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Organic–inorganic hybrid materials incorporating phosphorus centres. Evidence for some factors controlling the accessibility of phosphorus centres

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The accessibility of phosphorus centres incorporated into hybrid organic–inorganic materials prepared from various phosphines bearing two or three hydrolysable SiX_3 groups has been investigated by using some classical reactions at phosphorus centres. Estimation of the yields of the reaction has been established by high power proton decoupling magic angle spinning (HPDEC MAS) solid state ^{31}P NMR spectroscopy. It was found that reagents such as H_2O_2, S_8 as well as $THF{\cdot}BH_3$ and MeI can reach all the phosphorus centres whatever the starting material. In contrast, remarkable differences of accessibility of phosphorus centres in the studied solids were found for the more bulky reagent $THF{\cdot}W(CO)_5$. From these results, it appears that the accessibility of the phosphorus centres depends on the structure of the precursor, the degree of condensation of the polysilsesquioxane network, and the specific surface area of the material.

Introduction

The monophasic hybrid materials obtained by hydrolysis and polycondensation of organically substituted alkoxysilanes constitute a rapidly expanding area of research in materials science.[1–3] They are opening interesting perspectives and wide possibilities for changing the nature of the organic moiety which cannot be achieved by other materials. Thus the introduction of phosphino moieties in a silica matrix by a sol–gel process from phosphines including one hydrolysable $Si(OEt)_3$ group[4–6] was successfully investigated for the preparation of immobilized catalysts.[7–9]

In the course of our studies concerning nanostructured hybrid materials we have found that monosilylated precursors lead to solids in which the organic moieties are always at the surface of the solid.[10] In contrast the hydrolysis and polycondensation of bisilylated precursors give rise to solids in which the organic moieties can be in the core of the solid with short range order, the structure of the material being highly dependent on the organic moiety.[1b,2c,3a,11–13] That led us to study materials obtained by hydrolysis and polycondensation of organophosphorus precursors **1**, **2**, and **3**, all of them bearing more than one hydrolysable SiX_3 group.[14]

In this paper we examined the accessibility of the phosphorus centres incorporated into the solids prepared from these precursors, by using some classical chemical reactions at phosphorus centres (oxidation, sulfuration, quaternization, formation of complexes). The purpose of the present study is to inquire about a possible relation between the structure of the molecular precursor bearing two or three hydrolysable SiX_3 groups and the accessibility of the phosphorus atoms inside the corresponding solid. This study allowed us to determine some factors governing the accessibility of phosphorus centres, factors which will be discussed.

Results

The accessibility of the phosphorus centres has been investigated for the xerogels **X1–X3**, the preparations of which have been previously described[14] starting from the precursors **1–3**. The hydrolysis conditions for the phosphines **1–3** as well as some textural data for the corresponding xerogels **X1–X3** are summarized in Table 1. **X1** which was obtained from the precursor **1** bearing two hydrolysable $Si(OPr^i)_3$ groups is nonporous. **X2A** and **X2B** have been prepared under different experimental conditions (Table 1), both from the precursor **2**, which contains three hydrolysable $Si(OPr^i)_3$ groups. **X2A** has a very low BET surface area ($30\ m^2\ g^{-1}$) while the surface area of **X2B** is rather large ($460\ m^2\ g^{-1}$). **X3** results from hydrolysis and polycondensation of **3** which bears three hydrolysable SiH_3[1c,14] groups giving rise to a solid with a very large BET surface area ($870\ m^2\ g^{-1}$). The adsorption–desorption isotherms for the xerogels **X2B** and **X3** indicate that the solids are microporous (see Table 1).

All these xerogels have been treated by an excess of the following reagents: H_2O_2, S_8, $THF{\cdot}BH_3$, MeI, $PhCH_2Br$, and $THF{\cdot}W(CO)_5$ (Scheme 1). As we have previously demonstrated[14] that the hydrolysis and the polycondensation of derivatives **4–8** give rise after the usual work-up to the xerogels **X4A–X8A** and **X4B–X8B** depending on the experimental conditions [eqn. (1)] without any change at the phosphorus centres, the ^{31}P NMR chemical shifts displayed by the xerogels **X4–X8** may therefore be used as references. Estimation of the yields of the reactions has been established by high power proton decoupling magic angle spinning (HPDEC MAS) solid state ^{31}P NMR spectroscopy.

We prepared and characterized xerogels **X9** and **X10** from the precursors **9** and **10** [eqn. (2)] to have further ^{31}P NMR references for this study. During the sol–gel process of **9** there is a partial cleavage of the P–B bond (estimated from ^{31}P HPDEC MAS NMR spectroscopy at about 50%), as had previously been observed during the hydrolysis of **6**. The hydrolysis and polycondensation of **10** occurred without cleavage of the P–W bond to give the xerogel **X10** which was characterized by solid IR and NMR spectroscopies.

Reactivity of the xerogels X1, X2A and X2B towards H_2O_2

As an initial probe for the accessibility of the phosphorus centres within the xerogels **X1, X2A**, and **X2B**, we studied the oxidation of phosphorus centres by H_2O_2. This reaction was performed in the presence of an excess of an aqueous solution of H_2O_2 (60 equiv.). For a better impregnation of the solids by the solvent it was necessary to add CH_2Cl_2. After 13 h of treatment at room temperature the solids obtained were washed and dried (see Experimental section). Solid state ^{31}P

Table 1 Textural data[a] for materials prepared from compounds **1–3** (0.5 M in THF) in the presence of the stoichiometric amount of water at 30 °C

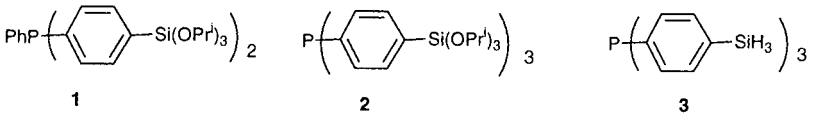
Precursor	Catalyst	Xerogel	S_{BET}/ $m^2\ g^{-1}$	Pore volume/ $cm^3\ g^{-1}$	Micropore volume/ $cm^3\ g^{-1}$	Mean pore diameter/Å
1	HCl 10%	**X1**	<10		—	—
2	PTSA[b] 1%	**X2A**	30		—	—
2	HCl 10%	**X2B**	460	0.225	0.175	15
3	TBAF[c] 1%	**X3**	870	0.426	0.265	17

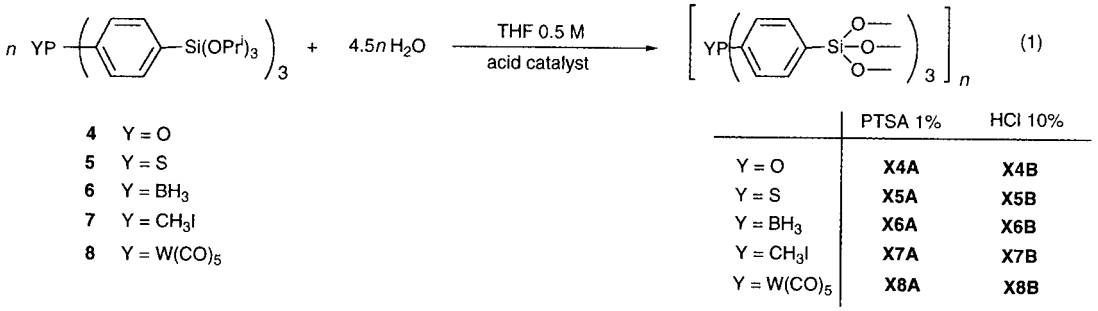
[a]Pores volumes and micropore volumes were determined by t-plot analysis; mean pore diameters from Horvath–Kawazoe analysis of adsorption isotherms. [b]*p*-Toluenesulfonic acid. [c]Tetrabutylammonium fluoride.

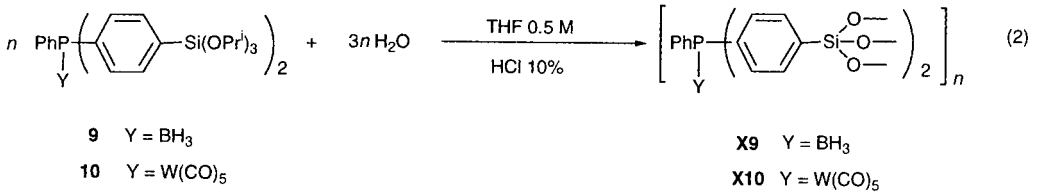
NMR spectroscopy of the xerogels after treatment revealed one signal at about δ 29 (see Table 2) flanked by spinning side bands. This signal was assigned to the phosphoryl centres as the chemical shift of **X4A**[14] was δ 31.4 and that of **X4B**[14] δ 30.7. Thus all the phosphorus atoms incorporated into the xerogels **X1**, **X2A** and **X2B** were oxidized under these conditions indicating that they are all accessible by H_2O_2.

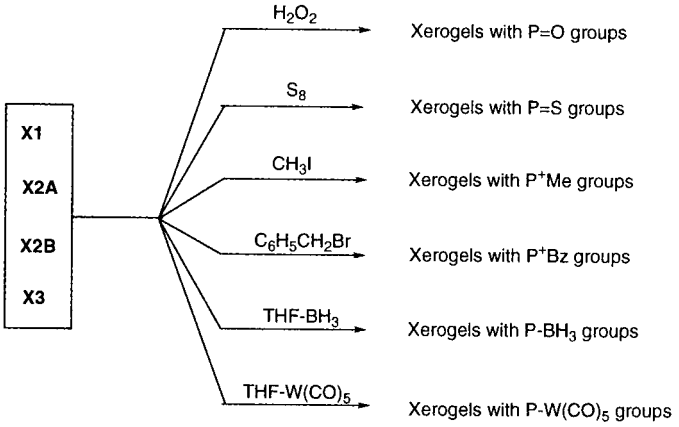
Reactivity of the xerogels X1–X3 towards S_8

The reactivity of the phosphorus centres inserted into the xerogels **X1–X3** was studied by treating these xerogels with sulfur (13 equiv.) in *n*-butanol heated under reflux for 48 h. After reaction and the usual work-up, the solid state ^{31}P NMR spectra of the solids displayed one signal centred at about δ









Scheme 1

Table 2 ^{31}P HPDEC MAS NMR chemical shifts (δ, ppm) of phosphorus atoms after treatment of the xerogels **X1–X3** with different reagents. The % of each signal is indicated in parentheses

Reagent	H_2O_2	S_8	$THF{\cdot}BH_3$[a]	CH_3I	$PhCH_2Br$	$THF{\cdot}W(CO)_5$
X1	29.8 (100)	41.7 (100)	22.5 (90); −5.6 (10)	20.9 (100)	22.1 (100)	21.1 (100)
X2A	29.8 (100)	41.6 (100)		21.1 (95); −4.6 (5)	22.9 (70); −5.3 (30)	21.0 (5); −4.8 (95)
X2B	28.8 (100)	41.9 (100)	22.8 (80); −5.0 (20)	21.1 (100)	22.0 (85); −4.5 (15)	20.8 (80); −5.9 (20)
X3		41.7 (100)		21.3 (100)	22.6 (90); −5.0 (10)	21.2 (60); −4.9(40)

[a]Reactions on silylated xerogels.

42 in all cases (see Table 2), flanked by spinning side bands. This signal was assigned to the thiophosphoryl centres by comparison with the chemical shift of **X5A**[14] (δ 42.5) and of **X5B**[14] (δ 42.0). Thus all the phosphorus centres incorporated into the xerogels **X1**, **X2A**, **X2B** and **X3** are accessible to sulfur.

Reactivity of the xerogels X1 and X2B towards $THF{\cdot}BH_3$

Formation of phosphine–borane from the phosphorus centres incorporated into the xerogels **X1** and **X2B** was investigated. First, **X2B** was treated with an excess of $THF{\cdot}BH_3$ (10 equiv.) for 24 h at room temperature in THF. The solid state ^{31}P NMR spectrum of the xerogel **X2B** after reaction revealed that there was complexation of only 40% of the phosphorus atoms. However, the B : P ratio calculated from the elemental analysis was found to be greater than 1 : 1. Furthermore, diffuse reflectance IR spectrum (DRIFTS) of the xerogel **X2B** after reaction exhibited a broad absorption band at 1380 cm^{-1} attributed to B–O stretching vibrations. Hence, the high boron content probably originates from side-reactions between $THF{\cdot}BH_3$ and the remaining SiOH groups. Therefore silylation[4c] of **X1** and **X2B** with a large excess of Me_3SiCl in the presence of triethylamine was performed prior to the treatment of the xerogel with $THF{\cdot}BH_3$. The analysis of the DRIFT spectra of these materials revealed that the silylation was very effective (see Fig. 1) with an important decrease in the ν_{SiOH} band intensity and the appearance of the expected IR bands for $Si(CH_3)_3$ groups (1253 and 850 cm^{-1}). It is worth noting that the texture of **X1** as well as that of **X2B** was not modified

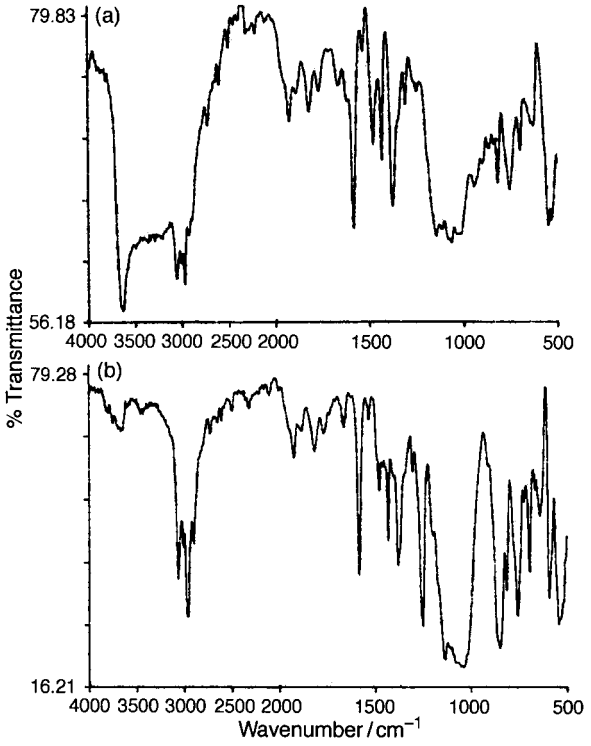


Fig. 1 IR spectra (DRIFTS method) of xerogel **X1**: (a) before silylation, (b) after silylation.

by Me_3SiCl/Et_3N treatment, whilst in the absence of Et_3N it was observed that release of HCl occurring during the silylation induced a rearrangement of the **X2B** solid with complete loss of the S_{BET}. These solids were subsequently treated with an excess of $THF{\cdot}BH_3$ (5 equiv.) in THF heated under reflux for 48 h. After the work-up, the solid state ^{31}P NMR spectra of both solids displayed two signals, one at *ca.* δ −5 (see Table 2) assigned to unchanged phosphorus centres and the other at about δ 22 which was attributed to the phosphine–borane centres, the chemical shifts of **X6A**,[14] **X6B**[14] and **X9** [eqn. (2)] being at about δ 22. The yields of complexation were estimated by ^{31}P NMR spectroscopy to be 90% for silylated **X1** and 80% for silylated **X2B** (Table 2). These results indicate that the phosphorus centres in the silylated xerogel **X1** are slightly more accessible that those in the silylated xerogel **X2B**.

Reactivity of the xerogels X1–X3 towards MeI and $PhCH_2Br$

Formation of phosphonium salts from the phosphorus centres incorporated into the xerogels **X1–X3** was investigated. Addition of an excess of methyl iodide (7 equiv.) to xerogels **X1–X3** resulted in almost quantitative quaternization of the phosphorus atoms after 48 h of treatment in toluene heated under reflux (Table 2). In all cases, the ^{31}P NMR spectra of solids **X1–X3** after treatment displayed one signal at about δ 21 which was attributed to quaternary phosphorus centres (the chemical shift of **X7A**[14] was δ 20.9 and that of **X7B**,[14] δ 21.0). It is to be noted that a further weak signal at δ −4.6 (5%) was displayed in the ^{31}P NMR spectrum of **X2A** thus showing a very slight difference of accessibility for the phosphorus centres incorporated into **X2A.**

As no notable difference concerning the accessibility of phosphorus centres incorporated into the different xerogels was shown by the preceding studies, the reactivity of the phosphorus atoms towards a more bulky reagent was investigated. The quaternization of the phosphorus atoms with benzyl bromide was carried out in the presence of an excess of reagent (7 equiv.) in toluene heated under reflux. The ^{31}P NMR spectra of solids **X1–X3** after treatment all display a signal at about δ 22 which was attributed to quaternary phosphorus centres (Table 2). Furthermore, except for **X1**, the ^{31}P NMR spectra of the other solids displayed a further signal at about δ −5 attributed to the unchanged phosphorus centres. This signal was estimated to be 30% for **X2A**, 15% for **X2B** and 10% for **X3**. Thus, from these results the order of accessibility of the phosphorus centres in the solids seems to be: **X1** > **X2B**, **X3** > **X2A**. Furthermore, these results confirm the trend previously observed, *i.e.* that the phosphorus centres in the solid **X1** are more easily accessible than those incorporated in the other solids.

Reactivity of the xerogels X1–X3 towards $THF{\cdot}W(CO)_5$

Complexation of the phosphorus atoms by the rather bulky reagent $THF{\cdot}W(CO)_5$ (diameter *ca.* 8 Å estimated by modelling studies) was undertaken. The complexation reactions of phosphorus centres included in the xerogels **X1–X3** were carried out in the presence of an excess of $THF{\cdot}W(CO)_5$ (4 equiv.) in THF heated under reflux for 96 h. After the usual work-up, DRIFTS analysis of the materials revealed the

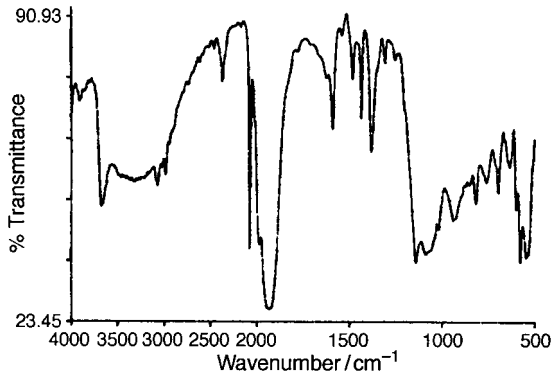


Fig. 2 IR spectra (DRIFTS method) of xerogel **X1** after reaction with $W(CO)_5$·THF.

presence of CO stretching bands characteristic of the expected $LW(CO)_5$ complex (see Fig. 2 and Experimental section) and previously observed for the solids **X8**[14] and **X10** [eqns. (1) and (2)]. The solid state ^{31}P NMR spectra for all the solids after reaction displayed a signal at about δ 21 which was attributed to the complexed phosphorus centres, the ^{31}P NMR chemical shifts of **X8A**[14] and **X8B**[14] being around δ 21 and that of **X10** δ 20.7. Furthermore, a resonance at about δ −5 was observed in all cases, except for **X1**, this being assigned to unchanged phosphorus centres (Table 2 and Fig. 3). From solid state ^{31}P NMR spectroscopy, it can be concluded that the complexation was almost quantitative for **X1**, *ca.* 80% for **X2B**, *ca.* 60% for **X3**, and *ca.* 5% for **X2A**. Furthermore, after only 4 h heating, complexation was found to be 95% for **X1** and 50% for **X2B**. This result shows that the accessibility of phosphorus centres is easier in the case of **X1** than for **X2B**. Thus, this last study demonstrated a remarkable decrease in the accessibility of phosphorus centres in the case of the rather bulky reagent THF·$W(CO)_5$, in the order: **X1** > **X2B** > **X3** > **X2A**.

Discussion

From these investigations, it is evident that phosphorus centres incorporated into the solid **X1** are more easily accessible to a given reagent than those incorporated into the other solids, though the specific surface area of **X1** is very low ($<10\ m^2\ g^{-1}$). **X1** was prepared from **1** which bears two hydrolysable $Si(OR)_3$ groups (the functionality around the silicon atoms f being 6) whilst **X2A**, **X2B**, and **X3** have been prepared respectively from **2** and **3** which both contain three hydrolysable SiX_3 groups ($f=9$). The value of f seems to play an important role controlling the accessibility of the phosphorus centres towards reagents. This should be connected to the average number N of the Si–O–Si bonds attached to each organic unit. The number of Si–O–Si bonds depends on the degree of condensation of the polysilsesquioxane network and on f. The degree of condensation can be semiquantitatively determined by deconvoluting the ^{29}Si NMR resonances of the T^1, T^2, and T^3 silicons.[15,16] Hence it was found that the degree of condensation was 62, 57 and 53% respectively for **X1**, **X2B**, and **X2A**. These values are not sufficiently different to result in significant modifications, and we therefore limit the discussion to the functionality around the silicon atoms.

Thus, we consider that the fewer the number of Si–O–Si bonds attached, on average, to each organic unit in **X1**, should result in an increased mobility of the network facilitating the penetration of the solvent and the diffusion of even rather bulky molecules through 'the stationary phase' according to Lindner *et al.*,[17,18] *i.e.* through the hybrid organic–inorganic

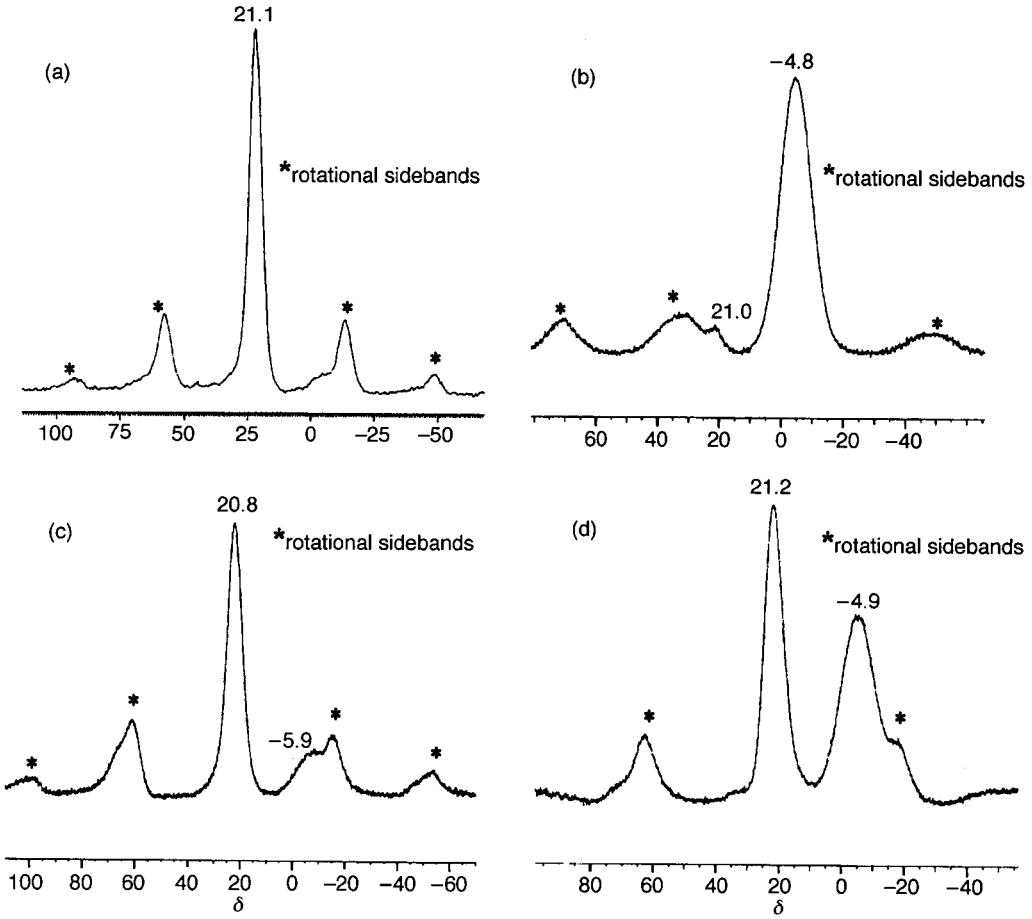


Fig. 3 ^{31}P HPDEC MAS NMR spectra of xerogels **X1**–**X3** after reaction with $W(CO)_5$·THF: (a) xerogel **X1**, (b) xerogel **X2A**, (c) xerogel **X2B**, (d) xerogel **X3**.

material. This process could be related to the swelling process occurring in the organic polymers and should explain the easier accessibility of the phosphorus centres to reagents in **X1**. In other respects, as **X1** presents a very low specific surface area, we can conclude that the specific surface area is not the dominating factor for the accessibility of the phosphorus centres. Nevertheless it is clear that, for a given functionality at silicon, the higher the specific surface area, the easier is the accessibility of the reactive phosphorus centres (compare in Table 2, **X2A** and **X2B**). While only 5% of the phosphorus centres in **X2A** reacted with $THF{\cdot}W(CO)_5$, 80% of the phosphorus centres incorporated into **X2B** were complexed.

Concerning the reactions carried out on **X3**, we expect that the phosphorus centres included in this solid should be at least as reactive as those of **X2B**, as both of them have been prepared from a precursor with the same value of *f* and that furthermore **X3** presents a higher BET surface area ($870\ m^2\ g^{-1}$) than **X2B** ($460\ m^2\ g^{-1}$), both displaying isotherms characteristic of microporous materials with a micropore ratio of 78% for **X2B** and of 62% for **X3**. However only 60% of the phosphorus centres of **X3** reacted with $THF{\cdot}W(CO)_5$ as compared to 80% for **X2B**. It is not very likely that the difference of accessibility between **X3** and **X2B** is due to a difference of pores sizes as in both cases the mean pore diameters (Table 1) are estimated in the same range (15, 17 Å), the size of the reagent being 8 Å. This moderate yield of complexation could be most porbably attributed to the higher degree of condensation of the polysilsesquioxane network for **X3** than for the others. Though this degree of condensation cannot be calculated by deconvolution of ^{29}Si CP MAS NMR signals for **X3** because of the remaining Si–H bonds[14] (presence in the spectrum of $CSi(H)O_2$ substructures) nevertheless it appears from the ^{29}Si CP MAS NMR spectrum of **X3** that the substructures T^3 are of importance while for the other solids, **X1** and **X2A** and **X2B**, they are very weak. This means that the number of Si–O–Si bonds attached to the organic unit, on average, is higher in **X3** than in **X2B** and should be the major factor controlling the accessibility of phosphorus centres in this materials. This should result in a more difficult penetration of the solvent into the solid, and consequently a lower diffusion of the reagent, the mobility of the organic unit being restricted.

Conclusion

We have shown that all the phosphorus centres incorporated in the xerogels **X1**, **X2** and **X3** are accessibile by small reagents. This is no longer the case with the rather bulky reagent $THF{\cdot}W(CO)_5$. With this reagent we showed that the accessibility of the phosphorus centres depends on the structure of the precursor and the texture of the material for a given functionality.

The greater the number *N* of Si–O–Si bonds attached to each organic unit on average, the more difficult is the diffusion of the reagent due to restricted mobility of the organic unit. Hence, a great number of Si–O–Si bonds induces a less solution-like behaviour of the organic moiety. In order to investigate this hypothesis, materials prepared from precursors with a functionality at silicon atoms greater than 9 are currently being studied.

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, solution NMR spectra on a Bruker AC-200 (^{29}Si), DPX-200 (^1H and ^{13}C) and WP 250 SY (^{31}P) spectrometers. Chemical shifts (δ in ppm) were referenced to Me_4Si (^1H, ^{13}C, ^{29}Si) or H_3PO_4 (^{31}P). The CP MAS ^{29}Si solid state NMR spectra were recorded on a Bruker FTAM 300 as instrument, CP MAS ^{13}C solid state NMR spectra using the total suppression of spinning side bands (TOSS) technique. In both cases the repetition time was 5 and 10 s with contact times of 5 and 2 ms. The HPDEC MAS ^{31}P solid state NMR spectra were recorded on a Bruker FTAM 300, ASX 200, or ASX 400 spectrometer with repetition time of 5 s. FAB mass spectra [matrix, *m*-nitrobenzyl alcohol] were registered on JEOL JMS-D3000 spectrometer. Specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method on Micromeritics ASAP 2010 and Gemini III 2375 analysers. Elemental analyses were carried out by the Service Central de Micro- Analyse du CNRS.

Preparations

Phenyl[bis(*p*-triisopropyloxysilylphenyl)]phosphine–borane 9. A 1 M solution of $THF{\cdot}BH_3$ in THF (3.2 ml, 3.2 mmol) was added dropwise, at 0 °C, to 2.14 g (3.19 mmol) of phosphine **1** in THF (25 ml). After stirring for 15 min at 0 °C and 30 min at 20 °C, the solvent was removed and the crude phosphine–borane recrystallized in 2-propanol to give 1.68 g (2.46 mmol, 77%) of white crystals of compound **9**, mp (decomp.) 100 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 1.25 (d, $^3J_{H\text{-}H}=6.1$, 39 H, Me and BH_3), 4.31 (spt, $^3J_{H\text{-}H}=6.1$ Hz, 6 H, OCH), 7.33–7.80 (m, 13 H, aromatic) ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.9 (Me), 66.1 (OCH), 129.0–137.4 (m, aromatic) ^{31}P NMR (100 MHz, $CDCl_3$): δ 21.1 ^{11}B NMR (80 MHz, $CDCl_3$): δ −38.0 (broad signal) ^{29}Si NMR (40 MHz, $CDCl_3$): δ −63.2 (d, $^5J_{P\text{-}Si}=1.4$ Hz). IR ($\bar{\nu}/cm^{-1}$, CCl_4) 2389. Calc. for $C_{36}H_{58}BO_6PSi_2$: C, 63.16; H, 8.48. Found: C, 62.82; H, 8.86%.

Pentacarbonyl{phenyl[bis(*p*-triisopropyloxysilylphenyl)]-phosphine}tungsten 10. A 0.071 M THF solution of $THF{\cdot}W(CO)_5$[19] (130 ml, 9.23 mmol) was added to 3.09 g (4.61 mmol) of phosphine **1** in THF (20 ml). The reaction mixture was stirred for 1 h at room temperature and the solvent removed under vacuum. After elimination of excess of $W(CO)_6$ by sublimation at 60 °C under vacuum, the crude product was recrystallized in 2-propanol to give 2.48 g (2.49 mmol, 54%) of a white powder, mp (decomp.) 103.7 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 1.25 (d, $^3J_{H\text{-}H}=6.1$, 36 H, Me), 4.32 (spt, $^3J_{H\text{-}H}=6.1$ Hz, 6 H, OCH), 7.41–7.80 (m, 13 H, aromatic) ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.7 (Me), 65.9 (OCH), 128.8 (d, $J_{P\text{-}C}=9.8$, aromatic), 130.5 (d, $J_{P\text{-}C}=1.9$, aromatic), 132.1 (d, $J_{P\text{-}C}=11.3$, aromatic), 133.4 (d, $J_{P\text{-}C}=12.0$, aromatic), 135.0 (d, $J_{P\text{-}C}=40.9$, aromatic), 135.1 (d, $J_{P\text{-}C}=9.3$, aromatic), 136.1 (d, $J_{P\text{-}C}=1.7$, aromatic), 137.0 (d, $J_{P\text{-}C}=40.2$, aromatic), 197.4 (d, $^2J_{P\text{-}C}=6.9$, CO *cis*), 199.4 (d, $^2J_{P\text{-}C}=21.6$ Hz, CO *trans*) ^{31}P NMR (100 MHz, $CDCl_3$): δ 21.3 (s and d, satellite ^{183}W, $^1J_{P\text{-}W}=243$ Hz) ^{29}Si NMR (40 MHz, $CDCl_3$): δ −63.1, (d, $^5J_{P\text{-}Si}=1.5$ Hz). IR ($\tilde{\nu}/cm^{-1}$, CCl_4) 1941, 1980, 2071. MS (FAB+): *m/z* 994 (M^+, 1%), 966 [$(M-CO)^+$, 1], 938 [$(M-2CO)^+$, 1], 910 [$(M-3CO)^+$, 3], 854 [$(M-5CO)^+$, 3], 671 [$(M-W(CO)_5+H)^+$, 7%]. Calc. for $C_{41}H_{55}O_{11}PSi_2W$: C, 49.50; H, 5.53. Found: C, 49.88, H, 5.83%.

Xerogel X9. To a solution of compound **9** (1.0 g, 1.46 mmol) in THF (1.4 ml) were added dropwise 1.5 ml of a 3 M water (4.5 mmol) and 0.1 M HCl solution (0.15 mmol) in THF. After stirring for 5 min at room temperature the reaction mixture was heated at 30 °C without stirring. Gel formation occurred after 70 min but a very slight release of gas was observed so that the cork of the flask was pierced. The wet colourless gel was allowed to age for 5 d at 30 °C after which it was powdered, 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; 535 mg of a white powder were obtained. ^{31}P NMR (120 MHz): δ −5.4, 21.7. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1380 (BO), 2376 (BH). S_{BET} < 10 m^2 g^{-1}. Calc. for $C_{36}H_{18}BO_3PSi_2$: C, 57.14; H, 4.23; B, 2.91; P, 8.20; Si, 14.81. Found: C, 49.62; H, 4.48; B, 1.80; P, 6.40; Si, 13.90%, *i.e.* $C_{20.02}H_{21.70}B_{0.79}O_{7.20}P_{1.00}Si_{2.40}$.

Xerogel X10. To a solution of compound **10** (2.0 g, 2.01 mmol) in THF (2 ml) were added dropwise 2 ml of a 3 M water (6 mmol) and 0.1 M HCl solution (0.2 mmol) in THF. After stirring for 5 min at room temperature the reaction mixture was heated at 30 °C without stirring. A dark blue gel was formed after 4 h. After aging, powdering, washing, and drying, 535 mg of a yellow powder were obtained. ^{31}P NMR (120 MHz): δ 20.7 ^{29}Si NMR (CP MAS, 60 MHz): δ −61.4 (T^1), −69.2 (T^2), −76.4 (T^3). IR ($\tilde{\nu}$/cm^{-1}, KCl) 1936, 1985, 2072. S_{BET} < 10 m^2 g^{-1}. Calc. for $C_{23}H_{13}O_8PSi_2W$: C, 40.11; H, 1.89; P, 4.50; Si, 8.14; W, 26.75. Found: C, 38.77; H, 2.33; P, 3.40; Si, 7.90; W, 24.70%, *i.e.* $C_{22.90}H_{16.51}O_{10.14}P_{0.78}Si_{2.00}W_{0.95}$.

Reactivity of xerogels

Before reaction, all the xerogels were systematically dried again under vacuum for 2 h at 120 °C. All the reagents being used in large excess, the molar mass of the xerogels has been calculated from an ideal formula (complete condensation).

X1, X2A, and X2B towards H_2O_2. ***X1.*** To a suspension of 182 mg (0.50 mmol) of the xerogel **X1** in CH_2Cl_2 (10 ml) were added dropwise at room temperature 2.5 ml of a 35% aqueous H_2O_2 solution (30 mmol). After 13 h stirring at room temperature the suspension was filtered off and the precipitate washed with water, ethanol, acetone and diethyl ether. After drying, 155 mg of a white powder were obtained. ^{31}P NMR (162 MHz): δ 29.8. S_{BET} < 10 m^2 g^{-1}. Calc. for $C_{18}H_{13}O_4PSi_2$: C, 56.84; H, 3.42; P, 8.16; Si, 14.73. Found: C, 52.11; H, 4.26; P, 7.05; Si, 13.45%, *i.e.* $C_{19.09}H_{18.73}O_{6.35}P_{1.00}Si_{2.11}$.

X2A. The same treatment of xerogel **X2A** (415 mg, 1 mmol) gave rise after drying to 364 mg of a white powder. ^{31}P NMR (162 MHz): δ 29.8. S_{BET} 80 m^2 g^{-1}. 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, 47.1; H, 4.64; P, 5.85; Si, 16.95%, *i.e.* $C_{20.80}H_{24.59}O_{8.43}P_{1.00}Si_{3.21}$.

X2B. The same treatment of xerogel **X2B** (415 mg, 1 mmol) gave rise after drying to 363 mg of a white powder. ^{31}P NMR (162 MHz): δ 28.8. S_{BET} 260 m^2 g^{-1}. 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, 46.04; H, 4.37; P, 5.65; Si, 16.85%, *i.e.* $C_{21.05}H_{23.97}O_{9.29}P_{1.00}Si_{3.30}$.

X1–X3 towards S_8. ***X1.*** 320 mg (0.88 mmol) of xerogel **X1**, 366 mg (11.4 mmol) of sulfur and 20 ml of *n*-butanol were heated under reflux for 48 h. The hot suspension was then filtered (in order to remove the excess of sulfur) 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, 344 mg of a whitish solid were obtained. ^{31}P NMR (120 MHz, HPDEC MAS): δ 41.7. S_{BET} < 10 m^2 g^{-1}. Calc. for $C_{18}H_{13}O_3PSSi_2$: C, 54.54; H, 3.28; P, 7.83; S, 8.08; Si, 14.14. Found: C, 56.26; H, 5.23; P, 5.35; S, 5.42; Si, 12.25%, *i.e.* $C_{21.43}H_{23.91}O_{4.42}P_{0.79}S_{0.77}Si_{2.00}$.

X2A. The same treatment of xerogel **X2A** (359 mg, 0.87 mmol) afforded after drying 394 mg of a white powder. ^{31}P NMR (120 MHz): δ 41.6, −5. S_{BET} 20 m^2 g^{-1}. 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, 49.55; H, 5.28; P, 5.20; S, 3.81; Si, 15.00%, *i.e.* $C_{24.61}H_{31.47}O_{7.88}P_{1.00}S_{0.71}Si_{3.19}$.

X2B. The same treatment of xerogel **X2B** (442 mg, 1.06 mmol) afforded after drying 470 mg of a white powder. ^{31}P NMR (120 MHz): δ 41.9. S_{BET} 280 m^2 g^{-1}. 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, 50.31; H, 4.83; P, 4.80; S, 4.86; Si, 14.55%, *i.e.* $C_{27.07}H_{31.19}O_{8.33}P_{1.00}S_{0.98}Si_{3.35}$.

X3. The same treatment of xerogel **X3** (480 mg, 1.15 mmol) afforded after drying 518 mg of a white powder. ^{31}P NMR (120 MHz): δ 41.7. S_{BET} 660 m^2 g^{-1}. 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, 49.63; H, 4.89; P, 5.30; S, 5.39; Si, 15.95%, *i.e.* $C_{24.19}H_{28.60}O_{6.89}P_{1.00}S_{0.98}Si_{3.33}$.

X2B towards THF·BH_3. To a suspension of 436 mg (1.05 mmol) of **X2B** in 5 ml of THF were added dropwise 10 ml of a 1 M THF solution of THF·BH_3 (10 mmol) and the reaction mixture was stirred at room temperature. During the reaction evolution of gas occurred. After 24 h the suspension was filtered and the precipitate washed with THF (under argon), ethanol then with acetone and ethyl ether. After drying 416 mg of a white powder were obtained. ^{31}P NMR (162 MHz): δ −5.1, 21.6. ^{29}Si NMR (60 MHz, CP MAS): δ −70.34 (T^2, large signal). S_{BET} 230 m^2 g^{-1}. Calc.: C, 50.35; H, 3.50; B, 2.56; P, 7.22; Si, 19.58. Found: C, 46.91; H, 3.50; B, 2.15; P, 5.20; Si, 17.40%, *i.e.* $C_{23.20}H_{20.86}B_{1.16}O_{9.25}P_{1.00}Si_{3.70}$.

Silylation. ***X1.*** A suspension of 910 mg (2.50 mmol) of **X1** in a solution of Me_3SiCl (10 ml, 78.8 mmol) and triethylamine (14 ml, 100 mmol) in THF (15 ml) were stirred under reflux for 7 h. The suspension was then filtered off and the solid washed with THF (3 × 40 ml), water (3 × 40 ml) then with ethanol, acetone and diethyl ether. After drying under vacuum for 2 h at 120 °C, 1.03 g of a white powder were obtained. ^{13}C NMR (75 MHz, CP MAS): δ 1.8 ($SiCH_3$), 25.5 (Me), 66.6 (OCH), 128.7–139.3 (aromatic) ^{29}Si NMR (60 MHz, CP MAS): δ 11.8 ($SiCH_3$), broad signal centred at −70. ^{31}P NMR (162 MHz): δ −5.9. IR ($\tilde{\nu}$/cm^{-1}, KCl) 850, 1253. S_{BET} < 10 m^2 g^{-1}. Found: C, 54.74; H, 5.68; P, 6.00; Si, 18.30%, *i.e.* $C_{23.57}H_{29.35}O_{4.87}P_{1.00}Si_{3.38}$.

X2B. The same treatment starting from 1.04 g (2.50 mmol) of **X2B**, 15 ml (118 mmol) of Me_3SiCl, 20 ml (143 mmol) of Et_3N in THF (15 ml) led to 1.19 g of a white powder. ^{13}C NMR (75 MHz, CP MAS): δ 1.2 ($SiCH_3$), 25.2 (Me), 66.0 (OCH), 134.2–138.5 (aromatic). ^{29}Si NMR (60 MHz, CP MAS): δ 11.1 ($SiCH_3$), −69.6 (T^2), −78.4 (T^3). ^{31}P NMR (162 MHz): δ −4.1. IR ($\tilde{\nu}$/cm^{-1}, KCl) 843, 1253. S_{BET} 530 m^2 g^{-1}. Found: C, 49.35; H, 5.72; P, 4.90; Si, 19.20%, *i.e.* $C_{26.02}H_{36.19}O_{8.08}P_{1.00}Si_{4.34}$.

Silylated xerogels X1 and X2B towards THF·BH_3. ***X1.*** A suspension of 618 mg (1.50 mmol) of silylated **X1** in 7.5 ml of a 1 M THF solution of THF·BH_3 (7.5 mmol) was heated under reflux for 48 h. It was then filtered and the precipitate washed with THF (under argon), ethanol then with acetone and ethyl ether. After drying 614 mg of a white powder were obtained. ^{31}P NMR (162 MHz): δ −6.0; 21.5. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1380 (ν_{BO}, weak band), 2386 (ν_{BH}). S_{BET} 15 m^2 g^{-1}. Found: C, 50.41; H, 5.75; B, 2.20; P, 5.65; Si, 16.80%, *i.e.* $C_{23.05}H_{31.55}B_{1.10}O_{8.68}P_{1.00}S_{13.29}$.

X2B. The same reaction starting from 638 mg (1.34 mmol) of silylated **X2B** and 7.0 ml of a 1 M THF solution of THF·BH_3 (7.0 mmol) afforded 620 mg of a white powder. ^{31}P NMR (162 MHz): δ −5.0; 22.8. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1380 (ν_{BO}, weak band), 2391 (ν_{BH}). S_{BET} 460 m^2 g^{-1}. Found: C, 44.36; H, 5.67; B, 1.95; P, 4.75; Si, 17.80%, *i.e.* $C_{24.2}H_{37.00}B_{1.16}O_{10.39}P_{1.00}Si_{4.15}$.

X1–X3 towards MeI. ***X1.*** 345 mg (0.95 mmol) of xerogel **X1** and 0.40 ml (6.42 mmol) of methyl iodide were heated under reflux in toluene (20 ml) for 48 h. After filtration, the precipitate was washed with ethanol, acetone and ethyl ether, and dried to give 416 mg of a yellow powder. ^{31}P NMR (162 MHz): δ 20.9. S_{BET} <10 m^2 g^{-1}. Calc. for $C_{19}H_{16}IO_3PSi_2$: C, 45.06; H, 3.16; I, 25.10; P, 6.12; Si, 11.07. Found: C, 44.50; H, 4.36; I, 18.68; P, 9.20; Si, 10.95%, *i.e.* $C_{18.96}H_{22.30}I_{0.75}O_{3.93}P_{1.52}Si_{2.00}$.

X2A. The same reaction starting from 828 mg (2.0 mmol) of xerogel **X2A** gave rise to 905 mg of a yellow powder. ^{31}P NMR (162 MHz): δ -4.6, 21.1. ^{29}Si NMR (60 MHz, CP MAS): δ -64.5 (T^1), -73.1 (T^2), -81.0 (T^3). S_{BET} <10 m^2 g^{-1}. 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, 41.96; H, 4.57; I, 14.66; P, 5.05; Si, 13.45%, *i.e.* $C_{21.46}H_{28.00}I_{0.71}O_{7.79}P_{1.00}Si_{2.95}$.

X2B. The same reaction starting from 261 mg (0.629 mmol) of xerogel **X2B** afforded 266 mg of a yellow powder. ^{31}P NMR (162 MHz): δ 21.1. S_{BET} <10 m^2 g^{-1}. 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, 42.06; H, 3.98; I, 10.60; P, 5.80; Si, 15.10%, *i.e.* $C_{18.73}H_{15.84}I_{0.45}O_{7.50}P_{1.00}Si_{2.88}$.

X3. The same reaction starting from 793 mg (1.91 mmol) of xerogel **X3** gave rise to 908 mg of a yellow powder. ^{31}P NMR (162 MHz): δ 21.3. S_{BET} 290 m^2 g^{-1}. 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, 38.40; H, 3.88; I, 16.18; P, 4.98; Si, 14.21%, *i.e.* $C_{19.92}H_{24.15}I_{0.79}O_{8.69}P_{1.00}Si_{3.16}$.

X1–X3 towards PhCH$_2$Br. ***X1.*** 364 mg (1.0 mmol) of xerogel **X1** and 1.20 ml (7.0 mmol) of benzyl bromide were heated under reflux in toluene (20 ml) for 48 h. After filtration, the precipitate was washed with ethanol, acetone and ethyl ether, and dried to give 416 mg of a white powder. ^{31}P NMR (162 MHz): δ 22.1. S_{BET} <10 m^2 g^{-1}. Calc. for $C_{25}H_{20}BrO_3PSi_2$: C, 56.07; H, 3.74; Br, 14.95; P, 5.79; Si, 10.47. Found: C, 54.24; H, 4.34; Br, 12.00; P, 5.20; Si, 9.80%, *i.e.* $C_{26.95}H_{25.87}Br_{0.89}O_{5.37}P_{1.00}Si_{2.09}$.

X2A. The same reaction starting from 415 mg (1.0 mmol) of xerogel **X2A** afforded 418 mg of a white powder. ^{31}P NMR (162 MHz): δ -5.3, 22.9. S_{BET} <10 m^2 g^{-1}. Calc. for $C_{25}H_{19}BrO_{4.5}PSi_3$: C, 51.19; H, 3.24; Br, 13.65; P, 5.20; Si, 14.33. Found: C, 48.62; H, 4.51; Br, 4.04; P, 5.20; Si, 15.80%, *i.e.* $C_{24.15}H_{26.89}Br_{0.30}O_{8.16}P_{1.00}Si_{3.36}$.

X2B. The same reaction starting from 415 mg (1.0 mmol) of xerogel **X2A** gave rise to 487 mg of a white powder. ^{31}P NMR (162 MHz): δ -4.5, 22.0. S_{BET} 15 m^2 g^{-1}. Calc. for $C_{25}H_{19}BrO_{4.5}PSi_3$: C, 51.19; H, 3.24; Br, 13.65; P, 5.20; Si, 14.33. Found: C, 48.12; H, 4.19; Br, 7.58; P, 4.90; Si, 15.20%, *i.e.* $C_{22.16}H_{26.51}Br_{0.60}O_{7.91}P_{1.00}Si_{3.43}$.

X3. The same reaction starting from 420 mg (1.01 mmol) of xerogel **X3** gave rise to 500 mg of a white powder. ^{31}P NMR (162 MHz): δ -5.0, 22.6. S_{BET} 270 m^2 g^{-1}. Calc. for $C_{25}H_{19}BrO_{4.5}PSi_3$: C, 51.19; H, 3.24; Br, 13.65; P, 5.20; Si, 14.33. Found: C, 48.57; H, 4.16; Br, 8.65; P, 5.60; Si, 14.90%, *i.e.* $C_{22.40}H_{23.04}Br_{0.60}O_{6.27}P_{1.00}Si_{2.95}$.

X1–X3 towards THF·W(CO)$_5$. ***X1.*** 417 mg (1.14 mmol) of xerogel **X1** and 80 ml of a 0.057 M THF solution of THF.W(CO)$_5$ (4.56 mmol) were heated under reflux and stirred for 96 h. The greenish suspension was then filtered and the precipitate washed twice with THF (2×30 ml) then with ethanol, acetone and ethyl ether. After drying under vacuum for 2 h at 120 °C, 751 mg of a pale green solid were obtained. ^{31}P NMR (120 MHz): δ 21.1. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1929, 1984, 2072. S_{BET} 13 m^2 g^{-1}. Calc. for $C_{23}H_{13}O_8PSi_2W$: C, 40.11; H, 1.89; P, 4.50; Si, 8.14; W, 26.75. Found: C, 37.15; H, 2.54; P, 4.30; Si, 8.20; W, 26.90%, *i.e.* $C_{22.32}H_{18.31}O_{9.42}P_{1.00}Si_{2.11}W_{1.05}$.

X2A. The same reaction starting from 895 mg (2.15 mmol) of xerogel **X2A** gave 824 mg of a beige powder. ^{31}P NMR (120 MHz): δ -4.8, 21.0. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1937, 1982, 2072. S_{BET} 70 m^2 g^{-1}. Calc. for $C_{23}H_{12}O_{9.5}PSi_3W$: C, 37.35; H, 1.62; P, 4.19; Si, 11.36; W, 24.88. Found: C, 45.84; H, 4.51; P, 4.70; Si, 14.32; W, 5.32%, *i.e.* $C_{25.19}H_{29.75}O_{10.43}P_{1.00}Si_{3.37}W_{0.19}$.

X2B. The same reaction starting from 403 mg (0.97 mmol) of xerogel **X2B** gave rise to 572 mg of a light green powder. ^{31}P NMR (120 MHz): δ -5.9, 20.8. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1931, 1985, 2072. S_{BET} 360 m^2 g^{-1}. Calc. for $C_{23}H_{12}O_{9.5}PSi_3W$: C, 37.35; H, 1.62; P, 4.19; Si, 11.36; W, 24.88. Found: C, 37.88; H, 3.03; P, 3.85; Si, 11.55; W, 18.65%, *i.e.* $C_{25.42}H_{24.40}O_{12.60}P_{1.00}Si_{3.32}W_{0.82}$.

X3. The same reaction starting from 755 mg (1.82 mmol) of xerogel **X3** afforded 1.03 g of a beige powder. ^{31}P NMR (120 MHz): δ -4.9, 21.2. IR ($\tilde{\nu}$/cm^{-1}, KCl) 1942, 1985, 2073. S_{BET} 620 m^2 g^{-1}. Calc. for $C_{23}H_{12}O_{9.5}PSi_3W$: C, 37.35; H, 1.62; P, 4.19; Si, 11.36; W, 24.88. Found: C, 37.82; H, 3.26; P, 4.39; Si, 12.48; W, 18.56%, *i.e.* $C_{22.25}H_{23.02}O_{10.37}P_{1.00}Si_{3.14}W_{0.71}$.

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