JOURNAL OF Materials CHEMISTRY

Preparation and characterization of new organic–inorganic hybrid materials incorporating phosphorus centres

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The reaction of *p*-bromo(triisopropyloxysilyl)benzene **2** with magnesium led to stable THF solutions of the corresponding Grignard reagent. The reaction of this latter with PCl_3 or $PhPCl_2$ allowed the preparation of phosphines **4** and **5** respectively. $LiAlH_4$ reduction of **4** afforded phosphine **6**. Compounds **4** and **6** have been transformed into phosphorus derivatives including BH_3, $W(CO)_5$, platinum and palladium complexes, all of them bearing three hydrolysable groups. Hydrolysis and condensation of these phosphorus derivatives in the presence of an acid catalyst result in the formation of new hybrid organic–inorganic silica gels incorporating phosphorus centres. Solid state ^{13}C, ^{29}Si, ^{31}P NMR spectroscopies were used to evaluate the integrity of the organic moiety and to determine the degrees of hydrolysis and condensation in the network materials. It was shown that during the sol-gel process there is no alteration around the phosphorus centre. The xerogels are amorphous microporous materials with specific surface areas lying between less than 10 $m^2\ g^{-1}$ and 800 $m^2\ g^{-1}$ depending on the experimental conditions. In contrast with these results, complete cleavage of the Si—C bonds was observed during the hydrolysis and polycondensation of the tris-(triisopropyloxysilylmethyl)phosphine **7** and of tris(trihydrosilylmethyl)phosphine **8**.

Introduction

Over the past few years, there has been increasing interest in the elaboration of solids by the sol–gel process.[1–7] This method permits access to materials through a very simple one pot procedure and under smooth conditions. In our laboratory[7–12] we have focussed our interest on the study of monophasic organic–inorganic hybrid[4,5,13,14] materials obtained by hydrolysis and polycondensation of organically substituted alkoxysilanes. During the elaboration of such materials, the inorganic matrix is built up around the organic moiety through hydrolytic polycondensation, both organic and inorganic units being bound through stable Si—C bonds.

Our interest in organic–inorganic hybrid materials led us to investigate solids resulting from hydrolysis and polycondensation of phosphines bearing hydrolysable SiX_3 groups. Such materials can incorporate metal centers, (most transition metals form stable phosphine complexes), and can show interesting physical properties (electronic, optical or magnetic). They can also be attractive as catalysts. Indeed, the preparation of immobilized catalysts *via* the sol–gel route[15–22] has been recently explored. It has been shown that this route has inherent advantages compared to the more conventional methods which consist of anchoring metal complex moieties to the silica surface.[23–27] One of the main advantages of the sol–gel route is the higher stability of the catalysts and the possibility of tailoring the texture of the solid. Phosphines like $Ph_2P(CH_2)_3Si(OEt)_3$[27–31] and $Ph_2P(CH_2)_2Si(OEt)_3$[21,28,32] are easily prepared. They have been commonly used for this purpose as well as phosphine ethers such as $Ph(CH_3OCH_2CH_2)P(CH_2)_xSi(OEt)_3$.[33,34] However to our knowledge there have been few reports concerning the hydrolysis and polycondensation of phosphines including two hydrolysable $Si(OR)_3$ groups[35] and none with three $Si(OR)_3$ groups. As it has been demonstrated that monophasic organic–inorganic hybrid materials prepared from precursors bearing at least two hydrolysable $Si(OR)_3$ groups covalently linked to the organic part could show short range organization,[8,10] it seemed to us interesting to extend this approach to the case of phosphines in order to try to incorporate the phosphorus atoms in the core of the amorphous solid instead of keeping them at the surface as was the case previously. The advantage of this approach could be in affording structures in which phosphines could have a co-operative interaction. A possible effect of the inorganic matrix around the metal centre could also be foreseen if the phosphorus atoms are incorporated in the core of the material.

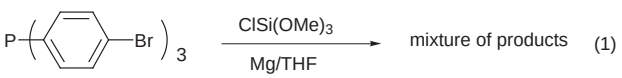
In this paper we present the first step of our approach, *i.e.* a general route to organic–inorganic hybrid materials incorporating free phosphines or phosphine derivatives *via* the sol–gel process.

Results and Discussion

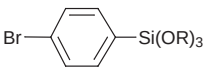
Synthesis of precursors 4–17

We first investigated the formation of silylated phosphines $P[C_6H_4Si(OR)_3]_3$ by two routes.

The first was the direct silylation of the tris(*p*-bromophenyl)phosphine[36] with chlorotrimethoxysilane in the presence of magnesium. This reaction, which is an extension of the Calas–Dunogues silylation reaction[37] for the trimethoxysilyl derivatives, allowed the preparation of a variety of bis(trimethoxysilyl) compounds.[9] However, in this case the reaction did not lead to complete trimethoxysilylation and a mixture of products including $P[C_6H_4Si(OCH_3)_3]_3$ in poor yield was obtained [eqn. (1)].

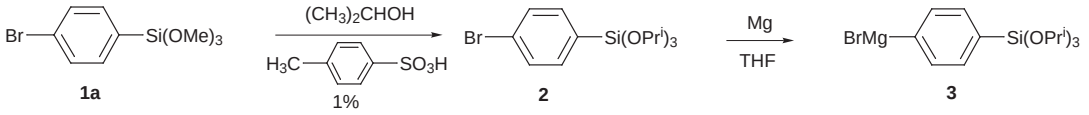


The second route involved the preparation of an organometallic derivative of the *p*-bromotrialkoxysilylbenzenes **1a** or **1b** followed by their reaction with PCl_3 or $PhPCl_2$. But this route

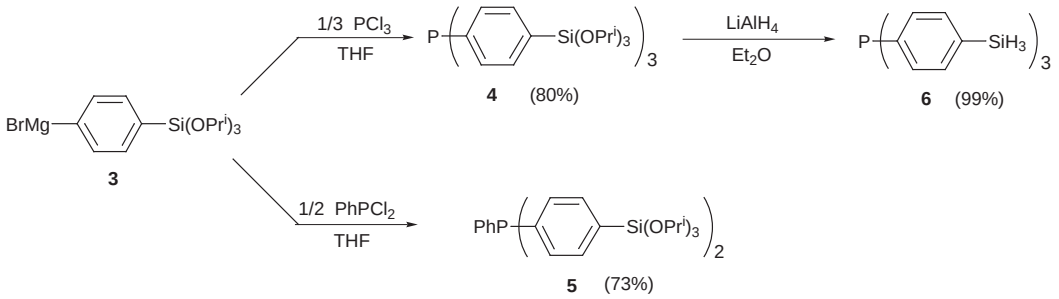


1a R = Me
b R = Et

failed, neither the lithium derivative of **1a** nor the Grignard derivative of **1b** being stable at room temperature. Therefore, we decided to prepare the *p*-bromotriisopropyloxysilylbenzene **2,** the bulky isopropyloxysilyl groups being weakly reactive.



Scheme 1



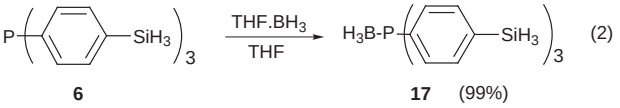
Scheme 2

Exchange reaction from **1a** (Scheme 1) led to **2** from which the corresponding Grignard reagent **3** was easily prepared. Compound **3** was found to be stable in THF at room temperature as the (triisopropyloxysilyl)methyl Grignard reagent previously described.[38] Reagent **3** reacted with PCl_3 to give phosphine **4** in 80% yield and with $PhPCl_2$ to give phosphine **5** in 73% yield (Scheme 2). These phosphines, like other triarylphosphines, are not air-sensitive. $LiAlH_4$ reduction of **4** afforded the air stable tris(*p*-trihydrosilylphenyl)phosphine **6**. The (triisopropyloxysilyl)methyl Grignard reagent reacted also with a stoichiometric amount of PCl_3 to afford the corresponding phosphine **7** in 66% yield. $LiAlH_4$ reduction of **7** gave tris(trihydrosilylmethyl)phosphine **8** in good yield (Scheme 3).

Scheme 3

Thus the reaction of a Grignard reagent bearing a triisopropyloxysilyl group with PCl_3 or $RPCl_2$ can lead to a variety of phosphines incorporating more than one hydrolysable SiX_3 group.

Phosphine **4** was converted (Scheme 4) into the corresponding phosphine oxide **9** by H_2O_2 in CH_2Cl_2 and into the sulfide phosphine **10** by sulfur in propan-2-ol. Addition of methyl iodide to **4** in toluene at 110 °C afforded the corresponding phosphonium salt **11**. The air-stable phosphine-borane **12** was prepared by the smooth reaction of **4** with BH_3·THF. This conversion is reversible in the presence of Et_2NH and can be used therefore for the protection of the phosphino group. Compound **4** reacted at room temperature with an excess of $W(CO)_5$·THF in THF to afford the expected complex **13** (as a beige powder) from which excess of $W(CO)_6$ was removed by sublimation under vacuum without decomposition of **13**. The ^{31}P NMR spectrum displays a $^1J(^{31}P–^{183}W)$ coupling constant of 240.3 Hz and the infrared spectrum exhibits the expected pattern of $\nu(CO)$ frequencies for $LW(CO)_5$. Treatment of **4** with a stoichiometric amount of K_2PtCl_4 in *o*-xylene at reflux resulted in complex **14** as a colourless powder. It is noteworthy that while the synthesis of $(Ph_3P)_2PtCl_2$ requires 6 hours under reflux in xylene,[39] 80 h under the same conditions were necessary to obtain 86% yield of **14**. The ^{31}P NMR spectrum of this complex in $CDCl_3$ solution displays two resonances separated by 7.2 ppm. From the magnitude of the $^1J(^{31}P–^{195}Pt)$ coupling constants[40] it can be inferred that the complex is constituted of 95% *cis* isomer [$^1J(^{31}P–^{195}Pt)$= 3614 Hz] and 5% of the *trans* isomer [$^1J(^{31}P–^{195}Pt)$= 2607 Hz]. When the same reaction is performed in a mixture of propan-2-ol and water as solvent, only the *trans* isomer **15** was obtained after crystallisation from propan-2-ol. The palladium complex **16** was quantitatively prepared by reaction of **4** with a stoichiometric amount of $PdCl_2$ in THF. The phosphine **6** was converted into the phosphine-borane **17** by treatment with BH_3·THF [eqn. (2)].

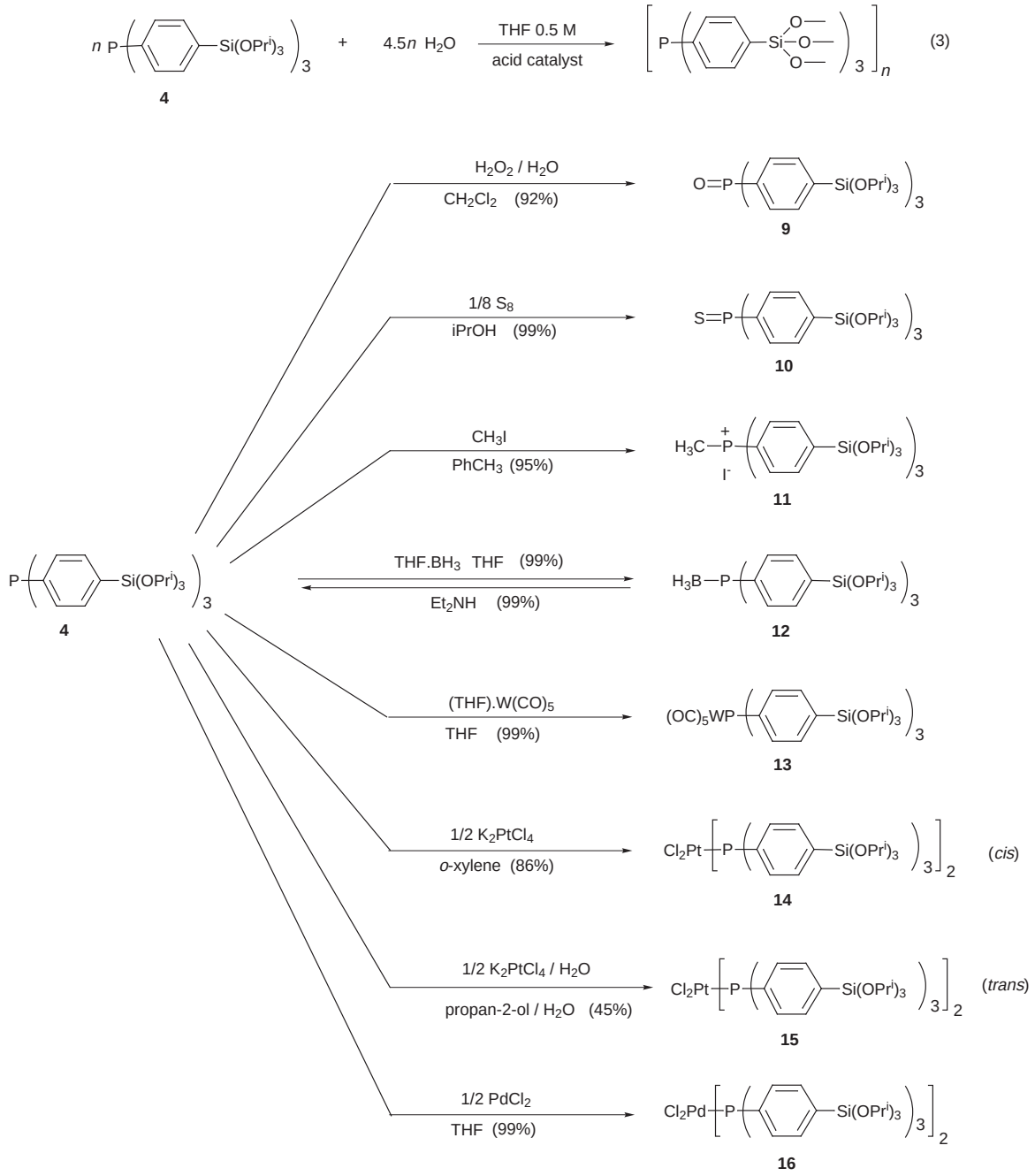


Sol–gel processing

Sol–gel processing of 4. It has been pointed out that the formation of monophasic organic–inorganic hybrid[9–12,41–45] materials is kinetically controlled. This means that all the parameters (catalyst, solvent, concentration, temperature *etc.*) which modify the kinetics of the polycondensation are of importance for the morphology of the elaborated solid. Therefore gel formation from phosphine **4** was first examined under various reaction conditions. While alcohol (ethanol) was often the preferred solvent for most sol–gel polymerizations,[1,9,13] gelations of monomer **4** were carried out in THF (because of the low solubility of **4** in propan-2-ol) with 4.5 equiv. of water. Furthermore, fluoride ions having proved to be very efficient for sol–gel polymerization,[9,46] we first attempted gelation of **4** in the presence of fluoride ions. But **4** failed to polymerize in the presence of a nucleophilic catalyst (see Table 1 entries 11 and 12) or under basic conditions (entry 13). In contrast, acidic catalyst (*p*-toluenesulfonic acid 1 or 10 mol%, HCl 1 or 10 mol%) polymerization of **4** afforded gels [eqn. (3)] within a few hours at relatively low monomer concentrations (0.5 mol l^{-1}). In all cases gelation occurs faster as the temperature increases. Thus, though in general, the longer and the bulkier the alkoxide group, the slower the rate constant of hydrolysis,[1] the gelification times under acidic conditions were quite acceptable. The gels were allowed to age for five days at the gelation temperature, and were then powdered and washed twice with ethanol, acetone and diethyl ether and dried *in vacuo* at 120 °C for 2 h.

Spectroscopic data for xerogels derived from 4. These xerogels were studied by ^{13}C, ^{31}P and ^{29}Si CP-MAS NMR spectroscopies which proved to be the most useful technique for providing chemical information regarding these polymers.

The ^{13}C CP-MAS NMR spectrum of the xerogel **X4F** (Table 1, entry 6) is given as an example (Fig. 1). It displays a



Scheme 4

resonance at 134.1 ppm which was assigned to aromatic carbons and two others at 24.9 and 66.8 ppm attributed to isopropoxy substituents which were left in the material. Furthermore, from the elemental analysis of the xerogel, the ratio of $OCH(CH_3)_3$ substituents remaining was estimated to be about 10%. This ratio was not substantially affected by the experimental conditions.

^{29}Si CP-MAS NMR spectroscopy was used to evaluate the degree of condensation in the network polysiloxanes. The ^{29}Si CP-MAS NMR spectrum of **X4F** is shown in Fig. 2. It displays two main resonances, one being assigned to substructures T^1 [C-Si(OR)$_2$OSi, −61.1 ppm] and the other to T^2 [C-Si(OR)(OSi)$_2$, −68.5 ppm]. CP-MAS spectroscopy is not quantitative. However Shea and coworkers[13*b*] have shown that single-pulse experiments did not reveal any significant variation in relative peak intensity from the CP-MAS spectra in systems without hydrogen atoms directly bound to the studied nucleus. So the ratio of the different T groups was estimated from deconvoluted T peaks when the overlap of the peak areas was not too large. The percentage of T groups are reported in Table 1. The T^2/T^1 ratio varies with the experimental conditions. However no relationship was found between the T^2/T^1 ratio, the temperature and the concentration of the acid catalyst. A minor resonance assigned to the substructure T^3 [C-Si(OSi)$_3$] was occasionally observed while T^0 peaks were absent in all the solid state ^{29}Si NMR spectra. Thus whatever the experimental conditions, hydrolysis was extensive but the condensation incomplete. The absence of any Q signal corresponding to the SiO_4 substructure (region of −100 ppm) is noteworthy indicating that the integrity of the organic moiety had been maintained during the sol–gel process.

The ^{31}P CP-MAS NMR spectra of the silsesquioxanephosphines display one signal, the chemical shift of which is very similar to that of phosphine **4** in solution (−4.5 ppm, $CDCl_3$) since they lie between −4.8 and −5.4 ppm. Thus no oxidation of the phosphorus atom occurred during the sol–gel process (see for example Fig. 3).

The surface areas (N_2 BET measurements) lie between 20

Table 1 Hydrolysis and polycondensation of **4** (0.5 mol l^{-1} in THF) in the presence of 4.5 equiv. of water. Characterization of the obtained xerogels

entry	catalyst[a]	T/°C	xerogel	S_{BET}/m^2 g^{-1}	^{31}P CP-MAS NMR, δ	^{13}C CP-MAS NMR, δ	^{29}Si CP-MAS NMR, δ
1[b]	PTSA 1%	21	**X4A**	20	−5.4	25.0, 66.8, 134.3	−60.5 (T^1), −68.4 (T^2)
2	PTSA 1%	30	**X4B**	30			−61.6 (T^1 46%), −69.5 (T^2 49%), (T^3 sh[c] 5%)
3	PTSA 1%	60	**X4C**	340	−5.1	25.0, 67.0, 134.4	−61.4 (T^1 33%), −69.2 (T^2 55%), (T^3 sh[c] 12%)
4	PTSA 1%	110	**X4D**	550			−70.9
5	PTSA 10%	30	**X4E**	480			−64.8 (T^1 35%), −70.7 (T^2 55%), −81.1 (T^3 10%)
6[b]	HCl 1%	19	**X4F**	50	−4.8	24.9, 66.8, 134.1	−61.1 (T^1 34%), −68.5 (T^2 60%), (T^3 sh[c] 6%)
7	HCl 1%	60	**X4G**	230	−4.9		−57.2 (T^1), −69.6 (T^2)
8[b]	HCl 1%	110	**X4H**	510			−69.9 (T^2), −80.7 (T^3)
9[d]	HCl 10%	30	**X4I**	570			−61.7 (T^1 21%), −69.7 (T^2 62%), −81.2 (T^3 17%)
10	HCl 10%	30	**X4J**	420	−4.8		−60.3 (T^1 41%), −67.4 (T^2 47%), (T^3 sh[c] 12%)
11[e]	NH_4F 5%	20		—			
12[e]	TBAF 1%	30		—			
13[e]	NaOH 10%	30		—			

[a]PTSA = *p*-toluenesulfonic acid. [b]1 mol l^{-1} of **4** in THF. [c]Shoulder. [d]9 equiv. of water. [e]No gelation after several weeks.

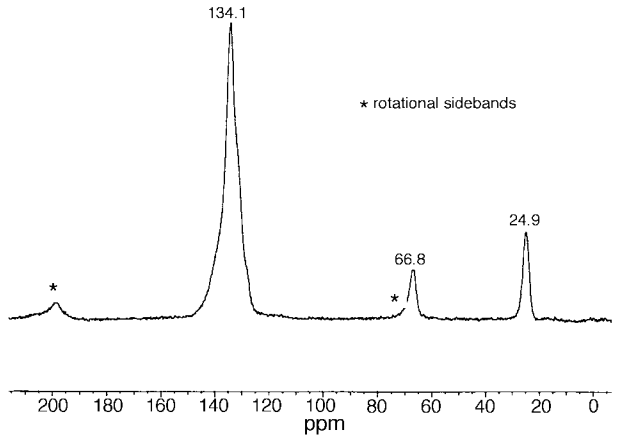


Fig. 1 ^{13}C CP-MAS NMR spectrum of xerogel **X4F**

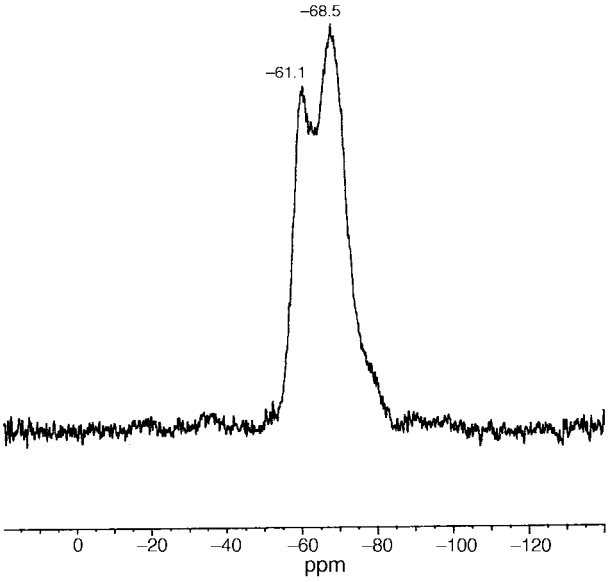


Fig. 2 ^{29}Si CP-MAS NMR spectrum of xerogel **X4F** showing T^1 and T^2 resonances

and 570 m^2 g^{-1} depending on the experimental conditions (Table 1). For a given concentration of acid, the higher the temperature, the higher the surface areas (compare entries 1, 2, 3, 4 and also entries 6, 7, 8). Furthermore with both acids it was observed that the surface area increases with the concentration of the acid (compare entries 2, 5, and 6, 10). Gelation was also carried out with 9 equiv. of water (see entry 9, Table 1). However, as no drastic change was observed, 4.5 equiv. of water were afterwards used for gelation, which is the amount theoretically necessary to convert **4** into the fully condensed polymer. The adsorption–desorption isotherms for the xerogels prepared from **4** indicate that the solids are microporous.

Sol–gel processing of 5. Phosphine **5** was polymerized at 30 °C in 0.5 M THF solution with 3 equiv. of water and 10 mol% of HCl as catalyst to afford a gel within 3 h. After the same processing as for **4** (ageing, washing and drying) the xerogel **X5** obtained was studied by solid state NMR spectroscopies. From these studies it appears that there is neither cleavage of the Si—C bond nor oxidation of the phosphorus atom during the sol–gel process and that the condensation is incomplete. Furthermore the N_2 BET surface area was found to be 7 m^2 g^{-1} which is considerably lower than that of the xerogel obtained from **4** (420 m^2 g^{-1}) and prepared under the same conditions.

Sol–gel processing of 9–16 and spectroscopic data for the corresponding xerogels. Phosphorus derivatives **9–16** were polymerized at 30 °C in 0.5 M THF solution with 4.5 equiv. of water and in the presence of an acid catalyst. The polymerisation of **9–16** in the presence of *p*-toluenesulfonic acid (PTSA 1%) as catalyst afforded the xerogels **X9A–X16A** after the usual work up, and in the presence of 10% HCl as catalyst, the xerogels **X9B–X16B** (Table 2). They were studied by solid state NMR spectroscopies.

From the ^{31}P CP-MAS NMR study it appears that during the polycondensation reaction of phosphorus derivatives **9–16** the structure around the phosphorus centre is maintained. There is neither decomposition, nor decomplexation, nor oxidation. Thus all the ^{31}P CP-MAS NMR spectra of the xerogels **X9A,B–X16A,B** exhibit one signal the chemical shift of which is very similar to those observed in ^{31}P NMR spectra of the corresponding monomer in solution (Table 2). It is worth noting that the platinum satellites are not observed in the ^{31}P CP-MAS NMR spectra of xerogels **X14B** and **X15B** which contain platinum complexes because of the line width (7800 Hz

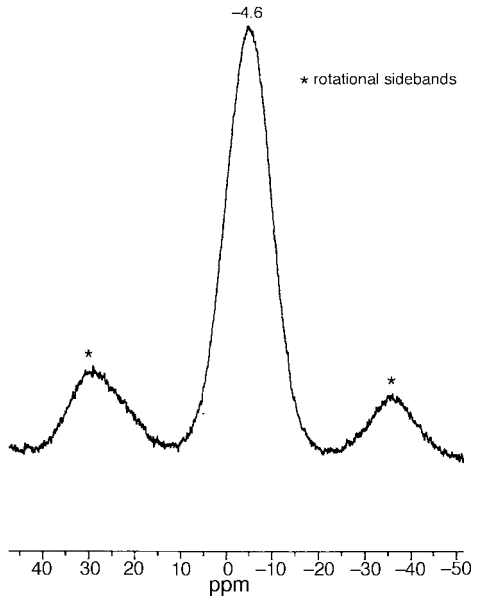


Fig. 3 ^{31}P C-MAS NMR spectrum of xerogel **X4F**

for **X14B** and 7500 Hz for **X15B**). The only side-reaction observed was the partial cleavage of the P—B bond during the hydrolysis and polycondensation of **12**. This cleavage was estimated from ^{31}P CP-MAS NMR at about 60% from **X12B** and at about 50% from **X12A**. It is noteworthy that ^{31}P CP-MAS NMR spectrum of the solid resulting from the polymerisation of platinum complex **14** displays only one signal which was attributed to the *cis* isomer, the poor resolution of the ^{31}P CP-MAS NMR spectrum not allowing the observation of the very minor *trans* isomer in the precursor.

From the ^{13}C CP-MAS NMR spectroscopy it can be concluded that residual isopropoxy groups are present in the materials and that the organic moiety is preserved (see Table 2); this is confirmed by ^{29}Si CP-MAS NMR spectroscopy which reveals the absence of a signal in the region −100 ppm corresponding to SiO_4 substructures. Furthermore, the ^{29}Si CP-MAS NMR spectra exhibit signals (see Table 2) indicating that the condensation is incomplete (substructures T^1 and T^2). The N_2 BET surface areas of xerogels **X9A,B**–**X16A,B** (see Table 2) increase notably with the concentration of the acid except for the xerogel **X11** which has a very low surface area with both acid catalysts.

Sol–gel processing of trihydrosilanes 6 and 17. The hydrolysis and polycondensation of trihydrosilanes catalysed either by $ClRh(PPh_3)_3$ or by fluoride anion has proved to be an alternative route to hybrid organic–inorganic materials.[47] This method avoids the formation of alcohols, the leaving group being removed as dihydrogen. It allows the formation of other types of solids with textures different from those of solids prepared by hydrolysis and polycondensation of the corresponding alkoxysilanes (higher N_2 BET surface area and porosity). Furthermore the xerogels obtained by fluoride anion catalysis exhibited N_2 BET surface areas higher than those obtained by rhodium catalysis. It is in this context that we have studied the hydrolysis and polycondensation of the phosphine **6** and of the corresponding phosphine borane **17**.

The reactions were performed in THF at a low precursor concentration (0.5 mol l^{-1}) with 4.5 equiv. of water and in the presence of a catalytic amount of tetrabutylammonium fluoride (1 mol%). The reagents were mixed at 0 °C and the solutions were allowed to warm up to room temperature after 5 min. Gels were formed within about 4 h with release of dihydrogen. After the same treatment as previously described (ageing, washing *etc.*) xerogels **X6** and **X17** were produced. Their physical characteristics are reported in Table 3. In both cases the ^{13}C CP-MAS NMR spectra exhibit a signal attributed to the aromatic groups which indicates that the organic moiety is preserved. This is confirmed by their ^{29}Si CP-MAS NMR spectra which reveal the absence of any peak corresponding to the SiO_4 substructure (region of −100 ppm) indicating that there is no cleavage of the Si—C bonds during the sol–gel process in these cases also. Furthermore the ^{29}Si CP-MAS NMR spectra display a set of three signals attributed to substructures, T^1, T^2, and T^3, as well as a broad resonance which was attributed to $CSi(H)O_2$ substructures. This is consistent with their FTIR spectra which show in both cases an Si—H absorption band. Thus the xerogels deviated notably from the silsesquioxane stoichiometry. Finally the ^{31}P CP-MAS NMR spectrum of **X6** displays one broad signal at −4.5 ppm, very close to that of the phosphine precursor (−4.9 ppm) while that of **X17** displays two resonances, one at −5.3 ppm (40%) attributed to the free phosphine and the other at 22.0 ppm attributed to the expected phosphine borane (60%). Thus during the hydrolysis and polycondensation of **17** there was partial decomplexation as previously observed from **12**. The N_2 BET surface areas of xerogels **X6** and **X17** are rather large (800 m^2 g^{-1} for **X6** and 570 m^2 g^{-1} for **X17**). In both cases they are larger than those found for the materials prepared from the corresponding alkoxysilanes. The

Table 2 Hydrolysis and polycondensation of precursors **9**–**16** (0.5 mol l^{-1} in THF) with 4.5 equiv. of water at 30 °C. Characterization of the obtained xerogels

precursor	acid catalyst	xerogel	S_{BET}/ m^2 g^{-1}	^{31}P NMR δ (precursor)	^{31}P CP-MAS NMR, δ (xerogel)	^{13}C CP-MAS NMR, δ (xerogel)	^{29}Si CP-MAS NMR, δ (xerogel)
9	PTSA 1%	**X9A**	85	29.8	31.4	24.0, 67.0, 131.2, 134.5	−62.3 (T^1) −69.8 (T^2)
	HCl 10%	**X9B**	410		30.7		−63.1 (T^1) −70.7 (T^2), −79.4 (T^3)
10	PTSA 1%[a]	**X10A**	4	43.8	42.4	25.1, 66.6, 134.4	−61.2 (T^1) −69.3 (T^2)
	HCl 10%	**X10B**	530		42.0		−62.7 (T^1) −70.5 (T^2)
11	PTSA 1%	**X11A**	3	22.1	20.9		−63.4 (T^1) −71.2 (T^2), −80.0 (T^3)
	HCl 10%	**X11B**	8		21.0		−65.4 (T^1) −73.4 (T^2), −83.2 (T^3)
12	PTSA 1%	**X12A**	60	21.1	−5, 22.4		
	HCl 10%	**X12B**	490		−5, 21.5		−62 (T^1) −70.2 (T^2)
13	PTSA 1%	**X13A**	5	21.3	21.2	24.8, 66.8, 134.6, 197.4	−60.9 (T^1) −68.8 (T^2)
	HCl 10%	**X13B**	290		21.1		−62.3 (T^1) −71.7 (T^2)
14	HCl 10%	**X14B**	460	13.5, 20.7	11.3[b]		−63.9 (T^1) −71.3 (T^2)
15	HCl 10%	**X15B**	520	20.6	20.8[b]		
16	PTSA 1%[c]	**X16A**	4	23.7	27.5	24.8, 66.7, 134.1	−61.9 (T^1) −69.7 (T^2)
	HCl 10%	**X16B**	370		27.3		−62.8 (T^1) −71.7 (T^2)

[a]1 M solution at 20 °C. [b]Platinum satellites are not observed in the ^{31}P CP-MAS NMR spectrum because of the width of the signal (7800 Hz for **X14B** and 7500 Hz for **X15B**). [c]At 22 °C.

Table 3 Hydrolysis and polycondensation of precursors **6** and **17** (0.5 M solution in THF) with 4.5 equiv. of water at 0 °C, then room temperature, catalysed by Bu^n_4NF (1%). Characterization of the obtained xerogels

xerogel	$S_{BET}/m^2\ g^{-1}$	IR (DRIFT, KCl), ν/cm^{-1}	^{31}P CP-MAS NMR, δ	^{13}C CP-MAS NMR, δ	^{29}Si CP-MAS NMR, δ
X6	800	2160	−4.5	133.4	−60.9 (T^1), −68.7 (T^2), −77.4 (T^3) −40 to −50 (D substructures)
X17	570	2159	−5.3, 22.0		−61.5 (T^1), −70.0 (T^2), −77.8 (T^3) −30 to −50 (D substructures)

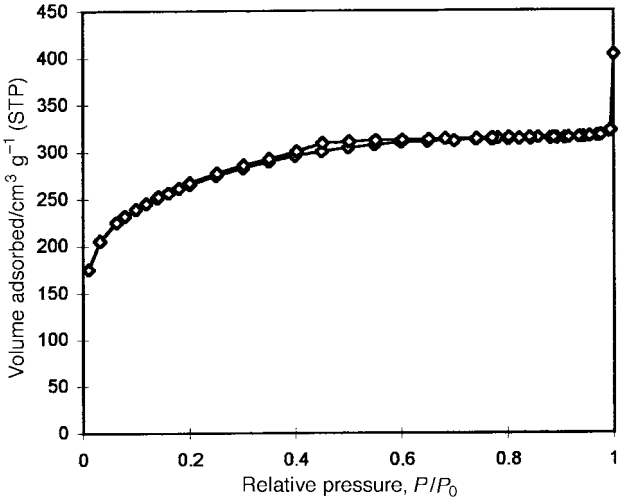
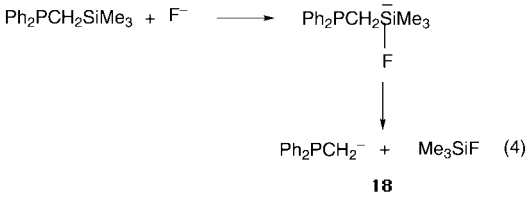


Fig. 4 Nitrogen adsorption–desorption isotherm for microporous xerogel **X6**

adsorption–desorption isotherms indicating that the solids are microporous (see Fig. 4 given as example).

Sol–gel processing of phosphines 7 and 8. The polycondensation of phosphine **7** was studied at 30 °C in THF as solvent in the presence of 4.5 equiv. of water under acidic conditions (*p*-toluenesulfonic acid 1 mol% and HCl 10 mol%). Gelation did not occur even after several weeks. In contrast, in the presence of TBAF (1 mol%) gelation occurred after 13 h. Following the usual treatment, the xerogel was studied by solid state NMR spectroscopy. The ^{29}Si CP-MAS NMR spectrum displays only signals corresponding to SiO_4 substructures (Q^2, −91.2; Q^3, −100.7; Q^4, −109.1) indicating complete cleavage of the Si—C bonds during the hydrolysis and polycondensation. Cleavage of the Si—C bonds was also observed during hydrolysis and polycondensation of **8**. The polymerisation was performed in THF at a low precursor concentration (0.5 mol l^{-1}) with 4.5 equiv. of water and in the presence of 1 mol% of TBAF. The reagents were mixed at −10 °C and after about 15 min gelation occurred. The ^{29}Si CP-MAS NMR spectrum of the xerogel displayed only signals corresponding to SiO_4 substructures (Q^2, −90.4; Q^3, −100.4, Q^4, −107.7). It is noteworthy that Si—C bond cleavage has been previously observed for diphenyl(trimethylsilyl)methylphosphine in the presence of fluoride ions as catalyst[48] and that formation of the carbanion **18** [eqn. (4)] has been suggested.



Conclusion

In this study we have described the preparation of phosphines and of phosphine derivatives bearing two or three hydrolysable SiX_3 groups covalently linked to the organic part. These derivatives have been prepared *via* the stable functional Grignard reagent of *p*-bromo(triisopropyloxysilyl)benzene. We have demonstrated that a variety of phosphorus derivatives can be incorporated into an inorganic network *via* the sol–gel process without alteration around the phosphorus atom. This process allows the deliberate tailoring of materials, the potential of which remains to be explored.

Experimental

All reactions were carried out under argon by using a vacuum line. Solvents were dried and distilled just before use. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR data were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer. The solution ^1H and ^{13}C NMR spectra were recorded at 200 MHz and 50 MHz respectively on a Bruker DPX-200 spectrometer and the solution ^{29}Si NMR spectra were recorded at 40 MHz on a Bruker WP-200 SY spectrometer. Chemical shifts were obtained relative to Me_4Si. The solution ^{31}P and ^{11}B NMR spectra were recorded at 100 MHz and 80 MHz respectively on a Bruker AC-250 and the chemical shifts were referenced to H_3PO_4 and $BF_3 \cdot Et_2O$. Cross-polarization magic angle spinning (CP-MAS) ^{13}C, ^{29}Si, and ^{31}P NMR spectra were obtained on a Bruker AM-300 operating at 75 MHz, 60 MHz and 120 MHz respectively. Carbon and silicon chemical shifts were referenced to Me_4Si while phosphorus chemical shifts were referenced to H_3PO_4. Mass spectra and FAB mass spectra [matrix, *m*-nitrobenzyl alcohol (NBA) or thioglycerol (GT)] were registered on JEOL JMS-D100 or JEOL JMS-SX102 spectrometers. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2400 analyser. Elemental analyses were carried out by the Service Central de Micro-Analyse du CNRS.

p-Bromo(triisopropyloxysilyl)benzene 2

To a solution of chlorotrimethoxysilane (33.3 g, 213 mmol) in THF (100 ml) placed, under argon, in a three-necked flask equipped with a mechanical stirrer, a condenser and an addition funnel, was added dropwise at 0 °C a solution of *p*-bromophenylmagnesium bromide (212 mmol) in THF (210 ml). The reaction mixture was stirred at room temperature overnight, then heated under reflux for 1 h. The solvent was removed and the resulting orange residue was dissolved in pentane (250 ml). After filtration and concentration of the filtrate, 48.8 g of **1a** as an orange pale oil was obtained.

A solution of the crude product in propan-2-ol (100 ml) was stirred at room temperature for 1 h in the presence of *p*-toluenesulfonic acid (0.4 g). Then the solvent was removed. The residue was dissolved again in propan-2-ol (100 ml) and the mixture was stirred for one further hour. In order to have complete exchange reaction, this operation was repeated three times. After removal of the solvent, the excess of 1,4-dibromo-

benzene was removed by sublimation at 90 °C under vacuum. The residual oil was distilled to give 38.1 g (106 mmol, 49%) of **2**. Bp 103–105 °C at 0.04 mmHg; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.26 (d, $^3J_{H-H}$ = 6.1 Hz, 18H, Me), 4.31 (spt, $^3J_{H-H}$ = 6.1 Hz, 3 H, OCH), 7.59 (m, 4 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.0 (OCH), 125.3, 131.3, 132.3, 136.9 (aromatics); ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −62.3; IR (ν/cm^{-1}, neat) 1381. Anal. calc. for $C_{15}H_{25}BrO_3Si$: C, 49.86, H, 6.92%. Found: C, 49.82, H, 7.13.

Tris(*p*-triisopropyloxysilylphenyl)phosphine 4

Magnesium turnings (7.40 g, 308 mmol) and 20 ml of THF were placed in a three-necked flask equipped with a mechanical stirrer, a condenser and an addition funnel. After activation of the magnesium by some drops of 1,2-dibromoethane, a solution of *p*-bromo(triisopropyloxysilyl)benzene **2** (93.7 g, 260 mmol) in THF (550 ml) was added dropwise so that the reaction mixture was not heated under reflux. The grey solution of Grignard reagent **3** was stirred at room temperature for 3 h, then a solution of PCl_3 (7.50 ml, 85.9 mmol) in THF (100 ml) was added dropwise at 0 °C and stirred overnight at room temperature and then heated under reflux for one hour. After removal of the solvent, the beige residue was dissolved in pentane (500 ml). After filtration of the salts and concentration of the filtrate, 75.1 g of a colourless powder was obtained. Crystallisation from propan-2-ol gave **4** (59.50 g, 68.1 mmol, 80%) as white crystals. Mp (propan-2-ol) 135–136 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H-H}$ = 6.1 Hz, 54 H, Me), 4.31 (spt, $^3J_{H-H}$ = 6.1 Hz, 9 H, OCH), 7.27–7.69 (m, 12H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (CH_3), 65.9 (OCH), 133.3 (d, J_{P-C} = 18.6 Hz, aromatic), 133.8 (s, aromatic), 135.2 (d, J_{P-C} = 6.6 Hz, aromatic), 139.1 (d, J_{P-C} = 11.1 Hz, aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) −4.51; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −62.0. MS (FAB+, NBA), 875 [$(M+H)^+$, 13%], 891 [$(M+OH)^+$, 48%]. Anal. calc. for $C_{45}H_{75}O_9PSi_3$: C, 61.78, H, 8.58%. Found: C, 61.69, H, 8.68.

Phenyl[bis(*p*-triisopropyloxysilylphenyl)]phosphine 5

Dichlorophenylphosphine (3.3 ml, 24.3 mmol) in THF (30 ml) was added dropwise, at 0 °C, to a solution of Grignard reagent **3** (50.6 mmol) in THF (100 ml). The reaction mixture was stirred for 12 hours at room temperature and then was heated under reflux for one hour. The THF was removed and pentane (300 ml) was added. After filtration and removal of the solvent under vacuum, the oily residue was distilled to afford 11.9 g (17.8 mmol, 73%) of **5**. Bp 220–230 °C at 0.02 mmHg; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H-H}$ = 6.1 Hz, 36 H, Me), 4.31 (spt, $^3J_{H-H}$ = 6.1 Hz, 6 H, OCH), 7.25–7.70 (m, 13 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 65.9 (OCH), 128.8–139.5 (aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) −4.6; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −61.8. MS (FAB+, NBA) 671 [$(M+H)^+$, 35%], 672 [$(M+2H)^+$, 39%]. Anal. calc. for $C_{36}H_{55}O_6PSi_2$: C, 64.48, H, 8.21%. Found: C, 64.16, H, 8.20.

Tris(*p*-trihydrogenosilylphenyl)phosphine 6

Phosphine **4** (4 g, 4.57 mmol) in diethyl ether (20 ml) was added dropwise, within one hour, at 0 °C, to a stirred suspension of $LiAlH_4$ (0.88 g, 23.1 mmol) in diethyl ether (50 ml). After stirring for 12 h at room temperature the solvent was removed under vacuum and pentane (150 ml) was added to the grey residual solid. After filtration of salts and evaporation of the pentane, 1.60 g (4.54 mmol, 99%) of **6** was obtained as an oil which becomes solid at room temperature. Mp 82–83.5 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 4.24 [s and d (satellite ^{29}Si, $^1J_{Si-H}$ = 202 Hz), 9 H, SiH], 7.30–7.63 (m, 12 H, aromatic), ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 129.7 (s, aromatic), 133.7 (d, J_{P-C} = 19 Hz, aromatic), 136.3 (d, J_{P-C} = 6.6 Hz, aromatic), 139.1 (d, J_{P-C} = 12.1 Hz, aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) −4.91; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −58.7 (d, $^5J_{P-Si}$ = 0.7 Hz); IR (ν/cm^{-1}, CCl_4) 2159; MS (FAB+, NBA) 352 (M^+, 100%). Anal. calc. for $C_{18}H_{21}PSi_3$: C, 61.36, H, 5.97%. Found: C, 60.58, H, 5.92.

Tris(triisopropyloxysilylmethyl)phosphine 7

PCl_3 (6.5 ml, 74.5 mmol) in THF (50 ml) was added dropwise, at 0 °C, to a solution of (triisopropyloxysilyl)methylmagnesium chloride[38] (225 mmol) in THF (230 ml). The reaction mixture was stirred for 12 h at room temperature and then was heated under reflux for a further 2 h. The THF was removed under vacuum to give a grey solid which was taken in pentane (400 ml). After filtration of salts, removal of the solvent under vacuum and distillation 34.2 g (49.7 mmol, 66%) of **7** was obtained as an oil which crystallised on standing. Bp 104–130 °C at 0.02 mmHg; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.04 (s, 6 H, CH_2Si), 1.22 (d, $^3J_{H-H}$ = 6.1 Hz, 54 H, Me), 4.3 (spt, $^3J_{H-H}$ = 6.1 Hz, 9 H, OCH); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 16.6 (d, $^1J_{P-C}$ = 30.8 Hz, PC), 26.0 (Me), 65.3 (OCH); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) −41.3; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −51.1 (d, $^2J_{P-Si}$ = 12.2 Hz); MS (FAB+, GT) 688 (M^+, 100%). Anal. calc. for $C_{30}H_{69}O_9PSi_3$: C, 52.32, H, 10.03%. Found: C, 51.86, H, 9.96.

Tris(trihydrosilylmethyl)phosphine 8

Phosphine **7** (7.05 g, 10.2 mmol) in diethyl ether (60 ml) was added dropwise, at 0 °C, to a suspension of $LiAlH_4$ (1.71 g, 45 mmol) in diethyl ether (60 ml). The reaction mixture was stirred for 12 hours at room temperature and the solvent was then evaporated under vacuum to give a grey solid which was dissolved in pentane (200 ml). After filtration of the salts and removal of the solvent under vacuum, 1.45 g (8.73 mmol, 85%) of raw phosphine was obtained. ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.02 (d of q, $^3J_{H-H}$ = 4.1 Hz, $^2J_{P-H}$ = 0.7 Hz, 6 H, CH_2Si), 3.65 [d of t, $^3J_{H-H}$ = 4.1 Hz, $^3J_{P-H}$ = 9.9 Hz) and d of d of t (satellites ^{29}Si, $^1J_{Si-H}$ = 200 Hz, 9 H, SiH)]; ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 6.96 (d, $^1J_{P-C}$ = 28.4 Hz, PC); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) −23.5; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −65.1 (d, $^2J_{P-Si}$ = 15.0 Hz); IR (ν/cm^{-1}, neat) 2153; MS (FAB+, NBA), 183 [$(M+OH)^+$, 100%].

Tris(*p*-triisopropyloxysilylphenyl)phosphine oxide 9

H_2O_2 (5 ml, 35% aq. solution) was added dropwise to 3.14 g (3.59 mmol) of phosphine **4** in CH_2Cl_2 (20 ml). After stirring for 5 min, 30 ml of H_2O were added and the phosphine oxide was extracted with CH_2Cl_2 (3 × 30 ml). After drying and evaporation of the solvent, 2.92 g (3.28 mmol, 92%) of **9** was obtained. Mp 163–164.5 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.24 (d, $^3J_{H-H}$ = 6.1 Hz, 54 H, Me), 4.30 (spt, $^3J_{H-H}$ = 6.1 Hz, 9 H, OCH), 7.6–7.82 (m, 12 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.1 (OCH), 131.5 (d, J_{P-C} = 9.5 Hz, aromatic), 134.1 (d, J_{P-C} = 102.9 Hz, aromatic), 135.1 (d, J_{P-C} = 12.1 Hz, aromatic), 138.2 (d, J_{P-C} = 2.3 Hz, aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 29.8; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −63.4; IR (ν/cm^{-1}, CCl_4) 1201; MS (FAB+, NBA) 891 [$(M+H)^+$, 100%]. Anal. calc. for $C_{45}H_{75}O_{10}PSi_3$: C, 60.67, H, 8.42%. Found: C, 60.40, H, 8.42.

Tris(*p*-triisopropyloxysilylphenyl)phosphine sulfide 10

Phosphine **4** (765 mg, 0.87 mmol) and 28 mg (0.87 mmol) of sulfur in propan-2-ol (10 ml) were heated under reflux for 9 hours. Compound **10** (786 mg, 0.867 mmol, 99%) was obtained after evaporation of the solvent. Mp (propan-2-ol) 193–194 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H-H}$ = 6.1 Hz, 54 H, Me), 4.31 (spt, $^3J_{H-H}$ = 6.1 Hz, 9 H, OCH), 7.65–7.81 (m, 12 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.1 (OCH), 131.6 (d, J_{P-C} = 10.2 Hz, aromatic), 134.5 (d, J_{P-C} =

82.9 Hz, aromatic), 135.2 (d, $J_{P-C}=12.1$ Hz, aromatic); 137.8 (d, $J_{P-C}=2.6$ Hz, aromatic), ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 43.8; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −63.3 (d, $^5J_{P-Si}=1.5$ Hz); MS (FAB+, NBA) 907 [$(M+H)^+$, 100%]. Anal. calc. for $C_{45}H_{75}O_{10}PSi_3$: C, 59.60, H, 8.28%. Found: C, 60.30, H, 7.96.

Methyl[tris(*p*-triisopropyloxysilylphenyl)]phosphonium iodide 11

Phosphine **4** (4.32, 4.94 mmol) and 0.6 ml (9.63 mmol) of methyl iodide were heated under reflux in toluene (20 ml) for 3 h. After evaporation of the solvent, 4.77 g (4.7 mmol, 95%) of **11** were obtained. Mp 163.5–166 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.22 (d, $^3J_{H-H}=6.1$ Hz, 54 H, Me), 3.25 (d, $^2J_{P-H}=13.0$ Hz, 3 H, PMe), 4.30 (spt, $^3J_{H-H}=6.1$ Hz, 9 H, OCH), 7.60–7.96 (m, 12 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 12.1 (d, $^1J_{P-C}=56$ Hz, PMe), 25.9 (Me), 66.5 (OCH), 120.4 (d, $J_{P-C}=87.4$ Hz, aromatic), 132.3 (d, $J_{P-C}=10.2$ Hz, aromatic), 136.7 (d, $J_{P-C}=12.3$ Hz, aromatic), 143.2 (s, aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 22.1; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −65.7 (d, $^5J_{P-Si}=1.8$ Hz); MS (FAB+, NBA) 889 [$(M-I)^+$, 100%]. MS (FAB−, NOBA) 127 (I^-, 100%). Anal. calc. for $C_{46}H_{78}IO_9PSi_3$: C, 54.33, H, 7.68%. Found: C, 54.58, H, 7.97.

Tris(*p*-triisopropyloxysilylphenyl)phosphine borane 12

A molar solution of $BH_3\cdot THF$ in THF (3.5 ml, 3.5 mmol) was added dropwise, at 0 °C, to 2.91 g (3.33 mmol) of phosphine **4** in THF (10 ml). After stirring for 1 h at room temperature, the solvent was removed to give 2.94 g (3.31 mmol, 99%) of **12**. Mp (propan-2-ol), 167–170.5 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H-H}=6.1$ Hz, 57 H, Me and BH_3), 4.31 (spt, $^3J_{H-H}=6.1$ Hz, 9 H, OCH), 7.50–7.80 (m, 12 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.1 (OCH), 130.9 (d, $J_{P-C}=57.0$ Hz, aromatic), 132.7 (d, $J_{P-C}=9.2$ Hz, aromatic), 135.4 (d, $J_{P-C}=9.8$ Hz, aromatic), 137.4 (d, $J_{P-C}=2.1$ Hz, aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 21.1 (broad signal); ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −63.2 (d, $^5J_{P-Si}=1.3$ Hz); ^{11}B NMR (δ, 80 MHz, $CDCl_3$) −37.9 (broad signal). Anal. calc. for $C_{45}H_{78}BO_9PSi_3$: C, 60.79, H, 8.84%. Found: C, 60.96, H, 8.33.

Tris(*p*-triisopropyloxysilylphenyl)phosphine tungsten pentacarbonyl 13

A THF solution of $(THF)W(CO)_5$[49] (260 ml, 14.2 mmol) was added to 6.2 g (7.1 mmol) of phosphine **4** in THF (20 ml). The reaction mixture was stirred for 1 h at room temperature and the solvent was evaporated under vacuum. After elimination of excess of $W(CO)_6$ by sublimation at 60 °C under vacuum, 8.24 g (6.88 mmol, 97%) of **13** were obtained. Mp (propan-2-ol), 158.5–160 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H-H}=6.1$ Hz, 54 H, Me), 4.32 (spt, $^3J_{H-H}=6.1$ Hz, 9 H, OCH), 7.42–7.78 (m, 12 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.1 (OCH), 132.5 (d, $J_{P-C}=11.4$ Hz, aromatic), 135.3 (d, $J_{P-C}=9.3$ Hz, aromatic), 136.3 (d, $J_{P-C}=1.7$ Hz, aromatic), 137.0 (d, $J_{P-C}=40.5$ Hz, aromatic), 197.6 [d, $^2J_{P-C}=7.0$ Hz, and d of d (satellite ^{183}W, $^1J_{C-W}=126.0$ Hz), CO (*cis*)], 199.7 [d, $J_{P-C}=21.7$ Hz, CO (*trans*)]; ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 21.3 [s and d (satellite ^{183}W, $^1J_{P-W}=240.3$ Hz]; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −63.1 (d, $^5J_{P-Si}=1.4$ Hz); IR (ν/cm^{-1}, CCl_4) 1941, 1980, 2071; MS (FAB+, GT) 1198 (M^+, 3%), 1170 [$(M-CO)^+$, 2.4%], 1143 [$(M-2CO+H)^+$, 5.3%], 1114 [$(M-3CO)^+$, 8.2%], 875 [$(M-W(CO)_6+H)^+$, 18.6%]. Anal. calc. for $C_{50}H_{75}O_{14}PSi_3W$: C, 50.08, H, 6.26%. Found: C, 49.75, H, 6.19.

cis-Bis[tris(*p*-triisopropyloxysilylphenyl)phosphine] dichloroplatinum 14

Compound **14** was prepared following the procedure described by Gillard and Pilbrow[39] for the preparation of $(PPh_3)_2PtCl_2$. K_2PtCl_4 (0.79 g, 1.9 mmol) and 3.32 g (3.8 mmol) of phosphine **4** were heated under reflux for 80 h in *o*-xylene (5 ml). After removal of the solvent under vacuum, the residue was taken again in pentane and the precipitate of KCl was filtrated. Pentane was evaporated under vacuum and 3.3 g (1.64 mmol, 86%) of **14** was obtained as a white powder. Mp 202–204 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.24 (d, $^3J_{H-H}=6.1$ Hz, 108 H, Me), 4.28 (spt, $^3J_{H-H}=6.1$ Hz, 18 H, OCH), 7.4–7.8 (m, 24 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.0 (OCH), 130.3–137.0 (aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 13.5 [s and d (satellite ^{195}Pt, $^1J_{P-Pt}=3614$ Hz), *cis*, 95%], 20.7 [s and d, (satellite ^{195}Pt, $^1J_{P-Pt}=2607$ Hz), *trans*, 5%]; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −63.5 (*cis*), −62.7 (*trans*). Anal. calc. for $C_{90}H_{150}Cl_2O_{18}P_2PtSi_6$: C, 53.63, H, 7.51, Cl, 3.47%. Found: C, 53.67, H, 7.37, Cl, 3.35.

trans-Bis[tris(*p*-triisopropyloxysilylphenyl)phosphine] dichloroplatinum 15

Phosphine **4** (3.46 g, 3.96 mmol) and 822 mg (1.98 mmol) of K_2PtCl_4 were refluxed for 1 h in a mixture of propan-2-ol (25 ml) and water (15 ml). After cooling, the product was extracted with diethyl ether which was washed with water and dried over $MgSO_4$. After elimination of diethyl ether and crystallisation from propan-2-ol, 1.70 g (0.844 mmol, 43%) of pure **15** was obtained. Mp 184–191 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H-H}=6.1$ Hz, 108 H, Me), 4.30 (spt, $^3J_{H-H}=6.1$ Hz, 18 H, OCH), 7.71–7.75 (m, 24 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 65.9 (OCH), 130.4–136.1 (aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 20.6 [s and d, (satellite ^{195}Pt, $^1J_{P-Pt}=2609$ Hz)]; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −62.5. Anal. calc. for $C_{90}H_{150}Cl_2O_{18}P_2PtSi_6$: C, 53.63, H, 7.51. Found: C, 53.62, H, 7.42.

Bis[tris(*p*-triisopropyloxysilylphenyl)phosphine] dichloropalladium 16

Phosphine **4** (5.86 g, 6.7 mmol) and 595 mg (3.35 mmol) of $PdCl_2$ were heated under reflux in THF (40 ml) for 3 h. The reaction mixture was filtered and the solvent was removed under vacuum to afford 6.4 g (3.32 mmol, 99%) of **16** as a yellow powder. Mp (propan-2-ol) 197–198.5 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.24 (d, $^3J_{H-H}=6.1$ Hz, 108 H, Me), 4.30 (spt, $^3J_{H-H}=6.1$ Hz, 18 H, OCH), 7.69, 7.71, 7.72 (3 s, 24 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.0 (OCH), 134.7 (aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 23.7; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −62.5. Anal. calc. for $C_{90}H_{150}Cl_2O_{18}P_2PdSi_6$: C, 56.09, H, 7.79, Cl, 3.69%. Found: C, 55.07, H, 7.69, Cl, 3.64.

Tris(*p*-trihydrosilylphenyl)phosphine borane 17

A molar solution (5.30 ml, 5.30 mmol) $BH_3\cdot THF$ in THF were added dropwise, at 0 °C to 1.86 g (5.28 mmol) of phosphine **4** in THF (15 ml). After 30 min at 0 °C and 1 h at room temperature, the reaction mixture was filtered and the THF was evaporated. The sticky product obtained was precipited by addition of pentane (25 ml). After evaporation of pentane, 1.80 g (4.91 mmol, 93%) of **17** was obtained as a white powder. Mp 115–117 °C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 0.5–2 (broad signal, 3 H, BH_3), 4.26 [s and d (satellite ^{29}Si, $^1J_{Si-H}=204$ Hz), 9 H, SiH], 7.54–7.75 (m, 12 H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 130.9 (d, $J_{P-C}=56.6$ Hz, aromatic), 132.9 (d, $J_{P-C}=9.3$ Hz, aromatic), 134.4 (d, $J_{P-C}=2.2$ Hz, aromatic), 136.5 (d, $J_{P-C}=9.8$ Hz, aromatic); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 22.5 (broad signal); ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) −58.2 (d, $^5J_{P-Si}=1.8$ Hz); ^{11}B NMR (δ, 80 MHz, $CDCl_3$) −38.1 (broad signal). IR (ν/cm^{-1}, CCl_4) 2162; MS (FAB+, NBA) 365 [$(M-H)^+$, 71%)], 352 [$(M-BH_3)^+$, 87%], 245 [$(M-BH_3-C_6H_5SiH_3)^+$, 100%]. Anal. calc. for $C_{18}H_{24}BPSi_3$: C, 59.01, H, 6.56%. Found: C, 58.32, H, 6.48.

Sol–gel processing. General procedure for the preparation of xerogels from 4 and from 9–16

The procedure for xerogel **X4J** is given as an example. To a solution of **4** (2.00 g, 2.28 mmol) in THF (2.3 ml) placed in a 12.5 ml flask were added dropwise at room temperature 2.3 ml (10.35 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The mixture was stirred for 5 min, then the flask was placed in a water-bath at 30 °C without stirring. Gelation occurred after 3 h 15 min. The wet whitish gel was allowed to age for 5 d at 30 °C after which it was powdered and washed with ethanol, acetone and diethyl ether. The powdering and washing were repeated once and the gel was powdered again and dried in vacuum for 2 h at 120 °C yielding 1.08 g of xerogel as a white powder.

Xerogels **X4C** and **X4G** were prepared at 60 °C in a 20 ml sealed tube while xerogels **X4D** and **X4H** were also prepared in a 20 ml sealed tube but at 110 °C.

Specific surface areas, ^{31}P (CP-MAS) NMR, ^{13}C (CP-MAS) NMR and ^{29}Si (CP-MAS) NMR spectroscopic results for xerogels **X4** are indicated in Table 1.

Elemental Anal. calc. for $C_{18}H_{12}O_{4.5}PSi_3$: C, 52,05; H, 2.89; P, 7.47; Si, 20.24. Found for: **X4A** (gelation time, 8 h): C, 49.84; H, 5.04; P, 6.10; Si, 14.30 which corresponds to $C_{21.10}H_{25.61}O_{7.85}PSi_{2.59}$; **X4B** (gelation time, 11 h): C, 48.64; H, 5.10; P, 6.15; Si, 14.85 which corresponds to $C_{20.43}H_{25.70}O_{7.95}PSi_{2.67}$; **X4C** (gelation time, 8 h): C, 46.22; H, 4.43; P, 5.45; Si, 17.58 which corresponds to $C_{21.90}H_{25.20}O_{9.35}PSi_{3.57}$; **X4D** (gelation time, 1 h): C, 50.92; H, 4.97; P, 5.65; Si, 16.70 which corresponds to $C_{23.28}H_{27.27}O_{7.46}PSi_{3.27}$; **X4E** (gelation time, <15 h): C, 47.88; H, 5.25; P, 6.00; Si, 16.25 which corresponds to $C_{20.61}H_{27.12}O_{7.85}PSi_{3.00}$; **X4G** (gelation time, 4 h): C, 49.64; H, 4.57; P, 5.80; Si, 16.80 which corresponds to $C_{22.11}H_{24.42}O_{7.74}PSi_{3.20}$; **X4I** (gelation time, 4.5 h): C, 47.52; H, 4.36; P, 5.15; Si, 19.10 which corresponds to $C_{17.41}H_{19.17}O_{6.56}P_{0.73}Si_{3.00}$; **X4J** (gelation time, 3 h): C, 49.28; H, 4.83; P, 7.10; Si, 16.65 which corresponds to $C_{17.93}H_{21.09}O_{6.04}PSi_{2.60}$.

Specific surface areas, ^{31}P CP-MAS NMR, ^{13}C CP-MAS NMR and ^{29}Si CP-MAS NMR spectroscopic results for xerogels **X9–X16** are indicated in Table 2.

Xerogel X5B

To a solution of 4.29 g (6.40 mmol) of **5** in THF (6.40 ml) placed in a 20 ml flask were added dropwise at room temperature 6.40 ml (19.20 mmol of H_2O) of a 3.0 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 3 h 10 min. After drying, 2.32 g of white xerogel **X5B** was obtained. ^{13}C NMR (δ, 75 MHz) 25.0, 66.3, 129.0; ^{31}P NMR (δ, 120 MHz) −5,5; ^{29}Si NMR (δ, 60 MHz) −60.6 (T^1 21%), −68.6 (T^2 68%), −76.2 (T^3 11%). Elemental Anal. calc. for $C_{18}H_{13}O_3PSi_2$: C, 59.34; H, 3.57; P, 3.51; Si, 15.38. Found: C, 56.66; H, 4.41; P, 7.35; Si, 14.00 which corresponds to $C_{19.91}H_{18.60}O_{4.63}PSi_{2.11}$.

Xerogel X9A

To a solution of 1 g (1.12 mmol) of **9** in THF (1.1 ml) placed in a 5 ml flask were added dropwise at room temperature 1.2 ml (5.4 mmol of H_2O) of a 4.5 m aqueous 0.01 M PTSA solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 4 h. After drying, 0.515 g of white xerogel **X9A** was obtained. Elemental Anal. calc. for $C_{18}H_{12}O_{5.5}PSi_3$: C, 50.11; H, 2.78; P, 7.19; Si, 19.49. Found: C, 43.83; H, 4.42; P, 5.85; Si, 15.80 which corresponds to $C_{19.35}H_{23.42}O_{9.97}PSi_{2.99}$.

Xerogel X9B

To a solution of 2.10 g (2.32 mmol) of **9** in THF (2.3 ml) placed in a 12.5 ml flask were added dropwise at room temperature 2.3 ml (10.35 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 20 min. After drying, 1.08 g of white xerogel **X9B** was obtained. Elemental Anal. calc. for $C_{18}H_{12}O_{5.5}PSi_3$: C, 50.11; H, 2.78; P, 7.19; Si, 19.49. Found: C, 45.51; H, 4.79; P, 6.35; Si, 18.05 which corresponds to $C_{18.51}H_{23.38}O_{7.72}PSi_{3.15}$.

Xerogel X10A

To a solution of 1.05 g (1.16 mmol) of **10** in THF (0.6 ml) placed in a 5 ml flask were added dropwise at room temperature 0.6 ml (5.4 mmol of H_2O) of a 9 M aqueous 0.02 M PTSA solution in THF. The reaction mixture was stirred for 5 min and kept at 19 °C without stirring. Gel formation occurred after 104 h. After drying, 0.443 g of white xerogel **X10A** was obtained. Elemental Anal. calc. for $C_{18}H_{12}O_{4.5}PSSi_3$: C, 48.32; H, 2.68; P, 6.93; S, 7.16; Si, 18.79. Found: C, 46.24; H, 4.90; P, 5.15; S, 5.20; Si, 16.75 which corresponds to $C_{23.19}H_{29.48}O_{8.18}PS_{0.98}Si_{3.60}$.

Xerogel X10B

To a solution of 2.26 g (2.49 mmol) of **10** in THF (2.50 ml) placed in a 12.5 ml flask were added dropwise at room temperature 2.50 ml (11.25 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 1 h. After drying, 1.20 g of white xerogel **X10B** was obtained. Elemental Anal. calc. for $C_{18}H_{12}O_{4.5}PSSi_3$: C, 48.32; H, 2.68; P, 6.93; S, 7.16; Si, 18.79. Found: C, 43.43; H, 4.62; P, 5.55; S, 5.72; Si, 17.30 which corresponds to $C_{20.21}H_{25.80}O_{8.16}PS_{1.00}Si_{3.45}$.

Xerogel X11A

To a solution of 2 g (1.97 mmol) of **11** in THF (2.0 ml) placed in a 12.5 ml flask were added dropwise at room temperature 2 ml (9 mmol of H_2O) of a 4.5 M aqueous 0.01 M PTSA solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 54 h. After drying, 1.28 g of yellow xerogel **X11A** was obtained. Elemental Anal. calc. for $C_{19}H_{15}IO_{4.5}PSi_3$: C, 40.93; H, 2.69; I, 22.80; P, 5.56; Si, 15.06. Found: C, 43.56; H, 4.86; I, 17.03; P, 3.37; Si, 11.82 which corresponds to $C_{33.39}H_{44.70}I_{1.23}O_{11.13}PSi_{3.88}$.

Xerogel X11B

To a solution of 2 g (1.97 mmol) of **11** in THF (2.0 ml) placed in a 12.5 ml flask were added dropwise at room temperature 2 ml (9 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 2 min. After drying, 1.22 g of yellow xerogel **X11B** was obtained. Elemental Anal. calc. for $C_{19}H_{15}IO_{4.5}PSi_3$: C, 40.93; H, 2.69; I, 22.80; P, 5.56; Si, 15.06. Found: C, 39.61; H, 4.38; I, 16.89; P, 4.34; Si, 12.99 which corresponds to $C_{23.57}H_{31.28}I_{0.95}O_{9.72}PSi_{3.31}$.

Xerogel X12A

To a solution of 1.68 g (1.89 mmol) of **12** in THF (1.9 ml) placed in a 12.5 ml flask were added dropwise at room temperature 1.9 ml (8.55 mmol of H_2O) of a 4.5 M aqueous 0.01 M PTSA solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 23 h but, after about 30 min a very slight release of gas was observed so that the cork of the flask

was pierced. After drying, 0.884 g of white xerogel **X12A** was obtained. Elemental Anal. calc. for $C_{18}H_{15}BO_{4.5}PSi_3$: C, 50.35; H, 3.50; B, 2.56; P, 7.22; Si, 19.58. Found: C, 49.26; H, 5.18; B, 1.50; P, 4.05; Si, 16.95 which corresponds to $C_{31.42}H_{39.65}B_{1.04}O_{11.03}PSi_{4.63}$.

Xerogel X12B

To a solution of 2.18 g (2.45 mmol) of **12** in THF (2.4 ml) placed in a 12.5 ml flask were added dropwise at room temperature 2.5 ml (11.25 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 1 h 10 min. However, after about 30 min a slight release of gas was observed so that the cork of the flask was pierced. After drying, 1.18 g of white xerogel **X12B** was obtained. Elemental Anal. calc. for $C_{18}H_{15}BO_{4.5}PSi_3$: C, 50.35; H, 3.50; B, 2.56; P, 7.22; Si, 19.58. Found: C, 46.36; H, 5.06; B, 1.15; P, 3.90; Si, 15.65 which corresponds to $C_{30.71}H_{40.22}B_{0.83}O_{13.85}PSi_{4.44}$.

Xerogel X13A

To a solution of 1.96 g (1.63 mmol) of **13** in THF (1.60 ml) placed in a 5 ml flask were added dropwise at room temperature 1.65 ml (7.42 mmol of H_2O) of a 4.5 M aqueous 0.01 M PTSA solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 5 h. After drying, 1.23 g of white xerogel **X13A** was obtained. IR (DRIFT, ν/cm^{-1}, KCl) 1940, 1982, 2072. Elemental Anal. calc. for $C_{23}H_{12}O_{9.5}PSi_3W$: C, 37.35; H, 1.62; P, 4.19; Si, 11.36; W, 24.90. Found: C, 37.27; H, 3.09; P, 3.65; Si, 10.75; W, 16.55 which corresponds to $C_{26.38}H_{26.24}O_{15.23}PSi_{3.26}W_{0.76}$.

Xerogel X13B

To a solution of 2.12 g (1.77 mmol) of **13** in THF (1.80 ml) placed in a 12.5 ml flask were added dropwise at room temperature 1.80 ml (8.10 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 50 min. After drying, 1.34 g of light yellow xerogel **X13B** was obtained. IR (DRIFT, ν/cm^{-1}, KCl) 1930, 1985, 2072. Elemental Anal. calc. for $C_{23}H_{12}O_{9.5}PSi_3W$: C, 37.35; H, 1.62; P, 4.19; Si, 11.36; W, 24.90. Found: C, 35.11; H, 3.02; P, 3.45; Si, 10.40; W, 23.15 which corresponds to $C_{26.29}H_{27.13}O_{13.97}PSi_{3.33}W_{1.13}$.

Xerogel X14B

To a solution of 1.92 g (0.95 mmol) of **14** in THF (1.90 ml) placed in a 12.5 ml flask were added dropwise at room temperature 1.90 ml (8.55 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 25 min. After drying, 1.23 g of light yellow xerogel **X14B** was obtained. Elemental Anal. calc. for $C_{36}H_{24}Cl_2O_9P_2PtSi_6$: C, 39.41; H, 2.19; Cl, 6.48; P, 5.65; Pt, 17.79; Si, 15.33. Found: C, 40.83; H, 4.52; Cl, 4.86; P, 4.41; Pt, 13.23; Si, 12.81 which corresponds to $C_{47.83}H_{63.54}Cl_{1.92}O_{16.99}P_2Pt_{0.95}Si_{6.43}$.

Xerogel X15B

To a solution of 1.58 g (0.78 mmol) of **15** in THF (1.50 ml) placed in a 12.5 ml flask were added dropwise at room temperature 1.60 ml (7.20 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 30 min. After drying, 0.93 g of light yellow xerogel **X15B** was obtained. Elemental Anal. calc. for $C_{36}H_{24}Cl_2O_9P_2PtSi_6$: C, 39.41; H, 2.19; Cl, 6.48; P, 5.65; Pt, 17.79; Si, 15.33. Found: C, 38.31; H, 4.26; Cl, 5.08; P, 4.90; Pt, 13.25; Si, 14.15 which corresponds to $C_{40.39}H_{53.90}Cl_{1.81}O_{15.86}P_2Pt_{0.86}S_{6.40}$.

Xerogel X16A

To a solution of 1.05 g (0.55 mmol) of **16** in THF (1.10 ml) placed in a 12.5 ml flask were added dropwise at room temperature 1.10 ml (4.95 mmol of H_2O) of a 4.5 M aqueous 0.01 M PTSA solution in THF. The reaction mixture was stirred for 5 min and kept at 22 °C without stirring. Gel formation occurred after 24 h. After drying, 0.59 g of orange xerogel **X16A** was obtained. Elemental Anal. calc. for $C_{36}H_{24}Cl_2O_9P_2PdSi_6$: C, 42.88; H, 2.38; Cl, 7.05; P, 6.15; Pd, 10.56; Si, 16.67. Found: C, 39.12; H, 3.93; Cl, 5.03; P, 5.10; Pd, 8.55; Si, 14.75 which corresponds to $C_{32.36}H_{47.78}Cl_{1.72}O_{17.87}P_2Pd_{0.98}Si_{6.40}$.

Xerogel X16B

To a solution of 1.69 g (0.88 mmol) of **16** in THF (1.75 ml) placed in a 12.5 ml flask were added dropwise at room temperature 1.75 ml (7.87 mmol of H_2O) of a 4.5 M aqueous 0.1 M HCl solution in THF. The reaction mixture was stirred for 5 min and kept at 30 °C without stirring. Gel formation occurred after 25 min. After drying, 1.03 g of orange xerogel **X16B** was obtained. Elemental Anal. calc. for $C_{36}H_{24}Cl_2O_9P_2PdSi_6$: C, 42.88; H, 2.38; Cl, 7.05; P, 6.15; Pd, 10.56; Si, 16.67. Found: C, 41.27; H, 4.52; Cl, 5.47; P, 4.74; Pd, 8.01; Si, 13.37 which corresponds to $C_{44.98}H_{59.12}Cl_{2.01}O_{18.49}P_2Pd_{0.98}Si_{6.24}$.

Xerogel X6

To a solution of **6** (1.25 g, 3.55 mmol) in THF (3.5 ml) placed in a 20 ml test tube was added dropwise at 0 °C in 5 min, under stirring, 3.6 ml (16.2 mmol of H_2O) of a 4.5 M aqueous 0.01 M Bu^n_4NF solution in THF. The reaction mixture was then kept at room temperature without stirring. Release of dihydrogen was observed until gel formation (4 h). The wet gel was left to age for 5 d at room temperature and the solid was subsequently treated as described before to give 1.44 g of white xerogel **X6**. Specific surface area, IR (DRIFT), ^{31}P (CP-MAS) NMR, ^{13}C (CP-MAS) NMR, and ^{29}Si (CP-MAS) NMR results are indicated in Table 3. Elemental Anal. calc. for $C_{18}H_{12}O_{4.5}PSi_3$: C, 52.05; H, 2.89; P, 7.47; Si, 20.24. Found: C, 51.45; H, 4.14; P, 7.00; Si, 19.20 which corresponds to $C_{18.98}H_{18.33}O_{5.04}PSi_{3.03}$.

Xerogel X17

To a solution of **17** (1.25 g, 3.41 mol) in THF (3.4 ml) placed in a 20 ml test tube were added dropwise at 0 °C, in 8 min, under stirring, 3.4 ml (15.3 mmol of H_2O) of a 4.5 M aqueous 0.01 M Bu^n_4NF solution in THF. The reaction mixture was kept at room temperature without stirring. Release of dihydrogen was observed until gel formation (9 h 30 min). After drying, 1.36 g of white xerogel **X17** was obtained. Specific surface area, IR (DRIFT), ^{31}P (CP-MAS) NMR, and ^{29}Si (CP-MAS) NMR results are indicated in Table 3. Elemental Anal. calc. for $C_{18}H_{15}BO_{4.5}PSi_3$: C, 50.35; H, 3.50; B, 2.56; P, 7.22; Si, 19.58. Found: C, 41.71; H, 4.64; B, 2.00; P, 6.20; Si, 18.90 which corresponds to $C_{17.38}H_{23.20}B_{0\cdot91}O_{8.30}PSi_{3.37}$.

Hydrolysis of 7

To a solution of **7** (3.0 g, 4.36 mmol) in THF (4.3 ml) placed in a 20 ml test tube were added dropwise at room temperature, 4.4 ml (19.8 mmol of H_2O) of a 4.5 M aqueous 0.01 M solution of Bu^n_4NF in THF. The mixture was stirred for 5 min and kept without stirring until gel formation (12 h). After drying,

0.926 mg of white xerogel was obtained, which was identified as silica by ^{29}Si CP-MAS NMR δ −91.2 (Q^2), −100.7 (Q^3), −109.1 (Q^4). Elemental Anal. calc. for $C_3H_6O_{4.5}PSi_3$: C, 15.72; H, 2.62; P, 13.54; Si, 36.68. Found: C, 11.94; H, 3.02; P, 0.15; Si, 34.80 which corresponds to $C_{0.80}H_{2.42}O_{2.52}P_{<0.01}Si$.

Hydrolysis of 8

To a solution of **8** (0.31 g, 1.86 mmol) in THF (1.8 ml) placed in a 20 ml test tube were added dropwise, at −10 °C, 1.9 ml (8.55 mmol of H_2O) of a 4.5 M aqueous 0.01 M solution of Bu^n_4NF in THF. The mixture was stirred for 30 min at −10 °C and kept without stirring until gel formation (15 min). After drying, 0.024 g of white xerogel was obtained, which was identified as silica by ^{29}Si CP-MAS NMR δ −90.4 (Q^2), −100.4 (Q^3), −107.7 (Q^4). Elemental Anal. calc. for $C_3H_6O_{4.5}PSi_3$: C, 15.72; H, 2.62; P, 13.54; Si, 36.68. Found: C, 4.70; H, 1.86; P, 0.40; Si, 38.15 which corresponds to $C_{0.29}H_{1.36}O_{2.45}P_{0.01}Si$.

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Paper 8/01077C; *Received* 6*th February*, 1998