Journal of Organometallic Chemistry, 369 (1989) 17–28
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09884

Insoluble ligands and their applications

II *. Polysiloxane-phosphine ligands, their complexes, and hydrogenation catalysts

R.V. Parish *, **D. Habibi, and V. Mohammadi**

Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester, M60 1 QD (Great Britain)

(Received February 1st, 1989)

Abstract

Solid polysiloxane ligands containing phosphine groups have been prepared by the hydrolytic condensation of $(EtO)_3Si(CH_2)_nPPh_2$ ($n = 2, 3$) with $Si(OEt)_4$. They have been characterised by solid-state NMR spectroscopy and by reaction with cobalt(II) and nickel(II). Both metals formed complexes of the type MCl_2-$[Ph_2P(CH_2)_n$-$S]_2$ (where S is the polysiloxane matrix), but it was not usually possible to complex all the phosphine groups. The ligands were also treated with $[IrCl(cod)]_2$ (cod = cyclo-octa-1,5-diene), which gave reproducible complexes having significant activity as hydrogenation catalysts. The system appears to be analogous to the homogeneous complex $[Ir(L)_2(cod)$ (L = tertiary phosphine), since both show first-order dependence on the metal and zero-order for hex-1-ene. During hydrogenation with the polysiloxane catalysts, hex-1-ene undergoes isomerisation, but the isomers are hydrogenated at the same rate as the terminal alkene. The catalysts show slight deterioration on re-use, but are still active after 10 cycles.

Introduction

Heterogenized catalysts, in which an analogue of a homogeneous transition-metal catalyst is attached to a solid support, combine the best features of heterogenous and homogeneous systems [1]. The active site is a definable, discrete complex, whose mechanism of action is similar to that of its truly homogeneous counterpart. At the same time, the ease of separation and recovery which characterise heterogeneous catalysts are retained. In recent years, many such systems have been described,

---

* For Part I, see Ref. 2.

0022-328X/89/$03.50

many of which are functionalised organic resins (e.g. polystyrene) or contain ligands bound to inorganic oxides (e.g. silica). The former suffer from the disadvantages of solvent-dependent swelling and porosity, the latter from insecurity of ligand attachment and relatively low concentrations of ligand groups. The preceding paper [2] described some polymeric ligands in which organic amine groups formed an integral part of an insoluble siloxane polymer. We now show the extension of this system to phosphine ligands which are used as supports for hydrogenation catalysts. As far as we are aware, this method has only been briefly described previously [3,4].

Results

The ligands

The novel siloxane ligands were prepared by the hydrolytic condensation of $(EtO)_3Si(CH_2)_nPPh_2$ ($n = 2, 3$) with $Si(OEt)_4$ in the presence of $Bu_2Sn(OAc)_2$ as catalyst. In the absence of $Si(OEt)_4$, chloroform-soluble oils were obtained, presumably similar to the oligomeric siloxanes described by Brisdon [5]. The $Si(OEt)_4$ acts as a cross-linking agent, giving porous, solid polymers, $S\text{-}(CH_2)_nPPh_2$, where S stands for the siloxane matrix. Various mole ratios of the reactants were used, and reactions were performed in ethanol or toluene as solvent. Preparative and analytical details are given in Table 1. As was observed previously [2], the absolute percentages of C, H, and P are generally lower than those expected for the simplest formulation corresponding to the reaction stoicheiometry. This indicates a loss of

Table 1

Preparative and analytical data for phosphine-polysiloxanes $S\text{-}(CH_2)_nPPh_2$

Batch	Solvent	Method [a]	Reactant ratio [b]	%C	%H	%P	C/P
n = 2							
1	EtOH	A	2	39.5	4.2	6.8	14.3
2	EtOH	A	1.5	42.9	5.1	6.3	17.5
3	(EtOH)	B	(2)	20.7	3.6	1.5	35.6
n = 3							
4	(EtOH)	C	(2)	25.8	4.2	1.7	39.2 [c]
5	EtOH	A	2	39.4	4.7	6.1	16.2
6	EtOH	A	3	35.7	4.4	5.4	17.1
7	EtOH	A	4	32.8	4.2	4.6	18.4
8	Toluene	A	2	40.7	4.0	6.5	16.2
9	Toluene	A	3	35.1	4.1	5.0	18.1
10	Toluene	A	4	33.2	3.7	4.4	19.5
11	EtOH	D	2	40.2	4.2	6.6	15.7
12	EtOH	D	3	37.5	3.9	5.6	17.3
13	EtOH	D	4	32.4	4.1	4.6	18.2
14	Toluene	D	2	35.9	4.2	5.5	16.8
15	Toluene	D	3	34.3	4.0	5.0	17.7
16	Toluene	D	4	35.7	4.1	5.0	18.4

[a] A = $Si(OEt)_4$ added before $(EtO)_3(CH_2)_nPPh_2$. B = $Si(OEt)_4$ polymerised with $(EtO)_3SiCH{:}CH_2$, and the product reacted with $HPPh_2$. C = $Si(OEt)_4$ polymerised with $(EtO)_3Si(CH_2)_3Cl$, and the product reacted with $HPPh_2$. D = $(EtO)_3Si(CH_2)_3PPh_2$ added before $Si(OEt)_4$. [b] Mole ratio of $Si(OEt)_4$ to $(EtO)_3(CH_2)_nPPh_2$. [c] Cl = 5.8%; Cl/P = 3.0.

some phosphine-bearing oligomers during the condensation or washing processes. In addition, the C/P mole ratios are usually greater than expected, for which there are two major causes. First, the hydrolysis may be incomplete, especially when conducted in ethanol, resulting in the presence of some residual ethoxy groups. Second, the catalyst may become incorporated into the polymer (^{119}Sn Mössbauer and NMR evidence is given below). Both these effects would increase the proportion of carbon.

Two other preparative methods were briefly investigated. In the first, a vinyl-functionalised polymer was prepared by co-condensation of $Si(OEt)_4$ with $(EtO)_3SiCH:CH_2$. The resulting polymer was treated with diphenylphosphine under ultra-violet irradiation. Analytical data (Table 1, batch 3) showed that only about 10% of the vinyl groups had reacted after 100 h, presumably because of the difficulty of irradiating an opaque suspension. In the second method, the analogous 3-chloropropyl polymer was prepared from $(EtO)_3Si(CH_2)_3Cl$, and then refluxed with diphenylphosphine. In this case, about 25% of the functional groups reacted in 24 h. This result is consistent with the suggestion made below that some of the functional groups in these polymers are inaccessible to relatively bulky reagents. In confirmation, it was found that the 3-chloropropyl-functionalised polymer reacted well (75%) with aniline but only about 5% with the bulkier diphenylamine.

The ^{29}Si CPMAS NMR spectra of two of the polymers both show two major resonances, centred on about -105 and -60 ppm (relative to TMS). These correspond to $Si(O)_4$ and $RSi(O)_3$ units respectively ($R = (CH_2)_nPPh_2$). Each of these, fairly broad, resonances is composed of at least two peaks, indicating the presence of units with different sets of neighbouring groups, e.g. $Si(OSiO_3)_4$, $Si(OSiO_2R)(OSiO_3)_3$, $Si(OSnBu_2)(OSiO_3)_3$, etc. The ^{13}C spectra showed, in addition to strong phenyl resonances at 130 ppm, signals characteristic of $-OCH_2-$ (51, 60 ppm), CH_3COO (179, 186 ppm), and $-CH_2-$ (14, 18, 27 ppm), indicating the presence of ethoxy, acetate and butyl groups. The ^{31}P spectra showed strong signals (9, 17 ppm) consistent with $-(CH_2)_nPPh_2$ groups, and confirmed the absence of phosphine oxide.

The presence of tin in the polymer with $R = (CH_2)_3Cl$ was confirmed by the ^{119}Sn Mössbauer spectrum. No spectrum was obtainable at room temperature, but at 80 K a doublet was observed: $IS(SnO_2) = 1.26$ mm s^{-1}, $QS = 2.82$ mm s^{-1}. These parameters are consistent with a four-co-ordinate diorganotin(IV) species [6], the other two ligands presumably being oxygen atoms of the polymer matrix.

These data are consistent with the formation of rigid, three-dimensional siloxane matrices in which 15–25% of the silcon atoms carry ligand groups.

Metal-uptake

The polymers were further characterized by their ability to form complexes with cobalt(II) and nickel(II). In all cases, uptake of the metal ions from ethanolic solution was relatively slow, reaching saturation only after 24–48 h: the data given in Table 2 for ligands $S-(CH_2)_3PPh_2$ are typical. The sluggish uptake indicates that many of the phosphine sites are situated in narrow pores, access to which is limited by slow diffusion. In the majority of cases, significant fractions of the sites are completely inaccessible, or possibly are blocked by the earlier bound metal ions, since in only two cases did the P/M ratio approach 2/1 (Table 2). The colours of the metal-treated polymers (blue and dark red) suggested that the complexes formed were tetrahedral $(P)_2CoCl_2$ and square-planar $(P)_2NiCl_2$ respectively. These assign-

Table 2

Metal-uptake data for the S-$(CH_2)_3PPh_2$ ligands

Batch	Time (h) 0.5			6.0			24			48		
	%P	%M	P/M	%P	%M	P/M	%P	%M	P/M	%P	%M	P/M
Cobalt												
5	6.0	0.3	38	6.1	1.0	11	6.0	2.3	5.0	5.8	3.5	5.5
7	4.2	0.2	40	6.1	1.0	9.5	4.6	1.8	4.9	4.5	2.4	3.6
8	6.4	0.5	24	6.3	1.0	12	6.2	3.2	3.6	5.8	3.5	3.2
10	4.7	0.7	13	4.3	1.4	5.9	4.4	2.6	3.2	4.4	1.9	4.4
11	6.5	0.2	61	6.2	0.3	39	6.5	1.8	6.8	6.3	1.9	6.3
13	4.6	0.1	86	4.6	0.1	86	4.6	1.2	7.2	4.6	1.2	7.2
14	6.6	0.2	63	6.6	0.2	63	6.5	1.7	7.3	4.8	4.9	1.9
16	4.3	1.3	6.3	4.6	2.6	3.5	4.7	3.6	2.5	4.7	4.6	1.9
Nickel												
5	5.5	0.2	52	6.0	0.9	13	5.8	1.6	6.8	5.5	1.9	5.5
7	4.0	0.2	38	4.6	0.6	15	4.6	1.8	4.8	4.6	1.6	5.4
8	6.3	0.3	39	6.4	0.8	15	6.3	1.9	6.2	6.0	1.6	7.0
10	4.7	0.4	22	4.7	1.1	8.0	4.3	1.9	4.2	4.3	1.8	4.5
11	6.3	0.1	118	6.4	0.5	24	6.5	0.6	20	6.4	0.8	15
13	4.4	0.1	82	4.6	0.4	22	4.7	0.6	15	4.7	1.0	8.8
14	6.6	0.1	125	6.5	0.2	62	5.0	1.9	5.0	4.8	2.0	4.5
16	4.4	1.2	7.0	4.3	1.5	5.4	4.7	2.3	3.9	4.8	3.0	3.0

ments were confirmed by comparison of the visible reflectance spectra of the complexes with those for the known complexes $MCl_2(PPhPr^n_2)_2$, diluted with the metal-free polymer; the spectra were essentially identical, giving absorption at $\bar{\nu} = 15.2$, 15.8, and 16.9 kK (M = Co), and 20.8 and 26.3 kK (M = Ni) for the polymers, and 15.2, 15.8, 16.9 kK (M = Co), and 21.7, 26.2 kK (M = Ni) for the propyldiphenylphosphine complexes. It is noticeable that the uptake of cobalt(II) by any given polymer was usually both quicker and greater than that of nickel(II). In the ethanolic solution employed, both metals would be present as octahedrally solvated ions, of which that containing cobalt is expected to be slightly the more labile. It is also possible that the differences are related to the different stereochemistries adopted by the two metals. Tetrahedral cobalt(II) and *trans*-planar nickel(II) would require different optimum spacings of adjacent phosphine groups.

In the metal-uptake experiments, with cobalt(II) and nickel(II) and with the catalytic metals, it was found that stirring the polymer with the solution gave a much higher uptake than when the mixture was simply shaken. This is due to the reduction in particle size which occurs on prolonged stirring, effectively increasing the available surface area and number of accessible ligand sites.

Catalysis

For the catalytic work, two polymeric ligands S-$(SCH_2)_nPPh_2$ were chosen [batches 1 ($n = 2$) and 16 ($n = 3$)] on the basis of their metal uptake which indicated relatively open structures. Catalysts were prepared by treating the solid ligand with a solution of $[RuCl_2(PPh_3)_3]$, $[RhCl(PPh_3)_3]$, $[RhCl(cod)]_2$, $[RhCl(coe)_2]_2$, $[IrCl(coe)_2]_2$, or $[IrCl(cod)]_2$ (coe = cyclo-octene, cod = cyclo-octa-1,5-diene). Chloroform solutions were found to give higher loading of metal than toluene. Activity was assessed by following the rate of hydrogen uptake at 1 atm (gas burette) and room temperature, using a solution of hex-1-ene in ethanol. The catalysts derived from the rhodium and ruthenium complexes were found to give relatively low activity or to become deactivated during the course of a single experiment. Those based on $[IrCl(cod)]_2$ had good activity and re-usability, and were examined in detail.

Three methods for the preparation of the catalysts were investigated. Initially, a solution of $[IrCl(cod)_2]_2$ was stirred with the ligand using a magnetic stirrer.This led to good metal uptake but also to severe degradation in particle size: much fine dust was produced which would not readily settle when stirring was stopped. There were also correlations between metal uptake and stirring time and between metal uptake and initial particle size, showing that reduction in particle size made available a greater surface area, by exposing some the narrower pores. However, these materials were prone to decomposition under hydrogenation conditions, becoming dark coloured and sometimes producing a dark colouration in the liquid phase.

Materials produced by shaking the ligand with the iridium solution in the cold (K2, K16), or refluxing the solution (R6–9) had good stability under hydrogenation conditions. Refluxing gave, in general, rather higher metal-uptake (Table 3). However, when used for the hydrogenation of hex-1-ene, the rate of reaction was very dependent on the metal-content, even though the same total amount of iridium was employed in each experiment (Table 4, expts. 1–3); leaching of the active species into the solution was suspected. This was confirmed by adding the free, unmetallated ligand to catalyst R7 so that the overall P/Ir ratio was the same as that for

Table 3

Analytical data for catalysts

No.	%P	%Ir	P/Ir	
R6	5.4	11.6	2.9	< 100 mesh
R7	6.0	6.3	5.4	< 100 mesh
R8	6.6	3.6	11	< 100 mesh
R9	6.7	1.1	38	< 100 mesh
K2	6.0	2.1	18	80–100 mesh
K16	4.1	6.3	4.0	80–100 mesh

catalyst R8. The rates for the two systems were the same (expt. 4). That is, increasing the number of free ligand sites allows leached metal to be recomplexed [7], and rendered less active. When R7 was recovered from expt. 1 and used again,

Table 4

Hydrogenation data for catalysts from batch 1

Expt. No.	No.	Catalyst		Olefin [a] (mmol)	Solvent [b] (cm^3)	Initial rate ($cm^3(H_2)$ min^{-1} $mmol(Ir)^{-1}$)	Comments
		Amount (mg)	Ir (μmol)				
1	R7	70	25	4	3	19	P/Ir = 5.4
2	R8	140	25	4	3	11	P/Ir = 11
3	R9	440	25	4	3	7.2	P/Ir = 38
4	R7+L		25	4	3	12	P/Ir = 11
5	R6	40	24	8	3.0	10	ethanol solvent
6	R6	40	24	8	3.0	1.3	toluene solvent
7	K2	150	16	2	3.5	11	ethanol solvent
8	K2	150	16	30	none	1.9	neat hex-1-ene
9	K2	150	16	2	3.5	11	hex-1-ene
10	K2	150	16	2	3.5	9.1	oct-1-ene
11	K2	150	16	2	3.5	4.3	cyclo-hexene
12	K16	100	32	4	18	31	hex-1-ene
13	K16	96	31	4	18	21	3,3-Me_2but-1-ene
14	K16	123	39	4	18	13	cyclo-hexene
15	K16	101	32	4	18	4.4	cyclo-octa-1,5-diene
16	K2	75	82	2	3.5	15	first-order in catalyst
17	K2	30	33	2	3.5	11	
18	K2	15	16	2	3.5	11	
19	K16	100	32	16	18	30	
20	K16	150	48	16	18	31	
21	K16	200	64	16	18	32	
22	K2	150	16	2	3.5	12	zero-order in hex-1-ene
23	K2	150	16	4	3.25	11	
24	K2	150	16	8	2.75	11	
25	K16	100	32	16	3.0	26	
26	K16	100	32	16	8.0	30	
27	K16	100	32	16	13	28	
28	K16	100	32	16	18	31	

[a] Hex-1-ene unless specifed otherwise under Comments. [b] Ethanol unless specified otherwise under Comments.

the rate of reaction was almost halved and at the end of this reaction the iridium content was only 40% of that of the unused catalyst.

In marked contrast, catalysts prepared by shaking the support with $[IrCl(cod)]_2$-solution in the cold could be re-used without any appreciable metal loss. For instance, catalyst K16 was used in ten hydrogenation experiments, after which the analytical data were indistinguishable from those of the original catalyst (P, 4.1, 4.2%; Ir, 6.3, 6.3%). Lack of leaching was also confirmed by the fact that, when fresh reagents were added to the separated liquid products, no further hydrogenation occurred. These materials were therefore studied in some detail (Table 4).

For hex-1-ene, reaction was much faster with ethanol as solvent than in toluene or in the neat alkene (expts. 5–8). The rate of hydrogenation depended on the alkene: oct-1-ene reacted only slightly more slowly than hex-1-ene, but the rate decreased markedly for 3,3-dimethylbut-1-ene, cyclo-hexene and cod in that order (expts. 9–15). Systematic studies were therefore carried out with hex-1-ene in ethanol. Care was taken that the agitation of the mixture did not result in crushing of the solid catalyst: either the reaction vessel was shaken or a specially shaped blade stirrer was used, which provided adequate clearance from the sides of the vessel. Catalyst preparation was quite reproducible: two samples of the solid ligand were shaken with the same iridium solution, to yield catalysts containing 0.9 and 1.0% iridium which gave hydrogenation rates of 5.7 and 5.8 $cm^3(H_2)\ min^{-1}\ mol(Ir)^{-1}$.

When the initial hexane concentration was kept constant, the rate of uptake of hydrogen was accurately proportional to the amount of catalyst present (expts. 16–21), demonstrating first-order dependence on the catalyst. During any single run, the rate of uptake was effectively constant for at least 50% reaction (runs were not normally continued beyond this point), suggesting that the reaction is zero-order in hexane. This is confirmed by expts. 22–28, in which the concentration of the alkene was varied with no effect on the rate. Such behaviour is very similar to that

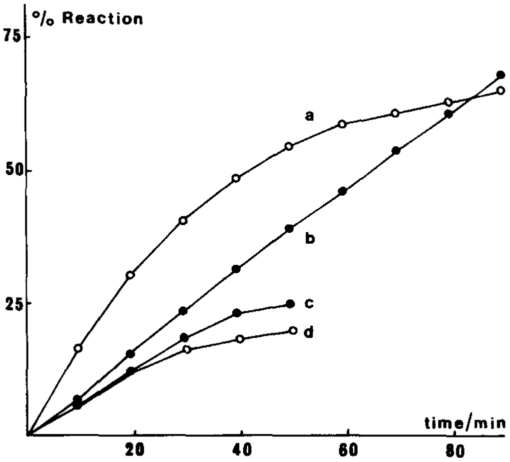

Fig. 1. Homogeneous vs. heterogeneous catalysts. (a) and (d) $[IrCl(cod)]_2 + 4PPh_2Pr$; (b) catalyst K2; (d) catalyst K16. Conditions: (a) and (b), hex-1-ene 2 mmol, Ir 33 μmol, EtOH 3.5 cm^3; (c) and (d), hex-1-ene 16 mmol, Ir 80 μmol, EtOH 18 cm^3.

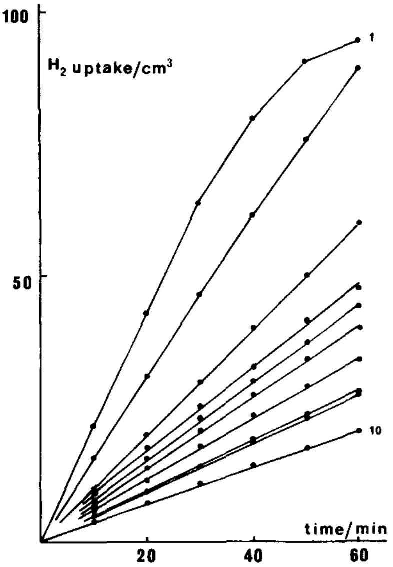

Fig. 2. Successive re-use of catalyst K_{16}. Conditions: hex-1-ene, 16 mmol; Ir, 65 μmol; EtOH 18 cm^3.

of the iridium(I)-phosphine-cod catalyst used by Crabtree [8] and, indeed, the rates of reaction are comparable (Fig. 1). However, the homogeneous catalyst deactivates rather rapidly, while the supported counterpart maintains its activity.

On re-use, there is slow loss of activity of the siloxane-supported catalyst. With catalyst K16, there was slight loss of activity during the first run, suggesting loss of a little active material or rearrangement within the catalyst. Subsequent runs showed only very slight decline in rate during any one run (typically about 15%), and a

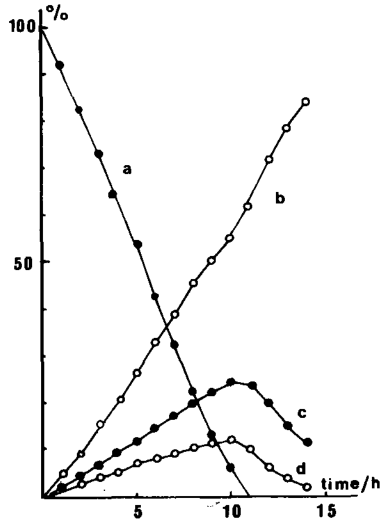

Fig. 3. Product profile during hydrogenation of neat hex-1-ene over catalyst K16. (a) hex-1-ene; (b) n-hexane; (c) *trans*-hex-2-ene; (d) *cis*-hex-2-ene.

small loss of activity between runs, e.g. the rate in run 10 (Fig. 2) is still 25% of that in run 2. It is possible that this decline in activity between runs may have been due to the difficulty of preventing exposure of the catalyst to the air during recovery and washing. The analytical data mentioned above show that there is no loss of iridium.

The majority of hydrogenation catalysts give rise to some concomitant isomerisation of the alkene. This may result in a decrease in rate, since internal alkenes are often hydrogenated more slowly than terminal alkenes. This possibility was investigated by gas-chromatographic analysis of the products during the course of a single run. For simplicity, no solvent was used. The data for the hydrogenation of hex-1-ene over K16 are shown in Fig. 3. Significant isomerisation does occur, giving a maximum of about 25% of hex-2-enes. However, the rates both of the formation of hexane and of the disappearance of hex-1-ene are effectively constant throughout the reaction. It can therefore be concluded that the rate of hydrogenation of the isomeric hexenes is very similar to that of hex-1-ene, and that the rate of isomerisation is comparable to that of hydrogenation. Indeed, the ratio of hexane to *trans*-hex-2-ene is constant while hex-1-ene is still present, 1/0.43, and the corresponding ratio for *cis*-hex-2-ene decreases only slowly, from 1/0.3 to 1/0.22.

Discussion

Heterogenized catalysts in which ligand groups are grafted on to silica sometimes suffer from leaching of active material under operating conditions, which may involve loss of the catalytic metal or of the anchoring ligand [9]. Both these disadvantages have been overcome by the present system, in which the ligand groups are securely incorporated into a siloxane polymer. The major disadvantage is that some of the ligand groups are relatively inaccessible, presumably being situated in narrow pores. No information is available about the distribution of the phosphine groups, but the solid-state NMR data show that all have similar environments. The spectra also show that no oxidation of the phosphine has occurred, in marked contrast to silica-supported systems [10].

Complexation of $S\text{-}(CH_2)_nPPh_2$ with cobalt(II) or nickel(II) shows the formation of bis-phosphine complexes, and in some cases products with a P/M ratio of 2/1 could be obtained. There appears to be no change in the nature of the complexes (as judged by their colours) with increasing metal-content. It is clear, therefore, that a large proportion of the phosphine groups are close enough that two groups may coordinate to the same metal atom, and that this is the preferred mode of coordination, even when a significant number of groups remain uncoordinated. Catalytically active materials were obtained by reaction of the ligand with $[IrCl(cod)]_2$. The stoicheiometry and coordination geometry of these complexes are not known but, in view of the nature of the cobalt and nickel complexes, it is likely that a bis-phosphine complex (**2**) is formed here also:

$$(cod)IrCl/2 \rightarrow \underset{(\mathbf{1})}{(cod)Ir(Cl)Ph_2P(CH_2)_n\text{-}S} \rightarrow \underset{(\mathbf{2})}{(cod)Ir[Ph_2P(CH_2)_n\text{-}S]_2^+}$$

Double attachment would also be consistent with the resistance to leaching which these catalysts show.

Species **2** is directly analogous to the homogeneous system described by Crabtree [8,11], and there is marked parallelism between the two. Thus, under comparable conditions, the rates of reaction and the kinetic behaviour are very similar (first-order in metal complex, zero-order in alkene). The heterogenized catalyst shows slightly more discrimination between alkenes, but this could be accounted for by some restriction of access due to the proximity of the polymer surface. It is also noticeable that the rates of reaction of the catalyst with the shorter chain (K2, $n = 2$) are slightly but consistently lower than for $n = 3$ (K16). We presume that the homogeneous and heterogenized systems function by the same mechanism [11], i.e. hydrogenative displacement of the diene and formation of a bis-alkene bis-phosphine iridium(I) complex (**3**) which reacts rapidly with hydrogen to form a dihydrido-iridium(III) species (**4**). Rearrangement to a monohydrido-alkyl-alkene complex (**5**) followed by loss of alkane and regeneration of **3** completes the catalytic cycle. The rearrangement of **4** to **5** is the rate-determining step, which accounts for the zero-order dependence on alkene concentration [8,11]. The considerable reduction in rate when toluene or hex-1-ene was used as solvent may indicate competition between the alkene and the chloride counterion in the formation of **3**.

$$\begin{tikzcd}
\underset{(2)}{(P)_2Ir(cod)^+} \arrow[r] & \underset{(3)}{(P)_2Ir(CH_2:CHR)_2{}^+} \arrow[dr] & \\
\underset{(5)}{(P)_2Ir(H)(CH_2:CHR)(CH_2CH_2R)^+} \arrow[ur] & & \underset{(4)}{(P)_2IrH_2(CH_2:CHR)_2{}^+} \arrow[ll]
\end{tikzcd}$$

A major drawback of the homogeneous $[Ir(cod)(L)_2]^+$ systems is their ease of deactivation. This appears to be due to the formation of dimeric species of the type $[L_2(H)Ir(\mu\text{-}H)_3Ir(H)L_2]^+$ which are inactive [8]. In the case of the heterogenized catalysts, such processes are unlikely, since the P/Ir ratios suggest that the metal atoms will be well separated and unable to dimerise; deactivation rates are low.

A further advantage of the heterogenized system is its ease of recovery and re-use. It is likely that exposure to the air must be avoided, but it is simple to maintain an atmosphere of hydrogen. Alternatively, the catalyst can be allowed to settle so that products can be withdrawn and replaced by fresh reactants. The polymer does appear to be rather soft and easily broken down into very small particles, so that care has to be taken with stirring; the best solution would be to use the hydrogen gas itself.

Thus, the polymeric siloxane appears to have considerable potential for use as a catalyst support, and we are currently investigating other catalytic systems and also the preparation of polymers with a more open pore structure which will allow more efficient use of ligand groups within the polymer.

Experimental

2-Diphenylphosphinoethyl(triethoxy)silane. $Ph_2P(CH_2)_2Si(OEt)_3$, was prepared as described by Allum et al. [12] from vinyltriethoxysilane and diphenylphosphine. The $(CH_2)_3$-analogue was prepared similarly from allyltriethoxysilane, obtained from trichlorosilane and allyl chloride [13].

Siloxane polymers, $S\text{-}(CH_2)_nPPh_2$

A typical preparation was as follows. Water (1.98 g, 0.11 mol) and ethanol (15 cm^3) were added to 3-diphenylphosphinopropyl(triethoxy)silane (7.82 g, 0.02 mol) at room temperature, with stirring. After 30 min, tetraethoxysilane (8.34 g, 0.04 mol) followed by dibutyltindiacetate (1.0 g) were added, and the mixture allowed to stand. After 4–8 h, the resulting solid was crushed, dried at 100 ° C, washed with and alcolhol and redried.

The effects of changing the order of addition or the ratio of reactants were investigated.

Cobalt and nickel uptake

About 1.0 g of the polymeric ligand was shaken or stirred with an ethanolic solution of the metal chloride (25 cm^3, 0.1 mol dm^{-3}) for the appropriate time. The solid was then filtered off, washed thoroughly with water, dried, and analysed.

Catalyst preparation

The polymeric ligand was shaken, stirred or refluxed with a solution of the appropriate metal complex for 24–72 h. The solid was separated by filtration, thoroughly washed with the solvent, and dried in vacuum.

Hydrogenation experiments

The reaction vessel was a three-necked 25 cm^3 pear-shaped flask equipped with a gas-inlet and -outlet and a serum cap, and attached to a gas burette. The vessel was either shaken or stirred by mechanical stirrer with a glass blade shaped to avoid crushing the solid catalyst. The flask was charged with the catalyst and solvent, and it and the gas burette were flushed with hydrogen for 30 min. The alkene was injected by syringe, and the consumption of hydrogen monitored at 10-min intervals.

For product-analysis, the reaction was conducted without solvent, replenishing the hydrogen as necessary. Samples of the liquid phase (10 μl) were withdrawn by syringe and analysed by GLC (50 m × 0.32 mm Plot Al_2O_3/KCl fused silica capillary column).

Acknowledgements

We are indebted to the SERC Solid-State NMR Service at Durham for providing spectra.

References

1 D.C. Bailey and S.H. Langer, Chem. Rev., 81 (1981) 109; A. Guyot, M. Bartholin, Prog. Polym. Sci., 8 (1982) 277; P. Hodge, Chem. Brit., 14 (1978) 237.
2 I.S. Khatib and R.V. Parish, J. Organometal. Chem., 369 (1989) 9.
3 A. Guyot and M. Bartholin, Inf. Chem., 166 (1977) 221, 227.
4 F.G. Young, Ger. Pat., (1974) 2330; Chem. Abstr., 80 (1974) 121737.
5 B.J. Brisdon and A.M. Watts, J. Chem. Soc., Dalton Trans., (1985) 2191.
6 R.V. Parish in G.J. Long (Ed.), Mössbauer Spectroscopy Applied to Inorganic Chemistry, Plenum, New York, Vol. 1, 1984, p. 527.
7 R.V. Parish and M.I. Vania, J. Organomet. Chem., 263 (1984) 139.
8 R.H. Crabtree, Acc. Chem. Res., 12 (1979) 331.
9 R.V. Parish and M.I. Vania, J. Organomet. Chem., 260 (1984) 41.
10 L. Bemi, C. Clark, J.A. Davies, C.A. Fyfe, and R.A. Wasylishen, J. Amer. Chem. Soc., 104 (1982) 438.

11 R.H. Crabtree, P.C. Demou, D. Eden, J.M. Mihelcic, C.A. Parnell, J.M. Quirk, and G.E. Morris, J. Amer. Chem. Soc., 104 (1982) 6994.

12 K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.C. Pitkethly, and P.J. Robinson, J. Organomet. Chem., 87 (1975) 203.

13 N. Furuya and T. Sukawa, J. Organomet. Chem., 96 (1975) C1.