

Insoluble Poly(alkylarylphosphine)siloxanes and Their Application as Supports for Catalytic Transition-Metal Complexes

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Synopsis

Light induced addition of diphenylphosphine (DPP) to methylvinylcyclotetrasiloxane (MVS) yielded poly(2-diphenylphosphinoethyl) cyclotetrasiloxane (DPPS). Similar treatment of allyldiphenylphosphine (ADPP) with linear poly(methylhydrogenosiloxane)-co-hexamethyldisiloxane (PMS) led to formation of poly(3-diphenylphosphinopropyl)methylsiloxane-co-hexamethyldisiloxane (PPMS). DPPS and PPMS were condensed by acid treatment to give insoluble rubbery phosphine bearing materials P₁ and P₂, respectively. Iridium and rhodium complexes were immobilized on P₁ and P₂. The ability of a high molecular weight substrate (PMS) to migrate to active catalytic centers within support matrix was examined. The effect of varying metal: phosphine ratio and total percentage metal on the support were examined during catalysis of O-silylation of ethanol with PMS and triethoxysilane (TES).

INTRODUCTION

A variety of rigid polymer backbones such as polystyrenes,¹ cellulose,² and silica³ have been used to immobilize transition metal complexes. Purely organic resins used as supports tend to swell in organic solvents which constitute the medium of application of the resins. Pore sizes of swollen resins become narrower and this in turn hinders free diffusion of substrate within the polymer matrix.⁴ Inorganic supports such as silica interact with the active centers and renders identification of active centers difficult. In an earlier report³ we stated that immobilized platinum complexes on silica were associated with an induction period during catalysis of hydrosilylation. Such induction period was shown to occur when the form of the metal complex on the support is transformed into an active catalytic species before catalytic cycle can be initiated.

It has been observed that ease of diffusion of high molecular weight substrates into the matrix of supports during catalysis can limit the rate and extent of reaction.⁴ Other workers⁵ have reported that rhodium(I) phosphine complexes attached to soluble polyphenylsiloxane which in turn was impregnated on macroporous silica showed superior activity compared to the silica-immobilized or the homogeneous analogue of the complex. This and other reports^{6,7} have dealt with the characteristics and possible advantages of

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soluble polysiloxane ligands. However insoluble polysiloxanes have not been investigated as potential support materials, we have addressed these problems by synthesis of insoluble "rigid" polysiloxanes, which unlike silica itself should permit easier diffusion due to wider pores. We also expect lower solvent swelling index when compared to polystyrene and other organic based resins.

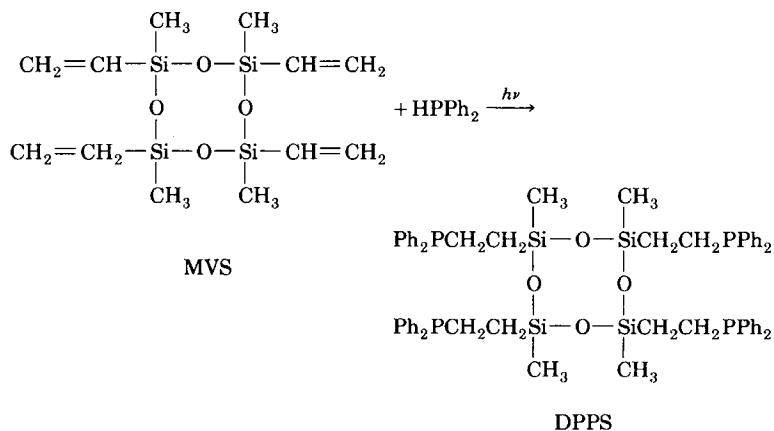
EXPERIMENTAL

All reagents were of commercial reagent grade: methylvinylcyclotetrasiloxane (MVS), poly(methylhydrogenosiloxane)-co-hexamethyldisiloxane (PMS) were supplied by Dow-Corning Ltd., Barry, Wales as DC 1100 98% and DC 1107, respectively. Diphenylphosphine (DPP), allyldiphenylphosphine (ADPP), μ, μ' -dichlorobis(dicyclooctadiene)diiridium(II) and μ, μ' -dichlorobis(dicyclooctadiene)dirhodium(II) were prepared according to reported procedures.^{8,9} Cobalt chloride hexahydrate (Aldrich), triphenylphenylphosphine 99% (Koch-Light), and triethoxysilane (TES) (Aldrich) were used as supplied. All solvents were purified and deoxygenated by standard procedures.¹⁰ Infrared spectra were obtained on a Perkin-Elmer 197 and a Beckman IR720M. Elemental analysis was performed by (UMIST) services.

The following synthetic procedures are typical:

Immobilized High Density Phosphine Ligands, P₁

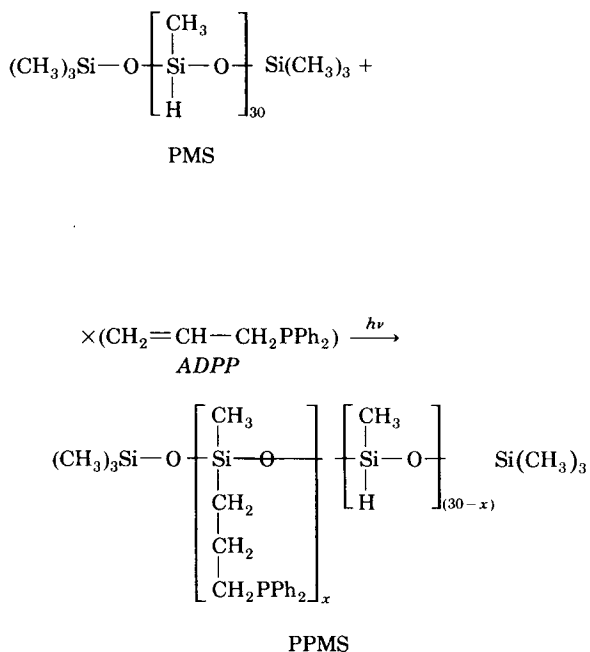
MVS (8.6 g) [0.1 mol CH₂=CHSi(Me)O] taken in 20 mL dichloromethane (DCM) was treated with 55.8 g (0.3 mol) DPP in 30 mL DCM. The mixture stirred under nitrogen was kept under high intensity UV lamp for 48 h. Solvent was flashed off and product distilled to remove excess DPP (150°C, 0.5 mm Hg). Fractions distilling between 190 and 230°C (0.5 mm Hg) (12 g) were collected. Analysis showed this to contain (DPSP):



DPSP (10 g) taken in 50 mL tetrahydrofuran (THF) was deoxygenated and treated under nitrogen with 80% sulfuric acid (5 mL). The mixture was kept under reflux for 2 h, and filtered under nitrogen with a Schlenk-type apparatus. The white rubbery residue (P₁) was washed with THF and DCM and dried in vacuum (0.5 mm Hg) at 50°C.

Immobilized Low Density Phosphine Ligands, P₂

PMS (3.86 g) (0.002 mol) in 20 mL DCM was treated with ADPP (22.6 g) (0.1 mol) in 30 mL DCM. The mixture taken under nitrogen was allowed to react while being stirred under a UV lamp for 5 days. The solvent was flashed off. The viscous product was subjected to flash chromatography over activated alumina using a 1:1 mixture of chloroform and DCM as eluent. Fractions containing silane were collected, pooled, and freed of solvent. Analysis showed this to contain PPMS:



PPMS (10 g) taken in THF 30 mL was treated with 80% sulfuric acid (5 mL). After a 3 h reflux a white rubbery residue P₂ was filtered out, washed with THF and DCM, and dried in vacuum (0.5 mm Hg) at 50°C. The properties of P₁ and P₂ are shown in Tables I and II.

TABLE I
Elemental Analysis of Prepolymers and Their Condensates

Resin	Observed		Expected	
	%C	%P	%C	%P
DPMS	28.1	7.4	66.2	11.4
P ₁	23.9	2.8	28.1	11.4
PPMS	44.6	2.3	66.6	10.6
P ₂	24.3	1.6	44.6	2.3

TABLE II
Physical Properties of Insoluble Siloxanes P₁ and P₂

	P ₁	P ₂
Bulk density (g/L)	310	320
Surface area (m ² /g) ^a	410	380
Average pore Diameter (Å)	120	115
Pore volume ^b (cm ³ /g)	1.3	1.0
Particle size		
On 1.2 mm	0%	2%
On 1.0 mm	5%	7%
On 0.2 mm	95%	85%
Thru 0.2 mm	5%	3%

^aBET (nitrogen adsorption).

^bMercury porosimeter.

Immobilized Rhodium and Iridium Complexes

The following description represents a typical procedure:

P₁ (4.714 g) taken in DCM (15 mL) was treated with μ, μ' -dichloro-bis(dicyclooctadiene)dirhodium(II) (0.18 g) in DCM (10 mL). The mixture kept under nitrogen was stirred for 48 h. The brown solid product was filtered and washed under nitrogen with DCM, toluene, and THF, and then dried in vacuum (0.5 mm Hg) at 35°C.

Soluble Cobalt Complexes Containing Polymeric Ligands

Cobalt complex with DPPS as ligand was prepared by treating CoCl₂ · 6H₂O (2 g) (0.014 mol) in ethanol (10 mL) with DPPS (3.8 g) (0.014 mol) in DCM 10 mL. The solution was chromatographed on activated alumina. The solvent-free product had the following for infrared signals: 186 and 150 cm⁻¹ ν (Co-P) and 106 cm⁻¹ δ (Co-Cl).¹¹ Similar signals were obtained when P₁ was treated with a large amount of CoCl₂ · H₂O.

Catalytic Activity of Supported Complexes

The activity of immobilized complexes were evaluated as catalysts for *O*-silylation of ethanol at 25°C.

(i) Ethanol (0.5 mL) (0.014 mol) was treated with PMS 0.3 m (5×10^{-4} mol) in dry toluene (10 mL). An amount of catalyst containing 5×10^{-6} mol metal was used. The mixture of silane and catalyst taken in a sealed flask connected to a 100 mL gas burette was deoxygenated. The deoxygenated ethanol was introduced to the stirred mixture with a syringe via a septum cap. The rate of evolution of hydrogen was monitored. Occasionally samples were withdrawn from the reaction flask, quenched in a mixture of pyridine and decane, and analyzed by GLC. Decane was used as internal standard for GLC.

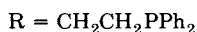
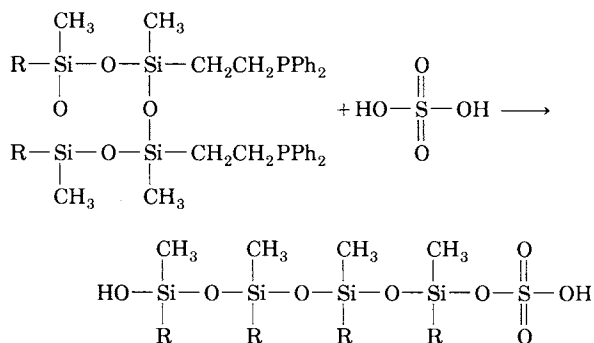
(ii) Ethanol (0.5 mL) (0.014 mol) and triethoxysilane 0.7 mL (4.5×10^{-3} mol) were allowed to react as described above.

RESULTS AND DISCUSSION

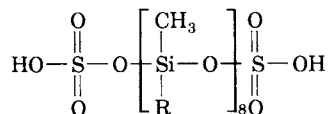
Prepolymer Preparation and Condensation

The elemental analysis for the soluble prepolymers DPPS and PPMS are given in Table I. The figure for DPPS indicates 64.9% reaction between the vinyl moieties and DPP. The molar ratio 1 : 3 maintained for the reaction was intended to ensure a high yield of DPPS and to suppress polymerization between the vinyl groups. Unreacted vinyl groups were identified by weak infrared signals at 1500 cm^{-1} . At 3050 cm^{-1} phosphorus phenyl vibrations were recorded. Previous workers⁷ have reported similar photoinduced additions. Elemental analysis for carbon and silicon was subject to some uncertainty due to formation of "SiC" species in the furnace.

In accordance with the mechanism proposed in the literature¹² for acid-catalyzed condensation of alkylsiloxanes, the formation of silanol groups constitute the first important step:



These silanols may now condense intermolecularly by dehydration between the terminal hydroxyl groups. The first of such condensation would result in a linear molecule capped with sulphate groups:



Condensation can also occur between the terminal sulfate groups and the silanols. These processes lead to increased chain length. In the presence of acid, however, the reverse process (rupture of silicon—oxygen bonds) will also occur. At equilibrium, however, under the conditions maintained rubbery gels are formed. These gels bear hydroxyl groups which cure to produce high molecular weight porous solids. The material consists of linear units of the functionalized siloxanes.

Lower than expected percentage phosphorus was observed due to cleavage of silicon—carbon bonds of 2-(diphenylphosphino)ethyl siloxane. Such cleavage¹³ was shown to be enhanced when a hetero-atom is attached to the carbon atom β to the silicon. Enhanced cleavage of silicon—vinyl bonds in

TABLE III
Weight Swelling Ratios (WSR) of Siloxane Condensates^a

Solvent	P ₁	P ₂
Toluene	0.1	0.0
Benzene	0.1	0.0
Hexane	0.0	0.0
Ethanol	0.1	0.1
THF	1.8	0.3

^a P₁ and P₂ swelled at 25°C for 24 h. WSR = (V₂ - V₁)/W, where V₁ = volume (mL) of polymer before swelling, V₂ = volume (mL) of polymer after swelling, and W = weight (g) of polymer.

sulfuric acid has also been reported.¹⁴ Under our conditions some cleavage is advantageous because the linear chains can be crosslinked by such mechanism. Crosslinking conferred greater rigidity to the products. Extensive cleavage would lead to formation of silica within the polymer matrix.

Only 21.7% of the silicon—hydrogen bonds of PMS reacted with ADPP to give PPMS. This was as expected because of the high molecular weight of the siloxane substrate. This product was intended to serve as a support with a lower density of phosphine moieties. Infrared absorptions at 750, 1475, and 3050 cm⁻¹ indicate presence of phenyl phosphine groups.

The physical properties of the condensates are presented in Table II. The surface area and pore volumes are both higher than that of silica supplied by manufacturers of Grace silica gels,¹⁵ which in turn are higher than figures for most polystyrene based resins. Table III shows the weight swelling ratios of the resins in various solvents. The values are quite low, which suggests that crosslinkage index must have been high. This agrees with the rather high cleavage of the silane substituents observed in Table I. The ability of organic polymers to swell in solvents when they are not highly crosslinked is one of their less desirable features as supports. However, highly crosslinked organic polymers tend to have low pore volumes, which limits diffusion. These results would suggest that the better features of inorganic and organic polymeric supports have been achieved in this synthesis.

Anchorage of Metal Complexes on Siloxane Polymers

Insertion of diphenylphosphine species into the complexes [IrCl(C₈H₁₂)₂]₂ and [RhCl(C₈H₁₂)₂]₂ occurred during equilibration of solutions containing these complexes with the polymers P₁ and P₂. The level of metal required for catalytic activity is usually very low so that infrared spectra have very low intensities, which we could not resolve without specialized instruments. The reaction of cobalt complex (a d⁹ metal) with P₁ and P₂ and DPPS to show that in this case soluble ligands (DPPS) and P₁ have the same kind of response in infrared excitation. It is therefore concluded that phosphine—metal bonds were formed during anchorage of iridium and rhodium on P₁ and P₂. The amount of iridium on P₁ and P₂ is presented in Tables IV and V. These supported metal complexes have been designated C₁–C₉. Similar data for rhodium are presented in Tables VI and VII. The catalysts here have been designated B₁–B₉.

TABLE IV
Iridium Catalysts Immobilized on High Density Phosphine Polymer P₁^a

Catalyst	% Iridium	Iridium/phosphine ratio	Rate ^b	Yield ^c
C ₁	1.2	1 : 11.5	39.4	95
C ₂	1.6	1 : 10.9	38.6	95
C ₃	2.3	1 : 7.2	40.7	95
C ₄	3.1	1 : 5.6	45.3	95
C ₅	3.5	1 : 5.1	57.5	90

^aSilane substrate is PMS; substrate/catalyst ratio 100 : 1.

^bMol of product (hydrogen)/mol of catalyst/time (min).

^cDetermined by GLC of ethanol left unreacted.

TABLE V
Iridium Catalyst Immobilized on Low Density Phosphine Polymer P₂^a

Catalyst	% Iridium	Iridium/phosphine ratio	Rate ^b	Yield ^c
C ₆	0.9	1 : 11	37.5	
C ₇	1.4	1 : 7.1	42.2	
C ₈	2.1	1 : 4.7	38.6	
C ₉	2.6	1 : 3.8	52.7	

^aSilane substrate is PMS; substrate/catalyst ratio 100 : 1.

^bMol of product (hydrogen)/mol of catalyst/time (min).

^cDetermined by GLC of ethanol unreacted.

TABLE VI^a
Rhodium Catalyst Immobilized on High Density Phosphine Polymer P₁

Catalyst	% Rhodium	Rhodium/phosphine ratio	Rate ^b	Yield ^c
B ₁	1.0	1 : 9.3	32.4	85
B ₂	1.3	1 : 7.2	34.3	88
B ₃	1.8	1 : 5.2	32.6	87
B ₄	2.7	1 : 3.4	38.6	86
B ₅	3.6	1 : 2.6	40.4	—

^aSilane substrate is PMS; substrate/catalyst ratio 100 : 1.

^bMol of product (hydrogen)/mol of catalyst/time (min).

^cDetermined by GLC of ethanol unreacted.

Evaluation of Immobilized Iridium and Rhodium Complexes

The results of catalysis with immobilized complexes are presented in Tables IV–VII. The test reaction is the transformation of the silicon—hydrogen bond to silicon—ethoxide bond (*O*-silylation):

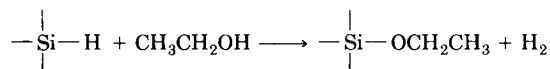


TABLE VII^a
 Rhodium Catalyst Immobilized on Low Density Phosphine Polymer

Catalyst	% Rhodium	Rhodium/phosphine ratio	Rate ^b	Yield ^c
B ₆	0.7	7.6	36.9	70
B ₇	1.1	4.8	38.7	72
B ₈	1.7	3.1	44.2	95
B ₉	2.0	2.7	46.3	95

^aSilane substrate is PMS; substrate/catalyst ratio is 100:1.

^bTurnover number = mol of product/mol of catalyst/time (min).

^cDetermined by GLC of ethanol unreacted.

When the silane substrate is PMS, the turnover number is less than for triethoxysilane (TES) substrate (Table IX). Other workers⁴ have also recorded diminished catalytic activity in relation with polymeric substrates. These workers used homogeneous catalysts. In our work we note that, although we have used polymeric catalysts, the decrease in activity is not as dramatic as that in reference⁴ above. This is due to the excellent characteristics of the support material, being similar and compatible with the high molecular weight substrate. Therefore, these macroporous rubbery solids appear in this respect to permit unhindered diffusion of reagents within its matrix. Tables IV and VII illustrate increased activity with increase in total percentage metal and lower metal-phosphine ratio of the support within each table. This

 TABLE VIII
 Repeated^a Use of Catalysts^b

Catalyst	% Metal ^c	%P ^c	Rate ^d
C ₁	0.6	2.1	26
C ₂	—	—	32
C ₃	—	—	25
C ₄	2.0	2.3	30
C ₅	2.0	2.4	35
C ₆	0.3	0.9	22
C ₇	0.7	1.0	25
C ₈	—	—	28
C ₉	1.2	1.3	41
B ₁	0.8	2.6	28
B ₂	—	— ^e	12
B ₃	—	— ^e	10
B ₄	—	— ^e	17
B ₅	2.5	2.1	22
B ₆	0.2 ^c	2.3	7
B ₇	0.3	0.9	8
B ₈	—	—	7
B ₉	0.9	—	7

^aThree runs.

^bSilane substrate is PMS; substrate/catalyst ratio is 100:1.

^cAfter use.

^dTurnover number, mol of product (hydrogen)/mol of catalyst/time (min).

^eFive runs.

TABLE IX
Influence of Polymer Matrix on Diffusion of Substrate^e

Catalyst ^a	% Metal ^b	Rate ^c	Yield ^d
C ₁₀	1.0	76	
C ₁₁	1.6	84	
C ₁₁	3.3	73	
C ₆	0.9	78	
C ₈	2.1	109	
B ₁	1.0	55	
B ₁₀	2.3	78	

^a Catalyst labeled C contain iridium while those labeled B contain rhodium.

^b Initial percentage metal.

^c Turnover number = mol of product/mole of catalyst/time (min).

^d 95% in all cases presented, determined by GLC of ethanol.

^e Silane substrate is TES; substrate/catalyst ratio is 100:1.

finding agrees well with the mechanism¹⁶ generally accepted for catalysis by transition metal complexes.

The difference in activity between iridium and rhodium complexes is probably fundamental involving less steric hindrance in the larger iridium atom which shares the same d⁹ configuration with rhodium. Both metals, however, exhibit similar characteristics as the density of ligands on the support is increased—compare Tables IV and VI; V and VII where rate increases in the latter.

There was no induction period associated with the reaction. This means that the active form of the complex must be already present on the support. The ability of the support to stabilize such active forms is noteworthy. Many^{3,1} catalytically active complexes go through an induction period during which process the complexes are rearranged to the active form. Table VIII shows that catalysis is associated with loss of metal from support, which leads to lower rates on subsequent use. This has been somewhat controlled by use of a mixture of the supported complex and the support without any metal.¹⁷ The problem appears to involve ligand/substrate insertion and deinsertion¹⁶ on the metal. This particular system of polymer support would appear to deserve further attention especially for substances like enzymes, where activity could be removed from the point of attachment to support.

CONCLUSION

The physical properties of P₁ and P₂ confer good support properties on them as shown by the nearly equivalent ease of diffusion of two substrates with molecular weight ratio of about 2000 (see Table IX). Enhanced diffusion within the polymer matrices is also due to inertness of the support material with respect to the substrates. The polymers do not swell in either hydrophobic or hydrophilic solvents which makes choice of solvent easy during application of these polymers.

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