Preparation and characterization of organic-inorganic hybrid materials incorporating diphosphino moieties. Study of the accessibility of the phosphorus atoms included into the material

Jean-Philippe Bezombes, Claude Chuit, Robert J.P. Corriu, and Catherine Reyé

Abstract: The hydrolysis-polycondensation by the sol-gel process of the aromatic diphosphines $(X_3SiC_6H_4)_2PC_6H_4P(C_6H_4SiX_3)_2$, which are rigid molecules bearing four hydrolysable SiX_3 groups (X = O^iPr, H), leads to new organic-inorganic hybrid materials, characterized by solid state ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopies. The accessibility of the phosphorus centres incorporated into the xerogel obtained from the diphosphine with X = O^iPr has been studied. All the phosphorus atoms reacted quantitatively with H_2O_2, S_8, and CH_3I but only 20% with the more bulky reagent $W(CO)_5·THF$. This result is explained by the rigidity of the inorganic network resulting from the high number of hydrolysable Si-O^iPr groups in the precursor.

Key words : Diphosphines, sol-gel process, xerogels, solid ^{31}P NMR.

Résumé : L'hydrolyse-polycondensation via le procédé sol-gel des diphosphines aromatiques $(X_3SiC_6H_4)_2PC_6H_4P(C_6H_4SiX_3)_2$, molécules rigides portant quatre groupements SiX_3 hydrolysables (X = O^iPr, H), conduit à de nouveaux matériaux hybrides organique-inorganiques qui ont été caractérisés par la RMN à l'état solide du ^{13}C, du ^{29}Si et du ^{31}P. L'étude de l' accessibilité des centres phosphorés incorporés dans le xérogel obtenu à partir de la diphosphine avec X = O^iPr est décrite. Tous les atomes de phosphore réagissent quantitativement avec H_2O_2, S_8, et CH_3I, mais seulement 20% réagissent avec $W(CO)_5·THF$ réactif plus volumineux que les précédents. Ce résultat est expliqué par la rigidité du réseau inorganique qui est la conséquence du nombre élevé de groupements hydrolysables Si-O^iPr porté par le précurseur.

Mots clés : diphosphines, procédé sol-gel, xérogels, RMN solide ^{31}P.

Introduction

The sol-gel process allows the preparation of organic–inorganic hybrid materials under smooth conditions (1–4). In a recent publication (5) we described the preparation of phosphines **1**, **2**, and **3** as well as their hydrolysis and polycondensation via the sol-gel process, giving rise to the corresponding xerogels. The accessibility of the phosphorus centres included in these xerogels was investigated by using some classical reactions at phosphorus. We found that the phosphorus centres react quantitatively with H_2O_2, S_8, and MeI, whilst their reactivity towards $W(CO)_5·THF$ (6) varied depending on the xerogel studied. We noticed that the phosphorus atoms became more readily accessible when the number of $Si(OR)_3$ groups in the precursor is low. Thus the phosphorus atoms in the xerogel derived from precursor **1** (with two $Si(O^iPr)_3$ groups) reacts more readily with $W(CO)_5·THF$ than when included into the xerogels derived from precursors **2** and **3** (with three SiX_3 groups).

As a continuation of this study, we prepared the aromatic diphosphines **4** and **5** (with four SiX_3 groups) and studied their hydrolysis and polycondensation as well as the accessibility of the phosphorus centres included into the xerogel **X4** obtained from the diphosphine **4**. This diphosphine was chosen with rigid substituents around the phosphorus centres as in the case for the phosphines **1** and **2**. This study was undertaken to verify if the high number of $Si(O^iPr)_3$ groups in the precursor **4** gives rise to a low accessibility of the phosphorus centres included into the corresponding xerogel as predicted by our previous study (6).

Results and discussion

1) Preparation of diphosphines 4 and 5 and of phosphine derivatives 7–9.

The diphosphine **4** was prepared in 53% yield by reaction of the previously described functional Grignard reagent **6** (5) with *P,P,P′,P′*-tetrachloro-*p*-phenylenediphosphine (7) in

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This paper is dedicated to Professor Adrian Brook in recognition to his very important contribution in silicon chemistry.

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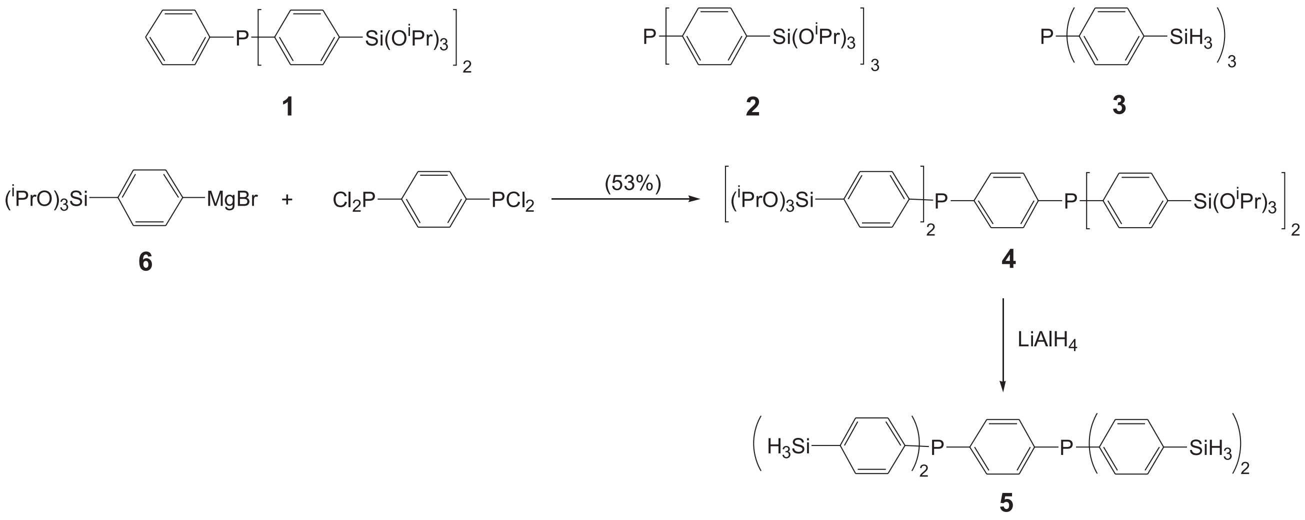
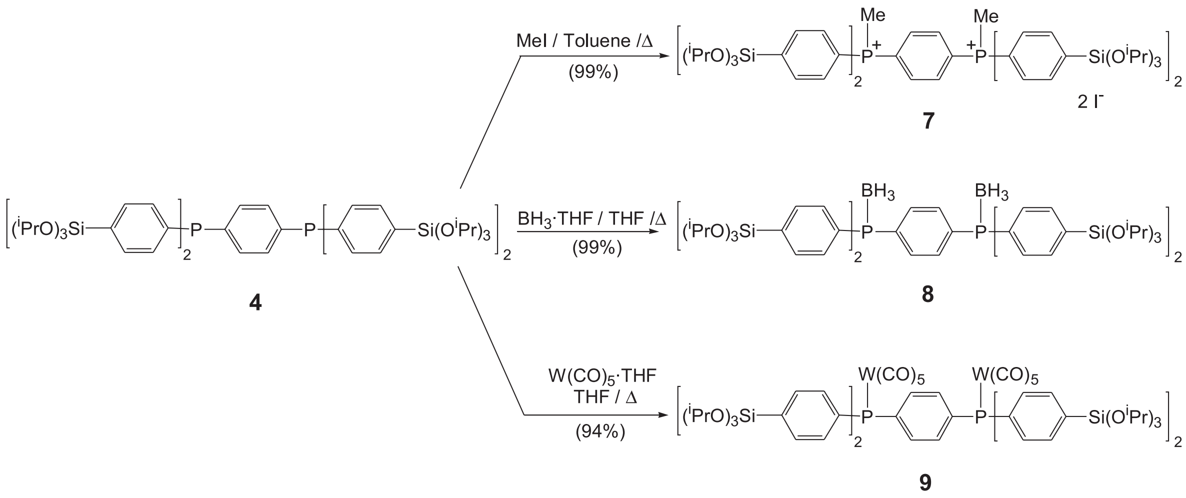
Scheme 1.



Scheme 2.



THF (Scheme 1). $LiAlH_4$ reduction of **4** gave the diphosphine **5** in good yield (Scheme 1). Treatment of **4** by methyl iodide, BH_3·THF, and $W(CO)_5$·THF gives rise respectively and quantitatively to the diphosphonium salt **7**, to the diphosphine borane complex **8**, and to the diphosphine tungsten pentacarbonyl complex **9** (Scheme 2).

2) Sol-gel processing of diphosphines 4 and 5 and of diphosphine derivatives 7–9

We previously showed (5) that phosphines **1** and **2** required an acidic catalyst to be hydrolyzed, therefore diphosphine **4** was hydrolyzed and polycondensed with 6 equivalents of water in the presence of 10% of HCl in THF solution (eq. [1] and Table 1). At 30°C, the gelation occurs within 2 h which is close to the gelation time for phosphine **2** (5). Xerogel **X4** was obtained after ageing at 30°C for five days. It was then powdered and washed twice with ethanol, acetone, and diethyl ether and dried in vacuo at 120°C for two hours. The solid state ^{31}P NMR spectrum of **X4** displays only one signal at –5.0 ppm which indicates that no oxidation of the phosphorus atom occurred during the sol-gel process. The solid state ^{13}C NMR spectrum of **X4** displays one signal at 134.4 ppm attributed to the aromatic carbons and two further signals at 24.8 and 66.7 ppm attributed to remaining O^iPr groups. Thus the hydrolysis is incomplete; however the elemental analysis indicates that only about 10% of the $Si(O^iPr)_3$ groups were not hydrolyzed. The solid state ^{29}Si NMR spectrum of **X4** displays two main resonances at –60.5 ppm [substructure T^1, $C\text{-}Si(OR)_2OSi$] and –69.1 ppm [substructure T^2, $C\text{-}Si(OR)(OSi)_2$]. A minor resonance assigned to the substructure T^3 [$C\text{-}Si(OSi)_3$] was observed while substructure T° was absent. The ratio of the T groups was estimated from deconvoluted T peaks (8, 9) at 42% for T^1, 52% for T^2, and 6% for T^3 corresponding to a degree of condensation τ of 55%.[2] Thus while the hydrolysis is important, the polycondensation is rather weak. The absence of any Q signal corresponding to the SiO_4 substructure (region of –100ppm) is noteworthy indicating that the

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[2] The degree of condensation was calculated according to the equation: $\tau = [(0.5)(\text{area } T^1) + (1.0)(\text{area } T^2) + (1.5)(\text{area } T^3)]/1.5$.

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Table 1. Textural and solid state NMR data for xerogels **X4**, **X5**, and **X7**–**X9**.

Precursor	Gelification time	S_{BET} (m^2 g^{-1})	^{31}P CP-MAS NMR (δ)	^{13}C CP-MAS NMR (δ)	^{28}Si CP-MAS NMR (δ)
4	2 h	460	–5.0	24.8, 66.7, 134.4	–60.5 (T^1), –69.1 (T^2)
7	1 min	<10	+22.0		–67.7 (T^2)
8	15 min	75	–5.8, +22.0 (50/50)		
9	20 min	380	+20.9		
5	30 h	570	–5.1		–61.6 (T^1), –69.3 (T^2), –77.0 (T^3) –50 to –30 (D)

Table 2. Textural data for the materials prepared by hydrolysis and polycondensation of phosphines **1**, **2**, and **4**.

Precursor	Xerogel	S_{BET} (m^2 g^{-1})	τ^a	N^b	Micropore vol. (mL g^{-1})	Mean pore dia. (Å)
1 (f^c = 6)	**X1**^{d}	< 10	62	3.7	—	—
2 (f^c = 9)	**X2**^{d}	400	57	5.1	0.175	15
4 (f^c = 12)	**X4**^{d}	460	55	6.6	0.182	15.5

[a] Degree of condensation, determined by ^{29}Si CP-MAS NMR.

[b] Average number of Si—O—Si bonds by precursor ($N = f \times \tau$).

[c] Functionality at silicon.

[d] HCl, 10% as catalyst.

integrity of the organic moiety had been maintained during the sol-gel process. The surface area (N_2 BET measurement) is of 460 m^2/g, value comparable to that found for the hydrolysis of phosphine **2** (Table 2). The adsorption–desorption isotherms for **X4** indicated that the solid is microporous with a microporous volume of 0.182 mL g^{-1} and mean pore diameter of 15.5 Å.

The hydrolysis of diphosphine **5** was performed in THF solution in the presence of a catalytic amount of tetrabutylammonium fluoride (10) with 6 equivalents of water. The reagents were mixed at 0°C and the solution was allowed to warm to 24°C after 8 min. The gel was formed after 30 h. After the usual work-up, xerogel **X5** was obtained. Its N_2 BET surface area was found of 570 m^2 g^{-1}, with a microporous volume of 0.247 mL g^{-1}. There is no oxidation of the phosphorus atoms during the hydrolysis as indicated by the solid state ^{31}P NMR spectrum of **X5** which displays only one signal at –5.1 ppm. The solid state ^{29}Si NMR spectrum of **X5** displays a set of three resonances at –61.6 ppm (substructure T^1), –69.3 ppm (substructure T^2), and –77.0 ppm (substructure T^3); and a broad resonance (–50 to –30 ppm) corresponding to $CSi(H)O_2$ substructures. This is consistent with the FTIR spectrum which shows a Si—H absorption band at 2160 cm^{-1}. No peak corresponding to an SiO_4 substructure was found around –100 ppm indicating that no Si—C cleavage occurred during the sol-gel process.

Phosphorus derivatives **7**–**9** were hydrolyzed and polycondensed under the same conditions as those previously described for phosphine **4** to give xerogels **X7**-**X9** (eqs. [2]–[4] and Table 1). The solid state ^{31}P NMR spectra of xerogels **X7** and **X9** showed that there was neither oxidation nor decomplexation during the polycondensation reactions. In the case of the diphosphine derivative **8** partial decomplexation took place during the hydrolysis. The P—B bond cleavage was estimated by ^{31}P NMR spectroscopy to be about 40% after reaction without drying the xerogel. After heating for one night at 120°C, the cleavage of the P—B bond was increased to 70%. This P—B bond cleavage occurred probably either by hydrolysis or by reaction of the Si-OH present in the xerogel or by both processes. The participation of the Si-OH groups in the cleavage of the P—B bonds is likely as elemental analysis showed that most of the B atoms are incorporated in the xerogel after washing, probably as Si-O-B groups.

Thus the behaviour of diphosphines **4** and **5** and diphosphine derivatives **7**–**9** during the hydrolysis process is very similar to those of phosphines **2** and **3** as well as that of the corresponding derivatives of phosphine **2** (5).

3) Reactivity of the xerogel X4 with H_2O_2, S_8, CH_3I, and $W(CO)_5 \cdot THF$

To investigate the accessibility of the phosphorus centers included into **X4**, we treated it with an excess of the following reagents: H_2O_2, S_8, CH_3I, and $W(CO)_5 \cdot THF$ (Scheme 3).

First we studied the oxidation of the phosphorus centres by reacting **X4** with an aqueous solution of H_2O_2 (60 equiv). The solid state ^{31}P NMR spectrum of the resulting xerogel showed the absence of the signal attributed to the phosphino group (–5.0 ppm) and the presence of a signal at 28.1 ppm assigned to the phosphine oxide centers (5).

X4 was treated with sulphur (13 equiv) in *n*-butanol heated under reflux for 48 h. The solid state ^{31}P NMR spectrum of the resulting xerogel exhibited only a signal at 41.3 ppm assigned to the thiophosphoryl centres (5).

Treatment of **X4** with an excess of methyl iodide for 48 h in toluene heated under reflux gave rise to a xerogel, the solid state ^{31}P NMR spectrum of which displayed a signal at 21.5 ppm, close to that for **X7** (δ = 22 ppm). This signal indicates that all the phosphino groups were transformed into phosphonium salts.

Finally **X4** was treated with an excess of $W(CO)_5 \cdot THF$ (4 equiv) in THF heated under reflux for 96 h. After the usual work-up, FTIR analysis of the resulting xerogel revealed the presence of the same CO stretching bands as those observed in **X9**, which characterize the expected $LW(CO)_5$. The solid state ^{31}P NMR spectrum of this xerogel displays a weak signal at 22.0 ppm corresponding to about 20% of complexed

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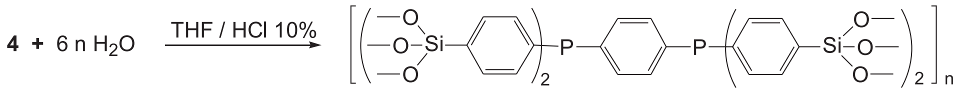
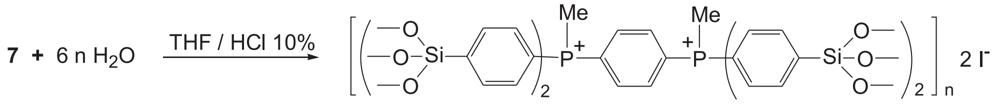
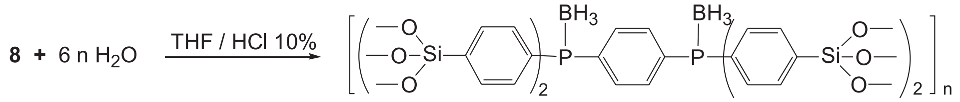


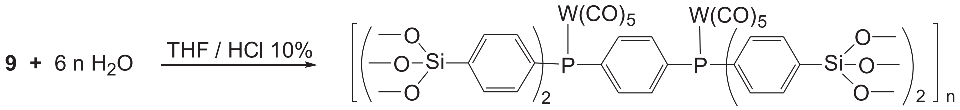
X4 (1)



X7 (2)

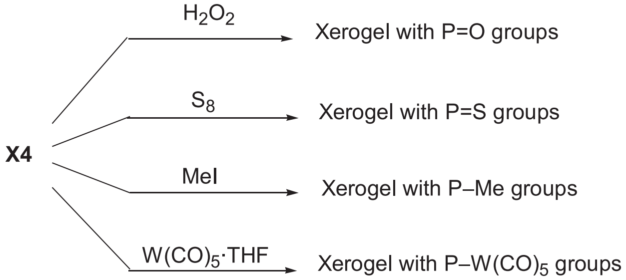


X8 (3)



X9 (4)

Scheme 3.



phosphino centres and a large signal at –7.3 ppm corresponding at about 80% of unchanged phosphino groups (Fig. 1). Thus, most of the phosphino groups in xerogel **X4** are not accessible by $W(CO)_5{\cdot}THF$ under the conditions used for the reaction.

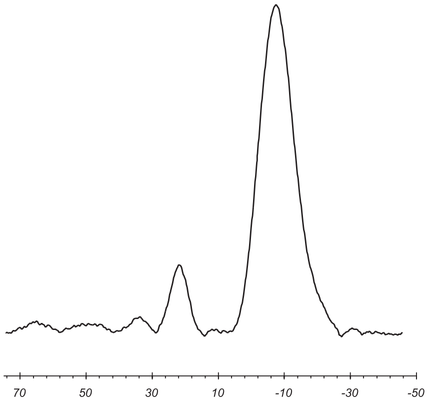
Discussion

All the phosphorus atoms of the xerogel **X4** are accessible to the small reagents H_2O_2, S_8, and CH_3I as was previously observed for the xerogels **X1** and **X2** obtained from the phosphines **1** and **2** respectively (Table 2) (5). In contrast, the reaction with the rather bulky reagent $W(CO)_5{\cdot}THF$ allowed discrimination between the xerogels **X1**, **X2**, and **X4**. Indeed, only 20% of phosphorus atoms included into **X4** were complexed by $W(CO)_5$ while the complexation was complete for **X1** and was 80% for **X2** (Table 3).

In our previous publication (6) we have observed that the average number (*N*) of Si-O-Si bonds attached to each organophosphorous moiety in the material was an important parameter controlling the accessibility of the phosphino centres. This number *N* is a function of both the degree of condensation τ of the xerogel and the number *f* of hydrolysable SiX_3 groups of the precursor ($N = f \times \tau$) (see Table 2). We observed that the greater the *N* value, the more difficult was the accessibility of the phosphorus centres by the rather bulky reagent $W(CO)_5{\cdot}THF$. The present study of the accessibility of the phosphorus centres incorporated into **X4** confirms this observation.

We consider that the number of Si—O—Si bonds should have an influence on the mobility of the network of the xerogel. The more important the mobility of the organic moieties, the easier is the penetration and the diffusion of the reagents into the hybrid organic-inorganic material (11, 12). Thus the diffusion of the reagent through **X1**, material in which the average number of Si—O—Si bonds by organic moiety is $N = 3.7$, is much easier than through **X4** in which the organic moieties are more rigid ($N = 6.6$). This interpretation is supported by ^{31}P NMR data of xerogels **X1**, **X2**, and **X4**. Indeed as shown on Fig. 2, the broadening of the ^{31}P NMR signals for xerogels increases with the average number *N* of Si—O—Si bonds attached to the organic moieties. The less flexible the organophosphorus moieties, the larger is the ^{31}P NMR signal of the phosphorus atoms (13).

Fig. 1. Solid state ^{31}P NMR spectrum of the xerogel **X4** after reaction with $W(CO)_5 \cdot THF$



Thus these NMR data confirm that the mobility of organophosphorous moieties decreases as *N* increases, the phosphorus atoms being less readily accessible to reagents owing to a lower swellability of the matrix.

In conclusion, this study and the preceding one (6) clearly show that the average number *N* of Si—O—Si bonds attached to the organic moiety is an important parameter controlling the accessibility of the phosphorus centers included in an hybrid organic-inorganic material. This shows the importance of the number of the hydrolysable SiX_3 bonds in the organic precursor. This parameter has been well evidenced because the precursors **1**, **2**, as well as **4** all bear rigid groups around the phosphorus centres. It is likely that in the case of phosphines with flexible groups around the phosphorus atoms, the situation is different.

Experimental

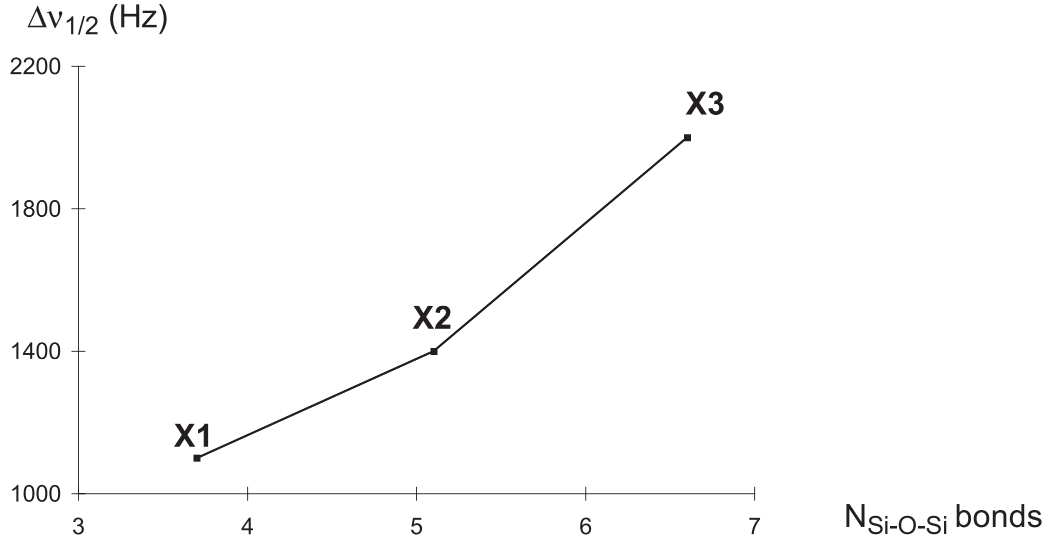
All reactions were carried out under argon by using a vacuum line. Solvents were dried and distilled just before use. Melting points were determined with a Gallenkamp apparatus and are uncorrected. IR data were obtained on a Perkin-Elmer 1600 FTIR spectrophotometer by the DRIFT method. The solution NMR spectra were recorded on a Bruker AC-200 (^{29}Si), Bruker DPX-200 (^{1}H and ^{13}C), and Bruker WP 250 SY (^{31}P, ^{11}B). Chemical shifts (δ in ppm) were referenced to Me_4Si (^{1}H, ^{13}C, ^{29}Si), $BF_3 \cdot THF$ (^{11}B), or H_3PO_4 (^{31}P). The CP MAS solid state ^{29}Si NMR spectra were recorded on a Bruker FTAM 300 as well as CP MAS ^{13}C solid state NMR spectra in that case by using the TOSS technique. In both cases the repetition time was 5 and 10 s with contact times of 5 and 2 milliseconds. The HPDEC MAS ^{31}P solid state NMR spectra were recorded on a Bruker FTAM 300, a Brucker ASX 200, or a Brucker ASX 400 with repetition time of 5 s. FAB mass spectra (matrix, *m*-nitrobenzyl alcohol (NBA), thioglycerol (GT)) were registered on Jeol JMS-D3000 spectrometer. Specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method on Micromeritics ASAP 2010 and Micromeritics Gemini III 2375 analysers. Elemental analyses were carried out by the Service Central de Micro- Analyse du CNRS.

Table 3. Solid state ^{31}P NMR chemical shifts (δ in ppm) of phosphorus atoms after treatment of the xerogels **X1**, **X2**, and **X4** with $W(CO)_5 \cdot THF$. The percent of each signal is indicated in parentheses.

	^{31}P HPDEC MAS NMR	
Xerogel	Complexed centers	Unchanged centers
X1 ($f = 6$)	21.1 (100%)	—
X2 ($f = 9$)	20.8 (80%)	–7.3 (20%)
X4 ($f = 12$)	22.0 (20%)	–5.9 (80%)

*P,P,P′,P′-tetrakis(4-triisopropyloxysilylphenyl)p-phenylenediphosphine (**4**)*: *P,P,P′,P′*-tetrachloro-*p*-phenylenediphosphine (14) (5.28 g, 18.9 mmol) in THF (50 mL) are added dropwise, at 0°C, to a solution of 4-triisopropyloxysilylphenylmagnesium bromide (77.4 mmol) in THF (200mL). The reaction mixture was stirred for 12 h at room temperature and then was heated under reflux for one hour. The THF was removed under vacuum and pentane (250 mL) was

Fig. 2. Half line width ($\Delta\nu_{1/2}$, 1100 Hz for **X1**, 1400 Hz for **X2**, 2000 Hz for **X4**) of the solid state ^{31}P NMR signals of xerogels **X1**, **X2**, and **X4** as a function of the average number *N* of Si-O-Si bonds (3.7 for **X1**, 5.1 for **X2**, 6.6 for **X4**).



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added. After filtration and removal of the solvent under vacuum, 2-propanol (30 mL) was added under stirring to the oily residue (23.6 g). The resulting powder was recrystallised from 2-propanol to give 11.7 g, (10.1 mmol, 53%) of white crystals. Mp (2-propanol) 172–175°C; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.24 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 72H, Me), 4.30 (spt, $^3J_{H\text{-}H}$ = 6.1 Hz, 12H, OCH), 7.25–7.36 (m, 12H, aromatic), 7.65–7.70 (m, 8H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 65.9 (OCH), 133–139 (aromatic); ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) –61.9; ^{31}P NMR (δ, 100 MHz, $CDCl_3$) –4.9; MS (FAB+, GT) 1263 [(M + H)$^+$, 32%], 1295 [(M + 2 oxygen + H)$^+$, 45%]. Anal. calc. for $C_{66}H_{104}O_{12}P_2Si_4$: C 62.75, H 8.24%; found: C 62.76, H 8.39.

P,P,P′,P′-tetrakis(4-trihydrosilylphenyl)p-phenylenediphosphine (5): Diphosphine **4** (10.4 g, 8.23 mmol) in diethyl ether (80 mL) was added dropwise at 0°C to a suspension of $LiAlH_4$ (1.92 g, 50.5 mmol) in diethyl ether (60 mL). The reaction mixture was stirred for 3 h at room temperature and the solvent was then evaporated under vacuum to give a white solid which was dissolved in pentane (500 mL). After filtration of the salts and evaporation of the solvent under vacuum, 4.24 g (7.49 mmol) of raw diphosphine was obtained. Mp 172 (decomp.); ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 4.23 (s and d (satellite ^{29}Si, $^1J_{Si\text{-}H}$ = 202 H), 9H, SiH), 7.23–7.62 (m, 20H, aromatic ; ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 130–139 (aromatic) ; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) –58.7 ; ^{31}P NMR (δ, 80 MHz, $CDCl_3$) –4.6 ; IR (ν/cm^{-1}, CCl_4) 2160; MS (FAB+, NBA) 567 [(M + H)$^+$, 40%], 583 [(M + 1 oxygen + H)$^+$, 56%]. Anal. calc. for $C_{30}H_{32}P_2Si_4$: C 63.60, H 5.65%; found: C 61.86, H 5.96.

Dimethyl[P,P,P′,P′-tetrakis(4-triisopropyloxysilylphenyl)p-phenylene]diphosphonium diiodide (7): Diphosphine **4** (2.38 g, 1.88 mmol) and methyl iodide (0.5 mL, 8.03 mmol) were heated under reflux in toluene (20 mL) for 3 h. After evaporation of the solvent, 2.87 g (1.86 mmol, 99%) of crude **7** was obtained. Mp (2-propanol) 284.6 (decomp.) ; ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.20 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 72H, Me), 3.23 (d, $^2J_{P\text{-}H}$ = 13.3 Hz, 6H, PMe), 4.28 (spt, $^3J_{H\text{-}H}$ = 6.1 Hz, 12H, OCH), 7.78–8.03 (m, 20H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 11.8 (d, $^1J_{P\text{-}C}$ = 56.7 Hz, PC), 25.9 (Me), 66.5 (OCH), 112–143 (aromatic) ; ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) –65.8 ; ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 22.7 ; MS (FAB+, GT) 1293 [(M – 2I)$^+$, 100%]. Anal. calc. for $C_{68}H_{110}O_{12}P_2Si_4$: C 52.78, H 7.11%; found: C 52.01, H 7.41.

P,P,P′,P′-tetrakis(4-triisopropyloxysilylphenyl)p-phenylenediphosphine diborane (8): A molar solution of BH_3·THF in THF (4.1 mL, 4.1 mmol) was added dropwise, at 0°C, to 2.56 g (2.03 mmol) of **4** in THF (10 mL). After stirring one hour at room temperature the solvent was removed to give 2.61 g (2.02 mmol, 99%) of crude **8**. Mp 163.7 (decomp.); ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 78H, Me+BH), 4.31 (spt, $^3J_{H\text{-}H}$ = 6.1 Hz, 12H, OCH), 7.54–7.81 (m, 20H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.1 (OCH), 128–138 (aromatic); ^{11}B NMR (δ, 80 MHz, $CDCl_3$) –38.5 (broad signal); ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) –63.5 (d, $^5J_{P\text{-}Si}$ = 1.2 Hz); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 22.1 (broad signal); MS (FAB+, GT) 1263 [(M – $2BH_3$ + H)$^+$, 41%]. Anal. calc. for $C_{66}H_{110}O_{12}B_2P_2Si_4$: C 61.39, H 8.53%; found: C 60.86, H 8.35.

P,P,P′,P′-tetrakis(4-triisopropyloxysilylphenyl)p-phenylenediphosphine bis tungsten pentacarbonyl (9): A THF solution of $W(CO)_5$·THF (15) (150 mL, 8.55 mmol) was added to 2.61 g (2.07 mmol) of **4**. After stirring for two hours at room temperature, the solvent was evaporated under vacuum. After elimination of excess of $W(CO)_5$·THF by sublimation at 60°C under vacuum, 3.71 g (1.94 mmol, 94%) of crude **9** was obtained. Mp (2-propanol) 203.6 (decomp.); ^{1}H NMR (δ, 200 MHz, $CDCl_3$) 1.25 (d, $^3J_{H\text{-}H}$ = 6.1 Hz, 72H, Me), 4.31 (spt, $^3J_{H\text{-}H}$ = 6.1 Hz, 12H, OCH), 7.44–7.80 (m, 20H, aromatic); ^{13}C NMR (δ, 50 MHz, $CDCl_3$) 25.9 (Me), 66.1 (OCH), 132.4–138.9 (aromatic), 197.4 (s and d $^2J_{P\text{-}C}$ = 6.8 Hz, CO cis), 199.4 (s and d $^2J_{P\text{-}C}$ = 22 Hz, CO trans); ^{29}Si NMR (δ, 40 MHz, $CDCl_3$) –63.3 (d, $^5J_{P\text{-}Si}$ = 1.2 Hz); ^{31}P NMR (δ, 100 MHz, $CDCl_3$) 21.7 (s d, $^5J_{P\text{-}Si}$ = 1.2 Hz); IR (ν/cm^{-1}, CCl_4) 1942, 1980, 2071; MS (FAB+, NBA) 1911 [(M + H)$^+$, 14%], 1587 [(M – $W(CO)_5$ + H)$^+$, 18%], 1263 [(M – $2W(CO)_5$ + H)$^+$, 16%]. Anal. calc. for $C_{76}H_{104}O_{22}P_2Si_4\ W_2$: C 47.75, H 5.44%; found: C 47.89, H 5.84.

Xerogel X4: To a THF (3.2 mL) solution of **4** (2.00 g, 1.58 mmol) in a 12.5 mL flask were added dropwise at room temperature 1.6 mL of a 6 M H_2O (9.6 mmol) and 0.1 M HCl (0.16 mmol) 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 3h. The wet whitish gel was allowed to age for 5 days at 30°C after which it was powdered and washed with ethanol, acetone and ether. The powdering and washing were repeated once and the gel was powdered again and dried in vacuum for 2 h at 120°C to yield 1.14 g of **X4** as a white powder. Specific surface area, ^{31}P, ^{13}C, and ^{29}Si CP-MAS NMR are indicated in Table 1. Elemental anal. calc. for $C_{30}H_{20}O_6PSi_4$: C 55.38, H 3.07, O 14.77, P 9.54, Si 17.23; found: C 51.80, H 5.13, O 20.87, P 8.05, Si 14.15 which corresponds to $C_{33.24}H_{39.51}O_{10\cdot04}P_{2.00}Si_{3.89}$.

Xerogel X5: To a THF (5.7 mL) solution of **5** (1.76 g, 3.10 mmol) in a 20 mL test tube was added dropwise at 0°C in 5 min, under stirring, 3.1 mL of a 6 M H_2O (16.2 mmol) and 0.01 M nBu_4NF (0.03 mmol) solution in THF. The reaction mixture was then kept at room temperature without stirring. A release of dihydrogen was observed until gel formation (30h). The wet gel was left to age for 5 days at room temperature and the solid was subsequently treated as it was described before to give 1.93 g of white xerogel **X5**. Specific surface area, ^{31}P and ^{29}Si CP-MAS NMR are indicated in Table 1. IR (DRIFT) (ν/cm^{-1}) 2159 (Si-H). Elemental anal. calc. for $C_{30}H_{20}O_6PSi_4$: C 55.38, H 3.07, O 14.77, P 9.54, Si 17.23; found: C 53.82, H 4.36, O 15.87, P 9.25, Si 16.70 which corresponds to $C_{30.06}H_{29.22}O_{6.65}P_{2.00}Si_{3.99}$.

Xerogel X7: To a THF (1.3 mL) solution of 2 g (1.29 mmol) of **7** in a 12.5 mL flask were added dropwise at room temperature 1.3 mL of a 6 M H_2O (7.8 mmol) and 0.1 M HCl (0.13 mmol) solution in THF. The reaction mixture was stirred and gel formation occurred after one min. After drying, 1.32g of yellow **X7** was obtained. Elemental anal. calcd. for

$C_{32}H_{26}I_2O_6P_2Si_4$: C 41.11, H 2.78, I 27.20, O 10.28, P 6.64, Si 11.99; found: C 41.30, H 4.80, I 20.45, O 17.50, P 5.80, Si 10.15 which corresponds to $C_{36.79}H_{41.30}I_{1.72}O_{11.69}P_{2.00}Si_{3.87}$.

Xerogel X8: To a THF (1.55 mL) solution of 2.0 g (1.55 mmol) of **8** in a 12.5 mL flask were added dropwise at room temperature 1.55mL of a 6 M H_2O (9.3 mmol) and 0.1 M HCl (0.15 mmol) solution in THF. The reaction mixture was stirred for 5 min and kept at 30°C without stirring. Gel formation occurred after 15 min. However, after about 10 min a slight release of gas was observed so that the cork of the flask was pierced. After ageing, powdering and washing, 1.31 g of white powder was obtained. Drying 2 h at 120°C of 1.01 g of crude xerogel gave 882 mg of **X8**. ^{31}P CP MAS NMR spectra indicated a cleavage of P—B bonds of 50%. Elemental anal. calcd. for $C_{30}H_{26}B_2O_6P_2Si_4$: C 53.10, H 3.83, B 3.24, O 14.16, P 9.14, Si 16.52; found: C 50.47, H 5.17, B 1.95, O 22.01, P 6.20, Si 14.20 which corresponds to $C_{42.06}H_{51.7}B_{1.77}O_{13.76}P_{2.00}Si_{5.07}$. The cleavage of the P—B bond of the crude xerogel is 40%. It is of 70% if the crude xereogel is heated one night at 120°C.

Xerogel X9: To a THF (1.0 mL) solution of 2.0 g (1.05 mmol) of **9** in a 12.5 mL flask were added dropwise at room temperature 1.1mL of a 6 M H_2O (6.6 mmol) and 0.1 M HCl (0.11 mmol) solution in THF. The reaction mixture was stirred for 5 min and kept at 30°C without stirring. Gel formation occurred after 20min. After drying, 1.38 g of light beige **X9** was obtained. IR (DRIFT ν/cm^{-1}, KCl) 1934, 1986, 2072. Specific surface area and ^{31}P CP-MAS NMR data are indicated in Table 1. Elemental anal. calcd. for $C_{40}H_{20}O_{16}P_2Si_4W_2$: C 36.98, H 1.54, O 19.72, P 4.78, Si 8.63, W 28.30; found : C 30.33, H 2.88, O 28.55, P 3.81, Si 7.58, W 26.85 which corresponds to $C_{41.13}H_{46.86}O_{29.03}P_{2.00}Si_{4.40}W_{2.37}$.

Reactivity of X4 with H_2O_2

To a suspension of 325 mg (0.50 mmol) of **X4** in CH_2Cl_2 (20ml) were added dropwise at room temperature 5 mL of a 35% aqueous H_2O_2 solution (60 mmol). After 13 h stirring at room temperature, the suspension was filtered off and the precipitate was washed with water, ethanol, acetone, and diethyl ether. After drying, 296 mg of a white powder were obtained. ^{31}P NMR (δ, 162 MHz, HPDEC MAS) 28.1. S_{BET} < 370 m^2/g. Elemental anal. calc for $C_{30}H_{20}O_8P_2Si_4$: C 52.78, H 2.93, O 18.77, P 9.09, Si 16.42; found: C 47.39, H 4.34, O 26.07, P 7.35, Si 14.85 which corresponds to $C_{33.31}H_{36.61}O_{13.74}P_{2.00}Si_{4.47}$.

Reactivity of X4 with S_8

333 mg (0.51 mmol) of **X4**, 426 mg (13.3 mmol) of sulphur, and 24 mL of *n*-butanol were heated under reflux for 48 h. The hot suspension was then filtered (to remove the excess of sulphur) and the precipitate was washed twice with hot *n*-butanol (2 × 20 mL) then with acetone and diethyl ether. After drying under vacuum for 2 h at 120°C, 346 mg of a whitish solid was obtained. ^{31}P NMR (δ, 120 MHz, HPDEC MAS) 41.3. S_{BET} = 415 m^2/g. Elemental anal. calc. for $C_{30}H_{20}O_6P_2S_2Si_4$: C 50.42, H 2.80, O 13.45, P 8.68, S 8.96, Si 15.69%; found: C 49.91, H, 4.68, O 18.75, P 6.90, S 6.19, Si 13.75%, which corresponds to $C_{37.37}H_{42.00}O_{10.53}P_{2.00}S_{1.74}Si_{4.41}$.

Reactivity of X4 with MeI

334 mg (0.514 mmol) of **X4** and 0.25 mL (4.0 mmol) of methyl iodide were heated under reflux in toluene (10ml) for 48 h. After filtration, the precipitate was washed with ethanol, acetone and diethyl ether, and dried to give 398 mg of a yellow powder. ^{31}P NMR (δ, 162 MHz, HPDEC MAS) 21.4. S_{BET} < 10 m^2/g. Elemental anal. calc. for $C_{36}H_{26}I_2O_6P_2Si_4$: C 41.11, H 2.78, I 27.20, O 10.28, P 6.64, Si 11.99%; found: C 43.40, H 4.53, I 15.32, O 17.25, P 7.30, Si 12.20 which corresponds to $C_{30.72}H_{38.47}I_{1.02}O_{9.16}P_{2.00}Si_{3.70}$.

Reactivity of X4 with $W(CO)_5{\cdot}THF$

302 mg (0.46 mmol) of **X4** and 70 mL of a 0.057 M THF solution of $W(CO)_5{\cdot}THF$ (4.0 mmol) were heated under reflux and stirring for 96 h. The greenish suspension was then filtered and the precipitate was washed twice with THF (2 × 30 mL) then with ethanol, acetone, and ethyl ether. After drying under vacuum for 2 h at 120°C, 344 mg of a pale green solid was obtained. ^{31}P NMR (δ, 120 MHz, HPDEC MAS) 20.8 (20%), –5 (80%). IR (DRIFT ν/cm^{-1}, KCl) 1935, 1984, 2072. S_{BET} = 380 m^2/g. Elemental anal. calc for $C_{40}H_{20}O_{16}P_2Si_4W_2$: C 36.98, H 1.54, O 19.72, P 4.78, Si 8.63, W 28.35; found: C 43.67, H 3.58, O 23.25, P 5.90, Si 11.80, W 11.80% which corresponds to $C_{38.24}H_{37.62}O_{15.27}P_{2.00}Si_{4.43}W_{0.67}$.

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