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SUPPORTED TRANSITION METAL COMPLEXES

III*. CATALYSTS FOR THE HYDROGENATION OF OLEFINS AND DIENES

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Summary

Phosphine complexes of rhodium, iridium, ruthenium and platinum have been chemically bonded to the surface of silica. These heterogeneous complexes catalyse the hydrogenation of olefins and dienes and most retain substantial hydrogenation activity in the presence of mercaptans. Variation of the phosphine and halide ligands in complexes of the type "MXP_2" (where M = Rh, Ir; X = halide; P = tertiary phosphine group linked to silica) has little effect on their hydrogenation activity in the presence of mercaptans.

Introduction

The field of supported transition metal complexes is attracting widespread interest at the present time [1–3]. The objective of this work is to combine the advantages of homogeneous catalysts with the greater ease of operation in industrial processes afforded by heterogeneous catalysts. The results of several groups of workers have demonstrated that the properties of transition metal complexes are largely retained when the metal is attached to the surface of a suitable macromolecular support via a liganding group, and some examples of the operation of such catalysts under continuous flow conditions have been reported [4,5].

In most of the work reported to date, organic polymers containing groups capable of co-ordinating to a metal centre have generally been used as the macromolecular support material. Work in our own laboratories has been concerned with both organic polymers [6] and silica [7] as the support. The use of silica can offer certain advantages, including the ability to prepare a ligand—silane

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* For part II see ref. 7.

complex in solution by conventional techniques and then to attach the complex to the silica in a separate stage via condensation between the ligand—silane and the silica surface (see Scheme 1). This method offers far greater control of the metal : ligand ratio in the complex, and is of particular value when complexes with several different metal : ligand ratios can be formed.

SCHEME 1

(a) $6(EtO)_3SiCH_2CH_2PPh_2 + [RhCl(COD)]_2 \rightarrow 2[[(EtO)_3SiCH_2CH_2PPh_2]_3RhCl]$

(ligand—silane) (complex precursor) (homogeneous complex)

(b) $\wr\!-OH + [(EtO)_3SiCH_2CH_2PPh_2]_3RhCl \rightarrow [\wr\!-O-Si-CH_2CH_2PPh_2]_3RhCl$

(silica surface) (homogeneous complex) (heterogeneous complex)

The present paper describes the preparation of tertiary phosphine complexes of transition metals (particularly rhodium and iridium) linked to the surface of silica, and the use of these materials as catalysts for the hydrogenation of both olefins and dienes. Since many petroleum based hydrocarbon feedstocks contain traces of sulphur compounds, the activity of these catalysts in the presence of low levels of mercaptans was investigated and these results are also described.

Results

1. Preliminary studies

In the initial investigation, a series of complexes of rhodium, iridium, ruthenium and platinum linked to silica were prepared. With the exception of the platinum complex, all were prepared by reaction of a complex precursor (e.g. $[RhCl(COD)]_2$) with the ligand—silane $(EtO)_3SiCH_2CH_2PPh_2$ in the desired stoichiometric ratio followed by condensation of the triethoxysilyl groups with hydroxyl groups on the surface of the silica. (The formula $SIL-(CH_2)_2-PPh_2$ is used to denote the tertiary phosphine ligand attached to silica). These complexes were then tested as heterogeneous catalysts for the hydrogenation of olefins (hex-1-ene, hept-3-ene and cyclohexene) and isoprene. (All conversions and yields are recorded as per cent mol. Metal: substrate molar ratios are generally about 1 : 4000 with respect to each olefin or diene. Full quantitative details are given in the Experimental section).

(a) Rhodium complexes

A rhodium complex believed to be analogous to Wilkinson's complex was prepared by the reaction of $[RhCl(COD)]_2$ with $(EtO)_3SiCH_2CH_2PPh_2$ with a molar ratio of Rh : P of 1 : 3 using the procedure of Ohno and Tsuji [8]. The product was obtained as a red oil and was linked to silica by refluxing a benzene solution with silica for 3 h. A deep red silica (Rh/1) was obtained, which typically contained 0.9% rhodium.

This complex was tested for the hydrogenation of a solution of hex-1-ene (20% vol in n-heptane) at 60°C. At 1 atm pressure of hydrogen a conversion of hex-1-ene of 50% with a 22% yield of n-hexane and a 23% yield of isomeric hexenes was obtained over 3.5 h. When the pressure was increased to 10 atm complete conversion to hexane was achieved within 2.5 h. Hydrogenation of internal olefins was slower, and with hept-3-ene (30% vol. in benzene) at 80°C under 15 atm over 1.5 h only 40% conversion to n-heptane occurred. When the temperature was raised to 100° C, the catalyst blackened during the reaction and examination by electron microscopy revealed the presence of crystallites of rhodium metal. With isoprene (30% vol. in benzene), there was only a trace of hydrogenation over 2 h at 50° C under 15 atm pressure. When the temperature was raised to 80° C, the yield of isopentenes increased to 11%, but at 100° C the catalyst blackened indicating some decomposition.

The effect of sulphur compounds on the activity of the rhodium complex was then examined [9]. It was found that mercaptans (e.g. n-butylmercaptan) reacted with the supported rhodium complex to give a new species which although less active as a hydrogenation catalyst than the original complex was thermally much more stable and did not decompose even when used at 200° C under 15 atm pressure of hydrogen. Thus, in the presence of n-butylmercaptan (at a concentration of 700 ppm of sulphur) a 98% conversion of hex-1-ene with an 85% yield of hexane was obtained in the hydrogenation of hex-1-ene (25% vol. in benzene) at 140° C under 15 atm pressure.

(b) Iridium complexes

$[IrCl(COD)]_2$ was reacted with $(EtO)_3SiCH_2CH_2PPh_2$ (Ir:P ratio 1:2) and linked to silica to give an orange silica containing 2.6% weight Ir (Ir/1). This was tested for the hydrogenation of hex-1-ene and cyclohexene both in the absence and presence of n-butylmercaptan (Table 1). The iridium complex is less readily decomposed in hydrogen than the rhodium complex Rh/1 and is stable at 120° C in the absence of mercaptan. The presence of mercaptan significantly lowers the hydrogenation activity as indicated particularly by the conversions of cyclohexene. The complex hydrogenated isoprene (20% vol. in benzene) in the presence of n-butylmercaptan to give isopentenes and isopentane in yields of 36% and 9% respectively at 140° C and 15 atm pressure over 3 h.

(c) Ruthenium complexes

Ruthenium acetate was reacted with an excess of $(EtO)_3SiCH_2CH_2PPh_2$ using a procedure analogous to that described by Wilkinson [10], and linked to the surface of silica in refluxing benzene to give a dark green silica containing 0.6% weight ruthenium (Ru/1). This complex was tested for the hydrogenation of hex-1-ene (20% vol. in benzene) at 130° C under 15 atm pressure over 3 h to give complete conversion of the hex-1-ene with a yield of n-hexane of 63%. The supported complex was treated with fluoroboric acid, which has been shown

TABLE 1

HYDROGENATION OF HEX-1-ENE AND CYCLOHEXENE WITH SIL—$CH_2CH_2PPh_2$ COMPLEXES [a]

Complex	Wt. of complex (g)	Temperature (°C)	Time (h)	Additive (0.15 ml)	Conversion of hex-1-ene (%)	Yield of hexane (%)	Yield of cyclohexane (%)
Ir/1	0.7	120	1	—	100	100	97
(2.6% wt. Ir)	0.7	140	2	n-BuSH	100	67	7
Ru/2	0.4	130	3	—	100	82	46
(0.5% wt. Ru)	0.6	125	3	Et_3N	100	90	33
	0.5	130	3	n-BuSH	100	64	26

[a] Conditions: Hex-1-ene : cyclohexene : benzene (1 : 1 : 3 by vol.; 70 ml); pressure 15 atm H_2.

to enhance the activity of some ruthenium acetate complexes [10], and then tested for the hydrogenation of hex-1-ene, cyclohexene, and benzene (1:1:3) at 140°C and 15 atm for 3 h. Hexane and cyclohexane yields of 92 and 34% respectively were obtained indicating that the acid treatment significantly enhanced the activity of the heterogeneous catalyst too.

An analogue of the complex $RuCl_2(PPh_3)_3$ was prepared by reaction of $(EtO)_3SiCH_2CH_2PPh_2$ with $RuCl_2(C_{10}H_{16})$ (made from ruthenium chloride and isoprene [11]) and linked to silica in refluxing benzene to give a red solid containing 0.5% weight Ru (Ru/2).

This complex was tested for the hydrogenation of hex-1-ene and cyclohexene in benzene (Table 1) and the effect of the addition of triethylamine and of n-butylmercaptan to the feed was examined. Triethylamine had little effect, but n-butylmercaptan reduced the activity of the complex to some extent. Unlike the rhodium complex, the complex Ru/2 showed no tendency to decompose at 130°C under hydrogen.

The complex Ru/2 also hydrogenated isoprene (20% vol. in benzene) containing n-butylmercaptan to give a conversion of 25% with a yield of isopentenes and isopentane of 23% and 2% respectively over 3 h at 140°C and 15 atm pressure.

(d) Platinum complex

A platinum complex was prepared by reaction of potassium tetrachloroplatinite with the tertiary phosphine ligand—silica SIL—$CH_2CH_2PPh_2$ and then treated with stannous chloride to give a silica containing 2.1% weight Pt (Pt/1). This complex was tested for the hydrogenation of hex-1-ene in methanol/benzene at 140°C under 15 atm pressure for 5 h. 64% of the hex-1-ene was converted, but the yield of n-hexane was low (6%), the major product being internal hexenes.

2. Studies using complexes of the type "MXP_2"

On the basis of the preliminary studies, complexes of rhodium and iridium were chosen for further investigation. Complexes of the type MXP_2 (M = Rh, Ir; X = Cl, Br, I; P = tertiary phosphine ligand—silane) were prepared and linked to silica. These were tested for the hydrogenation of hex-1-ene, cyclohexene, and isoprene in the presence of n-butylmercaptan.

(a) Rhodium complexes

Rhodium complexes, prepared by reaction of $[RhCl(C_8H_{14})_2]_2$ with a range of four tertiary phosphine ligand—silanes (Rh : P ratio 1 : 2), were linked to silica in refluxing benzene. The bromo complexes were prepared by reaction of the tertiary phosphine ligand—silanes with [RhBr(2,5-dimethylhexa-1,5-diene)]$_2$ (made from rhodium tribromide by analogous procedure to that described for the chloro complex [12]) followed by linkage to silica. The iodo complex $[RhI(SIL{-}(CH_2)_2{-}PPh_2)_2]$ was prepared from the bromo complex using lithium iodide in MEK by analogy with the preparation of $RhI(PPh_3)_2$ [13].

The complexes were tested for hydrogenation activity and the data are given in Tables 2-5. The molar ratio of rhodium to each substrate (hex-1-ene, cyclohexene, or isoprene) was approximately 1 : 3000 for all the tests. These show that variation of the phosphine-silane has only a small effect on the activity, the higher activity of the SIL—$(CH_2)_2P(n\text{-}C_6H_{13})_2$ complex for the hydrogenation

TABLE 2

EFFECT OF VARIATION OF PHOSPHINE ON ACTIVITY OF $MClP_2$ COMPLEXES IN THE HYDROGENATION OF OLEFINS [a]

Metal	Phosphine	Metal content (% wt.)	Wt. of complex (g)	Conversion hex-1-ene (%)	Yield of hexane (%)	Yield of cyclohexane (%)
Rh	SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	0.8	0.47	99	88	56
	SIL—$(CH_2)_2PPh_2$	0.8	0.47	100	71	81
	SIL—$(CH_2)_2Phex_2$ [b]	1.5	0.55	100	85	84
	SIL—$(CH_2)_2Pcy_2$ [c]	0.8	0.45	80	63	13
Ir	SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	2.4	0.45	100	86	0
	SIL—$(CH_2)_2PPh_2$	4.0	0.58	100	81	1
	SIL—$(CH_2)_2Phex_2$ [b]	3.0	0.48	100	79	5
	SIL—$(CH_2)_2Pcy_2$ [c]	2.9	0.47	100	78	3

[a] Conditions: Hex-1-ene : cyclohexene : benzene (1 : 1 : 3 by vol.: 70 ml) containing 0.15 ml of n-BuSH; temperature: 140°C; time: $1\frac{1}{2}$ h; pressure: 15 atm H_2. [b] hex = n-hexyl. [c] cy = cyclohexyl.

of isoprene probably being largely attributable to its higher rhodium content, but the lower activity of the SIL—$(CH_2)_2$—P(cyclo-$C_6H_{11})_2$ complex for cyclohexene hydrogenation may reflect the greater steric crowding around the rhodium centre in this complex, which becomes significant only in the hydrogenation rate for internal olefins. Variation of the halogen has a more pronounced effect than variation in the phosphine ligand, the activity being in the sequence: $Cl < Br \leqslant I$, although, even here, differences are relatively small.

(b) Iridium complexes

Iridium complexes with the four tertiary phosphine ligand-silanes were prepared by reaction of $[IrCl(C_8H_{14})_2]_2$ with the silanes (Ir:P ratio 1:2) by analogy

TABLE 3

EFFECT OF VARIATION OF PHOSPHINE ON ACTIVITY OF $MClP_2$ COMPLEXES IN THE HYDROGENATION OF ISOPRENE [a]

Metal	Phosphine	Metal content (% wt.)	Wt. of complex (g)	Conversion isoprene (%)	Yield of isopentenes (%)	Yield of isopentane (%)
Rh	SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	0.8	0.47	47	44	3
	SIL—$(CH_2)_2PPh_2$	0.8	0.49	51	46	5
	SIL—$(CH_2)_2Phex_2$ [b]	1.5	0.45	98	68	30
	SIL—$(CH_2)_2Pcy_2$ [c]	0.8	0.53	36	33	3
Ir	SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	2.4	0.50	85	77	8
	SIL—$(CH_2)_2PPh_2$	4.0	0.45	45	41	4
	SIL—$(CH_2)_2Phex_2$ [b]	3.0	0.48	68	59	9
	SIL—$(CH_2)_2Pcy_2$ [c]	2.9	0.51	99	82	17

[a] Conditions: Isoprene (15 ml) : benzene (55 ml) containing 0.15 ml of n-BuSH; temperature: 140°C; time: $1\frac{1}{2}$ h; pressure: 15 atm H_2. [b] hex = n-hexyl. [c] cy = cyclohexyl.

TABLE 4

EFFECT OF VARIATION OF HALIDE ON ACTIVITY OF $RhXP_2$ COMPLEXES IN THE HYDROGENATION OF OLEFINS [a]

Phosphine	Rh content (% wt.)	Halide	Wt. of complex (g)	Conversion of hex-1-ene (%)	Yield of hexane (%)	Yield of cyclohexane (%)
SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	0.8	Cl	0.47	99	88	56
SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	0.8	Br	0.49	100	95	76
SIL—$(CH_2)_2PPh_2$	0.8	Cl	0.47	100	71	81
SIL—$(CH_2)_2PPh_2$	1.0	Br	0.53	100	98	100
SIL—$(CH_2)_2PPh_2$	0.9	Br	0.54	73 [b]	55	24
SIL—$(CH_2)_2PPh_2$	0.7	I	0.66	97 [b]	95	45

[a] Conditions: Hex-1-ene : cyclohexene : benzene (1 : 1 : 3 by vol.: 70 ml) cintaining 0.15 ml of n-BuSH; temperature: 140°C; time: $1\frac{1}{2}$h; pressure: 15 atm H_2.
[b] Reaction time, $\frac{3}{4}$ h.

TABLE 5

EFFECT OF VARIATION OF HALIDE ON ACTIVITY OF $RhXP_2$ COMPLEXES IN THE HYDROGENATION OF ISOPRENE [a]

Phosphine	Rh content (% wt.)	Halide	Wt. of complex (g)	Conversion of isoprene (%)	Yield of isopentenes (%)	Yield of isopentane (%)
SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	0.8	Cl	0.47	47	44	3
SIL—$(CH_2)_4C_6H_4PPh_2$-*p*	0.8	Br	0.48	77	72	5
SIL—$(CH_2)_2PPh_2$	0.8	Cl	0.49	51	46	5
SIL—$(CH_2)_2PPh_2$	1.0	Br	0.55	100	30	70
SIL—$(CH_2)_2PPh_2$	0.9	Br	0.37	80 [b]	74	6
SIL—$(CH_2)_2PPh_2$	0.7	I	0.44	84 [b]	79	5

[a] Conditions: Isoprene (15 ml) : Benzene (55 ml) containing 0.15 ml of n-BuSH; temperature: 140°C; time: $1\frac{1}{2}$ h; pressure: 15 atm H_2. [b] Reaction time, $\frac{3}{4}$ h.

with the preparation of [$IrCl(PPh_3)_2$] [14] and then linked to silica in refluxing benzene. These complexes were tested as hydrogenation catalysts and the data are given in Tables 2 and 3. The molar ratio of iridium to each substrate (hex-1-ene, cyclohexene, or isoprene) was approximately 1:1500 in all the tests. As in the case of the rhodium complexes, variation of the phosphine made only a small difference to the catalyst activity. A significant difference between the rhodium and iridium species, however, was the much lower activity of the latter for the hydrogenation of cyclohexene.

Discussion

The preliminary studies showed that it is possible to prepare analogues of a variety of different phosphine complexes using tertiary phosphine ligands which can be linked to the surface of silica, and that the supported complexes can be used as heterogeneous catalysts for the hydrogenation of both olefins and dienes. The method of synthesis using a tertiary phosphine ligand—silane (e.g. $(EtO)_3SiCH_2CH_2PPh_2$) and forming a complex with this ligand in solution prior to attachment to the silica has the great advantage that the metal:ligand ratio can readily be controlled. This is especially useful in several of the systems used here, where complexes containing 1, 2 or 3 tertiary phosphine ligands attached to a metal atom can all be formed from the same precursor. For example, both rhodium and iridium can form complexes with different metal: phosphine ratios and in some cases the metal:phosphine ratio can have a critical effect on the hydrogenation activity. It has been reported [15] that, unlike the rhodium analogue $RhCl(PPh_3)_3$, the iridium complex $IrCl(PPh_3)_3$ has no hydrogenation activity as the phosphine groups are too firmly bound to the metal and do not readily dissociate. If, however, the species "$IrCl(PPh_3)_2$" is generated in situ, this is very active, even more so than the rhodium analogue. In the present studies, iridium complexes were always prepared using a ratio of metal : phosphine of 1 : 2 and the resulting products then linked to silica. These supported complexes all had high hydrogenation activity. A further advantage of the method involving formation of tertiary phosphine ligand—silane complexes is that the available phosphine groups are fully utilised, whereas with a pre-formed tertiary phosphine ligand—silica some phosphine groups may be inaccessible to the metal atoms in the complexing reaction.

The effect of the n-butylmercaptan in stabilising the rhodium complexes was quite unexpected. It has previously been reported that, in the hydrogenation of olefins, Wilkinson's complex shows some resistance to poisoning by sulphur compounds [16], and Wilkinson has isolated complexes of the type $RhHCl(SR)(PPh_3)_2$ from solutions containing $RhCl(PPh_3)_3$ and RSH (R = H or p-$CH_3C_6H_4$-SH) [17]. However, no detailed catalytic studies of these systems have been published. In our studies, it was found that only simple mercaptans stabilised the complex without completely poisoning its activity [9]. Carbon disulphide and thiophene reacted to give inactive species whereas di-n-butyl sulphide failed to prevent decomposition at elevated temperatures under hydrogen. Ethane-1,2-dithiol stabilised the complex but completely destroyed its activity. The nature of the mercaptan-treated complex is uncertain. Since it remains firmly bound to the silica throughout the hydrogenation sequence, it is clear that at least one tertiary phosphine group remains bound to the rhodium. Also, the steady trend in activity with change in the halide ligand in the sequence: Cl < Br ⩽ I strongly implies that the halide ligand remains in the complex. Furthermore, experiments with a complex prepared by reaction of "RhCl(PPh_3)$_2$" with SIL—(CH_2)$_3$—SH, which behaves in precisely the same way as the mercaptan-treated tertiary phosphine ligand—silica complex, showed that this ligand also remains attached to the metal throughout the hydrogenation sequence [9]. If species analogous to those described by Wilkinson, i.e. RhHCl(SBu)(phosphine)$_2$, are formed (i.e. the complex still contains two phosphine ligands co-ordinated to each rhodium atom), the mechanism of hydrogenation must presumably involve a stepwise rather than a concerted process — i.e. analogous to hydrogenations catalysed by $RhH(CO)(PPh_3)_3$ or $RuHCl(PPh_3)_3$ rather than $RhCl(PPh_3)_3$ [18]. It is rather surprising that, in view of the total destruction of catalytic activity by ethane-1,2-dithiol, the hydrogenation activity of the supported complexes is not fairly critically affected by the concentration of mercaptan in solution. In the present work, high molar ratios of mercaptan to rhodium (generally about 30 : 1) were used and yet good activity was observed, so that it appears that the poisoning effect of the dithiol must be attributable to the formation of a highly stable chelate species.

Under the test conditions used in this work, the effect of variation of substituents on the tertiary phosphine ligand in the species $MClP_2$ (M = Rh, Ir) linked to silica is small and no consistent trends are apparent. This is in sharp contrast to the results of studies of homogeneous catalysts where change in the phosphine from Ph_2PEt to PEt_3 in the species $RhClP_2$ resulted in a 40-fold reduction in activity for the hydrogenation of cyclohexene at 25°C [18]. However, all the homogeneous studies were carried out under sulphur-free conditions, whereas all the heterogeneous catalysts were examined in the presence of n-butylmercaptan, and it is possible that the mercaptan tends to reduce the effect of phosphine basicity on hydrogenation activity. Additional experiments using the heterogeneous complexes in the absence of mercaptan would be needed to clarify this. Isomerisation of hex-1-ene to hex-2-ene and hex-3-ene occurred to an appreciable extent under the test conditions used here, and, in all cases, the complexes possessed higher activity for the hydrogenation of terminal olefins than internal ones. With the iridium species, relatively low activity was observed for cyclohexene hydrogenation, indicating that the iridium complexes are less active than the rhodium analogues for the hydrogenation of internal olefins under the conditions used.

The hydrogenation tests were designed to indicate major differences between the activity of complexes containing different halide or phosphine ligands, rather than to give accurate detailed data on the relative rates under rigorously controlled conditions. Indeed, in many cases, 100% conversion of the hex-1-ene was achieved and activity differences between the complexes can only be detected in the hydrogenations of cyclohexene and isoprene where lower conversions took place. The results showed, from the point of view of activity alone, there was little difference between complexes with different phosphines and only a relatively small increase in activity across the halide series. However, for satisfactory operation as heterogeneous catalysts under continuous flow conditions, other properties are also very important. These include the stability of the complexes over prolonged reaction times, their sensitivity to traces of oxygen in the feedstocks, and the strength of the linkage between the metal centre in the complex and the silica. Cleavage of this link will lead to loss of metal from the catalyst and consequent loss of activity. Although some indication of stability and the ease of elution from the support can be gained from the results of the tests described here, tests under continuous flow conditions are necessary to establish the lifetime of the catalysts. Such tests have been carried out on several of the complexes described here and the detailed results will be published elsewhere [19]. They show that prolonged activity can be achieved in continuous operation in the liquid phase without detectable loss of rhodium from the support and that these complexes attached to silica are truly heterogeneous counterparts of homogeneous transition metal complex catalysts.

Experimental

All preparations were carried out under dry oxygen-free nitrogen. Solvents were dried and redistilled prior to use. The phosphine—silanes were prepared as described previously [7].

1. Preparation of complexes

(a) General reaction of linking silane complexes to silica

The complex (typically 1 g) dissolved in benzene (30 ml) was added to silica (5 g; Crosfield/Sorbsil U30 grade (surface area 500 m^2/g), which had been washed with dilute acid, then with distilled water and dried at 110°C before use). The mixture was refluxed for 3 h and the ethanol liberated azeotroped out using a Dean and Stark apparatus. The silica was then Soxhlet extracted with benzene or methanol for at least 6 h.

(b) Rhodium complexes

(i) $(EtO)_3SiCH_2CH_2PPh_2$ (3.63 g, 9.7 mmol) in benzene (10 ml) was added to $[RhCl(COD)]_2$ (0.79 g, 1.6 mmol) in benzene (20 ml) and the solution stirred for 16 h at room temperature. The benzene was then evaporated off to leave a red viscous material, which was dissolved in pentane and precipitated by cooling. The supernatant solution was decanted off and the remaining viscous material dried in vacuo at 60°C for 14 h. Analysis found: Rh, 7.7. $C_{60}H_{87}O_9P_3Si_3ClRh$ calcd.: Rh, 8.0%. This complex (1.14 g) was dissolved in benzene, added to silica (5 g) and refluxed for 3 h. The solution was then decanted off and the resulting dark red silica washed with benzene (3 × 30 ml) and Soxhlet extracted with benzene for 10 h. The silica was dried in vacuo. Analysis found: Rh, 0.9; P, 0.8% (Complex Rh/1A). A second preparation carried out on a larger scale yielded a similar product; analysis found: Rh, 0.7; P, 0.6% (Complex Rh/1B).

(ii) $(EtO)_3Si—(CH_2)_4—C_6H_4—PPh_2$-*p* (1.90 g, 4.0 mmol) in benzene (20 ml) was added to a stirred solution of $[RhCl(C_8H_{14})_2]_2$ [20] (0.72 g, 1.0 mmol) in benzene (50 ml) under nitrogen to give a red solution. Stirring was continued for 30 min, and then silica (5 g) was added and the mixture refluxed for 2½ h. The silica was then filtered off, Soxhlet extracted with benzene for 20 h and dried in vacuo to yield a brown silica containing 0.8% weight rhodium.

(iii) Using the same procedure described in *ii*, $(EtO)_3Si(CH_2)_2PPh_2$ (1.89

g, 5.0 mmol) and $[RhCl(C_8H_{14})_2]_2$ (0.71 g, 1.0 mmol) with silica (5 g) gave a red-brown silica containing 0.8% weight rhodium.

(iv) $(EtO)_3Si(CH_2)_2P(n\text{-}C_6H_{13})_2$ (1.56 g, 4.0 mmol) and $[RhCl(C_8H_{14})_2]_2$ (0.72 g, 1.0 mmol) gave an orange-brown silica containing 1.55% weight rhodium and 0.9% weight phosphorus.

(v) $(EtO)_3Si(CH_2)_2P(cyclo\text{-}C_6H_{11})_2$ (1.56 g, 4.0 mmol) and $[RhCl(C_8H_{14})_2]_2$ (0.72 g, 1.0 mmol) gave a red-brown silica containing 0.8% weight rhodium.

(vi) [RhBr(2,5-dimethylhexa-1,5-diene)]$_2$ was prepared using an analogous procedure to that described for the chloro complex [12]. 2,5-Dimethylhexa-1,5-diene (2.5 ml, 17 mmol) was added to rhodium tribromide (2.1 g, 4.5 mmol) in ethanol:water (5:1; 25 ml) and the mixture stirred for 24 h at room temperature. After standing for 6 days, the solution was filtered to yield dark brown needles, which were washed with methanol, and dried in vacuo (0.51 g). The infrared spectrum of the product was almost identical to an authentic sample of [RhCl(2,5-dimethylhexa-1,5-diene)]$_2$. Analysis found: Br, 25.9. $C_{16}H_{28}Br_2Rh_2$ calcd. Br, 27.2%. $(EtO)_3Si(CH_2)_4C_6H_4PPh_2\text{-}p$ (1.33 g, 2.7 mmol) and [RhBr-(2,5-dimethylhexa-1,5-diene)]$_2$ (0.37 g, 0.64 mmol) gave a red-brown silica containing 0.8% weight rhodium.

(vii) $(EtO)_3Si(CH_2)_2PPh_2$ (1.50 g, 4.0 mmol) and [RhBr(2,5-dimethylhexa-1,5-diene)]$_2$ (0.58 g, 1.0 mmol) gave a red-brown silica containing 1.0% weight rhodium.

(viii) $(EtO)_3Si(CH_2)_2PPh_2$ (1.16 g, 3.0 mmol) and [RhBr(2,5-dimethylhexa-1,5-diene)]$_2$ (0.45 g, 0.75 mmol) gave a red-brown silica containing 0.9% weight rhodium.

(ix) $(EtO)_3Si(CH_2)_2PPh_2$ (2.0 g, 5.2 mmol) and [RhBr(2,5-dimethylhexa-1,5-diene)]$_2$ (0.76 g, 1.3 mmol) in benzene (25 ml) were added to lithium iodide (1.17 g, 8 mmol) in MEK (50 ml) at 0°C. The mixture was stirred for 2 h and allowed to warm to room temperature. The solvent was evaporated off and the residue extracted with benzene, filtered, and added to silica (6 g) as described above. A dark red-brown silica containing 0.7% rhodium, 0.02% bromine, 1.22% iodine was obtained.

(c) Iridium complexes

(i) $(EtO)_3Si(CH_2)_2PPh_2$ (1.50 g, 4.0 mmol) was added to a solution of [IrCl(COD)]$_2$ [21] (0.67 g, 1.0 mmol) in benzene (20 ml). The pale orange solution was stirred for 1 h and then silica (5 g) was added. The mixture was refluxed for 2 h and the silica filtered off and Soxhlet extracted with benzene for 12 h. The bright orange silica was dried in vacuo. It contained 2.6% weight iridium (Complex Ir/1).

(ii) $(EtO)_3Si(CH_2)_4C_6H_4PPh_2\text{-}p$ (1.25 g, 2.6 mmol) and $[IrCl(C_8H_{14})_2]_2$ [15] (0.57 g, 0.64 mmol) with silica (3.2 g) yielded a yellow silica containing 2.4% weight iridium.

(iii) $(EtO)_3Si(CH_2)_2PPh_2$ (0.75 g, 2.0 mmol) and $[IrCl(C_8H_{14})_2]_2$ (0.45 g, 0.5 mmol) with silica (2.5 g) yielded a yellow silica containing 4.0% weight iridium.

(iv) $(EtO)_3Si(CH_2)_2P(n\text{-}C_6H_{13})_2$ (6.0 g, 12.5 mmol) and $[IrCl(C_8H_{14})_2]_2$ (3.6 g, 4.0 mmol) with silica (20 g) gave a bright yellow silica containing 3.0% weight iridium.

(v) $(EtO)_3Si(CH_2)_2P(cyclo\text{-}C_6H_{11})_2$ (1.56 g, 4.0 mmol) and $[IrCl(C_8H_{14})_2]$

(0.90 g, 1 mmol) with silica (5 g) gave a pale yellow silica containing 2.9% weight iridium.

(d) Ruthenium complexes

(i) $(EtO)_3Si(CH_2)_2PPh_2$ (4.0 g, 10.6 mmol) in methanol (5 ml) was added to ruthenium acetate [10] (1.60 g; 3.6 mmol) in methanol (20 ml). The mixture was stirred overnight and the methanol evaporated off. The product (containing excess $(EtO)_3SiCH_2CH_2PPh_2$) was dissolved in pentane from which it separated on cooling. The complex (1.95 g) was dissolved in benzene (10 ml) and added to silica (5 g) suspended in benzene (50 ml). The mixture was refluxed for 2½ h, the silica filtered off, and Soxhlet extracted with methanol. The dark green silica was dried in vacuo. Ruthenium content 0.6% weight (Complex Ru/1A).

(ii) Complex Ru/1A (1.0 g) was treated with methanol (20 ml) which had been saturated with hydrogen and contained fluoroboric acid (0.2 ml of 40% aqueous solution). The mixture was stirred for 1 h and then the silica was filtered off, washed with methanol, and dried in vacuo (Complex Ru/1B).

(iii) $(EtO)_3Si(CH_2)_2PPh_2$ (3.7 g; 9 mmol) was added to a suspension of $RuCl_2(C_{10}H_{16})$ (0.52 g, 1.7 mmol) — made from hydrated $RuCl_3$ and isoprene [11] — in methanol (40 ml). The mixture was refluxed for 3 h and cooled. The methanol was evaporated off, and the red viscous oil extracted with pentane and dried in vacuo. This complex was dissolved in benzene (10 ml) and added to silica (5 g) suspended in benzene (50 ml). The mixture was refluxed for 3 h and then the silica was filtered off, Soxhlet extracted with methanol for 6 h and dried in vacuo. Ruthenium content 0.5% weight.

(e) Platinum complex

SIL—$CH_2CH_2PPh_2$ (5 g, 0.75% phosphorus) was added to a solution of K_2PtCl_4 (1.0 g, 2.4 mmol) in water (35 ml). The mixture was stirred for 6 h at room temperature and allowed to stand overnight. The silica was then filtered off, washed with water, dried in vacuo, and treated with anhydrous stannous chloride (1.15 g, 6.0 mmol) in methanol (40 ml) for 30 min. The silica was filtered off, washed with methanol and dried in vacuo. Platinum content 2.1% weight.

2. Hydrogenation tests

(a) Standard test conditions

Hydrogenation tests were carried out in Fischer and Porter glass pressure vessels of approximately 100 ml capacity. The standard test solutions used were:

(i) Hex-1-ene (20% vol.), cyclohexene (20% vol.) and benzene (60% vol.). 70 ml of this solution were used for each test and n-butylmercaptan (0.15 ml) was added to give a solution containing approximately 700 ppm of sulphur.

(ii) Isoprene (15 ml) and benzene (55 ml) to which n-butylmercaptan (0.15 ml) was added to give a solution containing approximately 700 ppm of sulphur.

The standard hydrogenation tests (Tables 2-5) were carried out at 15 atm pressure of hydrogen at 140° C. Except where indicated otherwise (Tables 4 and 5), the duration of the tests was 1½ h at 140° C. The additional time needed for the solution to heat up from room temperature to 140° C was approximately 45 min.

(b) Hydrogenation tests with complex Rh/1

(i) Complex Rh/1A (0.5 g) was added to n-heptane (60 ml) saturated with hydrogen. Hex-1-ene (25 ml) was added and the reaction mixture stirred at 60°C under hydrogen at 1 atm. Analysis of the product after $3\frac{1}{2}$ h showed that 50% conversion of the hex-1-ene with a 22% yield of n-hexane and 23% yield of isomeric hexenes had occurred.

(ii) The reaction was repeated using complex Rh/1A (0.5 g) with hex-1-ene (15 ml) in n-heptane (40 ml) under a hydrogen pressure of 10 atm. After $2\frac{1}{2}$ h at 60°C, complete conversion of the hex-1-ene to n-hexane had occurred.

(iii) Complex Rh/1B (0.5 g) was added to hept-3-ene (20 ml) and benzene (50 ml), which had been saturated with hydrogen, and the mixture stirred at 80°C under 15 atm pressure of hydrogen for $1\frac{1}{2}$ h. Conversion of hept-3-ene 44%; yield of n-heptane, 40%.

(iv) Complex Rh/1B (0.5 g) was stirred with isoprene (20 ml) and benzene (50 ml) at 80°C under hydrogen (15 atm) for $1\frac{1}{2}$ h. 11% of the isoprene was hydrogenated to isopentenes.

(v) Complex Rh/1B (0.5 g) was stirred with hex-1-ene (20 ml) and benzene (50 ml) (to which n-butylmercaptan (0.15 ml) had been added) for $1\frac{1}{2}$ h at 140°C under hydrogen (15 atm). Conversion of hex-1-ene, 98%; yield of n-hexane, 85%.

(c) Hydrogenation tests with complex Ir/1

(i) Experimental details of hydrogenation tests with hex-1-ene and cyclohexene are given in Table 1.

(ii) Complex Ir/1 (0.47 g) was stirred with isoprene (15 ml) and benzene (50 ml) to which n-butylmercaptan (0.15 ml) had been added for 3 h at 140°C under hydrogen (15 atm). Conversion of isoprene, 45%; yield of isopentenes, 36%; yield of isopentane, 9%.

(d) Hydrogenation tests with complex Ru/1

(i) Complex Ru/1A (0.6 g) was stirred with hex-1-ene (14 ml) and benzene (56 ml) at 130°C for 3 h under hydrogen (15 atm). Conversion of hex-1-ene, 100%; yield of n-hexane, 67%.

(ii) Complex Ru/1B (0.5 g) was stirred with a solution of hex-1-ene (20% vol.), cyclohexene (20% vol.) and benzene (60% vol.) (70 ml) at 140°C for 3 h under hydrogen (15 atm). Conversion of hex-1-ene, 100%; yield of n-hexane, 92%; yield of cyclohexane, 34%.

(e) Hydrogenation tests with complex Ru/2

(i) Experimental details of hydrogenation tests with hex-1-ene and cyclohexene are given in Table 1.

(ii) Complex Ru/2 (0.4 g) was stirred with isoprene (15 ml) and benzene (55 ml) at 140°C for 3 h under hydrogen (15 atm). Conversion of isoprene, 25%; yield of isopentenes, 23%; yield of isopentane, 2%.

(f) Hydrogenation test with platinum complex

The complex (0.8 g) was stirred with hex-1-ene (15 ml), methanol (22 ml) and benzene (33 ml) under hydrogen (15 atm) at 140°C for 5 h. Conversion of hex-1-ene, 64%; yield of n-hexane, 6%.

Analysis

Analyses of hydrogenation products were carried out by gas chromatography using columns of dimethylsulpholane (25%) and dinonylphthalate (5%) on Embacel at 40°C or $\beta\beta'$-oxydipropionitrile (5%) on Embacel at 40°C.

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