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Studies of the functionalisation of organic–inorganic hybrid materials by using the Heck reaction†

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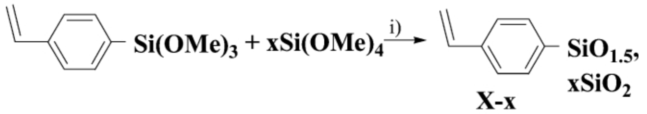
Cogelation of 4-styryltrimethoxysilane was performed using NH$_4$F as catalyst. The functionalisation of the styryl group was then studied by using Heck's reaction with ethyl 4-bromobenzyl- or 4-bromoarylvinylbenzyl-phosphonates. The efficiency of the solid-phase reaction was highly dependent on the texture of the solids.

Functionalisation of organic molecules in the solid phase by using transition metal catalysis has become a powerful tool in different fields.[1] In this context, the mild conditions of the Heck reaction allowed the preparation of elaborated materials[1a,b, g–j] in scopes such as solid support synthesis (Wang and Merrifield resins) for the preparation of chemical libraries, and polymer science.[1k] However, Heck's reaction performed on hybrid organic–inorganic materials such as silica-based solids is much less described. Due to the growing interest of these materials[2] in fields such as catalysis, non-linear optics, sensors, solid-phase methods of functionalisation are needed. Only one example deals with the Heck reaction at the surface of organo-modified silicas,[3] and to our knowledge, no example of Heck's reaction performed on xerogels has been reported. We present here our results concerning the functionalisation of hybrid materials with 4-bromobenzylphosphonate or 4-bromoarylvinylbenzylphosphonates, by using the Heck reaction.

Cogels **X-x** ($x = 0,2,5,10$) were prepared by nucleophilic cogelation (NH$_4$F cat.) of parastyryltrimethoxysilane[4] (Scheme 1) in the presence of different amounts of Si(OMe)$_4$. Solids were analysed by solid-state NMR, IR, BET.[10] CP MAS (Cross-Polarisation ^{1}H-^{29}Si Magic Angle Spinning) ^{29}Si NMR of **X** showed the classical resonances T (SiO$_3$ units) for $x = 0$, T and Q (SiO$_4$ units) for $x > 0$. The major resonances were T^3 at −79 ppm attributed to SiO$_3$ groups possessing 3 siloxane bridges and resonances at −101 ppm (Q^3), and −109 ppm (Q^4), corresponding to SiO$_4$ units possessing 3, 4 siloxane bridges respectively. (T^2) and (Q^2) were minor signals, indicating that the gels were well condensed. CP MAS ^{13}C NMR spectroscopy showed resonances at 139.4 and 125.4 ppm (Ar and =CH) and at 115 ppm (=CH$_2$).

BET analyses showed specific surface area for xerogels **X** for low value of x in contrary to related xerogels functionalised with arylene-vinylene chromophores[5] possessing a phosphonate unit. **X-0** possessed a microporous character. The mesoporous contribution increased by increasing x to (5, 10) and types I and IV isotherms were observed for **X-5**, **X-10**.

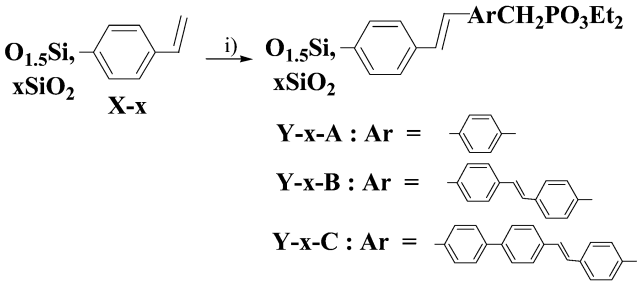
We then performed the Heck reaction by using ethyl 4-bromobenzylphosphonate (**A**) and ethyl 4-bromoarylvinylbenzylphosphonates (**B**, **C**) (Scheme 2).



Scheme 1 i) 2% NH$_4$F, MeOH–THF, (1.5 + 2x)H$_2$O

Table 1 BET of Xerogels X-x and Y-10-A

	Isotherm	Porous diameter (Å)	Surface area (m^2 g−1)	Microporous contribution
X-0	I	10 < Ø < 30	251	62
X-2			none	
X-5	I and IV	10 < Ø < 40	541	54
X-10	I and IV	10 < Ø < 40	645	36
Y-10-A	I and IV	10 < Ø < 40	325	33



Scheme 2 i) **Br–ArCH$_2$PO$_3$Et$_2$**, Heck's reaction.

Different conditions were tested. Macquarrie's phosphine free conditions,[3] which were very efficient in functionalising aliphatic alkene grafted on silica, gave poor results when applied to our cogels and bromoarylphosphonates **A**, **B**, **C**. Aqueous conditions which have been shown to sometimes facilitate the Heck reaction[6] failed in our case. The best results were obtained by using 4% Pd(OAc)$_2$, 15% triorthotolylphosphine (TOP), 6 Et$_3$N, in MeCN, at 120 °C in a sealed tube, which are the conditions used for cross-coupling in the liquid state.[7] Herrmann's procedure gave lower yields.[8] The optimum conditions were tested with solids **X-x**, varying x from 0 to 10. Solids were filtered, washed with water, and then a soxhlet extraction with THF for 24 h was performed. Yields were analysed on the basis of the Si/P ratio by using Energy Dispersive X-ray analyses (EDX). With this technique residual Pd was detected in low amounts (0.1–2%). TOP did not interfere with the evaluation of the Si/P ratio, as TOP was not detected by spectroscopic techniques. For $x = 0$, cross-coupling of **X-0** with **A** was studied. The Si/P ratio indicated a maximum coupling of 40%. The HPDEC (High Power Decoupling) ^{31}P MAS NMR spectra showed a signal at 20 ppm, with an important peak width at half maximum of 10 ppm (Table 2).

Table 2 Heck's reaction yields, HPDEC MAS ^{31}P NMR

	Yield (%)	^{31}P NMR (ppm) PO$_3$Et$_2$	^{31}P NMR (ppm) transesterification
Y-0-A	40 maxi	none	20.2 (large)
Y-2-A	90	26.9	none
Y-2-B	75	27.3	none
Y-2-C	70	26.9	none
Y-5-A	20	28	21.2
Y-10-A	60	26.1	none

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† Electronic supplementary information (ESI) available: isotherms of **X0**, **X5**, **X10** and **Y10A**. See http://www.rsc.org/suppdata/cc/b3/b301355c/

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This signal is characteristic of the transesterification of the phosphonate group with formation of P–O–Si bonds.[9] CPMAS ^{13}C NMR confirmed this fact as the ethoxy group were hardly detected. Thus, Heck reaction performed on xerogel **X-0** did not work properly and the phosphonate group was damaged. The vinyl groups seem not to be accessible, probably because organic moieties in **X-0** are too crowded and a part of the styryl groups are inside the solid.

By contrast the same reaction performed on **X-2** gave much better results. EDX indicated more than 90% coupling with **A**. Only one signal at 27 ppm with a peak width at half maximum of 5 ppm was observed by HPDEC ^{31}P MAS NMR (Table 2). This signal confirmed the presence of the benzylic ethyl phosphonate supported on silica, transesterification did not occur.[9] Note that CH_3CN must be used as the solvent, as a second minor signal at 20 ppm (transesterification) was observed when performing the reaction in DMF. CPMAS ^{13}C NMR showed appearance of the signal at 129.2 ppm (aromatics) and 61.5 and 15.2 ppm (ethoxy). The residual signal at 113 ppm confirmed the disappearance of the terminal $=CH_2$ vinyl groups. Fluorescence of **Y-2-A** (Fig. 1) confirmed the presence of the stilbene unit with a maximum at 465 nm. Indeed, direct cogelation of the same stilbene unit with 10 $Si(OMe)_4$ gave the same type of curve.[5] This red-shifted signal was attributed to the formation of aggregates of the stilbene units, in the ground state. Note that the styryl units of **X-x** gave no fluorescence between 400–800 nm. Thus, Heck's reaction was efficient even when the styryl units of **X-2** were close to each other. The more bulky bromoarylphosphonates **C** and **B** gave conversions of 70–75%, which were lower probably because **C** and **B** are more encumbered. Solid-state ^{13}C and ^{31}P NMR gave the same type of results as with **A** ($=CH_2$ more present). Fluorescence confirmed that cross-coupling occurred.

A bathochromic effect was observed with **Y-2-B** and **Y-2-C** compared to **Y-2-A** as the chromophores were longer and gave different kinds of aggregates. Thus texture of **X-2** was more favourable for the Heck reaction in the solid state than **X-0**, even if no specific surface area was detected by BET. Thus organic parts seem to be located at the surface of the solid.

We then silanized **X-2** with HMDS or TMSBr before studying the Heck reaction. Results were worse with **A** as conversion dropped to 20% and P–O–Si bonds were observed. It seems as Me_3Si groups have encumbered xerogel **X-2** preventing accessibility to styryl groups and favouring transesterification by silicon species *versus* Heck's reaction.

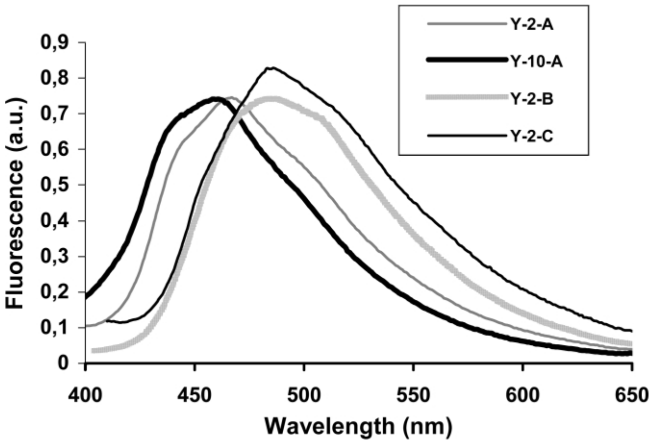

Fig. 1 Fluorescence of xerogels **Y**.

Xerogel **X-5** gave very bad results with **A** as less than 20% conversion was obtained. Again P–O–Si bonds were observed. Vinyl groups seem to be trapped inside the solid and porosity of **X-5** did not allow diffusion of organic species.

Xerogel **X-10** gave 55–60% conversion with **A**, the phosphonate group was not damaged and fluorescence of **Y-10-A** confirmed the presence of the stilbene unit (Fig. 1). A slight blue shift was observed compared to **Y-2-A**, aggregates of the stilbene units are still present with slightly different geometries from that of **Y-2-A**. **X-10** presented a porous texture with a low microporous contribution, which permitted accessibility to vinyl groups.

BET studies of **Y-0**, **Y-2**, **Y-5** showed no specific surface area and **Y-10-A** showed a specific surface area of 325 m^2g^{-1}. Thus, specific surface area dropped after performing the Heck reaction although **X-0**, **X-5**, **X-10** in Et_3N, CH_3CN at 120 °C showed no loss of specific surface area. The presence of the arylvinylbenzylphosphonate groups seems to prevent N_2 diffusion inside the solid matrix by blocking the pores.

In conclusion Heck's reaction was performed on solid phase to functionalize styrene-derived xerogels. The efficiency of the Heck reaction was highly dependent on the texture of the solids and steric hindrance of the bromoarene. The best results were obtained with **X-2** and **X-10**. In those cases the Heck reaction was kinetically favoured *versus* transesterification. Thus transition metals catalysis offers new perspectives for the preparation of hybrid materials.

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