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Selective Hydrogenation of Ketones and Olefins over Polymer-bound Rhodium Catalysts

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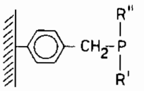
Selective hydrogenation of olefins and ketones promoted by polymer-bound cationic rhodium(I) catalysts is reported. A different catalytic behaviour is found depending on the substituents on the phosphorus atom of the polymeric ligand. The effect of the polymer on the stability of supported complexes towards reduction, and on the fate of the catalysts is discussed. In some cases polymer trapped Rh^{II} compounds are present at the end of the catalytic cycle.

Introduction

An heterogeneous catalyst is defined as one which can be easily separated from the reaction mixture by simple, economical, physical means. This ease in separation gives heterogeneous catalysts marked advantages over their homogeneous counterparts. On the other hand, an homogeneous catalyst is often more active and selective than an heterogeneous one. A substantial improvement may be achieved if both types of catalysts are combined together while retaining the properties and capabilities of each. Only recently a great deal of interest has been focused on heterogenizing catalysts.[1–3] Selective hydrogenation of polyenes to monoenes has been carried out with Pt^{II} and Pd^{II} complexes bound to polymeric phosphines.[4] Also, monoenes of different size such as 1-hexene or Δ^2-cholestene are hydrogenated by $Rh(PPh_3)_3Cl$ supported on a polymeric phosphine based on chloromethylated polystyrene with 2% of divinylbenzene cross-linking.[5] The high dependence of rate of reduction on the size and rigidity of the substrate has suggested the contention that reduction takes place within the resin rather than at its surface. Also the synthesis of a variety of rhodium, iridium, and cobalt complexes with a triphenylphosphine-substituted resin of type $[(Resin)C_6H_4PPh_2]$ as ligand has been reported.[6] In all cases a high degree of catalytic activity has been observed, which has been attributed to the inability of these catalysts to associate into aggregates of the types which are feasible in solution. Phosphinated resins have been used as ligands in reactions of hydrosilylation[7] or hydroformylation[8] with various transition metals. In all cases the insoluble catalyst could be filtered off from the reaction mixture and reused without appreciable loss of activity.

Asymmetric reductions of prochiral olefins by rhodium(I) catalysts supported on asymmetric polyphosphines have been described recently.[9] This system proved much less effective in inducing asymmetry than the analogous homogeneous one for which very high optical yields were achieved. The asymmetric hydrosilylation of acetophenone by the same catalyst has been shown to occur[9] with optical yields of up 58%. In our study we have reported on the hydrogenation of ketones and olefins with rhodium(I) complexes bound to polymeric substituted phosphines of type:



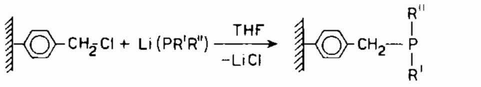
$R' = R'' = Ph$; $R' = Ph$, $R'' = Me$; $R' = Ph$, $R'' =$ Menthyl

We have also shown that it is possible to achieve different degrees of catalytic effectiveness by changes in the substituents R′ and R″, thereby getting selective reduction of carbonyl or carbon–carbon double bonds depending on the substituent on the phosphorus atom.

Results and Discussion

Synthesis of Supported Catalyst Complexes

In all cases Merrifield's[10] resin was used (0.7 or 3.5 meq. Cl/g, 200–400 mesh, 2% divinylbenzene), [I], which was treated with lithiumdiphenylphosphide or lithiummethylphenylphosphide in THF according to the reaction:

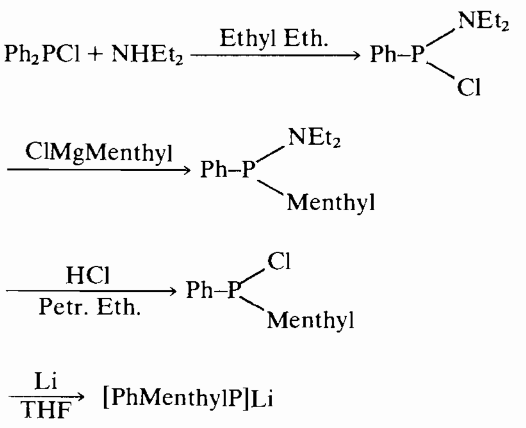


[1]

[I] [II, a, b, c]

R′ = R″ = Ph(IIa); R′ = Ph, R″ = Me(IIb)

We have also prepared an optically active polymeric phosphine (IIc; R′ = Ph, R″ = Menthyl):



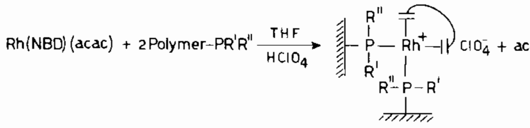
$$Ph_2PCl + NHEt_2 \xrightarrow{\text{Ethyl Eth.}} Ph\text{–}P(NEt_2)(Cl) \xrightarrow{\text{ClMgMenthyl}} Ph\text{–}P(NEt_2)(\text{Menthyl}) \xrightarrow[\text{Petr. Eth.}]{\text{HCl}} Ph\text{–}P(Cl)(\text{Menthyl}) \xrightarrow[\text{THF}]{\text{Li}} [\text{PhMenthylP}]Li$$

[2]

Menthylphenylphosphide is reacted with resin [I] according to reaction [1] to give an organic polymer containing benzylphenylmenthylphosphine as functional grouping. Polymeric complexes closely related to $[Rh(NBD)LL']^+$ (L, L′ polymeric phosphines of the type IIa, b, c) were prepared by routes analogous to those involved in the synthesis in homogeneous phase of cationic rhodium(I) complexes.[11] In particular, two procedures were adopted.

Method A

In a typical experiment, resins [IIa, b, c] suspended in THF are treated with a solution of [Rh(NBD)(acac)] in the same solvent with no particular contrivances and then with 70% $HClO_4$ in THF:



[3]

[III]

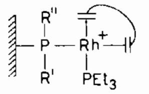
R′ = R″ = Ph; R′ = Ph, R″ = Me; R′ = Ph, R″ = Menthyl

In this way a rhodium complex immobilized in a polymeric network is obtained which is formulated as [III] on the basis of the following evidence: (*i*) the i.r. spectrum of [III] in KBr has no bands attributable to coordinated acetylacetone; (*ii*) norbornadiene is coordinated to the rhodium. [III], when treated with excess of 1,2-bisdiphenylphosphinoethane in THF gives a yellow solution containing a rhodium complex that has thereby been displaced from the resin (no attempts at characterization were made). In the same solution norbornadiene is detected by gas chromatography; (*iii*) the presence of the ClO_4^- ion was proved by suspending the resin in an aqueous solution of Li_2SO_4. After equilibration the mixture was filtered and the filtrate treated with excess NaI in acidic medium, whereupon I_2 was set free, indicating the presence of oxiding species such as ClO_4^-.

Of course, the structure of [III] as drawn above does not take into account the possibility that the coordinating phosphine groups may originate from the same polymeric chains or from different chains, although it has been shown[6] that 2% divinylbenzene–styrene copolymers are mobile enough to allow ligands attached to the polymer beads to act as "chelates".

Method B

The polyphosphines suspended in CH_2Cl_2 were equilibrated with a solution of $[Rh(NBD)(PEt_3)_2]^+$ in the same solvent. After 1–2 days the resin was filtered off and washed. The filtrate is colorless and no longer contains rhodium. Phosphine was detected, albeit not in quantitatively measurable extent due to the low concentrations involved. Both chemical properties and catalytic activity of these compounds differ substantially from those of their analogues prepared by method A. In particular, Table I (experiments No. 15, 26, 27 and 28) shows that some of the complexes from method A will reduce ketones and will be reduced to metallic rhodium, by hydrogen, whereas the complexes from method B will reduce ketones without being reduced themselves. The presence of ClO_4^- and norbornadiene was again detected as under method A. Based on the above evidence, although other formulations cannot be ruled out, we have tentatively formulated this complex as [IV]:



[IV]

ESR Spectra

Catalysts before use

Catalysts prepared by methods A and B show two small signals, a sharp one at g = 2.003 probably due to some organic radical generated in the polymer (this signal is present in the spectrum of the polyphosphine itself), and a more complex one at g = 1.99 and g = 2.12, most probably due to Rh^{II} impurities.

Used Catalysts

After use for some catalytic cycles, the ESR spectra of the polymer bonded complexes show remarkable modifications depending on the preparation and the rhodium content: (*i*) [Rh(NBD)(PolymerPPhMen-

TABLE I. Hydrogenation of Ketones and Olefins using Supported Cationic Rh(I) Complexes closely Related to $[(NDB)Rh(LL')]^+$. NBD = Norbornadiene; L,L' = Phosphine Ligands. Polymer = Merrifield Polymer (Chloromethylatedpolystyrene, 2% divinylbenzene, 3.5 meq Cl/g). Reaction Time = 18 hr; Temperature 20° C; Ratio Substrate/Rhodium = 1000; pH_2 measured in psig.[a]

Run	LL'	Substrate	Product	Yield%	pH_2 psig	Notes
1	L = L' = PolymPPhMe	Acetone	iso-Propanol	5	5	
2		Acetone	iso-Propanol	70	800	Subst./Rh = 100
3		MethylEthylKetone	sec-Butanol	30	45	
4		Cyclohexene	no reaction		5	
5		Cyclohexene	no reaction		45	Reaction Time 72 h
6		1-Hexene	no reaction		5	
7		1-Hexene	n-Hexane	5	45	
8	L = PolymPPhMe, L' = PEt_3	Acetone	iso-Propanol	8	5	
9		Acetone	iso-Propanol	70	45	Subst./Rh = 100
10		MethylEthylKetone	sec-Butanol	70	45	
11		Cyclohexene	no reaction		5	
12		Cyclohexene	Cyclohexane	2	45	
13		1-Hexene	no reaction		5	
14		1-Hexene	n-Hexane	5	45	
15	L = L' = PolymPPhMenthyl	Acetone	iso-Propanol	100	5	Rh Metal
16		MethylEthylKetone	sec-Butanol	70	15	see Table III
17		Acetophenome[b]	PhMethylCarbinol	10		
			CyMethylCarbinol	4	800	Reaction Time 48 h
			CyMethylKetone	6		
18		Cyclohexene	Cyclohexane	1	5	
19		Cyclohexene	Cyclohexane	100	45	
20		1-Hexene	no reaction		5	
21		1-Hexene	n-Hexane	5	45	
22		MethylEthylKetone	sec-Butanol	3	5	Polymer B Table II
23		MethylEthylKetone	no reaction		5	Polymer C Table II
24		MethylEthylKetone	sec-Butanol	5	45	Reaction Time 5 d
25		MethylEthylKetone	sec-Butanol	100	800	Reaction Time 18 h Subst./Rh = 100
26	L = PolymPMenthylPh, L' = PEt_3	MethylEthylKetone	no reaction		800	
27		Cyclohexene	Cyclohexane	7	5	
28		1-Hexene	n-Hexane	35	5	
29	L = L' = $PolymPPh_2$	Acetone	no reaction		45	
30		MethylEthylKetone	no reaction		45	
31		Cyclohexene	Cyclohexane	8	5	
32		1-Hexene	n-Hexane	35	5	
33	L = $PolymPPh_2$, L' = PEt_3	Acetone	no reaction		45	
34		MethylEthylKetone	no reaction		45	
35		Cyclohexene	Cyclohexane	<1	5	
36		1-Hexene	n-Hexane	10	5	

[a] Cy = Cyclohexyl. All runs were carried out in pure substrate. 1% H_2O or 1% MeOH was always added respectively to ketones or olefins. [b] Ethylbenzene is probably present in products in low concentration.

TABLE II. Behaviour toward Hydrogen of $[Rh(NDB)(PolymerPPhMenthyl)_2]^+$.[a]

Type	P/Rh	P meq/g	Rh meq/g	Ketone Moles	Ketone/Rh	Rh Metal
A	2/1	0.89	0.44	0.440	1000	yes
B	2/1	0.14	0.06	0.300	5000	yes
C	10/1	0.98	0.095	0.500	5000	no

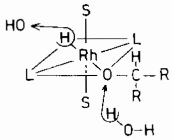
[a] In runs A and B a black material is obtained.

thyl)$_2$]$^+$ reacts with molecular hydrogen to give a green–yellow product (Type C, Table II) which shows at 77 °K a very peculiar spectrum with broad signals at g = 4.35 and g = 1.99. Where the sample is warmed at room temperature, besides further broadening of these lines a third signal appears. This signal shows a reversible temperature dependence, moving from g = 1.99 (at 77 °K) to g = 2.34 (at 303 °K). While we have no explanation for the species giving the signal at g = 2.34, the other signals could be attributed to a largely anisotropic species of Rh^{II}.[12] We are carrying out further studies to shed light on these results; (*ii*) the ESR spectrum of the black material obtained by reduction of the rhodium(I) supported complex (type A, Table II) shows a very broad symmetric signal centered g ~ 2.25. The signal which shows very little temperature dependence could be attributed to a very anysotropic Rh^{II} species or to rhodium metal particles of very small size. Although rhodium metal obtained by reduction of $RhCl_3$ and supported on the same polymeric phosphine gave no ESR signal; (*iii*) [Rh(NBD)(PolymerPPhMenthyl)$_2$]$^+$ reacts with molecular hydrogen in acetophenone (Table I, ex. 17) to give a yellow–green solid without reduction to rhodium metal. This shows two ESR lines, $g_\perp$ = 1.99 $g_{||}$ = 2.12, in accordance with previously reported spectra for Rh^{II} complexes.[13] The same results are obtained using catalysts prepared with method A with Polymer PMePh as ligand; (*iv*) catalysts prepared using method B are all active in the reduction of ketones and/or olefins, but the presence of rhodium metal was never observed. The catalysts after being used in hydrogenation catalysis do not show ESR signals.

Hydrogenation Catalysis

As can be seen in Table I, these supported catalysts, closely related to [Rh(NBD)LL′]$^+$, will hydrogenate selectively either olefins or ketones depending on the polymeric phosphine ligands. This appears to be a combination of an intrisically selective reactivity towards ketones or olefins of these complexes and some physical effect of the substrate itself, as the polymer is swollen to a much greater degree by ketones than by olefins. As a general trend, increasing the basicity of the rhodium-coordinated phosphine will enhance the ability to reduce ketones while at the same time reducing the catalytic effectiveness of olefin hydrogenation. At least as far as hydrogenation of olefins is concerned, this finding is partially at variance with what was found for the analogous reaction in homogeneous phase.[14, 15] In fact, it has been observed that complexes of type [$RhH_2(PPh_2Me)_2$(solvent)$_2$]$^+$ originating from [Rh(NBD)$(PPh_2Me)_2$]$^+$ also hydrogenate olefins,[15] although the reaction is inhibited by water and excess of phosphine. Various differences can be noted in analogous hydrogenation reactions when using related immobilized systems.

Thus, for instance, [Rh(NBD)(PEt_3)(PolymerPPhMenthyl)]$^+$ will not hydrogenate cyclohexene (H_2 pressure, 12 psig) if suspended in the olefin itself, whereas it will work, albeit very slowly, upon addition of CH_2Cl_2 or, faster, in the presence of trace amounts of methanol. Under the same conditions [Rh(NBD)(PEt_3)(PolymerPPhMe)]$^+$ will not hydrogenate cyclohexene. When hydrogenation of cyclohexene by [Rh(NBD)(PolymerPPhMe)$_2$]$^+$ is carried out in the presence of acetone (acetone/olefin ratio 1) fast reduction to cyclohexane is observed. These findings indicate that both chemical factors (such as steric and/or electronic properties of substituents on the phosphorus) and physical properties (such as swelling ability of the polymer in the presence of solvent) may play a primary role in these types of catalysts. The presence of small amounts of water (1%) either in homogeneous or in heterogeneous phase is also required for the hydrogenation of ketones. In this case water is likely to be directly involved in the reaction; in fact, the second hydrogen transfer – the first hydride transfers by nucleophilic attack at the α-carbon of the coordinated ketone – is thought to be promoted by water, as follows (charges are omitted):



For the complex [Rh(NBD)(PolymerPPhMenthyl)$_2$]$^+$ a discussion of its own is in order. Upon suspending this complex in acetone under H_2 atmosphere, immediate formation of a black material (probably rhodium metal) takes place (type A and B in Table II). However, if the P/Rh ratio is increased the compound is more stable and no reduction to metal is observed (type C in Table II). In this case methylethylketone is reduced quantitatively to *sec*-butanol (Table I, ex. 25) although the alcohol displays no appreciable optical purity.

As we have already noted, compounds of type IV (which we have formulated as having one single polymeric phosphine coordinated) are stable towards reduction even at high H_2 pressures, suggesting some sort of destabilization of the immobilized complex with increasing rhodium content at constant phosphorus contents, hence with increasing ability of "chelation" by the polymer. The mobility of the resin with low divinylbenzene content entails the possibility of linkage by even remote phosphines (due to the low rhodium content, type C in Table II). This will reduce possible strains in the polymeric chain and enhance the complex stability toward reduction, whereupon the complex will become closer in structure to species of type IV.

It must be noted that the fate of the catalysts prepared using methods A or B is very different. In the former case a Rh^{II} complex trapped in the polymer is obtained whereas no Rh^{II} is present in the used catalysts prepared by method B. These results might also be attributed to the possible "chelating" effect of the polymer in the case of complexes [III].

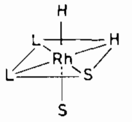
A study of the effect of divinylbenzene percentage will shed light on this matter. As a matter of fact, it is noteworthy that the activity of a catalyst can be enhanced by preventing it from aggregating or by trapping on rigid supports species that would be highly reactive in solution.[16] The reduction of A (Table II) with H_2 afforded a black active material. This substance will catalyze the hydrogenation of olefins, ketones, and nitriles, and exhibits reactivity and substrate selectivity close to 5% Rh/C[17] or 5% Rh/Al_2O_3.[18] When $RhCl_3$ is reduced in the presence of the same polyphosphine, supported rhodium metal is obtained. This material shows no catalytic activity. Assuming that the black material could consist of rhodium metal, the different behaviour could be attributed to the different size of metal particles. A diffractometric study of the samples obtained by these two methods indicate that the size of the polycrystalline rhodium metal deposited on the polyphosphine is smaller than 50–100 Å. Table III shows the reactions examined. When benzylmethylketone is the substrate, the aromatic ring also is hydrogenated, in accordance with the fact that rhodium was proved active for ring hydrogenation[19] and would be the metal of choice for total reduction.

One further important fact is pointed out by exp. 17 in Table I. In this case reduction of acetophenone does not produce rhodium metal. This differing behaviour depending on the ketone to be reduced, albeit requiring further investigation, may be related to the ability of aromatic ketones to form stable complexes thereby decreasing their ease of hydrogenation.

Conclusions

All supported catalysts employed can be reused without extensive loss of activity after filtration with no peculiar precautions. If the catalyst is dried under vacuum it becomes appreciably less active.

At the end of the hydrogenation, norbornane is present in the solution. In analogy with the process in homogeneous phase this might be taken as an indication that an active species closely related to a Rh^{III} dihydride is present[11–13] on the polymer



L = Phosphine; S = Solvent

Catalysts prepared with method B show no ESR signals after use, and possibly a reaction path similar to that found in homogeneous phase might be operative. At variance a more complex reaction pathway could be suggested in the case of catalysts prepared with method A where the presence of appreciable amount of Rh^{II} species could play an important role in the hydrogenation process. The i.r. spectrum of both types of catalysts in KBr, displays no band attributable to a ν(Rh–H) stretch in the region 2300–1900 cm^{-1}. This may be due to the high dilution of the complex in the resin compounded with a weakness of this band.

In conclusion, many factors affect the selectivity, activity, and stability of immobilized catalysts related to $[Rh(NBD)LL')]^+$, such as: (*i*) basicity of ligands. This seems to be the foremost parameter, together with the bulkyness of substituents on the phosphorus, in devising a "tailor-made" supported catalyst that will hydrogenate selectively ketones and olefins; (*ii*) the solvent or the substrate itself with their ability to cause swelling of the polymer. This also indicates that most of the reduction takes place inside the polymer bead; (*iii*) the "chelating" ability of the polymer – or the P/Rh ratio. These factors play an essential role in

TABLE III. Hydrogenation of Unsaturated Substrates using Rhodium Metal Supported on Polyphosphine (5% in Rhodium). Substrate/Rhodium = 1000; Temperature 20° C.[a]

Substrate	Product (Yield %)	Reaction Time, hr	pH_2 psig
Acetone	iso-Propanol (100%)	5	5
MethylEthylKetone	sec-Butanol (70%)	5	800
MethylPropylKetone	2-Pentanol (25%)	120	5
BenzylMethylKetone	Benzylmethylcarbinol (12%) 1 Cyclohexyl-2-butanol (3%)	120	20
Benzonitrile	no reaction	48	800
Proprionitrile	Propylamine (7%)	120	14
Cyclohexene	Cyclohexane (60%)	18	40

[a] All runs were carried out in pure substrate. 1% H_2O was always added to ketones and 1% MeOH to nitriles and olefins.

stabilizing the catalysts towards reduction to metal, at least with PolymerPPhMenthyl as the polyphosphine; (*iv*) apart from the cases where a destabilisation of the complex occurs in the polymer bonded catalysts the active species seems to be a trapped Rh^{II} complex, at variance with the related homogeneous reactions. These results probably indicate that either the catalytic reaction proceeds with a different mechanism in homogeneous *versus* heterogeneous phase, or in the latter case the further oxidation of Rh^{II} to Rh^{III} complexes has been hampered by attachement to the polymer.

Experimental

Materials

Analytical grade chemicals and solvents were employed, and were in most cases used without further purification. When even dry, oxygen-free solvents were needed, the commercial solvents were purified following the standard methods,[20] and stored under nitrogen. The purity of solvents and substrates used for hydrogenation experiments were checked by glc.

Complexes [(NBD)Rh(acac)] and $[(NBD)Rh(PEt_3)_2]^+ ClO_4^-$ were prepared by analogous methods reported in the literature for [(ethylene)Rh(acac)][21] or $[(NBD)RhL_2]^+$.[11,14,15]

Merrifield polymer Fluka (200–400 mesh, 2% divinylbenzene, 0.7 meq Cl/g and/or 3.5 meq Cl/g) was used throughout.

This polymer was treated in THF with $Li[PPh_2]$ or with Li[PPhMe][22] to obtain respectively an organic polymer containing benzyldiphenylphosphine or benzylphenylmethylphosphine functional groups prepared by the methods reported.[23] With these methods we obtained phosphinated polymers. Analytical data are reported in Table IV.

Synthesis of PolymerPPhMenthyl

Preparation of PPhMenthylCl

This compound was prepared by the method outlined by Issleib.[22]

$PPhCl_2$ (63 g, 3.5×10^{-1} mol) is put in a 500 ml 3-necked flask, under nitrogen and mechanical stirring; $HNEt_2$ (46 g, 6×10^{-1} mol) was added dropwise. Low temperature was maintained with the aid of a salt–ice bath. Then 200 ml of anhydrous ethyl ether were slowly added, and the reaction mixture was further stirred for 2 hours at room temperature. The white solid was filtered off, washed twice with 100 ml anhydrous ether under nitrogen, and the filtrate concentrated. The oily residue was distilled *in vacuo* to give 47.5 g of pure diethylaminophenylchlorophosphine (b.p. 108 – 115/7 mm; ν(P–N–C) 790 cm^{-1}; 63% yield).

TABLE IV. Analytical Data.[a]

Phosphinated Polymer	Analysis %		% Cl Substituted
	Cl	P	
$PolymerPPhMe$	1.48	7.12	85
PolymerPPhMenthyl	7.38	2.40	26
$PolymerPPh_2$	3.19	5.64	66

[a] Merrifield polymer 3.5 meq Cl/g as starting material.

MenthylMgCl dissolved in anhydrous THF (obtained from 63 g of Menthyl chloride[24–25]) was added dropwise under nitrogen to a cool solution of Et_2N–PPhCl (47.5 g, 2.2×10^{-1} mol) in 100 ml THF with vigorous stirring. Then the mixture was refluxed for 5 hours, cooled, maintained at room temperature overnight, filtered under nitrogen, concentrated, and distilled *in vacuo* to give 38 g of pure diethylaminophenyl-menthyl phosphine (b.p. 150–155/3 mm Hg: $\nu(PNC) = 790$ cm^{-1}; $[\alpha]_D^{20} = -52.4$, C 30.82 THF; 55% yield) as an oily, colourless, air sensitive liquid.

Through a solution of Et_2N–PPh menthyl (38 g, 1.2×10^{-1} mol) in 100 ml of anhydrous petroleum ether, dry hydrogen chloride was bubbled with stirring. Excess HCl was removed from the slurry by bubbling N_2; $HNEt_2HCl$ was filtered off under nitrogen, and the filtrate concentrated to give 30 g of phenylmenthylchlorophosphine (ν_{PCl} 500 cm^{-1}).

Preparation of PolymerPPhMenthyl

Lithium (1.5 g) is suspended in anhydrous THF (20 ml) under nitrogen with vigorous stirring. PPhMenthylCl (3 g, 1.1×10^{-2} mol) dissolved in THF (7 ml) is added dropwise. The mixture is refluxed for five hours, then cooled at room temperature and excess Li filtered off under nitrogen. Merrifield polymer (2% DVB; 3.5 mmol Cl/g; 200–400 mesh; 3 g) suspended in THF is added to the filtrate under N_2 with stirring. The solution is discoloured in few minutes. After 2 hr the white resin is filtered off, washed several times with H_2O, MeOH, THF and dried under vacuum (*Anal.:* C 82.51; H 7.63; Cl 7.38; P 2.40%).

Immobilization of Rh^I Cationic Complexes

Method A

[Rh(NBD)(acac)] (250 mg, 0.85×10^{-3} mol) dissolved in 25 ml of THF was added dropwise with stirring to a suspension of PolymerPPhMe (2 g, $P = 4.0 \times 10^{-3}$ mol) swollen in THF. To the resultant solution was added dropwise a 70% solution of $HClO_4$ (150 mg, 10^{-3} mol) in 2 ml of THF. After 15 hr, the mixture was filtered and the solid was washed with MeOH and THF until the washings were colorless, then with dichloromethane and hexane, and dried *in vacuo*.

Complexes immobilized on PolymerPPhMenthyl or $PolymerPPh_2$ were prepared in an analogous way. Resins B and C in Table II were also prepared with this procedure. For the former a lower phosphorus content resin (starting Merrifield resin 0.7 meq Cl/g) was used whereas for the latter a smaller amount of complex was employed.

Method B

PolymerPPhMe (1 g, $P = 2 \times 10^{-3}$ mol) suspended in 10 ml of CH_2Cl_2 was treated with a stoichiometric amount of $[Rh(NBD)(PEt_3)_2]^+$ dissolved in the same solvent. The suspension was allowed to equilibrate for 3 days under nitrogen. The solid was filtered off, washed with CH_2Cl_2, MeOH, THF, acetone, ether and dried *in vacuo*.

The same procedure was adopted to prepare complexes immobilized on PolymerPPhMenthyl of PolymerPPh_2.

Apparatus and Hydrogenation Reactions

For high-pressure hydrogenations the reactants were placed in a glass container fitted in a 200 ml stainless steel autoclave. A J. B. Thompson Co., Cumberland, Md, U.S.A. low-pressure hydrogenator was employed for reactions up to 50 psig.

Infrared spectra were recorded on a Perkin–Elmer 457 spectrophotometer. Gas chromatographic analysis was carried out with a Hewlett–Packard 5750 gas chromatograph. ESR spectra were recorded on a Varian E4 spectrometer in a temperature range 77–323 °K.

Acknowledgement

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References

1 N. Kohler and F. Dawans, *Revue de l'Istitut Francais du Petrol, XXVII,* (1972) 105 and references therein.

2 J. Manassen, D.D. Whitehurst, J.C. Bailar, S. Carrà, M. Graziani, K. Mosbach, R.C. Pitkethly, E.K. Pye, J.J. Rooney, *Catalysis, Progress in Research,* F. Basolo and R.L. Burwell Ed., Plenum Press, London, 1973, 177.

3 E. Cernia and M. Graziani, *J. Appl. Polym. Sci.,* (1974) in press.

4 H. Bruner and J.C. Bailar, *Inorg. Chem., 12,* (1973) 1465.

5 R.H. Grubbs and L.C. Kroll, *J. Am. Chem. Soc., 93,* (1971) 3062.

6 J.P. Collman, L.S. Hegedus, M.P. Cooke, J.R. Norton, G. Dolcetti, D.N. Marquardt, *J. Am. Chem. Soc., 94,* (1972) 1789.

7 M. Capka, P. Svodoba, M. Creny and J. Hetflejs, *Tetrahedron Letters,* 4787 (1971).

8 a) W.O. Haag and D.D. Whitehurst, *Proceedings of the Vth International Congress on Catalysis,* Amsterdam 1972, North Holland Publishing Co., Amsterdam, 1973, and *Patents* reported therein; b) K.G. Allum, P.D. Hancock, J. McKenzie and R.C. Pitkethly, *ibid.*, 1973, and *Patents* reported therein.

9 W. Dumont, J.C. Poulin, T.P. Dang and H.B. Kagan, *J. Am. Chem. Soc., 95* (1973) 8295.

10 R.B. Merrifield, *J. Am. Chem. Soc., 85* (1963) 2149.

11 R.R. Schrock and J.A. Osborn, *J. Am. Chem. Soc., 93* (1971) 2397.

12 M.A. Bennett, R. Bramley and P.A. Longstaff, *Chem. Commun.,* 806 (1966); M.A. Bennett and P.A. Longstaff, *J. Am. Chem. Soc., 91* (1969) 6266.

13 H.J. Keller and H. Wawersik, *J. Organometall. Chem., 8* (1967) 185; M.C. Baird, *Inorg. Chim. Acta, 5* (1971) 46.

14 J.R. Shapley, R.R. Schrock and J.A. Osborn, *J. Am. Chem. Soc., 91* (1969) 2816.

15 R.R. Schrock and J.A. Osborn, *Chem. Commun.,* (1970) 567.

16 R.H. Grubbs, C. Gibbons, L.C. Kroll, W.D. Bonds and C.H. Brubaker, *J. Am. Chem. Soc., 95* (1973) 2373.

17 E. Breitner, E. Roginski and P.N. Rylander, *J. Org. Chem., 24* (1959) 1855.

18 M. Freifelder, *J. Am. Chem. Soc., 82* (1960) 2386.

19 H.A. Smith and R.G. Thompson, *Advances in Catalysis,* Academic Press, New York, 1957.

20 J.A. Riddick and W.B. Bunger, *Organic Solvents,* A. Weissberger III Ed., Wiley–Interscience, New York, N.Y., 1970.

21 R. Cramer, *J. Am. Chem. Soc., 86* (1964) 217.

22 K. Issleib, *Rev. of Pure and Appl. Chem., 9,* (1967) 205.

23 Britisch Petroleum Co. Ltd., *Belgian Patent* 739, 607.

24 J.G. Smith and G.F. Wright, *J. Org. Chem., 17* (1952) 1116.

25 J.D. Morrison, R.E. Burnett, A.M. Aguiar, C.J. Morrow and C. Phillips, *J. Am. Chem. Soc., 93* (1971) 1301.

26 Only a low degree of quaternarization of the phosphine has been found in our case. T. O. Mitchell and D. D. Whitehurst, *Proc. Third North American Meeting of the Catalysis Society,* San Francisco, Calif., 3–6 Feb. 1974.