Journal of Organometallic Chemistry, 87 (1975) 203—216

SUPPORTED TRANSITION METAL COMPLEXES

II*. SILICA AS THE SUPPORT

K.G. ALLUM, R.D. HANCOCK, I.V. HOWELL*, S. McKENZIE, R.C. PITKETHLY and P.J. ROBINSON

The British Petroleum Company Limited, BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex (Great Britain)

(Received October 11th, 1974)

Summary

Liganding groups may be chemically bonded to silica by reaction of the surface silanols with molecules of the type $RSiX_3$, in which R is an organic group containing a ligand atom and X is a hydrolysable group (eg OC_2H_5). Ligand-silicas, so formed, may be used to prepare transition metal complexes. Alternatively complexes with a ligand containing a SiX_3 group may be prepared and subsequently bonded to the silica surface. The principles are illustrated by the preparation of some phosphorus, nitrogen, sulphur and oxygen donor ligands and ligand-silicas. Carbonyl containing rhodium complexes of these ligands are described.

Introduction

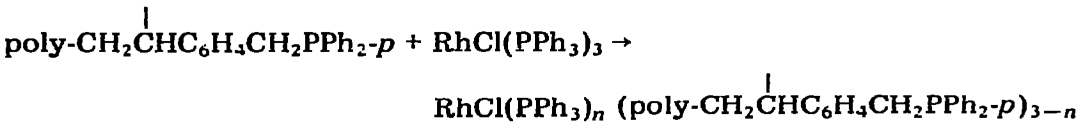
Many highly active and selective catalysts can be derived from transition metal complexes and the properties of these catalysts may often be varied widely by a change in the electronic and steric environment of the metal centre. However, these homogeneous catalysts are often more difficult to handle than heterogeneous catalysts particularly on an industrial scale — for instance in their separation from the reaction products. Attempts are now being made to combine the practical advantages of conventional heterogeneous catalysts with the versatility of homogeneous transition metal catalysts [1]. The objective is to obtain a well defined complex that can be highly dispersed throughout the reaction medium while remaining in a separate phase. This may be achieved by the

---

* For Part I see ref. 2.

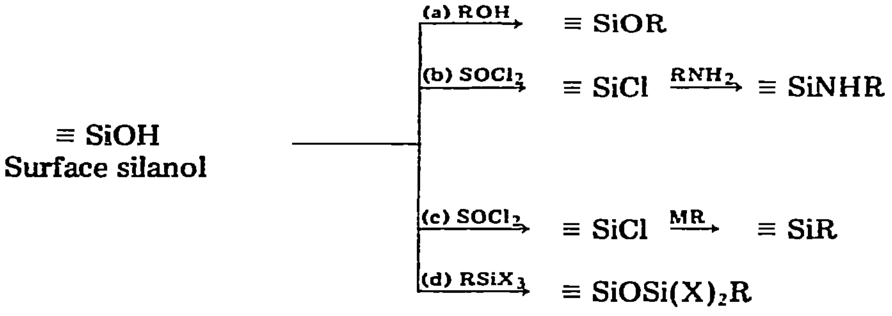
synthesis of a suitable transition metal complex in which one or more of the ligands is chemically bonded to the surface of a high surface area solid support.

Organic polymers have been used as the supporting macromolecule both in our group [2,3], and by other workers [4-6]. The polymer is chemically modified to introduce the liganding group. The desired complex is obtained by reaction of the product ligand-polymer with a transition metal compound precursor or by exchange for a monomeric ligand in an analogous complex, e.g. [7]:



$$\text{poly-CH}_2\overset{|}{\text{C}}\text{HC}_6\text{H}_4\text{CH}_2\text{PPh}_2\text{-}p + \text{RhCl(PPh}_3)_3 \rightarrow \text{RhCl(PPh}_3)_n\ (\text{poly-CH}_2\overset{|}{\text{C}}\text{HC}_6\text{H}_4\text{CH}_2\text{PPh}_2\text{-}p)_{3-n}$$

We have also investigated the use of inorganic materials as the macromolecular support [3], and have demonstrated that complexes may be prepared on silica, alumina, sepiolite and molecular sieves. However, silica has been used as the macromolecule for most of the work. To form a chemical bond between a ligand and the surface of silica, a molecule containing the liganding group, or a group that may readily be converted to a liganding group, is reacted with the surface silanols. In principle this may be done in several ways, all of which have been used to bond organofunctional groups to inorganic surfaces, for instance in chromatographic applications [8-12].



$$\equiv\text{SiOH (Surface silanol)} \xrightarrow{\text{(a) ROH}} \equiv\text{SiOR}$$

$$\equiv\text{SiOH} \xrightarrow{\text{(b) SOCl}_2} \equiv\text{SiCl} \xrightarrow{\text{RNH}_2} \equiv\text{SiNHR}$$

$$\equiv\text{SiOH} \xrightarrow{\text{(c) SOCl}_2} \equiv\text{SiCl} \xrightarrow{\text{MR}} \equiv\text{SiR}$$

$$\equiv\text{SiOH} \xrightarrow{\text{(d) RSiX}_3} \equiv\text{SiOSi(X)}_2\text{R}$$

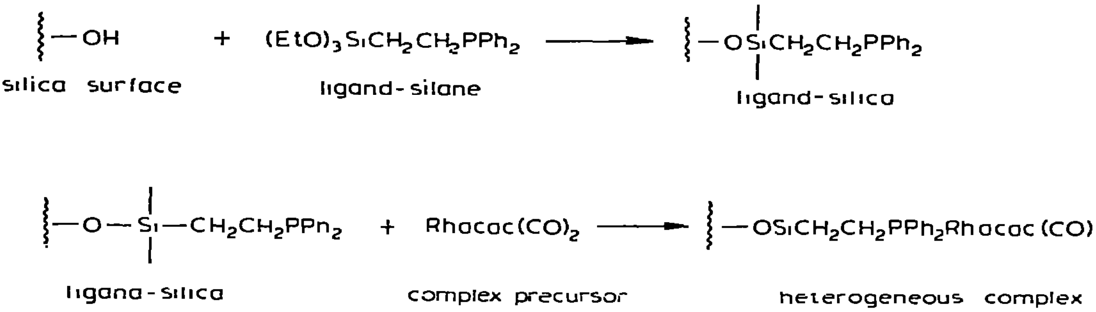
(R = an organofunctional group; X = a readily hydrolysable group, such as Cl, OR, NH_2, OCOR; MR = a metallo-organic compound such as LiR, XMgR)

We have preferred method (d) for bonding liganding groups to silica because (i) it produces an Si—C unit at the surface and this is much more hydrolytically and thermally stable than either an Si—O—C or an Si—N—C unit, (ii) a wide range of organofunctional compounds of the type $RSiX_3$ is readily available, (iii) it is a one step reaction that is simple to carry out under mild conditions.

The heterogeneous complex may be formed from the ligand-silica by the same methods used for ligand-polymers (Scheme 1). However, since the reaction with the surface takes place under relatively mild conditions and the reaction does not involve the ligand donor atom, there exists an alternative of forming the metal complex in solution prior to attaching the ligand to the surface (Scheme 2).

The purpose of this paper is to outline the methods that have been used to obtain ligand-silicas and heterogeneous complexes. Subsequent papers will de-

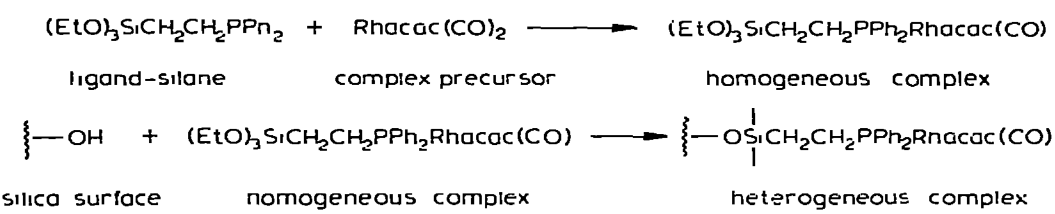
SCHEME 1



$$\{-OH + (EtO)_3SiCH_2CH_2PPh_2 \longrightarrow \{-OSiCH_2CH_2PPh_2$$

$$\{-O-Si-CH_2CH_2PPh_2 + Rhacac(CO)_2 \longrightarrow \{-OSiCH_2CH_2PPh_2Rhacac(CO)$$

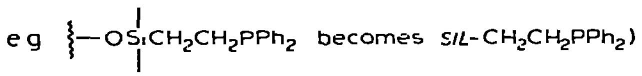
SCHEME 2



$$(EtO)_3SiCH_2CH_2PPh_2 + Rhacac(CO)_2 \longrightarrow (EtO)_3SiCH_2CH_2PPh_2Rhacac(CO)$$

$$\{-OH + (EtO)_3SiCH_2CH_2PPh_2Rhacac(CO) \longrightarrow \{-OSiCH_2CH_2PPh_2Rhacac(CO)$$

(The ligand-silica may be conveniently written as *SIL*-ligand



e g $\{-OSiCH_2CH_2PPh_2$ becomes *SIL*-$CH_2CH_2PPh_2$)

scribe the use of heterogeneous complexes as catalysts for the hydrogenation and hydroformylation of olefins.

Results

Ligands

In principle any ligand that forms part of an organic molecule can be introduced into a molecule of the type $RSiX_3$ and hence linked to the silica surface. However, in practice, it is sometimes easier to modify or replace an organic group already attached to the surface. Both methods have been used in this work to obtain a range of phosphorus, nitrogen, sulphur and oxygen donor ligands.

Four types of tertiary phosphine ligand-silane have been prepared: trialkyl-, alkyldicycloalkyl-, alkyldiaryl- and triaryl-phosphines. $(EtO)_3SiCH_2CH_2P(C_6H_{13})_2$, $(EtO)_3SiCH_2CH_2P(C_6H_{11})_2$ and $(EtO)_3SiCH_2CH_2PPh_2$ were synthesised by UV light-induced addition of the corresponding secondary phosphine to vinyltriethoxysilane [13]. The triarylphosphine ligand-silane, $(EtO)_3SiCH_2CH_2CH_2CH_2C_6H_4PPh_2$-*p*, was prepared by the UV light induced addition of Cl_3SiH to *p*-$Ph_2PC_6H_4CH_2CH_2CH = CH_2$, followed by ethanolysis of the $SiCl_3$ group. Each of these phosphines reacts with silica to give the corresponding ligand-silica. An alkyldiarylphosphine ligand-silica, *SIL*—$CH_2CH_2CH_2PPh_2$, has also been prepared by reaction of a chloroalkyl-silica, *SIL*—$CH_2CH_2CH_2Cl$, with potassium diphenylphosphide, following Issleib's procedure [14]. The chloroalkyl-silica had been treated previously with Me_3SiCl to convert any remaining accessible OH groups to $OSiMe_3$, thus preventing side reaction of the Ph_2PK with the surface.

Four types of nitrogen donor ligand have been synthesised: nitrile, primary amine, pyridine and tertiary amine. The nitrile ligand-silica, *SIL*—CH_2CH_2CN, and primary amine ligand-silica, *SIL*—$CH_2CH_2CH_2NH_2$, were prepared by reaction of $(EtO)_3SiCH_2CH_2CN$ and $(EtO)_3SiCH_2CH_2CH_2NH_2$ with silica. The pyridine ligand-silica, *SIL*—4-$CH_2CH_2CH_2CH_2C_5H_4N$ was prepared by the reaction of chloropropyl-silica with 4-picolinatolithium. Two tertiary amine ligand-silicas, *SIL*—$CH_2CH_2CH_2NEt_2$ and *SIL*—$CH_2CH_2CH_2N(CH_2)_4$ were prepared by reaction of *SIL*—$CH_2CH_2CH_2Cl$ with the corresponding secondary amine and the third, *SIL*—$C_6H_4CH_2N(CH_2Ph)_2$-*p*, by reaction of *SIL*—$C_6H_4CH_2Cl$-*p* with dibenzylamine.

Two examples of Group VI donor ligands have been used. A thiol ligand-silica was prepared by the reaction of $(EtO)_3SiCH_2CH_2CH_2SH$ with silica. An acetylacetone ligand-silane, $(EtO)_3SiCH_2CH_2CH_2CH(COCH_3)_2$ was prepared by a platinum-catalysed addition of triethoxysilane to 3-allylacetylacetone. This reacts with silica in the usual way.

The extent of reaction between the silane and the surface may be varied between wide limits. For example, by controlling the temperature and time of reaction and by using varying amounts of water in the reaction of $(MeO)_3SiCH_2$-CH_2CH_2Cl with silica, products were obtained that contained 2.4, 3.4, 4.0 and 5.4% weight chlorine.

It is evident that reaction of a ligand-silane with silica may not involve all the surface hydroxyl groups. The accessible ones that remain may be removed by reaction with a silylating reagent such as trimethylchlorosilane (as mentioned above) or hexamethyldisilazane. This has been shown to reduce side reactions during use of complexes of the ligand-silicas as catalysts at high temperatures [15].

Complexes

The ligand-silicas and ligand-silanes have been used to prepare a range of carbonyl-containing rhodium complexes, which are described below. Silica-supported complexes of cobalt [3], nickel [3], palladium, platinum, iridium and ruthenium have also been prepared as have other rhodium complexes [15].

Table 1 summarises reactions that have been carried out between rhodium(I)

TABLE 1

SCHEME 1 REACTIONS

Ligand-silica	Donor atom (%wt.)	Complex precursor	Product colour	Rh (%wt.)
SIL—$CH_2CH_2PPh_2$	0.2	$Rhacac(CO)_2$	pale yellow	0.4
SIL—$CH_2CH_2PPh_2$	1.2	$[RhCl(CO)_2]_2$	yellow	2.1
SIL—CH_2CH_2CN	0.3	$[RhCl(CO)_2]_2$	yellow	0.7
SIL—$CH_2CH_2CH_2NH_2$	3.1	$[RhCl(CO)_2]_2$	orange	1.6
SIL—$CH_2CH_2CH_2NEt_2$	1.1	$[RhCl(CO)_2]_2$	red-brown	3.7
SIL—$CH_2CH_2CH_2N(CH_2)_4$	1.0	$[RhCl(CO)_2]_2$	brown	1.7
SIL—4-$CH_2CH_2CH_2CH_2C_5H_4N$	0.4	$[RhCl(CO)_2]_2$	orange-brown	2.1
SIL—$C_6H_4CH_2N(CH_2Ph)_2$-*p*	1.1	$[RhCl(CO)_2]_2$	pale yellow	0.9
SIL—$CH_2CH_2CH_2SH$	0.6	$[RhCl(CO)_2]_2$	red-brown	1.8

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF COMPLEXES

Complex	Solvent or Nujol mull	Carbonyl stretching frequency[a] (cm^{-1})				Ref.
$Rhacac(CO)_2$	heptane		2086	2016		*b*
$Rhacac(CO)(Ph_2PEt)$	heptane				1983	*b*
$Rhacac(CO)(poly\text{-}CH_2CHC_6H_4CH_2\text{-}PPh_2\text{-}p)$	mull				1975	2
$Rhacac(CO)(SIL{-}CH_2CH_2PPh_2)$	mull				1975	*b*
$[RhCl(CO)_2]_2$	hexane	2105 m	2089	2035		25
trans-$RhCl(CO)(Ph_3P)_2$	mull				1961	26
cis-$RhCl(CO)(Ph_3P)_2$	mull				1978	27
cis-$RhCl(CO)_2(Ph_3P)$	hexadecane		2088	2002		28
$Rh_2Cl_2(CO)_2(Ph_3P)_2$	mull				1982	29
$RhCl(CO)_2(poly\text{-}CH_2CHC_6H_4CH_2\text{-}PPh_2\text{-}p)$	mull		2085	1993		24
$RhCl(CO)_2(SIL{-}CH_2CH_2PPh_2)$	mull		2090	2018		*b*
cis-$RhCl(CO)_2(Et_3N)$	*c*		2090	2002		21
cis-$RhCl(CO)_2(PhCH_2NMe_2)$	*c*		2088	2004		21
cis-$RhCl(CO)_2(poly\text{-}CH_2CHC_0H_4\text{-}CH_2NMe_2\text{-}p)$	mull		2083	2002		21
cis-$RhCl(CO)_2[SIL{-}C_6H_4CH_2N\text{-}(CH_2Ph)_2\text{-}p]$	mull		2085	2006		*b*
cis-$RhCl(CO)_2(SIL{-}CH_2CH_2CH_2\text{-}NH_2)$	mull		2095	2009		*b*
cis-$RhCl(CO)_2[SIL{-}CH_2CH_2CH_2\text{-}N(CH_2)_4]$	mull		2080	1998		*b*
cis-$RhCl(CO)_2(SIL{-}CH_2CH_2CH_2\text{-}NEt_2)$	mull		2078	2000		*b*
cis-$RhCl(CO)_2(CH_3CN)$	*c,d*		2090	2020		21
cis-$RhCl(CO)_2(poly\text{-}CH_2CHC_6H_4\text{-}CH_2CN\text{-}p)$	mull		2088	2018		21
cis-$RhCl(CO)_2(SIL{-}CH_2CH_2CN)$	mull		2087	2019		*b*
cis-$RhCl(CO)_2(C_5H_5N)$	*c*		2089	2005		21
cis-$RhCl(CO)_2(poly\text{-}2\text{-}CH_2CHC_5\text{-}H_4N)$	mull		2085	2010		21
cis-$RhCl(CO)_2(SIL{-}4\text{-}CH_2CH_2\text{-}CH_2CH_2C_5H_4N)$	mull		2084	2008		*b*
$[Rh(SBu)(CO)_2]_2$	CH_2Cl_2	2078 m	2059	2009		24
$[Rh(SPr)(CO)_2]_2$	CH_2Cl_2[e]	2075	2055	1998 m		21
$Rh_2Cl(poly\text{-}CH_2CHC_6H_4CH_2S\text{-}p)\text{-}(CO)_4$	mull	2070 m	2055	2022		21
$\{[RhCl(CO)_2]_2 + SIL{-}CH_2CH_2\text{-}CH_2SH\}$	mull	2084 m	2056	2009		*b*

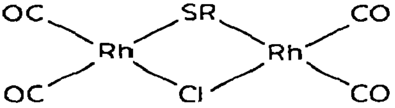
[a] Intensity strong unless otherwise indicated. [b] Present work. [c] CO saturated hexane or benzene. [d] Excess nitrile. [e] Excess PrSH.

carbonyl complexes and ligand-silicas. Table 2 gives the carbonyl stretching frequencies of the product complexes and those of some similar polymer supported and homogeneous complexes.

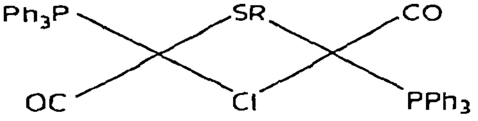
The reaction of $Rhacac(CO)_2$ with tertiary phosphine ligand-silica proceeds in a manner directly analogous to that with a monomeric tertiary phosphine in the substitution of one carbonyl [16]. The reaction of $[RhCl(CO)_2]_2$ with tertiary phosphines is more complicated since two reactions can occur, substitution of a carbonyl and splitting of the halide bridge [17]. The infrared evidence points to the splitting of the halide bridge and no substitution of a carbonyl when using $SIL{-}CH_2CH_2CH_2PPh_2$.

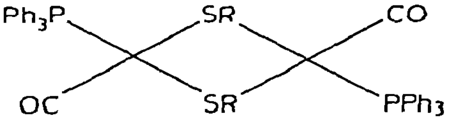
The reaction of $[RhCl(CO)_2]_2$ with nitrogen donor ligands generally leads to a splitting of the halide bridge [18-21]. The infrared evidence is consistent with this reaction taking place with all the nitrogen donor ligand-silicas.

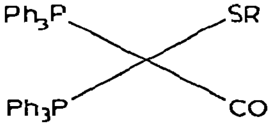
Thiols react with $[RhCl(CO)_2]_2$ to substitute the halide in the bridge by RS [22,23]. The thiol ligand-silica apparently reacts similarly since evolution of hydrogen chloride is observed during the reaction, but the extent to which this substitution takes place has not been determined. Rollman [21] postulated a structure of the type

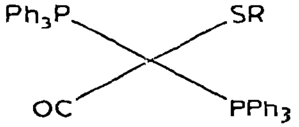


on the basis of the difference in relative intensities of the three carbonyl bands observed when using a monomeric thiol and polyvinylbenzylthiol (Table 2). However, the relative intensities that he reports for the monomeric thiol complex differ from those obtained with the thiol complexes which we have prepared [24] and those prepared by other workers [23]. Reaction of the thiol ligand-silica complex with triphenylphosphine gives a yellow product, the infrared spectrum of which has $\nu(CO)$ 1967 cm^{-1} with a shoulder at ca. 1976 cm^{-1}, indicating the presence of at least two distinct types of surface species in which one carbonyl group has been substituted. The rhodium and phosphorus contents of the material, 1.4 and 0.5% weight respectively, give a Rh/P ratio of 1/1.2. From this ratio it can be inferred that there is more than one surface species with different ratios of phosphine to rhodium. Possible structures for these species include:









Carbonyl-containing rhodium complexes have also been prepared with ligand-silanes and these subsequently reacted with a silica surface (Scheme 2). $[RhCl(CO)_2]_2$ reacts with four moles of a tertiary phosphine to give [RhCl(CO)(phosphine)$_2$] [25] which reacts with $NaBH_4$ in the presence of excess phosphine to give [RhH(CO)(phosphine)$_3$] [30]. Solid yellow complexes have been prepared in this way using the tertiary phosphine ligand-silane. $(EtO)_3SiCH_2CH_2PPh_2$. These complexes have been reacted with silica to give yellow materials containing 0.9 and 1.2% weight rhodium respectively.

Rhacac$(CO)_2$ is prepared by the reaction of $[RhCl(CO)_2]_2$ with acetylacetone in the presence of a base [16]. The reaction of $[RhCl(CO)_2]_2$ with 3-(3-triethoxysilylpropyl)acetylacetone gave a red oil, from which no crystalline materials could be obtained, but which reacted with silica to give a brown material containing 0.4% weight rhodium.

Discussion

Liganding groups can be chemically bonded to the surface of macromolecules. Thus transition metal complexes may be prepared which are highly dispersed on and chemically bonded to the surface of an insoluble macromolecule. Such complexes have been shown to produce catalyst systems, which combine the advantages in homogeneous catalysis of high activity and selectivity with the ease of handling associated with heterogeneous catalysts [4,5]. Most work in this field has concerned organic polymers as the macromolecular support, whereas inorganic macromolecules, such as silica, have physical properties which offer considerable advantages as supports for large scale applications of heterogeneous catalysts. As organic polymers do not have a rigid structure, so their conformation and hence the shape and size of the particles is strongly influenced by solvents, temperature and pressure. This may limit their use in large scale apparatus where long catalysts beds and large pressure drops are encountered. Silica, on the other hand, is mechanically rigid and is unaffected by all but the most severe solvent and temperature conditions.

The chemical bonding of organofunctional groups to the surface of inorganic solids has found application in many fields [8,31]. The most widely used method and the one leading to the most stable products is the reaction of $RSiX_3$ molecules with surface hydroxyl groups. This reaction has been demonstrated for many inorganic surfaces such as those of silica [32], diatomaceous earths [19], glass [31], and nickel oxide on nickel [33], but the most stable bonds are formed with silica. This and the inertness of its surface made silica the ideal choice for the initial investigation.

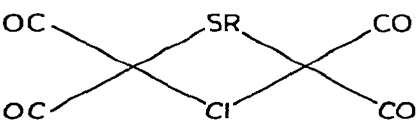
The course of the reaction of the silica surface with molecules containing an Si—X bond has been investigated extensively [32,34-45], particularly from the gas phase. Generally, at lower temperatures, adsorption occurs, but this is followed by condensation as the temperature is raised, the temperature at which condensation begins depending upon the nature of X. Reaction from a liquid phase appears to take place more readily [44,45] and certain groups, such as amines, catalyse the condensation with the surface [32]. In the presence of water the Si—X hydrolyses to Si—OH which can condense either with a surface silanol or with the silanol of another molecule. The former leads to individual linking of all ligand molecules to the surface, the latter to a cross linked polysiloxane network with few chemical bonds to the silica surface [46]. Intermediate structures are probably formed in most cases.

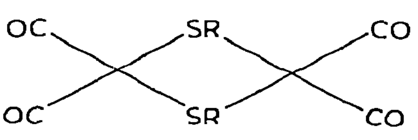
The presence of a surface to silane bond is difficult to establish conclusively in all but the simplest cases. However, the production of an alcohol, together with the fact that the ligand-silane cannot be removed from the surface by repeated washings with hot solvents, strongly suggests that the ligand-silane is chemically bonded to the surface.

Theoretically any ligand that contains an organic group can be included in a molecule of the type $RSiX_3$ and can thus be chemically attached to a silica surface. For instance, the reaction of triethoxyvinylsilane with secondary phosphines could be used to prepare a great variety of tertiary phosphine ligand-silanes and hence tertiary phosphine ligand-silicas. Preparation of a triarylphosphine ligand-silane is more difficult, but can be accomplished by hydrosilylation of a double bond in a substituted triaryl-phosphine (see experimental section). In practice there are cases where ligand-silicas are more easily obtained by reaction of an organofunctional group attached to the silica surface. This was shown to be a particularly useful route to tertiary amine ligand-silicas, by reaction of *SIL*—$CH_2CH_2CH_2Cl$ and *SIL*—$C_6H_4CH_2Cl$-*p* with secondary amines.

Ligand-silicas may be used as direct replacements for the more usual monomeric ligands in just the same way as ligand-polymers. Their reaction with complex precursors or ligand exchange reactions can then be used to prepare the desired complex. This is relatively straightforward where there is only one ligand required and one possible product, as in the reaction of $Rhacac(CO)_2$ with *SIL*—$CH_2CH_2PPh_2$ to give $Rhacac(CO)($*SIL*—$CH_2CH_2PPh_2)$. Where several ligands are required and there is a possibility of obtaining several products, the course of the reaction is complicated by the inhomogeneity of the surface. The liganding groups on the surface are randomly distributed so that there will not be a fixed distance between pairs. Thus the particular requirements for the formation of a certain complex may only be met by a small number of the groups and some other groups may be correctly placed for the formation of a different complex. Even if only one species is formed it is difficult to determined its structure unless the complex contains a suitable analytical 'handle' which can readily be identified, such as the CO stretching frequency in the infrared spectrum of carbonyl complexes. Elemental analyses are of little assistance since the complex is such a small proportion of the whole that all the figures are small and relatively inaccurate. Besides, it is unlikely, on steric grounds, that all the liganding groups will be available to complex with the metal centre.

$[RhCl(CO)_2]_2$ can form a variety of products on reaction with a tertiary phosphine. Since all the products contain at least one carbonyl group it was possible from the infrared spectrum to assign the species formed with *SIL*—$CH_2CH_2CH_2PPh_2$ the structure *cis*-$RhCl(CO)_2($*SIL*—$CH_2CH_2CH_2PPh_2)$ based on the infrared data of species formed in homogeneous reactions with triphenylphosphine (see Table 2). However the presence of carbonyl groups is not always sufficient. The reaction of $[RhCl(CO)_2]_2$ with *SIL*—$CH_2CH_2CH_2SH$ also gives a product containing carbonyl groups, but the infrared spectrum gives insufficient data to assign a structure to the surface species. This is because the two likely products:





are expected to have similar infrared spectra. However, the low chlorine content of the product indicates a preponderance of the latter. The reaction of the product {*SIL*—$CH_2CH_2CH_2SH + [RhCl(CO)_2]_2$} with triphenylphosphine appears on the basis of the infrared spectrum to give a mixture of products with an Rh/CO ratio of 1, but no further conclusion can be reached as there are insufficient data on homogeneous complexes for comparison.

Despite these uncertainties the method of Scheme 1 does have certain advantages:

(i) the range of ligands is readily extended by standard organic reactions of organofunctional groups attached to the surface, that are not applicable to the $RSiX_3$ species. For instance, *SIL*—$CH_2CH_2CH_2Cl$ may be reacted with $KPPh_2$ and 4-$LiCH_2C_5H_4N$ to give *SIL*—$CH_2CH_2CH_2PPh_2$ and *SIL*—4-$CH_2CH_2CH_2CH_2C_5H_4N$ whereas similar reactions with $(MeO)_3SiCH_2CH_2CH_2Cl$ and $(MeO)_3SiC_6H_4CH_2Cl$-*p* are precluded by the reactivity of the Si-OMe group.

(ii) Species that are unstable in solution may be isolated. In this case, the surface rigidity is put to good effect, in that species which are unstable in solution because they interact with each other to form dimeric species, for example, may be generated in a more stable form on a surface where the opportunity for intermolecular interactions is greatly reduced. This has been demonstrated by Grubbs [47] in the case of the Cp_2TiCl_2/alkyllithium hydrogenation system, where in solution there is a rapid decay in activity due to dimerisation of the titanium species but a very slow decay when one of the cyclopentadienyl ligands is chemically bonded to a polystyrene resin.

(iii) The surface properties of the silica may be altered prior to reaction with a sensitive metal centre. After reaction of the surface with a bulky organosilane, some silanol groups will still be present. The more accessible of these may be removed by silylation, thus decreasing the polarity of the surface. This opens up the possibility of controlling the microenvironment of a catalytic centre, which may prove to have beneficial effects on its activity and selectivity. It has been shown that silylation of the silica surface reduces the side reactions of the silica base [15].

The method of Scheme 2, by which a soluble complex is prepared that can subsequently be attached to the surface by one or more reactive ligands, is an alternative means of preparing heterogeneous complexes that is not available when organic polymers are used as supports. That this method is available with inorganic supports is due to the linking reaction proceeding at a point in the ligand molecule removed from the donor atom and under relatively mild conditions. The chief advantage of using this means of preparing heterogeneous complexes is the elimination of a large degree of doubt about the nature of the surface species. The complex that is to be linked can be made by a standard method, provided that this does not involve the use of aqueous solutions which would lead to polymerisation of the ligand-silane. In principle the complex may be separated and analysed by standard methods and then allowed to react with the surface. In practice some complexes containing the ligand-silane cannot be obtained as crystalline materials. This complicates the purification procedure, particularly as chromatographic separations could only be carried out using non-hydroxylic phases. For instance, $Rhacac(CO)_2$ can readily be obtained as a green crystalline solid, but $Rh[(EtO)_3SiCH_2CH_2CH_2C(COCH_3)_2](CO)_2$ could only be obtained as a red oil. However the complexes $RhCl(CO)[(EtO)_3SiCH_2CH_2PPh_2]_2$ and $RhH(CO)[(EtO)_3SiCH_2CH_2PPh_2)_3]$ were obtained as yellow solids and characterised. They reacted with silica to give $RhCl(CO)($*SIL*—$CH_2CH_2PPh_2)_2$ and $RhH(CO)($*SIL*—$CH_2CH_2PPh_2)_3$. These heterogeneous complexes would be difficult to obtain by other means: the former since the reaction of $[RhCl(CO)_2]_2$ with *SIL*—$CH_2CH_2CH_2PPh_2$ only led to splitting of the halogen bridge and no carbonyl substitution, the latter since it is very unlikely that three phosphine groups would be oriented correctly on the surface, without being previously attached to some kind of template.

Thus the method of Scheme 2 also has certain advantages:

(i) the ligand to metal ratio may be controlled.

(ii) Complexes that could not be prepared from a ligand-silica may be attached to the surface.

(iii) Separation and characterisation of a discrete complex is possible, even when direct reaction of the ligand-silica with the complex precursor would lead to a mixture of products on the surface.

Although there is no absolute certainty that the structure of the species will be maintained when it is attached to the surface, it is unlikely that the nature of the complex would be substantially altered under the relatively mild conditions of the linking reaction.

The methods of Scheme 1 and Scheme 2 are complementary. In some cases, complexes such as Rhacac(CO)(phosphine) may readily be prepared by either method, but in others one scheme is much preferred. For instance, RhCl-$(CO)_2$(phosphine) is more readily prepared by Scheme 1, whereas RhH(CO)-$(phosphine)_3$ can only be prepared by Scheme 2. Use of both these methods opens up a wide range of possibilities for the preparation of transition metal complexes that are chemically bound to the surface of an inert solid. These may be used as heterogeneous analogues of homogeneous catalysts and may extend the range of possible transition metal complex catalysts by the stabilisation of species that are too reactive when mobile in solution.

Experimental

All preparations were carried out in a dry, oxygen-free nitrogen atmosphere. Solvents were dried before use. Infrared spectra were measured with a Perkin—Elmer 257 spectrometer.

Carbonyl stretching frequencies are given in Table 2.

General reaction of a silane with silica

A solution of the silane in an aromatic solvent was stirred with silica and the mixture heated to reflux for two hours or more. If a Dean and Stark apparatus is used, some of the boiling solvent may be run off, to remove the alcohol formed in the reaction. After cooling the solid was transferred to a Soxhlet apparatus and extracted with benzene or toluene. Finally the ligand-silica was dried in vacuo.

Variation of reaction conditions for the reaction of $(MeO)_3SiCH_2CH_2CH_2Cl$ with silica

(a) $(MeO)_3SiCH_2CH_2CH_2Cl$ (32 ml) was added to silica (31.9 g) suspended in toluene (200 ml) and the mixture refluxed for seven hours. After extraction with toluene for 24 h and drying, the chlorine content was 2.4%.

(b) Silica (34 g) was suspended in toluene, water (3.5 ml) added and the mixture stirred at room temperature for one hour. $(MeO)_3SiCH_2CH_2CH_2Cl$ (35 ml) was added and the mixture stirred at room temperature. Samples were removed after (i) 24 h and (ii) 48 h, extracted with toluene for 24 h and dried. Found: (i) 3.4% Cl, (ii) 4.0% Cl.

(c) Silica (35.9 g) was suspended in xylene, water (7 ml) added and the mixture stirred at room temperature for 15 min. $(MeO)_3SiCH_2CH_2CH_2Cl$ (35 ml) was added and the mixture stirred at about 80° for 6 h. Finally most of the solvent was distilled off, the silica extracted with toluene for 24 h and dried. Found: 5.4% Cl.

Silylation of surface silanols

Typically, the silica was suspended in chlorotrimethylsilane, the mixture brought to reflux for about two hours and left to stand at room temperature overnight. The excess silane was distilled off and the silica dried in vacuo.

Preparation of ligand-silanes

(a) $(EtO)_3SiCH_2CH_2PR_2$. Equimolar quantities of vinyltriethoxysilane and secondary phosphine were irradiated with a high intensity UV lamp for about 100 h and the products distilled in vacuo. $(EtO)_3SiCH_2CH_2PPh_2$, b.p. 155-165°/ 0.1 Torr, 85% yield; $(EtO)_3SiCH_2CH_2P(C_6H_{13})_2$, b.p. 134° at 0.001 Torr, 89% yield: $(EtO)_3SiCH_2CH_2P(C_6H_{11})_2$ b.p. 180-205° at 0.3 Torr.

(b) $(EtO)_3SiCH_2CH_2CH_2CH_2C_6H_4PPh_2$-*p*. (i) Allyl bromide was added to *p*-$BrC_6H_4CH_2MgBr$ (prepared under standard Grignard conditions) to yield *p*-$BrC_6H_4CH_2CH_2CH{=}CH_2$ (b.p. 85-120°/10 Torr).

(ii) To the Grignard reagent made from *p*-$BrC_6H_4CH_2CH_2CH{=}CH_2$ (112 g, 0.53 mol) in THF (100 ml) cooled to below 0^c was added Ph_2PCl (85 ml, 0.46 mol) in THF (100 ml). After the addition was complete the solution was allowed to warm to room temperature and then heated under reflux for 20 min. After cooling to ca. 0°, a slight excess of dilute HCl, saturated with NaCl was added, and the organic layer was separated and dried. The THF was distilled off and the product extracted with pentane. The pentane was distilled off and the *p*-butenylphenyldiphenylphosphine distilled (b.p. 188-192° at 0.5 Torr). Yield 38%.

(iii) *p*-$Ph_2PC_6H_4CH_2CH_2CH{=}CH_2$ (64 g, 0.2 mol) were placed in a silica flask with $HSiCl_3$ (50 ml, 4 mol) and the solution refluxed while under irradiation from a high intensity UV lamp for 120 h. The excess $HSiCl_3$ was distilled off and the product diluted with ether (1 l). Pyridine (320 g, 4 mol) and ethanol (220 ml, 3.7 mol) were added from a dropping funnel. The pyridinium chloride was filtered off and washed with ether. The filtrate was distilled to remove ether, pyridine and ethanol and the residue distilled in vacuo (b.p. 208-220°/0.1 Torr). Yield of the ligand-silane 30%.

(c) $(EtO)_3SiCH_2CH_2CH_2CH(COCH_3)_2$. 3-allylacetylacetone (14 g, 0.1 mol) and triethoxysilane (16.4 g, 0.1 mol) were stirred at 100° in the presence of Pt-on-charcoal (0.25 g, 5% Pt) for 24h. The catalyst was filtered off and the filtrate distilled to give a clear liquid; b.p. 130-139°/1.0 Torr. Yield 60%.

Preparation of ligand-silicas

(a) SIL—$CH_2CH_2CH_2PPh_2$. Silylated *SIL*—$CH_2CH_2CH_2Cl$ (15 g, 1.2% Cl) was suspended in THF. An excess of $KPPh_2$ in THF was added and the mixture brought to reflux for one hour. Methanol was added and the silica soxhlet extracted with methanol for 24 h and then toluene for 24 h. Finally it was dried in vacuo to give a material containing 0.1% Cl and 0.4% P.

(b) SIL—4-$CH_2CH_2CH_2CH_2C_5H_4N$. Silylated *SIL*—$CH_2CH_2CH_2Cl$ (28.4 g,

1.0% Cl) was suspended in toluene. An excess of 4-$LiCH_2C_5H_4N$ in THF was added and the mixture brought to reflux for 2 h. Methanol was added and the silica extracted with methanol for 24 h. Finally it was dried in vacuo to give a material containing < 0.07% Cl and 0.2% N.

(c) SIL—$C_6H_4CH_2N(CH_2Ph)_2$-*p*. *SIL*—$C_6H_4CH_2Cl$-*p* (7.9 g, 3.6% Cl) was put into a glass pressure vessel with 25 ml $(PhCH_2)_2NH$ and the mixture heated at 150-160° under nitrogen (15 atm) for 7 h. The silica was extracted with methanol for 12 h and dried in vacuo to give a product containing 1.1% N and 0.1% Cl.

(d) SIL—$CH_2CH_2CH_2NEt_2$. *SIL*—$CH_2CH_2CH_2Cl$ (7.0 g, 3.3% Cl) was put into a glass pressure vessel with Et_2NH (25 ml) and the mixture heated at 155-165° under nitrogen (15 atm) for 7 h. The silica was extracted with methanol for 12 h and dried in vacuo to give a product containing 1.1% N and 0.1% Cl.

(e) SIL—$CH_2CH_2CH_2N(CH_2)_4$. *SIL*—$CH_2CH_2CH_2Cl$ (10.0 g, 3.3% Cl) was put into a glass pressure vessel with pyrrolidine (25 ml) and the mixture heated at 150-160° under nitrogen (15 atm) for 8 h. The silica was extracted with methanol for 12 h and finally dried in vacuo to yield a product containing 1.0% N and 0.1% Cl.

Reaction of SIL—$CH_2CH_2PPh_2$ with Rhacac$(CO)_2$

Rhacac$(CO)_2$ (0.201 g) was dissolved in heptane (75 ml). *SIL*—$CH_2CH_2PPh_2$ (5.1 g, 0.2% P) was added and the mixture stirred at room temperature for 2 h. The silica was extracted with hexane for 8 h and dried in vacuo to give a pale yellow product containing 0.4% Rh.

Reaction of ligand-silicas with $[RhCl(CO)_2]_2$

$[RhCl(CO)_2]_2$ (ca. 0.2 g) was dissolved in heptane (100 ml). The ligand-silica was added and the mixture stirred at room temperature for 6 h and then allowed to stand overnight. The product silica was washed with heptane (6 × 50 ml) and dried in vacuo.

(a) *SIL*—$CH_2CH_2PPh_2$ (3.1 g, 1.2% P) gave a yellow product (2.1% Rh).

(b) *SIL*—$CH_2CH_2CH_2NH_2$ (5.2 g, 3.1% N) gave an orange product (1.6% Rh).

(c) *SIL*—CH_2CH_2CN (3.4 g, 0.3% N) gave a yellow product (0.7% Rh).

(d) *SIL*—$C_6H_4CH_2N(CH_2Ph)_2$-*p* (3.2 g, 1.1% N) gave a pale yellow product (0.9% Rh).

(e) *SIL*—$CH_2CH_2CH_2N(CH_2)_4$ (4.8 g, 1.0% N) gave a brown product (1.7% Rh).

(f) *SIL*—4-$CH_2CH_2CH_2CH_2C_5H_4N$ (4.4 g, 0.4% N) gave an orange-brown product (2.1% Rh).

(g) *SIL*—$CH_2CH_2CH_2NEt_2$ (3.2 g, 1.1% N) gave a red-brown product (3.7% Rh).

(h) *SIL*—$CH_2CH_2CH_2SH$ (4.1 g, 0.6% S) gave a red-brown product (1.8% Rh).

Preparation of $RhCl(CO)((EtO)_3SiCH_2CH_2PPh_2)_2$

$[RhCl(CO)_2]_2$ (2.49 g, 6.4 mmol) was dissolved in benzene and $(EtO)_3SiCH_2CH_2PPh_2$ (9.60 g, 25.5 mmol) in benzene added. The reaction mixture was stirred for 15 min, whereupon the colour changed from red to yellow. The mixture was allowed to stand overnight, and then the solution was evaporated to a small bulk and pentane added to give a yellow precipitate. Analysis found: C, 53.8; H, 6.5; Cl, 3.6; P, 7.1; Rh, 11.1. $C_{41}H_{58}O_7P_2Si_2ClRh$ calcd.: C, 53.6; H, 6.3; Cl, 3.9; P, 6.7; Rh, 11.2%. ν(CO) 1966 cm^{-1} (nujol mull).

Preparation of $RhH(CO)((EtO)_3SiCH_2CH_2PPh_2)_3$

$RhCl(CO)[(EtO)_3SiCH_2CH_2PPh_2]_2$ (5.0 g, 5.5 mmol) was added to $NaBH_4$ (ca. 2 g) and $(EtO)_3SiCH_2CH_2PPh_2$ (8.3 g, 22.1 mmol) in refluxing ethanol to give a yellow solid. This was filtered off and recrystallized from benzene/pentane. Analysis found: Rh, 7.5; P, 6.8. $C_{61}H_{88}O_{11}P_3Si_3Rh$ calcd.: Rh, 8.3; P, 7.3%. Infrared bands at 1990 [ν(Rh—H)] and 1915 cm^{-1} [ν(CO)] (nujol mull).

Preparation of $SIL—CH_2CH_2CH_2C(COCH_3)_2Rh(CO)_2$

$[RhCl(CO)_2]_2$ (3.89 g, 0.01 mol) was dissolved in hexane and sodium propionate (1.88 g, 0.02 mol) added. The mixture was stirred for 2 h, warmed to reflux and $(EtO)_3SiCH_2CH_2CH_2CH(COCH_3)_2$ (18.2 g, 0.06 mol) added. After 24 h, the mixture was filtered and the red filtrate evaporated to a small bulk. This was then added to silica (10 g) suspended in refluxing benzene. The solid was extracted with ethanol for 24 h and dried in vacuo to give a brown product containing 0.4% Rh. ν(CO) 2060, 1995 cm^{-1} (nujol mull); (cf. Rhacac$(CO)_2$, ν(CO) 2086, 2016 cm^{-1}).

Acknowledgement

Permission to publish this paper has been given by The British Petroleum Company Limited.

References

1 F. Basolo and R.L. Burwell, (Eds.), Catalysis - Progress in Research, Plenum Press, London, 1973, p 177-185.
2 K.G. Allum, R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, J. Organometal. Chem., 87 (1975) 187.
3 K.G. Allum, R.D. Hancock, S. McKenzie and R.C. Pitkethly in J.W. Hightower (Ed.), Catalysis, Vol.1, North-Holland, Amsterdam, 1973, p. 477.
4 N. Kohler and F. Dawans, Rev. Inst. Fr. Petrole Ann. Combust. Liquides, 27 (1972) 105.
5 W.O. Haag and D.D. Whitehurst in J.W. Hightower (Ed.), Catalysis, Vol. 1, North-Holland, Amsterdam, 1973, p. 465.
6 Z.M. Michalska and D.E. Webster, Platinum Metals Rev., 18 (1974) 65.
7 R.H. Grubbs, L.C. Kroll and E.M. Sweet, J. Makromol. Sci. Chem., 7 (1973) 1047.
8 D.C. Locke, J. Chromatogr. Sci., 11 (1973) 120.
9 J.J. Kirkland and J.J. Destefano, J. Chromatogr. Sci., 8 (1970) 309.
10 O.E. Brust, I. Sebestian and I. Halász, J. Chromatogr., 83 (1973) 15.
11 D.C. Locke, J.T. Schmermund and B. Banner, Anal. Chem., 44 (1972) 90.
12 C.R. Hastings, W.A. Aue and F.N. Larsen, J. Chromatogr., 60 (1971) 329.
13 H. Niebergall, Makromol. Chem., 52 (1962) 218.
14 K. Issleib, Z. Chem., 2 (1962) 163.
15 Paper in preparation.
16 F. Bonati and G. Wilkinson, J. Chem. Soc., (1964) 3156.
17 Yu.S. Varshavsky, T.G. Cherkasova and N.A. Buzina, J. Organometal. Chem., 56 (1973) 375.
18 R. Ugo, F. Bonati and M. Fiore, Inorg. Chim. Acta, 2 (1968) 463.
19 W. Hieber, H. Heusinger and O. Vohler, Chem. Ber., 90 (1957) 2425.
20 D.N. Lawson and G. Wilkinson, J. Chem. Soc., (1965) 1900.
21 L.D. Rollman, Inorg. Chim. Acta, 6 (1972) 137.

22 W. Hieber and K. Heinicke, Z. Naturforsch. B, 16 (1961) 554.
23 E.S. Bolton, R. Havlin and G.R. Knox, J. Organometal. Chem., 18 (1969) 153.
24 Unpublished results.
25 J.A. McCleverty and G. Wilkinson, Inorg. Syn., 8 (1966) 211.
26 J. Chatt and B.L. Shaw, J. Chem. Soc. A, (1966) 1437.
27 J. Blum, E. Oppenheimer and E.D. Bergmann, J. Amer. Chem. Soc., 89 (1967) 2338.
28 R. Poilblanc and J. Gallay, J. Organometal. Chem., 27 (1971) C53.
29 F. Farone, G. Ferrara and E. Rotondo, J. Organometal. Chem., 33 (1971) 221.
30 D. Evans, G. Yagupsky and G. Wilkinson, J. Chem. Soc. A, (1968) 2660.
31 G.M. Cameron and J.G. Marsden, Chem. Brit., (1972) 381.
32 R.L. Kaas and H.L. Kardos, Polym. Eng. Sci., 11 (1971) 11.
33 H.H. Weetall and L.S. Hersh, Biochim. Biophys. Acta., 206 (1970) 54.
34 T.E. White, Proc. Soc. Plastics Industry 20th Annual Meeting, Chicago, 1965, Reinforced Plastics Division, Sect. 38, p. 1.
35 J.V. Duffy, J. Appl. Chem., 17 (1965) 35.
36 M.L. Hair and W. Hertl, J. Phys. Chem., 73 (1969) 2372.
37 C.G. Armistead and J.A. Hockey, Trans. Farad. Soc., 63 (1967) 2549.
38 F.O. Stark, O.K. Johannson, G.E. Vogel, R.G. Chaffee and R.M. Lacefield, J. Phys. Chem., 72 (1968) 2750.
39 W. Hertl, J. Phys. Chem., 72 (1968) 1248.
40 W. Hertl, J. Phys. Chem., 72 (1968) 3993.
41 K. Unger, K. Berg, E. Gallei and G. Erdel, Fortschr. Kolloid Polym., 55 (1971) 34.
42 W.J. Eakins, Ind. Eng. Chem., Prod. Res. Develop., 7 (1968) 39.
43 W.D. Bascom and R.B. Timmons, J. Phys. Chem., 76 (1972) 3192.
44 V.Ya. Davydov, A.V. Kiselev and L.T. Zhuralev, Trans. Farad. Soc., 609 (1964) 2254.
45 J.G. Koelling and K.E. Kolb, Chem. Commun., (1965) 6.
46 E.P. Plueddemann, J. Paint Technol., 42 (1970) 600.
47 R.H. Grubbs, C. Gibbons, L.C. Kroll, W.D. Bonds and C.H. Brubaker, J. Amer. Chem. Soc., 95 (1973) 2373.