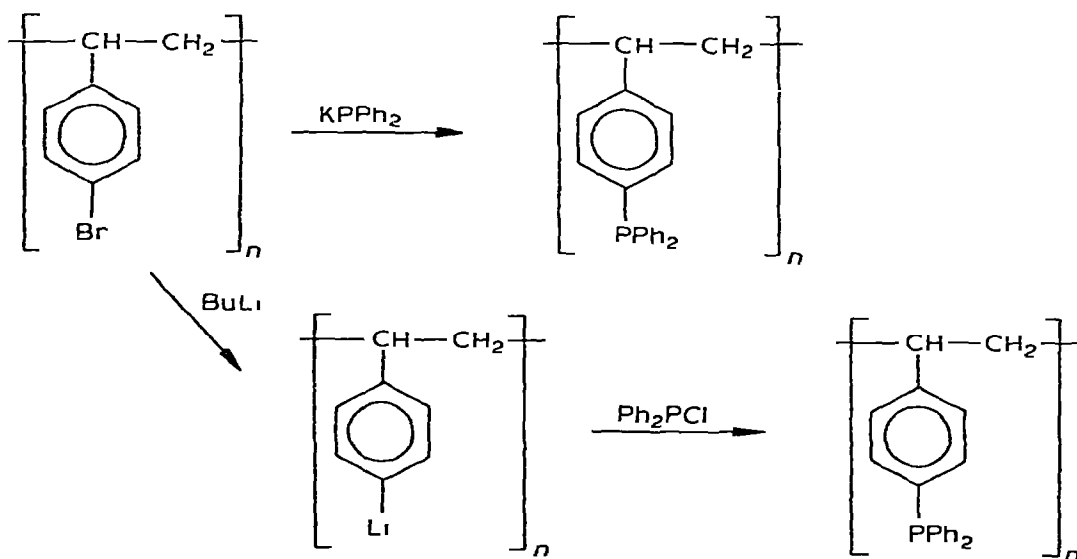
### Preparation of trivalent phosphorus ligand-polymers

*From polystyrene.* Several reactions have been employed to bond tertiary phosphine groups to styrene polymers:

(a) Poly-*p*-bromostyrene, prepared by polymerization of *p*-bromostyrene in the presence of benzoyl peroxide, reacted with potassium diphenylphosphide to give a polymer containing 3.4% weight of phosphorus.

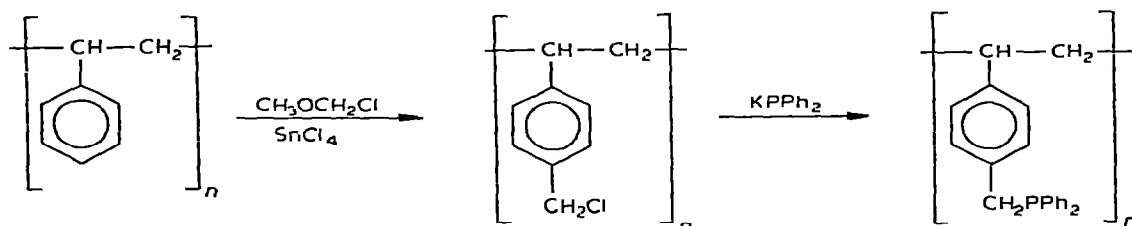
(b) Polymers containing up to 6% weight of phosphorus (e.g. ligand-polymer I — see Experimental) were obtained via a two stage route involving lithiation of the polymer with *n*-butyllithium followed by reaction with chlorodiphenylphosphine.

SCHEME 1



(c) Unsubstituted polystyrenes were treated with chloromethyl methyl ether and stannic chloride to introduce *p*-chloromethyl groups. Subsequent reaction with potassium diphenylphosphide gave polymers containing 4-5% weight phosphorus (e.g. ligand-polymers II and III).

SCHEME 2



These reactions were carried out with both cross-linked and non cross-linked polystyrenes of molecular weights in the region of 250000. In addition, a commercially available cross linked polystyrene (Amberlite XAD-2) in the form of spherical beads with high surface area ( $120 \text{ m}^2/\text{g}$ ) was also chloromethylated and reacted with potassium diphenylphosphide. Phosphorus contents of 2.0% weight were obtained (ligand-polymer IV).

*From PVC and polychloroprene.* Polyvinyl chloride and polychloroprene have also been used for the preparation of trivalent phosphorus ligand-polymers. Since these polymers already contained chlorine, direct reaction of the polymers with potassium diphenylphosphide gave products containing diphenylphosphino groups. In the PVC case, phosphorus contents up to 11% were obtained (e.g. ligand-polymer V); the polychloroprene-based material contained 3% weight phosphorus.

*From polybutadiene.* A number of routes for introducing phosphine groups to polybutadienes have been examined. Hydrogen bromide was added to poly-1,4-butadiene to give a material containing 34% weight bromine, and subsequent reaction with potassium diphenylphosphide resulted in partial replacement of the bromine by diphenylphosphino groups. The phosphorus contents of the resulting polymers were 6-8%. In addition, direct addition of diphenylphosphine to poly-1,2-butadiene was carried out in the presence of ultra-violet light to give a polymer containing 8% weight of phosphorus (ligand-polymer VI).

*From polyvinyl alcohol.* Polyvinyl alcohol was treated directly with diphenylchlorophosphine to give a product containing 1.7% weight of phosphorus. Unlike the polymers described previously, the phosphine group is linked to the polymer backbone by C—O—P linkages rather than direct C—P bonds. Reaction of polyvinyl alcohol with phenyldichlorophosphine gave a product with higher phosphorus contents (6-7% weight). In this case, the phosphorus atom may be linked to the polymer by one or two C—O—P bonds. A disadvantage with polymers of this type is that the C—O—P bond is hydrolytically unstable and reactions have to be carried out in non-hydroxylic solvents. However, the use of polyvinyl alcohol offers a route to polymers containing phosphite groups.

#### *Preparation of polymers containing acetylacetonone groups*

*From polystyrene.* Acetylacetonone groups have been linked to the surface

of cross-linked polystyrene beads (Amberlite XAD-2) via reaction of the chloromethylated polymer with sodium acetylacetonate. The low metal contents obtained in subsequent complex formation using this polymer suggest that a relatively low concentration of acetylacetonate groups are present on the surface.

*By polymerization of monomers.* Two polymers containing acetylacetonate groups have been obtained via this route from polymerization of methacryloylacetone and from copolymerization of methacryloylacetone and styrene in the presence of radical initiators [4].

#### *Characteristics of ligand-polymers*

The reactions described above demonstrate the feasibility of introducing trivalent phosphorus ligand groups into common organic polymers and that a similar halide substitution may be used to introduce acetylacetonate groups. However, the physical properties of some of the ligand-polymers limit their usefulness in transition metal complex catalysis.

The desirable characteristics of a catalyst support for use in commercial operations include physical robustness, chemical and thermal stability under reaction conditions, ease of access of the reagents to the supported catalytic centres, and negligible solubility in the reaction medium. However, many of the ligand-polymers prepared did not meet some of these criteria. A number proved to be either oily liquids or relatively low melting solids, and therefore unsuitable for use as catalyst supports in a fixed bed operation. Certain polymers containing residual halogen (e.g. polyvinyl chloride and halogenated polybutadiene) can undergo dehydrohalogenation on heating, leading to degradation of the polymer. The most satisfactory ligand-polymers were derived from high surface area cross-linked polystyrene beads (Amberlite XAD-2). Although the phosphorus contents were lower than those of PVC-based ligand-polymers, the total insolubility of these polystyrene materials in organic solvents and the relative ease of handling made them the preferred ligand-polymers for use in most further studies. Some experiments were also carried out with PVC-based ligand-polymers despite their slight solubility, as substantially higher metal contents could be achieved in complexes with these polymers.

#### *Preparation of metal complexes of trivalent phosphorus ligand-polymers*

The ligand-polymers described above have been shown to complex with many transition metals including iron, cobalt, nickel, ruthenium, rhodium, iridium, palladium, platinum and rhenium. Data on some of the complexes of cobalt, nickel, and rhodium are given in Table 1.

*Cobalt complexes.* Anhydrous cobalt chloride reacted with phosphorus ligand-polymers based on polystyrene, poly-*p*-bromostyrene, polyvinyl chloride and polybutadiene in refluxing THF or butanol/toluene to give blue complexes. The ultraviolet and visible diffuse reflectance spectra of these species closely resemble those of the complex  $[\text{CoCl}_2(\text{Ph}_3\text{P})_2]$ , suggesting a similar tetrahedral arrangement around the cobalt atom in all cases [5]. This indicates that for all the polymers some phosphine groups are suitably placed for coordination to form bis(phosphine) species.

TABLE 1

## METAL COMPLEXES OF TRIVALENT PHOSPHORUS LIGAND-POLYMERS

Polymer base	Ligand-polymer		Polymer-complex	
	Number	phosphorus (%)	Metal reagent	Metal (%)
Poly- <i>p</i> -bromostyrene	I	5.9	CoCl <sub>2</sub>	0.7
Non cross-linked polystyrene	II	4.7	CoCl <sub>2</sub>	4.3
Cross-linked polystyrene	III	4.35	CoCl <sub>2</sub>	2.8
Cross-linked polystyrene beads (Amberlite XAD-2)	IV	2.0	Ni(C <sub>8</sub> H <sub>12</sub> ) <sub>2</sub>	0.3
		2.0	Rh(acac)(CO) <sub>2</sub>	2.0
		2.2	[RhCl(C <sub>8</sub> H <sub>12</sub> ) <sub>2</sub> ] <sub>2</sub>	2.7
Polyvinyl chloride	V	4.3	CoCl <sub>2</sub>	4.6
		4.75	Rh(acac)(CO) <sub>2</sub>	7.3
Polybutadiene	VI	7.9	CoCl <sub>2</sub>	3.1

In some cases, such as a polyvinyl chloride-based ligand-polymer containing 4.3% weight of phosphorus, a cobalt/phosphorus ratio of about 1/2 was obtained, suggesting that virtually all the phosphine groups can be involved in complex formation. Examination of molecular models showed that neighbouring phosphine groups on the PVC backbone are suitably placed for coordination to a single cobalt atom, but, for many other ligand-polymers, phosphine groups on different parts of the polymer chain or on different polymer chains may be involved in complexing to the metal atom. In the formation of bis(phosphine)-metal complexes, the relative positions of the phosphine groups will be very important in determining the number of phosphine groups that can coordinate to the metal and thus in the amount of metal that can be bound to the polymer. There is some indication that the metal content of the ligand-polymer complexes decreases as the extent of cross linking of polystyrene ligand-polymers increases, but further work is necessary to substantiate this. In the case of PVC ligand-polymers, the concentration of phosphine groups will greatly affect the flexibility of the polymer chain and the number of neighbouring phosphine groups able to coordinate to the metal.

The effect of increasing the phosphorus content of the polymer on the amount of metal that can complex with the phosphine groups is worthy of further study.

**Nickel complexes.** Anhydrous nickel chloride reacted with trivalent phosphorus ligand-polymers derived from PVC and cross-linked polystyrene in butanol/toluene and ethanol to give red-brown and mauve complexes respectively. The diffuse reflectance spectra suggest that the complexes should be formulated as the more usual square planar bis(phosphine) species analogous to [NiCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>], although small amounts of the tetrahedral form may be present in the PVC-based ligand-polymer [3].

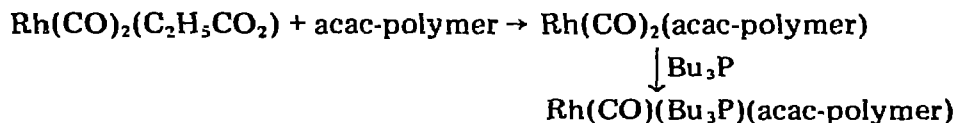
Bis(1,5-cyclooctadiene)nickel in toluene reacted with ligand-polymer IV to give an air-sensitive red complex. Subsequent reactions of this complex (see later) suggest that it is a bis(phosphine) species, analogous to  $[\text{Ni}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2]$  [6].

**Rhodium complexes.** Rhodium carbonyl complexes of trivalent phosphorus ligand-polymers were prepared by direct displacement of carbon monoxide by the ligand-polymer, in a manner analogous to that observed with monomeric phosphines [7]. Thus,  $[\text{Rh}(\text{acac})(\text{CO})_2]$  in heptane reacted with polystyrene and PVC ligand-polymers to give yellow solids with carbonyl bands in the range  $1900\text{--}2000\text{ cm}^{-1}$ . In the case of the complex with ligand-polymer IV, the carbonyl band was observed at  $1975\text{ cm}^{-1}$ . This value is close to that found for the related complex  $[\text{Rh}(\text{acac})(\text{CO})(\text{Ph}_2\text{PEt})]$ , which has a carbonyl band at  $1983\text{ cm}^{-1}$  in heptane solution, and supports the formulation of the supported species as  $[\text{Rh}(\text{acac})(\text{CO})(\text{P-polymer})]$ .

In efforts to prepare a supported species related to Wilkinson's complex  $\text{RhCl}(\text{PPh}_3)_3$ , ligand-polymer IV was treated with  $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]$  under hydrogen. The formulation of the yellow product is uncertain. Initially, the species  $[\text{RhCl}(\text{C}_8\text{H}_{12})(\text{P-polymer})]$  is probably formed, but, since the supported complex catalyses the hydrogenation of olefins, it is likely that a species of the type  $[\text{RhH}_2\text{Cl}(\text{P-polymer})_2]$  may be formed after hydrogenation and displacement of the cyclooctadiene ligand under a hydrogen atmosphere. Because of the steric restrictions imposed by the polymer structure, it is unlikely that more than two phosphine groups are coordinated to the rhodium centre.

#### *Preparation of metal complexes with acetylacetonate ligand-polymers*

**Rhodium complexes.** The copolymer of methacryloylacetonate and styrene reacted with rhodium dicarbonyl propionate to give a green polymer containing 2.3% weight rhodium. Treatment of this supported species with tributylphosphine gave a yellow species with evolution of carbon monoxide. The product had a phosphorus to rhodium ratio of approximately 1/1 and the reaction scheme may be represented as:



Reaction of a cross-linked polystyrene containing acetylacetonate groups with rhodium dicarbonyl propionate gave a species containing 0.2% weight of rhodium.

#### *Catalytic reactions*

Several complexes of the ligand-polymers described above have been examined as catalysts for reactions of olefins and dienes. Complexes of soluble ligand-polymers were found to have a much lower solubility in organic solvents than the free ligand-polymers, but many were still slightly soluble and thus not suitable for use in a fixed bed catalytic operation with liquid feedstocks or products. Consequently, most catalytic experiments with phosphine polymers were carried out using ligand-polymer IV, since this was totally insoluble in the reaction media.

**Hydroformylation.** A complex formed from  $[\text{Rh}(\text{acac})(\text{CO})_2]$  and ligand-polymer IV was tested for hydroformylation of 1-hexene at  $80^\circ$  and 43 atm pressure of  $\text{CO}/\text{H}_2$  (1/1) in an autoclave for 4 h. The molar ratio of olefin to rhodium was approximately 10000/1. A 61% conversion of 1-hexene was obtained with a yield of aldehyde of 41%. The normal/iso aldehyde ratio in the product was 2.5/1 and indicated that the phosphine group must be present in the catalytic species. (If the activity were derived from a rhodium carbonyl species containing no phosphine ligands in solution, much lower normal to branched ratios would be expected [8].) Furthermore, provided that oxygen was rigorously excluded from the reaction, the amount of rhodium in the products was less than 2 ppm [9].

**Hydrogenation.** The complex formed from the reaction of  $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]$  with the ligand-polymer IV was heated with 1-hexene and cyclohexene at  $50^\circ$  and 15 atm pressure of hydrogen. The olefin to rhodium ratio was approximately 500/1 for each olefin. After 4 h, 71% of the 1-hexene had been converted to hexane, and 37% of the cyclohexene to cyclohexane.

**Oligomerization.** Wilke has shown that complexes formed from  $[\text{Ni}(\text{C}_8\text{H}_{12})_2]$  and tertiary phosphines are good catalysts for the conversion of butadiene to  $\text{C}_8$  oligomers. With triphenylphosphine, 1,5-cyclooctadiene and 4-vinylcyclohexene are formed in a ratio of 2.4/1 [10]. In the absence of phosphine ligands, cyclotrimerisation of butadiene to cyclododecatriene occurs. A supported complex of nickel formed by reaction of  $[\text{Ni}(\text{C}_8\text{H}_{12})_2]$  with the phosphine polymer was examined for this reaction. The results are summarized in Table 2. The supported complex showed very low activity for the cyclodimerisation but, when diethyl-aluminium ethoxide was added, the activity under the same conditions increased dramatically. Analysis of the products showed that no cyclododecatriene was formed, indicating that a phosphine group remains attached to the nickel centre throughout the reaction. The need for the aluminium alkyl suggests that the interaction of  $[\text{Ni}(\text{C}_8\text{H}_{12})_2]$  with the phosphine polymer may give rise to chelated species which do not readily dissociate. However, the aluminium alkyl may displace the equilibrium between mono- and chelated phosphine species in favour of the mono-phosphine species by complexing with the dissociated phosphine groups, thereby preventing their recoordination to the nickel. This phenomenon has also been observed for certain cobalt complexes with chelating phosphines [11].

TABLE 2

## CYCLODIMERISATION OF BUTADIENE USING SUPPORTED NICKEL COMPLEXES

Conditions: temperature  $80^\circ$ ; 1 g catalyst, containing 0.3% wt. nickel and 2.0% wt. phosphorus; 30 ml toluene saturated with butadiene; 15 atm pressure nitrogen.

$\text{Et}_2\text{AlOEt}$ added	Productivity	Selectivity (% wt.)	
(ml)	(g/g Ni/h)	COD <sup>a</sup>	VCH <sup>b</sup>
0	3	0	100
0.5	60	68	32
2	100	72	28

<sup>a</sup> COD = 1,5-cyclooctadiene. <sup>b</sup> VCH = 4-vinylcyclohexene.

TABLE 3

## CYCLODIMERISATION OF BUTADIENE IN FLOW SYSTEM USING SUPPORTED NICKEL COMPLEXES

Conditions. temperature 90° C; atmospheric pressure; 6 g catalyst containing 0.4% wt. nickel and 1.6% wt. aluminium; butadiene flow rate 30-40 ml/min at NTP.

Hours on stream	Productivity	Selectivity (% wt.)	
	(g/g Ni/h)	COD	VCH
0-17	28	60.5	39.5
17-20	29	65.5	34.5
20-23	35	66.8	33.2
23-24.5	29	67.0	33.0
24.5-41.5	30	67.4	32.6

The supported complex does not require the presence of the aluminium alkyl after the initial activation has taken place. This was demonstrated in a flow system in which the catalyst was activated with  $\text{Et}_2\text{AlOEt}$  and then the excess of alkyl removed by washing the catalyst with toluene saturated with butadiene. The catalyst was then tested for the cyclodimerisation of butadiene in the gas phase at 1 atm and 90° in a flow system. The results (Table 3) show that the activity of the catalyst remains fairly steady over 40 h on stream to give a ratio of 1,5-cyclooctadiene to 4-vinylcyclohexene of 2/1 in the products, similar to that expected by analogy with Wilke's results in the homogeneous system.

### Conclusion

The results presented above show that trivalent phosphorus and acetyl-acetone ligand groups may be bonded to a wide range of organic polymers. The resulting ligand-polymers form complexes with transition metals by methods analogous to those used for simple monomeric ligands. It has also been shown that, in many cases, almost all the ligand groups on the polymer chains are readily accessible for complex formation and that the complexes formed remain accessible to hydrocarbon substrates as exemplified by their catalytic activity in hydrogenation, oligomerization and carbonyl insertion reactions.

Although a wide range of solvents may be used with supported complexes without the limitations of solubility imposed in homogeneous systems, the solvent may have a profound effect on the polymeric support in causing swelling and resulting in large changes in the size of the pores and available surface area. This can affect both the reaction rates and the selectivity of the active centre towards different sized substrates [12]. This limitation can be overcome by the use of inorganic oxides, such as silica, as the support to which liganding groups may be attached.

The results obtained using these inorganic supports are published in the following paper [13].

### Experimental

All preparations were carried out under dry oxygen-free nitrogen. Solvents



were dried and redistilled prior to use. Chloromethylation of polystyrenes was performed by the method of Pepper [14]. For the non cross-linked polystyrene the reaction was conducted using a dilute solution of polystyrene in cyclohexane. 1,3-Butadiene was purified by passage through columns of 3A molecular sieve and activated alumina.

#### *Preparation of ligand-polymer I*

Poly-*p*-bromostyrene (50 g) dissolved in tetrahydrofuran (250 ml) was added to a vigorously stirred solution of butyllithium (200 ml, 1.47 *N* in hexane; 0.3 mol) at  $-35$  to  $-40^{\circ}$ . During the addition period of 6 h a yellow solid was deposited. The temperature was raised to  $0^{\circ}$  and chlorodiphenylphosphine (63 g, 0.28 mol) in tetrahydrofuran (100 ml) slowly added. The reaction mixture was stirred for a further 4 h after the addition was complete and then degassed water (500 ml) added to produce two layers. The upper organic layer was added to pentane (3 l) whereupon the white polymer was precipitated. The product was isolated by filtration and purified by reprecipitation from tetrahydrofuran using pentane. The product was finally dried in *vacuo*. Phosphorus content of product = 5.9% weight.

#### *Preparation of ligand-polymer II*

Non cross-linked chloromethylated polystyrene (10 g, 12.6 per cent weight chlorine) in tetrahydrofuran (100 ml) was added to a stirred solution of potassium diphenylphosphide [prepared from potassium (7.8 g, 0.2 mol) and chlorodiphenylphosphine (22 g, 0.1 mol) in tetrahydrofuran (500 ml)]. After stirring for 1 h at ambient temperature, degassed water (500 ml) was added to the reaction mixture to produce two layers. The upper organic layer was slowly added to pentane (3 l) to precipitate the polymer. Purification of the polymer was achieved by reprecipitation from tetrahydrofuran using pentane followed by exhaustive extraction of the polymer with pentane. The product was dried in *vacuo*. Phosphorus content of product = 4.7% weight.

#### *Preparation of ligand-polymer III*

Ligand-polymer III was prepared by the procedure described for ligand-polymer II, but due to the insolubility of the chloromethylated species it was added in batches (0.5 g) over a 2 h period to the refluxing tetrahydrofuran solution of potassium diphenylphosphide. Purification of the polymer product was by extraction with methanol/water (1/1), methanol/acetic acid (10% vol acetic acid) and finally methanol. The white polymer product was dried in *vacuo*. Phosphorus content of product = 4.35% weight.

#### *Preparation of ligand-polymer IV*

Chloromethylated Amberlite XAD-2 polystyrene beads (20 g, 8% weight chlorine) were added in batches (0.5 g) over a 2 h period to a stirred refluxing solution of potassium diphenylphosphide [prepared from potassium (30 g, 0.75 mol) and chlorodiphenylphosphine (80 g, 0.37 mol) in tetrahydrofuran (750 ml)]. After refluxing the reaction mixture for a further hour, an additional quantity (20 g) of chloromethylated beads was added, again in 0.5 g batches over a 2 h period. Reflux was maintained for a further 3 h during which time

the red colour of the potassium diphenylphosphide was completely discharged. After cooling to ambient temperature, degassed water (250 ml) was cautiously added and the polymer beads isolated by filtration. The product was purified by Soxhlet extraction using degassed water and then tetrahydrofuran and finally dried in vacuo. Phosphorus content of product = 2.0% weight.

#### *Preparation of ligand-polymer V*

Ligand-polymer V was prepared according to the procedure described for the synthesis of polymer II but using polyvinyl chloride (3 g) in tetrahydrofuran (100 ml) and potassium diphenyl phosphide [prepared from potassium (3.9 g, 0.1 mol) and chlorodiphenyl phosphine (11.0 g, 0.05 mol)] in tetrahydrofuran (250 ml). Phosphorus content of product = 4.3% weight.

#### *Preparation of ligand-polymer VI*

Poly-1,2-butadiene (2.5 g) was dissolved in diphenylphosphine (50 ml) contained in a 250 ml silica flask and the mixture stirred and irradiated with ultraviolet light for 72 h at room temperature. Removal of the excess diphenylphosphine by distillation yielded a viscous product which was dissolved in toluene (10 ml) and precipitated by hexane (300 ml). This procedure was repeated five times and the product finally dried at 120° in vacuo. Phosphorus content of product = 7.9% weight.

#### *Preparation of a styrene-methacrylacetone copolymer*

Styrene monomer (20.8 g, 0.2 mol), methacrylacetone (12.6 g, 0.1 mol) and  $\alpha,\alpha'$ -azoisobutyronitrile (0.5 g) were heated at 70° for 3 h. The solid product was dissolved in tetrahydrofuran (200 ml) and precipitated by addition of pentane (3 l). This purification procedure was repeated and the white polymer product dried in vacuo.

#### *Reaction of chloromethylated Amberlite XAD-2 polystyrene beads with mono-sodio acetylacetonate*

Chloromethylated polystyrene beads (50 g, 8.0% weight chlorine) were added to mono-sodio acetylacetonate, prepared from sodium hydride (15 g, 0.625 mol) and acetylacetonate (40 g, 0.4 mol), in hexamethylphosphoramide (500 ml). The reaction mixture was heated to 150° and maintained at this temperature for 72 h. After cooling to room temperature the beads were filtered off and Soxhlet extracted with methanol prior to drying in vacuo.

#### *Reaction of ligand-polymer I with anhydrous cobalt chloride*

Ligand-polymer I (8.0 g, 5.9% weight phosphorus) in hot butanol (50 ml) was added to anhydrous cobalt chloride (1.1 g, 9 mmol) in hot butanol (25 ml). The solution was refluxed for 2 h during which time a blue solid was deposited. After cooling to ambient temperature the reaction mixture was poured into pentane (1 l). The polymer product was filtered, extracted with butanol until free from residual cobalt chloride and finally dried in vacuo. Cobalt content of product = 0.7% weight.

A similar procedure was employed to produce the cobalt chloride derivative of ligand-polymer VI using toluene/butanol (20% vol. butanol; 60 ml). The product contained 3.1% weight cobalt.

***Reaction of ligand-polymer II with anhydrous cobalt chloride***

Ligand-polymer II (10 g, 4.7% weight phosphorus) was dissolved in tetrahydrofuran (200 ml). Anhydrous cobalt chloride (1 g, 8 mmol) was added and the solution refluxed for 2 h. The mixture was cooled and a blue solid was precipitated. This was filtered off, extracted with tetrahydrofuran until free from residual cobalt chloride, and dried in vacuo. Cobalt content of product = 4.3% weight.

The cobalt chloride derivative of polymer V was prepared by a similar procedure in refluxing tetrahydrofuran/butanol (10% vol. butanol; 100 ml) for 4 h. The precipitated product was purified by extraction with butanol and dried in vacuo. Cobalt content of product = 4.6% weight.

***Reaction of ligand-polymer III with anhydrous cobalt chloride***

Ligand-polymer III (1.0 g, 4.35% weight phosphorus) and anhydrous cobalt chloride (1.0 g, 8 mmol) were refluxed in toluene/butanol (1/1, 50 ml) for 4 h. The blue-green product was filtered off, extracted with butanol until free from cobalt chloride and dried in vacuo. Cobalt content of product = 2.8% weight.

***Reaction of ligand-polymer IV with bis(1,5-cyclooctadiene)nickel(0) [polymer-complex I]***

Ligand-polymer IV (2.46 g, 2.2% weight phosphorus) and toluene (50 ml) were cooled to 0° and bis(1,5-cyclooctadiene)nickel(0) (0.41 g, 1.5 mmol) in toluene (25 ml) at 0° added via hypodermic tubing. The resulting mixture was stirred for 2 h at 0 to 5° during which time the polymer slowly became red in colour. The liquid was removed and the polymer product extracted with cold toluene (5 × 25 ml) until free from residual bis(1,5-cyclooctadiene)nickel(0). The product, which was air-sensitive, was dried in vacuo. Nickel content of product = 0.3% weight.

***Reaction of ligand-polymer IV with acetylacetonatodicarbonylrhodium(I) [polymer-complex II]***

Ligand-polymer IV (50 g, 2.0% weight phosphorus) was added to a solution of acetylacetonatodicarbonylrhodium(I) (3.5 g, 14 mmol) in hexane (150 ml). Addition of the polymer was accompanied by evolution of carbon monoxide. After stirring for 1 h at room temperature the yellow polymer product was filtered off, Soxhlet extracted with hexane and dried in vacuo. Rhodium content of product = 2.0% weight.

***Reaction of ligand-polymer V with acetylacetonatodicarbonylrhodium(I)***

Ligand-polymer V (1.25 g, 4.75% weight phosphorus) dissolved in tetrahydrofuran (25 ml) was added to a solution of acetylacetonatodicarbonylrhodium(I) (0.5 g, 2 mmol) in tetrahydrofuran (10 ml). Carbon monoxide was evolved. The reaction mixture was stirred for 2 h at room temperature and the product was precipitated by pentane (1 l). The solid was filtered off, washed with ethanol, then with pentane, and dried in vacuo. Rhodium content of product = 7.3 per cent weight.

***Reaction of ligand-polymer IV with chloro(1,5-cyclooctadiene)rhodium(I) dimer [polymer-complex III]***

Ligand-polymer IV (2.8 g, 2.2% weight phosphorus) was added to a solution of chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.49 g, 1 mmol) in benzene (50 ml), under hydrogen. After stirring at room temperature for 3 h, the polymer product was extracted with benzene until free from residual chloro-1,5-cyclooctadiene)rhodium(I) dimer and subsequently dried in vacuo. Rhodium content of product = 2.7% weight.

***Reaction of styrene-methacroylaceton copolymer with propionatodicarbonylrhodium(I) dimer***

The styrene-methacroylaceton copolymer (3.0 g) was added to a solution of propionatodicarbonylrhodium(I) dimer (0.25 g, 0.5 mmol) in hexane (100 ml) and refluxed for 15 min. After cooling to room temperature the green polymer was filtered off and purified by repeated extraction with heptane. Rhodium content of product = 2.3% weight.

Addition of tributylphosphine (0.8 g, 4 mmol) to the above rhodium-containing polymer (1.0 g) suspended in hexane resulted in the evolution of carbon monoxide and the formation of a yellow polymer product. Phosphorus content of product = 0.85% weight.

***Hydroformylation of 1-hexene***

The reaction was performed in a stainless steel autoclave. Deperoxidised 1-hexene (84 g, 1 mol), heptane (200 ml) and polymer-complex II (0.62 g,  $1.2 \times 10^{-3}$  mol Rh) were heated at 80° and 43 atm carbon monoxide/hydrogen (1/1) for 4 h. GLC analysis of the products showed 61% of the 1-hexene had reacted, with a yield of heptaldehydes of 41% and a normal/iso heptaldehyde ratio of 2.5/1. No alcohols or paraffins were detected, the only other products being internal hexenes.

***Hydrogenation of 1-hexene and cyclohexene***

Polymer-complex III (0.81 g,  $2.1 \times 10^{-4}$  mol Rh), benzene (42 ml), 1-hexene (14 ml, 0.11 mol) and cyclohexene (14 ml, 0.14 mol) were heated at 50 to 55° under 15 atm hydrogen pressure for 4 h in a glass pressure vessel. Analysis of the products showed 100% conversion of the 1-hexene, a 71% yield of hexane and 29% yield of internal hexenes. 37% hydrogenation of the cyclohexene to cyclohexane was observed.

***Cyclooligomerization of 1,3-butadiene***

(a) Polymer-complex I (0.32 g,  $1.6 \times 10^{-4}$  mol Ni) was mixed with toluene previously saturated with 1,3-butadiene at room temperature (30 ml) and heated at 80° for 16 h under 15 atm pressure of nitrogen. After cooling to ambient temperature the reaction vessel was vented to atmospheric pressure and the products analysed. Repeat experiments were performed using polymer-complex I (1.0 g,  $5 \times 10^{-4}$  mol Ni) and incorporating diethylaluminium ethoxide (0.5 ml and 2.0 ml) respectively. Results are summarized in Table 2.

(b) A glass reactor tube of 40 ml capacity was placed in an electrically heated furnace and connected to supplies of nitrogen and gaseous 1,3-butadiene.

A cold trap was incorporated on the outlet side of the reactor. The bottom third of the reactor was packed with glass wool. Polymer-complex I [prepared from ligand-polymer IV (6.0 g, 2.0% weight phosphorus) and bis(1,5-cyclooctadiene)nickel(0) (0.4 g, 1.5 mmol) according to the previously described procedure] was loaded into the reactor under a nitrogen/butadiene atmosphere, and washed with toluene saturated with 1,3-butadiene at room temperature (10 ml). Toluene saturated with 1,3-butadiene (20 ml) and containing diethylaluminium ethoxide (3 ml) was pumped over the catalyst and followed by a further quantity of toluene saturated with 1,3-butadiene (20 ml) to wash it free from excess diethylaluminium ethoxide. Purified gaseous 1,3-butadiene was then passed over the catalyst at 30 to 40 ml/min and the temperature was raised to 90°. The catalyst was tested under these conditions for the cyclooligomerization of 1,3-butadiene over 41.5 h on a continuous basis, samples from the cold trap being periodically removed for analysis. Full results are given in Table 3. The recovered catalyst contained: nickel = 0.4% weight; aluminium = 1.6% weight.

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### References

- 1 C.W. Bird, *Transition Metal Intermediates in Organic Synthesis*, Logos Press, London, 1967.
- 2 F. Basolo and R.L. Burwell (Eds.), *Catalysis - Progress in Research*, Plenum Press, London, 1973, p. 177-185.
- 3 K.G. Allum, R.D. Hancock, S. McKenzie and R.C. Pitkethly in J.W. Hightower (Ed.), *Catalysis*, Vol. 1, North-Holland, Amsterdam, 1963, p. 477.
- 4 P. Teyssié and G. Smets, *Makromol. Chem.*, 26 (1958) 245.
- 5 F.A. Cotton, O.D. Faut, D.M.L. Goodgame and R.H. Holm, *J. Amer. Chem. Soc.*, 83 (1961) 1780.
- 6 G. Wilke, E.W. Müller, M. Kroner, P. Heimbach and H. Breil, *Fr. Pat.*, (1963) 1320729.
- 7 F. Bonati and G. Wilkinson, *J. Chem. Soc.*, (1964) 3156.
- 8 R.L. Pruett and J.A. Smith, *J. Org. Chem.*, 34 (1969) 327.
- 9 Paper in preparation.
- 10 W. Brenner, P. Heimbach, H. Hey, E. Müller and G. Wilke, *Justus Liebigs Ann. Chem.*, 727 (1969) 161.
- 11 M. Iwamoto and S. Yuguchi, *Chem. Commun.*, (1968) 28.
- 12 R.H. Grubbs, L.C. Kroll and E.M. Sweet, *J. Makromol. Sci. Chem. A*, 7 (1973) 1047.
- 13 K.G. Allum, R.D. Hancock, J.V. Howell, S. McKenzie, R.C. Pitkethly and P.J. Robinson, *J. Organometal. Chem.*, 95 (1975)
- 14 K.W. Pepper, H.M. Paisley and M.A. Young, *J. Chem. Soc.*, (1953) 4097.