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Organic–inorganic hybrid materials containing metal phosphine complexes
Evidence for preferential *cis* configuration of Pd(II) and Pt(II) complexes within the materials

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Abstract

The hydrolysis–polycondensation of palladium (Pd) and platinum (Pt) complexes of phosphines $[p\text{-}(OiPr)_3SiC_6H_4]_2PC_6H_5$ and $[p\text{-}(OiPr)_3SiC_6H_4]_3P$ gives rise to xerogels in which the metal complexes are included within a silica matrix with retention of the arrangement around the metal centre. However, the *trans*-Pd as well as the *trans*-Pt complexes incorporated within the xerogels slowly isomerize into the more stable *cis* complexes. Direct reaction of $(CH_3CN)_2PdCl_2$ with xerogels prepared from both phosphines leads to the incorporation of the Pd salt, the corresponding complexes always adopting a *cis* arrangement of the ligands. Treatment with $n\mathrm{Bu}_3P$ of all the materials containing metal centres leads to the complete removal of the metal except for the materials obtained by hydrolysis of the metal–$[p\text{-}(OiPr)_3SiC_6H_4]_3P$ complexes. © 2002 Published by Elsevier Science B.V.

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1. Introduction

The economic importance of catalysts has led to much research into catalysts supported on organic polymers [1,2] or inorganic polymers such as silica. The anchorage of catalysts on silica is achieved by reacting the surface OH groups of the silica [3] with trialkoxysilyl derivatives $(RO)_3Si–X–D_0$ where X is an organic spacer and D_0 a metal coordinating group [4]. The metal can be introduced before or after the reaction of the trialkoxysilane with the silica [3,4]. However, in both cases, the metal loading remains rather low.

A more efficient method to anchor catalysts results from the sol–gel process [5]. It consists in co-hydrolysing a mixture of a trialkoxysilane of type $(RO)_3Si–X–D_0$ and a tetraalkoxysilane [6]. By this method, the organic moiety is ‘diluted’ into the silica matrix and the metal coordinating groups are located outside the polysiloxane matrix [7] and are easily accessible by bulky metallic reagents [8]. The metal can also be introduced by co-hydrolysing a mixture of a metal chelated trialkoxysilane of type $(RO)_3Si–X–D_0–M$ and a tetraalkoxysilane [9,10]. Both methods allow the control of the quantity of the metal introduced into the material. Moreover, the textural characteristics of the materials can be adjusted through the choice of the experimental conditions for the hydrolysis. The most frequently used alkoxysilane derivatives are the phosphines $Ph_2P(CH_2)_nSi(OEt)_3$ [6,8,11,12] ($n = 2$, 3). Catalysts have also been obtained by hydrolysis–polycondensation of complexed phosphines bearing two hydrolysable $Si(OEt)_3$ groups [13].

Recently, we studied the hydrolysis–polycondensation (catalysed by 10% HCl) of phosphine **1** [with three $Si(OR)_3$ groups], phosphine **2** [with two $Si(OR)_3$ groups], and metallic Pd (**3**), *cis*-Pt (**4**), and *trans*-Pt (**5**) complexes giving rise to xerogels **X1**–**X5** (Eq. (1)) [14]. We report in this paper the hydrolysis–polycondensation of the palladium (Pd) and platinum (Pt) complexes of phosphine **2** (catalysed by HCl 10%) giving xerogels

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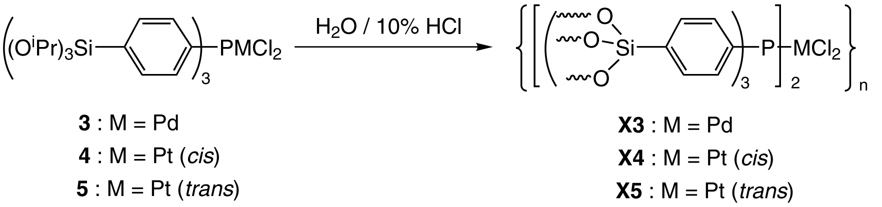
X6 and **X7** in order to compare the structures and properties of these xerogels with those of **X3**–**X5**. We have also studied the complexation of $PdCl_2$ by the P atoms incorporated within xerogels **X1** and **X2**, in a continuation of the study of the reactivity of these centres [15]. The *trans–cis* isomerisation of the Pd and Pt complexes included into these xerogels is shown. In order to obtain information about the structures of the xerogels resulting of the complexation of the phosphines before and after the hydrolysis, the decomplexation of the phosphorus atoms was also investigated by reacting these xerogels with an excess of $n\text{Bu}_3\text{P}$.



(1)

3 : M = Pd
4 : M = Pt (*cis*)
5 : M = Pt (*trans*)

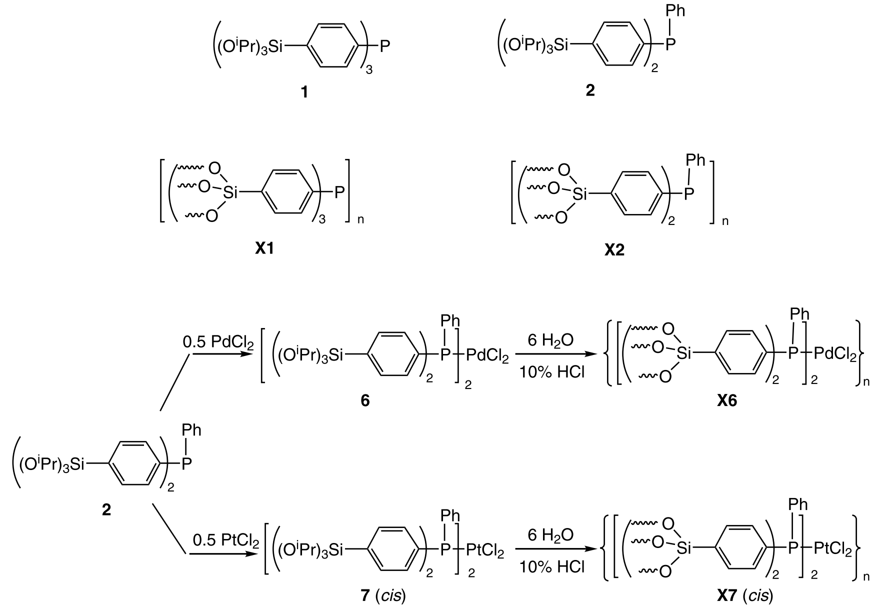
X3 : M = Pd
X4 : M = Pt (*cis*)
X5 : M = Pt (*trans*)

2. Result and discussion

2.1. Hydrolysis of the metallic complexes

The Pd and Pt complexes **6** and **7** were prepared as indicated in Scheme 1, but it was not possible to prepare the *trans*-Pt complex of phosphine **2**. The ^{31}P-NMR spectra of Pd complex **6** displays a single resonance at 23.6 ppm close to that of **3** (23.7 ppm) [14] and close to that of *trans*-$(Ph_3P)_2PdCl_2$ (23.1 ppm) [16] allowing attribution of a *trans* geometry to complexes **3** and **6**. The ^{31}P-NMR spectrum of the Pt complex **7** displays a resonance at 14.2 ppm and a large $^1J_{P-Pt}$ coupling constant (3670 Hz) characteristic of a *cis* geometry [17] as has **4** ($^1J_{P-Pt} = 3614$ Hz).

The hydrolysis–polycondensation of complexes **6** and **7** was performed under the same conditions (30 °C, 0.5 M THF solution, stoichiometric amount of water, 10% HCl as catalyst) as for complexes **3**–**5** [14]. Solid state NMR and textural data of the obtained xerogels **X6** and **X7** as well as of xerogels **X3**, **X4**, and **X5**, previously prepared [14], are indicated in Table 1. The ^{31}P CP MAS-NMR spectra of xerogels **X6** and **X7** display one signal, the chemical shift of which is very close to that of phosphine complexes **6** and **7** as were the chemical shifts of **X3**–**X5** [14]. The stereochemistry of the Pt complexes included into **X7** was inferred from the chemical shift of the ^{31}P CP MAS-NMR signal (10.5 ppm). The $^1J_{P-Pt}$ coupling constant could not be determined due to the width of the signal. Thus, neither decomplexation of the metal atom, nor isomerisation of the metallic complexes occurred during the sol–gel process. The ^{29}Si CP MAS-NMR spectra of all the xerogels **X3**–**X7** (Table 1) display signals corresponding to T^1, [C–Si(OR)$_2$OSi] and T^2, [C–Si(OR)(OSi)$_2$] substructures (a weak T^3 substructure, [C–Si(OSi)$_3$], was observed only for **X7**). The ratio of the different T groups was estimated by the method of deconvoluted T peak [18] which gives a degree of condensation for all



Scheme 1.

Table 1
Solid state ^{31}P-NMR (δ, ppm, $^{1}J_{P\text{–}Pt}$, Hz in bracket), solid state ^{29}Si-NMR (δ, ppm), degree of condensation (τ), and textural data for xerogels **X3**–**X7**

Xerogel	^{31}P-NMR	^{29}Si-NMR	τ (%)	S_{BET} (m^2 g^{-1})	Micropore volume (ml g^{-1})	Microporous surface (m^2 g^{-1})
X3	27.3	-62.8 (T^1), -71.7 (T^2)	58	510	0.225	490
X4	11.3 (3660)	-63.9 (T^1), -71.3 (T^2)	61	460	0.201	437
X5	20.8 (2590)			520	0.230	497
X6	24.9	-61.5 (T^1), -68.9 (T^2)	56	100		
X7	10.5	-62.1 (T^1), -70.0 (T^2), -78.9 (T^3)	58	410	0.153	349

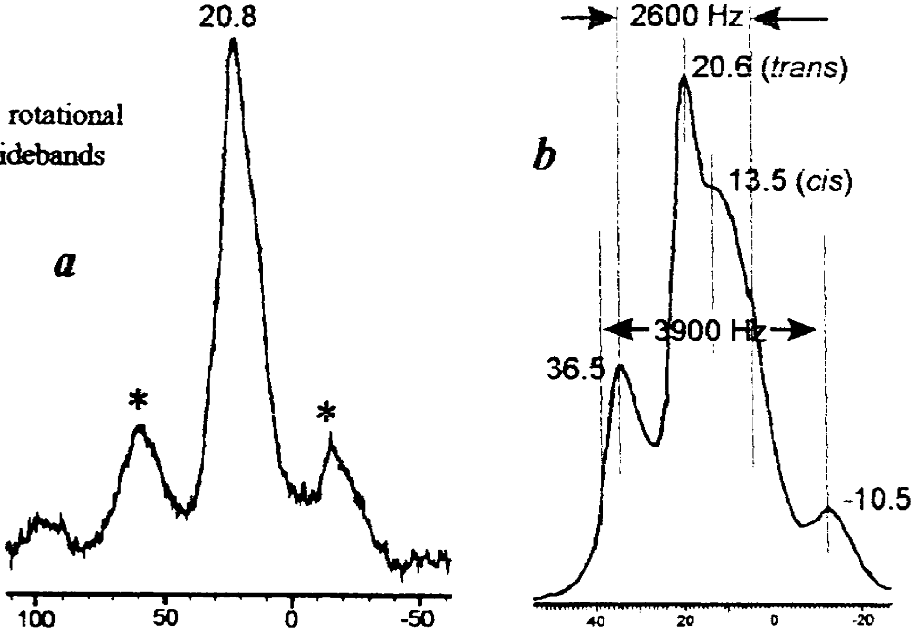


Fig. 1. Solid state ^{31}P-NMR spectrum of Pt xerogel **X5** as a function of time: (a) after reaction; (b) after one year.

the xerogels of about 60% (Table 1). Some OH and *i*Pr groups remain into the xerogels, the *i*Pr groups being detected by ^{13}C CP MAS-NMR spectroscopy and the OH groups by DRIFTS analysis. The texture of the xerogels was investigated using nitrogen adsorption–desorption measurements (Table 1). The absorption–desorption isotherms of all samples were of type I (characteristic of microporous material according to the BDDT) [19]. The N_2 Brunauer–Emmett–Teller (BET) surface areas are rather large (400–500 m^2 g^{-1}) except for **X6** (100 m^2 g^{-1}).

2.2. Trans–cis isomerisation of the complexes included into the xerogels

While the ^{31}P CP MAS-NMR spectrum of **X5** with a *trans*-Pt complexes at first exhibited one resonance at 20.8 ppm (Table 1), after one year two signals were observed at 20.6 and 13.5 ppm, signals which were tentatively attributed to the *trans* ($J_{P\text{–}Pt} = 2600$ Hz) and *cis* ($J_{P\text{–}Pt} = 3900$ Hz) complexes as indicated in Fig. 1. No change was apparent after a further year. A similar evolution of the ^{31}P CP MAS-NMR spectra of the *trans*-Pd complexes was observed for xerogels **X3** and **X6**. The original signal of **X3** at 27.3 ppm (corresponding to the *trans* complex) disappears after about one year to give another signal at 33.8 ppm. An analogous change of the trans signal was observed for **X6** but at a slower rate as shown in Fig. 2. The initial signal at 24.9 ppm (of the *trans* complexes) was transformed into two signals of the same intensity at 25.9 and 31.2 ppm after 8 months, and a major signal at 32 ppm and a weak signal at 26 ppm was formed after a further year. Thus the *trans*-Pd complexes incorporated within **X3** and **X6** are slowly transformed to the *cis* complexes with a chemical shift of about 30 ppm. The attribution for the chemical shifts for the *trans*- and *cis*-Pd complexes are in agreement with the values found for the *trans*- and *cis*-$[(EtO)_3Si(CH_2)_2PPh_2]PdCl_2$ complexes anchored to silica (respectively 21.3 and 30.0 ppm) [16]. In contrast, the ^{31}P CP MAS-NMR spectra of xerogels **X4** and **X7**

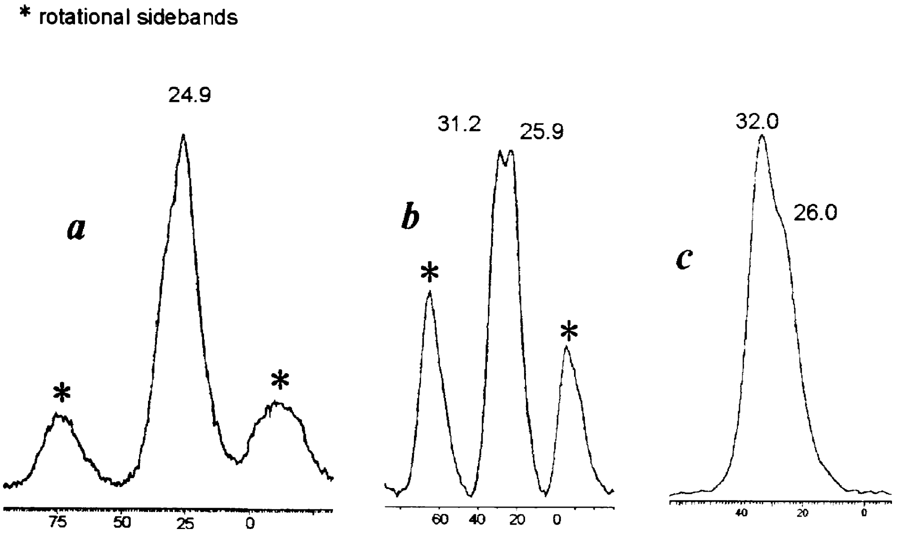


Fig. 2. Solid state ^{31}P-NMR spectrum of Pd xerogel **X5** as a function of time: (a) after reaction; (b) after 8 months; (c) after 20 months.

incorporating *cis*-Pt complexes are all the same after more than one year. Thus, in xerogels **X3**–**X7** the more stable geometry around the Pd or Pt atoms is the *cis* geometry. The *trans* complexes isomerise slowly into the *cis* complexes, the isomerisation of the Pd complexes being easier than that of the Pt complexes. The same difference is observed in solution, the Pt phosphine complexes being isomerised only in presence of an external nucleophile [20] which is not the case for the Pd complexes [21]. Thus, in these materials, the phosphorus atoms are sufficiently mobile to break a phosphorus metal bond and to build a new phosphorus metal bond with another phosphorus atom to give a more stable complex. Isomerisation by complexation–decomplexation was observed in the ruthenium complexes included into the xerogel resulting from hydrolysis of the Ru complex [22] obtained from $PhP[(CH_2)_4Si(OMe)_3](CH_2OCH_3)$.

2.3. Study of the accessibility of the phosphorus atoms within the materials

We have previously shown that the phosphorus atoms included into xerogels **X1** and **X2** can react with different reagents and that the accessibility of the phosphorus atoms is easier from the xerogel **X2** than from the xerogel **X1** [15]. To complete this work, we studied the complexing ability of the phosphorus atoms included into the two xerogels **X1** and **X2** as well as into xerogel **X1′** (obtained by hydrolysis of **1** catalysed by 1% of *p*-toluenesulfonic acid). **X1** has a rather large BET surface area (450 m^2 g^{-1}) while **X1′** and **X2** have low BET surface area (< 10 m^2 g^{-1}).

We found that the best conditions to incorporate $PdCl_2$ into the solids were the addition of a twofold excess of $(CH_3CN)_2PdCl_2$ in acetonitrile heated under reflux for 48 h. In all cases, the yield of incorporation of $PdCl_2$ determined by solid state ^{31}P-NMR spectroscopy is quantitative. The xerogels obtained, **X1′[Pd]**, **X1[Pd]**, and **X2[Pd]** were washed with acetonitrile, ethanol, acetone, and diethyl ether and dried under vacuum. The BET surface area of the new xerogels were not different from those of the starting xerogels except for **X1′**, the S_{BET} of which increases to 80 m^2 g^{-1}. The ^{31}P CP MAS-NMR spectra of the new xerogels show the disappearance of the signal attributed to the phosphines moieties (about −5 ppm) and the appearance of new signals at 31.8 ppm for **X1′[Pd]** and **X2[Pd]** and 29.9 ppm for **X1[Pd]**, corresponding to the *cis* complexes. Thus, all the phosphorus atoms have complexed the $PdCl_2$ salts. However, the microanalysis data indicate an excess of $PdCl_2$ into the xerogels **X1′[Pd]**, **X1[Pd]**, and **X2[Pd]**. The fact that no C≡N stretching band was observed by DRIFTS analysis and that only a very low percentage of nitrogen was found by elemental analysis, indicate that all the CH_3CN ligands were eliminated. As the excess of $PdCl_2$ salts was not eliminated by washing, it is likely that the $PdCl_2$ salts are retained into the xerogels by coordination. One explanation is part of the $PdCl_2$ salts was complexed by two phosphorus atoms in *cis* position while the rest is complexed by one phosphorus atom and probably by another nucleophile present in the xerogel (OH or OR groups), the ratio of both kinds of complexes depending on the nature of the xerogels (**X1**, **X1′** or **X2**). Thus, whatever the texture of the xerogels, all the phosphorus atoms of the xerogels **X1′**, **X1**, and **X2** are accessible by $(CH_3CN)_2PdCl_2$, as they were by H_2O_2, S_8, and CH_3I [15]. We can deduce that the first step is the coordination of the Pd atom by one phosphorus atom, a second nucleophile (P, OH, OR) giving the *cis*-Pd complex. The fact that the BET surfaces of

Table 2
Solid state ^{31}P-NMR chemical shifts (δ, ppm), ^{31}P-NMR yields (in brackets), and S_{BET} (m^2 g^{-1}, in square brackets) of metallated xerogels before and after treatment with nBu$_3$P

Xerogel	Starting xerogel	Xerogel after treatment with nBu$_3$P
X3	23.7 [510]	25.3 [a] (ca. 100%) [<10]
X6	24.9 [100]	−5.0 (ca. 100%) [30]
X4	11.4 [460]	4.1 (ca. 60%) and 13.1 [b] (ca. 40%) [14]
X5	20.8 [520]	4.2 (ca. 20%) and 21.6 (ca. 80%) [<10]
X7	10.5 [410]	−5.5 [c] (ca. 100%) [20]
X1[Pd]	29.9 [380]	−5.6 (ca. 70%) and 29.9 (ca. 30%) [350]
X2[Pd]	31.2 [<10]	−5.4 (ca. 100%) [<10]

[a] Two signals at 25.6 and 31.9 are obtained after 9 months.

[b] A weak unidentified signal was observed at 55 ppm.

[c] A weak signal (ca. 5%) at 31.3 ppm corresponding to oxidation of the phosphorus atoms is observed.

the metallated xerogels are not very different than those of the starting xerogels seems to indicate that the reaction with (CH$_3$CN)$_2$PdCl$_2$ does not greatly alter the texture of the xerogels.

2.4. Study of the demetallation of the complexes included into the xerogels

To study the accessibility of the metallic atoms within the xerogels **X3**–**X7** and within the xerogels **X1[Pd]** and **X2[Pd]**, we treated these xerogels with an excess (10 equivalents) of nBu$_3$P in acetonitrile heated under reflux for 120 h. The results obtained are indicated in Table 2. As shown in this table, no decomplexation occurred for the Pd complexes of **X3** and only partial decomplexation of the Pt of **X4** and **X5** was observed. On the contrary, total decomplexation of the Pd and Pt complexes of xerogels **X6** and **X7** occurred. Thus, the metallic atoms included into the xerogels **X6** and **X7** obtained from phosphine **2** with two hydrolysable Si(OR)$_3$ groups are much more easily accessible than the metallic salts included into xerogels **X3**–**X5** obtained from phosphine **1** with three hydrolysable Si(OR)$_3$ groups. The greater number of Si–O–Si attached to the organic units, the less easy is the diffusion into the xerogel, as it was previously observed with xerogels **X1** and **X2** [15,23]. For all these xerogels (**X3**–**X7**), there is a dramatic decrease of the BET specific surfaces after treatment with nBu$_3$P.

In contrast to these results, the decomplexation of the phosphorus atoms included into xereogels **X1[Pd]** and **X2[Pd]** is easy and quantitative (Table 2). After treatment with nBu$_3$P an additional signal, at 29.9 ppm was observed in the ^{31}P CP MAS-NMR spectra of xerogels **X1[Pd]**. This signal was attributed to oxidation of the phosphorus atoms during the treatment of the xerogel with nBu$_3$P. Indeed, the phosphine oxide incorporated into **X1** has a chemical shift of 30.7 ppm [14]. So, in xerogels **X1[Pd]** and **X2[Pd]** the Pd atoms are easily accessible by nBu$_3$P. The fact that **X1[Pd]** is easily demetallated may result from a possible conservation of the texture of the xerogel **X1** after reaction with (CH$_3$CN)$_2$PdCl$_2$ allowing the accessibility of the Pd atoms by nBu$_3$P.

Thus, the xerogels **X3** and **X1[Pd]**, obtained from the same phosphine **1** by two different routes, have different structures which render the accessibility of the Pd atom easy in **X1[Pd]**, but very difficult in **X3**. Moreover, we observed the same difference of reactivity between the xerogels **X6** and **X3** as previously observed between the xerogels **X2** and **X1** [15].

3. Conclusion

In conclusion, metallic complexes have been introduced into a silica matrice by two ways:

- Hydrolysis–polycondensation of a Pd (or Pt) phosphine complex, the phosphine bearing two or three hydrolysable (SiOR)$_3$ groups. In these cases, the geometry of the complex was preserved during the sol–gel process, but the *trans* complexes are slowly isomerised into the *cis* complexes.
- Reaction of (CH$_3$CN)$_2$PdCl$_2$ with the phosphorus atoms included into the xerogels **X1** [obtained from [p-(OiPr)$_3$SiC$_6$H$_4$]$_3$P] and **X2** [obtained from [p-(OiPr)$_3$SiC$_6$H$_4$]$_2$PPh]. In these cases, the yields of complexation are quantitative and the geometry of the complexes is *cis*. However, the Pd salt is retained not only by phosphines by also by other nucleophiles such as OH or OR groups.
- The metallic salts can be removed from the xerogels by treatment with nBu$_3$P. We found the same difference of reactivity between the xerogels **X3** and **X5** [obtained from [p-(OiPr)$_3$SiC$_6$H$_4$]$_3$P] and **X6** and **X7** [obtained from [p-(OiPr)$_3$SiC$_6$H$_4$]$_2$PPh] as that previously found for the reactivity of the phosphorus atoms included into xerogels **X1** and **X2**. The demetallation is very easy from xerogels **X6** and **X7** but difficult from xerogels **X3** and **X5**. On the contrary, the demetallation is very easy from the xerogels obtained by the second route, whatever the xerogel. Thus, the structure and the texture of the xerogels prepared by the two ways are different. The accessibility of the reaction centres is easier from **X1[Pd]** than from **X3**. That means that the reaction of (CH$_3$CN)$_2$PdCl$_2$ with the P atoms included into **X1** do not modify appreciably the structure of the xerogel and the accessibility of the reactive centres.

4. Experimental

All reactions were carried out under Ar by using a vacuum line. Solvents were dried and distilled just before use. M.p. were determined with a Gallenkamp apparatus and are uncorrected. 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). Chemical shifts (δ in ppm) were referenced to Me_4Si (^{1}H, ^{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 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 ms. The HPDEC MAS ^{31}P solid state-NMR spectra were recorded on a Bruker ASX-200 or a Bruker ASX-400 with repetition time of 5 s. FAB mass spectra [matrix, *m*-nitrobenzyl alcohol (NBA)] were registered on JEOL JMS-D3000 spectrometer. Specific surface areas were determined by the BET method on Micromeritics Gemini III 2375 analyser. Elemental analysis were carried out by the Service Central de Micro-Analyse du CNRS.

4.1. *trans-Bis{phenyl[bis(p-triisopropyloxysilylphenyl)]-phosphine}dichloropalladium* (***6***)

A mixture of phosphine **2** (3.74 g, 5.58 mmol) and of $PdCl_2$ (495 mg, 2.79 mmol) was heated under reflux in THF (30 ml) for 3 h. After elimination of the solvent and crystallisation from propan-2-ol, 3.45 g (2.27 mmol, 82%) of **6** were obtained as yellow needles. M.p. (propan-2-ol): 185.5–187 °C; ^{1}H-NMR (δ, 200 MHz, $CDCl_3$): 1.24 (d, $^{3}J_{H\text{–}H} = 6.1$ Hz, 72 H, Me), 4.30 (sept, $^{3}J_{H\text{–}H} = 6.1$ Hz, 12 H, OCH), 7.39–7.73 (m, 26 H, aromatic); ^{13}C-NMR (δ, 50 MHz, $CDCl_3$): 25.9 (Me), 66.0 (OCH), 128.3–136.2 (m, aromatic); ^{31}P-NMR (δ, 100 MHz, $CDCl_3$): 23.6; ^{29}Si-NMR (δ, 40 MHz, $CDCl_3$): −62.6. Anal. Calc. for $C_{72}H_{110}Cl_2O_{12}P_2PdSi_4$: C, 56.95; H, 7.25. Found: C, 56.83; H, 7.35%.

4.2. *cis-Bis{phenyl[bis(p-triisopropyloxysilylphenyl)]-phosphine}dichloroplatinum* (***7***)

To a warm solution of phosphine **2** (3.00 g, 4.47 mmol) in propan-2-ol (35 ml) was added a solution of 930 mg (2.24 mmol) of K_2PtCl_4 in water (15 ml). The pink suspension was heated at 40 °C for 1 h. After cooling, the product was extracted with Et_2O. The organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum. After crystallisation from propan-2-ol, 2.37 g (1.48 mmol, 66%) of **7** were obtained as a white powder. M.p. (propan-2-ol): 108 °C (dec.); ^{1}H-NMR (δ, 200 MHz, $CDCl_3$): 1.22 (d, $^{3}J_{H\text{–}H} = 6.1$ Hz, 72 H, Me), 4.28 (spt, $^{3}J_{H\text{–}H} = 6.1$ Hz, 12 H, OCH), 7.1–7.7 (m, 26 H, aromatic); ^{13}C-NMR (δ, 50 MHz, $CDCl_3$): 25.9 (Me), 66.0 (OCH), 128.1–136.9 (m, aromatic); ^{31}P-NMR (δ, 100 MHz, $CDCl_3$): 14.2 [s and d (satellite ^{195}Pt, d, $^{1}J_{P\text{–}Pt} = 3670$ Hz)]; ^{29}Si-NMR (δ, 40 MHz, $CDCl_3$): −63.3; MS (FAB^+, NBA): 1571 [$(M + Cl)^+$, 65%], 1535 [$(M - 2Cl + H)^+$, 59%]. Anal. Calc. for $C_{72}H_{110}Cl_2O_{12}P_2PtSi_4$: C, 53.80; H, 6.85. Found: C, 53.92; H, 6.95%.

4.2.1. *Xerogel* ***X6***

To a solution of 2.00 g (1.32 mmol) of **6** in THF (2.6 ml) placed in a 20 ml flask were added dropwise at room temperature (r.t.) 2.6 ml (7.8 mmol of H_2O) of a 3.0 M aq. 0.1 M HCl solution in THF. After stirring for 5 min at r.t., the reaction mixture was heated at 30 °C without stirring. An orange gel was formed after 30 min. The wet gel was allowed to age for 5 days at 30 °C after which it was powdered and washed with EtOH, C_3H_6O and Et_2O. The powdering and washing were repeated once and the gel was powdered again and dried under vacuum for 2 h at 120 °C. Orange powder (1.25 g) was obtained. ^{13}C-NMR (δ, 75 MHz, CP MAS): 24.7 (Me), 67.0 (OCH), 125.1–133.8 (aromatic); ^{29}Si-NMR (δ, 60 MHz, CP MAS): −61.5 (T^1), −68.9 (T^2), −80 (T^3, shoulder); ^{31}P-NMR (δ, 81 MHz, HPDEC MAS): 24.9. S_{BET}: 100 $m^2\ g^{-1}$. Anal. Calc. for $C_{36}H_{26}Cl_2O_6P_2PdSi_4$: C, 47.73; H, 2.87; Cl, 7.84; P, 6.85; Pd, 11.71; Si, 12.38. Found: C, 46.22; H, 3.59; Cl, 6.83; P, 6.25; Pd, 9.35; Si, 12.50%, i.e. $C_{38.21}H_{35.61}Cl_{1.91}O_{9.46}P_{2.00}Pd_{0.87}Si_{4.42}$.

4.2.2. *Xerogel* **7**

The same procedure starting from 2.00 g (1.18 mmol) of **7** led to 1.18 g of a yellow powder. ^{29}Si-NMR (δ, 60 MHz, CP MAS): −62.1 (T^1), −70.0 (T^2), −78.9 (T^3, shoulder); ^{31}P-NMR (δ, 162 MHz, HPDEC MAS): 10.5. S_{BET}: 410 $m^2\ g^{-1}$. Anal. Calc. for $C_{36}H_{26}Cl_2O_6P_2PtSi_4$: C, 43.46; H, 2.62; Cl, 7.14; P, 6.24; Pt, 19.63; Si, 11.27. Found: C, 41.67; H, 4.02; Cl, 6.10; P, 5.80; Pt, 16.60; Si, 10.50%, i.e. $C_{37.12}H_{42.97}Cl_{1.84}O_{10.23}P_{2.00}Pt_{0.91}Si_{4.01}$.

4.2.3. *Reactivity of xerogels* ***X1'***, ***X1***, *and* ***X2***

Before reaction, all the xerogels were systematically dried again under vacuum for 2 h at 120 °C. The reagent $(CH_3CN)_2PdCl_2$ was used in large excess. The molar mass of the xerogels has been calculated from an ideal formula (complete condensation). The following procedure is given as example.

4.2.3.1. *Xerogel* ***X1'[Pd]***. Xerogel **X1'** (320 mg, 0.77 mmol) and $(CH_3CN)_2PdCl_2$ (200 mg, 0.77 mmol) were heated under reflux in MeCN (30 ml) for 24 h. The orange suspension was then filtered and the precipitate was washed with MeCN, EtOH, C_3H_6O and Et_2O. After drying, 368 mg of an orange powder was obtained. ^{31}P-NMR (δ, 81 MHz, HPDEC MAS): 31.2.

S_{BET}: 80 m^2 g^{-1}. 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, 38.26; H, 4.29; Cl, 7.58; P, 3.92; Pd, 10.56; Si, 12.04%, i.e. $C_{54.44}H_{67.87}Cl_{3.38}O_{20.58}P_{2.00}Pd_{1.93}Si_{6.80}$.

*4.2.3.2. Xerogel **X1[Pd]**.* ^{31}P-NMR (δ, 81 MHz, HPDEC MAS): 29.9. S_{BET}: 380 m^2 g^{-1}. 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, 36.70; H, 3.84; Cl, 9.21; P, 4.70; Pd, 13.95; Si, 13.15%, i.e. $C_{40.34}H_{50.65}Cl_{3.42}O_{15.09}P_{2.00}Pd_{1.31}Si_{6.19}$.

*4.2.3.3. Xerogel **X2[Pd]**.* ^{31}P-NMR (δ, 81 MHz, HPDEC MAS): 31.2. S_{BET}: 10 m^2 g^{-1}. Elemental Anal. Calc. for $C_{36}H_{26}Cl_2O_6P_2PdSi_4$: C, 47.73; H, 2.87; Cl, 7.84; P, 6.85; Pd, 11.71; Si, 12.38. Found: C, 40.52; H, 3.78; Cl, 9.25; P, 5.70; Pd, 13.70; Si, 10.70%, i.e. $C_{36.73}H_{41.12}Cl_{2.83}O_{10.98}P_2Pd_{1.40}Si_{4.16}$.

4.3. Xerogels demetallation

All the demetallation reactions have been carried out in the same way, except that the reaction time was of 5 days for **X3**–**X7** and of 2 days for **X1**[**Pd**] and **X2**[**Pd**].The following procedure is given as an example.

*4.3.1. Xerogel **X3***

Xerogel **X3** (937 mg, 0.93 mmol) and nBu$_3$P (4.20 g, 20.7 mmol) were refluxed in $C_6H_5CH_3$ (20 ml) for 5 days. The suspension was filtered and the precipitate washed with $C_6H_5CH_3$, EtOH, C_3H_6O and Et_2O. After drying, 987 mg of an orange powder was obtained. ^{31}P-NMR (δ, 81 MHz, HPDEC MAS): 25.3. S_{BET}: <10 m^2 g^{-1}. Elemental Anal. Calc. for $C_{18}H_{12}O_{4.5}PdSi_3$: C, 52.05; H, 2.89; P, 7.47; Si, 20.24%.

*4.3.2. Xerogel **X4***

^{31}P-NMR (δ, 162 MHz, HPDEC MAS): -4.1, 13.1, 55.0. S_{BET}: 14 m^2 g^{-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: C, 46.17; H, 5.35; Cl, 3.36; P, 7.55; Pt, 10.50; Si, 11.15%.

*4.3.3. Xerogel **X5***

^{31}P-NMR (δ, 162 MHz, HPDEC MAS): -4.2, 21.6. S_{BET}: 10 m^2 g^{-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: C, 43.96; H, 4.81; Cl, 4.77; P, 7.00; Pt, 9.60; Si, 12.00%.

*4.3.4. Xerogel **X6***

^{31}P-NMR (δ, 81 MHz, HPDEC MAS): -5.0. S_{BET}: 30 m^2 g^{-1}. Elemental Anal. Calc. for $C_{18}H_{13}OP_2PdSi_6$: C, 59.34; H, 3.57; P, 8.51; Si, 15.38. Found: C, 55.82; H, 4.58; Cl, 0.47; P, 7.90; Pd, 0.80; Si, 12.80%.

*4.3.5. Xerogel **X7***

^{31}P-NMR (δ, 162 MHz, HPDEC MAS): -5.5. S_{BET}: 20 m^2 g^{-1}. Elemental Anal. Calc. for $C_{18}H_{13}O_3PSi_2$: C, 59.34; H, 3.57; P, 8.51; Si, 15.38. Found: C, 57.06; H, 4.82; Cl, 0.83; P, 8.00; Pt, 1.30; Si, 12.80%.

*4.3.6. Xerogel **X1[Pd]***

^{31}P-NMR (δ, 81 MHz, HPDEC MAS): -5.6, 29.9. S_{BET}: <10 m^2 g^{-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: C, 51.55; H, 5.60; Cl, 0.48; P, 4.80; Pd, 0.90; Si, 9.90%.

*4.3.7. Xerogel **X2[Pd]***

^{31}P-NMR (δ, 81 MHz, HPDEC MAS): -5.4. S_{BET}: <10 m^2 g^{-1} Elemental Anal. Calc. for $C_{18}H_{13}O_3PSi_2$: C, 59.34; H, 3.57; P, 8.51; Si, 15.20. Found: C, 57.18; H, 5.41; Cl, 820 ppm, P, 7.10; Pd, 0.10; Si, 12.40%.

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