Supported Aqueous-Phase Palladium Catalysts for the Reaction of Allylic Substitution: Toward an Understanding of the Catalytic System

Sylvia dos Santos, Yuye Tong, Françoise Quignard, and Agnès Choplin*

Institut de Recherches sur la Catalyse, CNRS, 2 Avenue Albert Einstein,
69626 Villeurbanne Cedex, France

Denis Sinou*

Laboratoire de Synthèse Asymétrique, associé au CNRS, CPE Lyon, Université Lyon-1,
43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Jean Pierre Dutasta

Laboratoire de Stéréochimie et Interactions Moléculaires, Ecole Normale Supérieure de Lyon,
46 Allée d'Italie, 69364 Lyon Cedex 07, France

Received August 18, 1997[⊗]

The heterogeneization of the catalytic biphasic system $Pd(OAc)_2$/5tppts/water/nitrile (tppts = sodium salt of tri(*m*-sulphophenyl)phosphine)) is performed by controlled deposition on silica of the catalyst in its aqueous phase (SAP catalyst). The resulting heterogeneous molecular catalysts are active for the alkylation of ethyl acetoacetate or morpholine by (*E*)-cinnamyl ethyl carbonate. They are very selective for the monoalkylated product, and the secondary reactions due to water itself, such as formation of cinnamyl alcohol, are suppressed. Finally, the active Pd(0) entity is stable toward decomposition into metallic particles. This method (SAP) is most appropriate with true biphasic media. Thus, with CH_3CN, the SAP catalyst is less active than the monophasic homogeneous catalyst, whatever the water content of the solid. On the contrary, with PhCN, the SAP catalyst is drastically more active than the biphasic homogeneous catalyst, a phenomenon which must be correlated to a large enhancement of the interphase surface area. The water content of the SAP catalyst intervenes in different ways. Thus, a minimum amount of water (*ca.* 15−20 wt %) is necessary to observe any catalytic activity, a phenomenon which is correlated with a certain mobility of the complex on the surface of silica, confirmed by ^{31}P MAS NMR, but also probably to a minimum concentration of the reactants in the aqueous phase. Activity increases when the water content reaches 30−50 wt %. Within these boundaries, no detectable palladium leaching is observed but the catalysts progressively loose part of their activity after several recyclings, a phenomenon which seems to be correlated with water leaching into the organic phase. ^{31}P MAS NMR reveals that the main surface complex is $Pd(0)(tppts)_3$. Its chemical shift corresponds to the weighted average of that of $Pd(tppts)_3$ (δ 22.6 ppm) and that of free tppts (δ −5.6 ppm), in accordance with a fast exchange between free tppts and coordinated tppts. No strong interaction between the complex and the silica surface could be evidenced; in the presence of small amounts of water, free tppts interacts with the silica surface ($\delta \approx$ 0 ppm) *via* hydrogen bonding. Above 50 wt % of water, a number of problems are encountered which lead to an overall drop in activity: the solid agglomerates and palladium and water leaching both become significant. The SAP catalysts supported on a nonporous silica present the same behavior, i.e., increasing activity with increasing water content up to a content corresponding roughly to the wetting volume.

Introduction

The synthesis of supported liquid-phase catalysts (SLPC) was reported for the first time in 1939.[1,2] Their domain of application and a first description of their operating mode was simultaneously reported later by Acres et al.[3] and by Rony.[4,5] The method is inspired from the theory of gas−liquid chromatography techniques and uses a catalyst deposited on the surface of

---

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

(1) Moravec, R. Z.; Schelling, W. T.; Oldershaw, C. F. Brit. Patent 511,556, 1939.

(2) Moravec, R. Z.; Schelling, W. T.; Oldershaw, C. F. Can. Patent 396,994, 1941.

(3) Acres, G. J. K.; Bond, G. C.; Cooper, B. J.; Dawson, J. A. *J. Catal.* **1966**, *6*, 139.

(4) Rony, P. R. *Chem. Eng. Sci.* **1968**, *23*, 1021.

(5) Rony, P. R. *J. Catal.* **1969**, *14*, 142.

S0276-7333(97)00729-2 CCC: $15.00
Publication on Web 01/05/1998

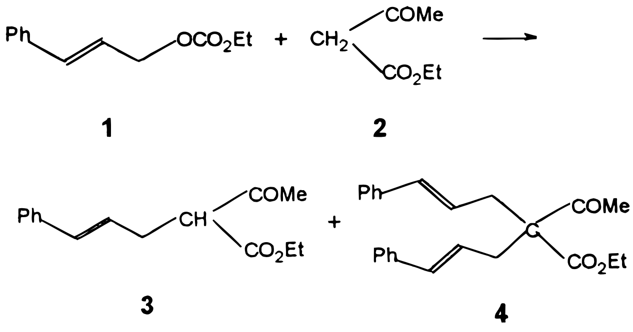
a high-surface-area porous inorganic oxide in a thin film of a nonvolatile solvent; reactants and products are in the gas phase. This technique was first applied to the $RhCl_3$-catalyzed isomerization of pentene-1 (catalyst in a film of ethylene glycol) and to the $(Ph_3P)_2Rh(CO)Cl$-catalyzed hydroformylation of propene (catalyst in a film of butyl benzyl phthalate). For this latter reaction, the highest activity of the catalyst corresponds to an amount of solvent such that one can consider it to be present as a thin film on the surface; with greater amounts, the activity decreases, a phenomenon which is attributed to a progressive plugging of the pores leading to long liquid diffusion paths. Later, variations of the Wilkinson SLP catalyst using the phosphine itself as the solvent, molten under the reaction conditions, were reported.[6-10] The SLP catalysts were finally adapted to the hydrogenation of ketones.[11]

The SLP method, as originally described, in its principle is restricted to gaseous reactants and products. Renewed interest for this type of catalyst appeared with their adaptation to biphasic media, water−organic solvent, the so-called supported aqueous-phase catalysts (SAPC); it is considered as an elegant way of heterogenizing biphasic catalysts.[12] The molecular catalyst is immobilized *via* its solvent, i.e., water, by hydrogen bonding with the surface silanol groups, reactants and products being in the organic phase. These SAP catalysts have been successfully tested for reactions such as hydroformylation of heavy[13-15] or functionalized olefins,[16] selective hydrogenation of α,β-unsaturated aldehydes,[17] and asymmetric hydrogenation.[18-20] Their main advantadges concern easy catalyst recovery and increased activity through a sharp increase of the interphase surface area through that of the silica support, a property particularly sensitive with sparingly water soluble reactants.

The precise operating mode of these catalysts and the nature of their interactions with the support are still a matter of debate. Thus, the stability of the catalysts toward metal leaching and the optimum amount of water necessary to achieve high activity are both dramatically dependent on the catalyst precursor system and the reaction itself. Thus, for example, only a few layers seem to be necessary for the hydroformylation of octene with $HRh(CO)(tppts)_3$, while amounts equal or superior to that corresponding to complete filling of the pores of the support are reported for the hydroformylation of methyl methacrylate with the same catalyst[16] or hydrogenation of 2-(6′-methoxy-2′-naphthyl)acrylic acid by SAP−Ru−Binap-$4SO_3Na$.[19] Above a certain amount of water, severe problems of metal leaching and/or stability of the catalyst were evidenced. We wish to report in this paper our results concerning palladium-based SAP catalysts for the Trost−Tsuji reaction; the influence of the nature of the silica support and the amount of water on the activity and the stability of the catalyst toward degradation and leaching in the liquid phase will be discussed. ^{31}P MAS NMR studies and variation of the nature of the nucleophile complete the description of the catalytic system.

Results and Discussion

In a preliminary study,[21] we have demonstrated that the SAP methodology can be applied to the palladium-catalyzed alkylation of ethyl acetoacetate by (*E*)-cinnamyl ethyl carbonate (eq 1) Total carbonate conversion could be reached under very mild conditions with a high selectivity for the monoalkylated product **3** (>90%), using $Pd(OAc)_2$/5tppts/silica as the catalyst. Only minor amounts of palladium were detected in the reaction solution. We have now optimized this catalyst and its operating conditions and identified some of the parameters which are crucial for the future use of such systems in a continuous flow reactor. The replacement of the poorly water-soluble ethyl acetoacetate by the more water-soluble morpholine completes this study.



(1)

1. Catalytic Properties of Palladium-Based SAP Catalysts for the Reaction of Allylic Alkylation. The catalytic system $Pd(OAc)_2$/5tppts was tested for reaction 1 under biphasic and SAP conditions with water/nitrile as the solvents. In order to ensure a valid comparison, in both types of experiments we used the same concentration of (*E*)-cinnamyl ethyl carbonate in the nitrile solvent and the same ratio of [Pd]/[carbonate]/[nucleophile] (1/25/30). Obviously, the amount of water is quite different: the ratio of H_2O/nitrile was chosen to be 1/1 in the biphasic experiments to allow for the solubilization of the catalyst in water.

We have deliberately chosen to precisely immobilize the optimized biphasic system, i.e., $Pd(OAc)_2$ and 5 equiv of tppts.[22] We avoid, thus, the tedious steps of

---

[6] Hjortkjaer, J.; Scurrel, M. S.; Simonsen, P. *J. Mol. Catal.* **1979**, *6*, 405.

[7] Gerritsen, L. A.; Herman, J. M.; Klut, W.; Scholten, J. J. F. *J. Mol. Catal.* **1980**, *9*, 158.

[8] Gerritsen, L. A.; Herman, J. M.; Scholten, J. J. F. *J. Mol. Catal.* **1980**, *9*, 241.

[9] de Munck, N. A.; Verbruggen, M. W.; de Leur, J. E.; Scholten, J. J. F. *J. Mol. Catal.* **1981**, *11*, 331.

[10] Uematsu, T.; Kawakami, T.; Saitho, F.; Miura, M.; Hashimoto, H. *J. Mol. Catal.* **1981**, *12*, 11.

[11] Strohmeier, W.; Graser, B.; Marcec, R.; Holke, K. *J. Mol. Catal.* **1981**, *11*, 257.

[12] Arhancet, J. P.; Davis, M. E.; Merola, J. S.; Hanson, B. E. *Nature* **1989**, *339*, 454. Davis, M. E. *Chemtech.* **1992**, 498.

[13] Horvath, I. T. *Catal. Lett.* **1990**, *6*, 43.

[14] Gou, I.; Hanson, B. E.; Toth, I.; Davis, M. E. *J. Organomet. Chem.* **1991**, *403*, 221.

[15] Gou, I.; Hanson, B. E.; Toth, I.; Davis, M. E. *J. Mol. Catal.* **1991**, *70*, 363.

[16] Fremy, G.; Monflier, E.; Carpentier, J. F.; Castanet, Y.; Mortreux, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 147; *J. Catal.* **1996**, *162*, 339.

[17] Fache, E.; Mercier, C.; Pagnier, N.; Despeyroux, B.; Panster, P. *J. Mol. Catal.* **1993**, *79*, 117.

[18] Wan, K. T.; Davis, M. E. *Nature* **1994**, *370*, 449.

[19] Wan, K. T.; Davis, M. E. *J. Catal.* **1994**, *148*, 1.

[20] Wan, K. T.; Davis, M. E. *J. Catal.* **1995**, *152*, 25.

[21] Schneider, P.; Quignard, F.; Choplin, A.; Sinou, D. *New J. Chem.* **1996**, *20*, 545.

[22] Blart, E.; Genêt, J.-P.; Safi, M.; Savignac, M.; Sinou, D. *Tetrahedron* **1994**, *50*, 505.

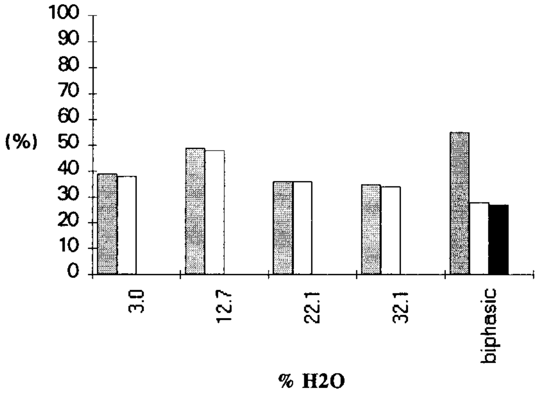


Figure 1. Influence of the water content of solid **SAP25P** (0.76% Pd) on its catalytic properties for the allylic alkylation of ethyl acetoacetate with (*E*)-cinnamyl ethyl carbonate. Experimental conditions: $m_{\text{cat.}} \approx 200$ mg, $T = 80$ °C, solvent CH_3CN. Carbonate conversion (%), monoalkylated product yield (%), and cinnamyl alcohol yield (%) after 8 h of reaction are shown by the grey, white, and black boxes, respectively.

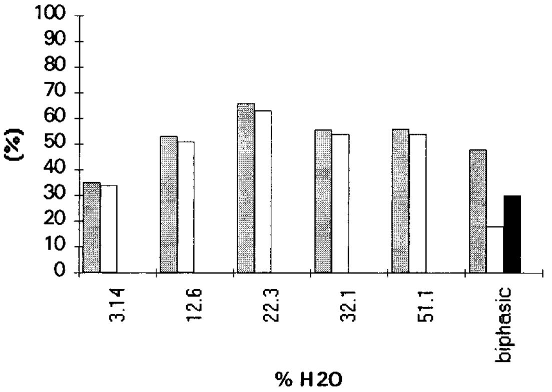


Figure 2. Influence of the water content of solid **SAP50P** (0.76% Pd) on its catalytic properties for the allylic alkylation of ethyl acetoacetate with (*E*)-cinnamyl ethyl carbonate. Experimental conditions: $m_{\text{cat.}} \approx 200$ mg, $T = 80$ °C, solvent CH_3CN. Carbonate conversion (%), monoalkylated product (**3**) yield (%), and cinnamyl alcohol yield (%) after 8 h of reaction are shown by the grey, white, and black boxes, respectively.

the synthesis and purification of $Pd(tppts)_n$[23] and the search for the optimum amount of phosphine necessary for the stabilization of the active species. Because the *in-situ* reduction of $Pd(OAc)_2$ by phosphine is known to be a slow reaction[24] and because we do not precisely know the influence of silica on this reduction, we synthesized two types of solid catalysts, which result from impregnation of silica with an aqueous solution of $Pd(OAc)_2$/5tppts maintained either at room temperature (**SAP25**) or at 50 °C (**SAP50**) before room temperature impregnation. Finally, we also used two types of silica differing essentially by their porosity; thus, **SAP25P** and **SAP50P** were catalysts supported on a mesoporous silica, while **SAP25NP** and **SAP50NP** were catalysts supported on a nonporous silica.

a. Allylic Alkylation of Ethyl Acetoacetate by (*E*)-Cinnamyl Ethyl Carbonate. Influence of the Water Content of the Solid Catalyst. We first tested the catalytic properties of solid **SAP25P** for different water contents of the solid; the desired amount of water was added to different portions of the same precursor sample. The catalytic reaction was performed at 80 °C, using acetonitrile as the organic solvent. The reaction is slow whatever the initial water content of the solid: carbonate conversion is nearly complete after only *ca.* 24 h. Although the activity of the catalyst under SAP conditions and under "biphasic" conditions is very similar (Figure 1), one can notice that the stability of the catalyst under the latter conditions is poor: black particles already precipitate after 6 h of reaction. The selectivities of the two systems for the monoalkylated product **3** are very different. While the **SAP25P** catalyst is highly selective for **3** (only trace amounts of the dialkylated product **4** are detected after 24 h), the same catalytic system under biphasic conditions leads to the formation of an important quantity of cinnamyl alcohol (selectivity ≈ 50%). With **SAP25P**, although the conversion of carbonate **1** and the yield of product **3**, determined independently, are almost identical (Figure 1), we have checked that cinnamyl alcohol, if it was formed, does not physisorb or chemisorb on silica under our experimental conditions: indeed, the composition of a standard solution of **1**, **2**, **3**, and cinnamyl alcohol in acetonitrile does not vary over time in the presence of silica at 80 °C.

Influence of the Method of Preparation of the Catalyst. The same type of experiment was then performed with solid **SAP50P**. The activity of this solid is similar to that of **SAP25P** when no water is added (Figure 2), but it increases with the water content of the catalyst. The activity of **SAP50P** reaches a plateau for 22 wt % H_2O, where it compares to that of the biphasic system. After 24 h, the reaction is near completion in all cases. The selectivity in the monoalkylated product **3** is always very high and close to 100%. The related biphasic system ($Pd(OAc)_2$/5tppts kept at 50 °C for 1 h before introduction of the reactants) shows a low selectivity for the monoalkylated product **3** (38%), associated with the formation of cinnamyl alcohol.

The different behaviors of the two catalysts **SAP25P** and **SAP50P** with increasing amounts of water are not easy to rationalize. It may be attributed to differences in the concentration of the active species on the solids and/or to variation of this concentration with time and/or water content of the solid. One cannot exclude *a priori* partial decomposition of the catalytically active species over time. Nevertheless, the most important point is that supporting $Pd(OAc)_2$/5tppts on silica leads to enhanced selectivity for the desired monoalkylated product **3**, a property which must be correlated to the low amounts of water necessary to obtain an active catalyst. Finally, one should also mention that the catalytic solution becomes yellow only with **SAP50P** (51.1 wt % H_2O); elemental analysis reveals that *ca.* 7% of the palladium introduced on the solid has leached into the solvent.

Influence of the Nature of the Nitrile. The solubility of water in acetonitrile is very high so that the medium H_2O/CH_3CN is in fact a monophasic system when the reaction is performed in the liquid phase. This suppresses the problems related to the small interphase surface area, encountered with biphasic systems, but

---

[23] Hermann, W. A.; Kellner, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103.

[24] Amatore, C.; Carre, E.; Jutand, A.; M'Barki, M. A. *Organometallics* **1995**, *14*, 1818.

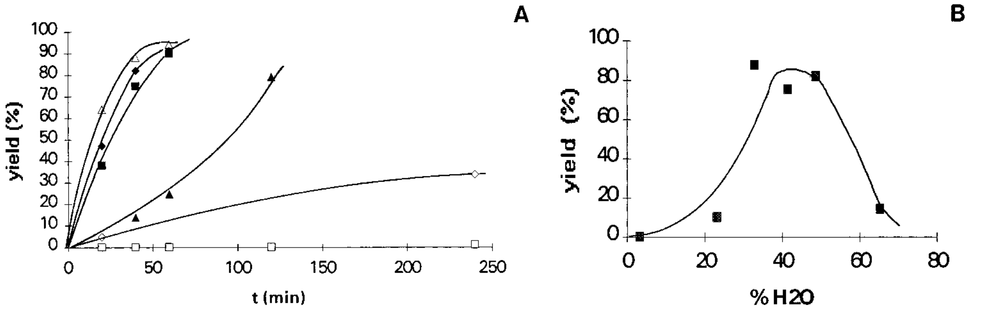


Figure 3. Influence of the water content of solid **SAP50P** (0.76% Pd) on its catalytic properties for the allylic alkylation of ethylacetoacetate with (*E*)-cinnamyl ethyl carbonate. Experimental conditions: $m_{\mathrm{cat.}} \approx 200$ mg, $T = 80$ °C, solvent PhCN. (A) Evolution with time of the yield of alkylated product **3**. Water content (%): (□) 3.4; (◇) 23.1; (△) 32.8; (■) 41.5; (◆) 48.7; (▲): 65.4. (B) Evolution of the yield of **3** with water content of the solid after $t_R = 40$ min.

renders the recovery of the catalyst more critical. When this medium is used under SAP conditions, the lower activity of the SAP catalysts when compared to that of the homogeneous H_2O/CH_3CN system may be explained by preferential adsorption of water on the surface of silica, so that the interphase surface area is then close only to that of the solid surface.

Interestingly, the activity of **SAP50P** for reaction 1 becomes several orders of magnitude higher in PhCN (Figure 3A); remarkably, it is strongly dependent on the water content of the solid. Thus, with 3 wt % H_2O, no carbonate conversion occurs within 3 h, a result which compares with that obtained with the biphasic H_2O/PhCN (1/1) homogeneous system. For water contents between 30 and 50 wt %, total carbonate conversion is achieved within 1 h (compare with the 24 h necessary in CH_3CN) and the selectivity for **3** is close to 100%. Above 50 wt % H_2O, the activity of **SAP50P** decreases (Figure 3B) but simultaneously we observe that the solid is poorly dispersed in the liquid phase and that the solution becomes shallow, suggesting that water has leached from the solid. This also explains the difficulties we encountered in obtaining reproducible data with these water-rich solids.

These data show clearly that the SAP methodology is well-adapted for the heterogeneization of truly biphasic catalytic systems; the surface of the silica support becomes the interphase surface and is, thus, large (several hundreds of square meters), larger that the values attainable in the liquid phase. Consequently, the activity of the SAP catalyst is sharply enhanced over that of the biphasic equivalent system, the water content of the solid being a critical parameter.

Conclusions. The results obtained for the $Pd(OAc)_2$/5tppts-catalyzed alkylation of ethyl acetoacetate by (*E*)-cinnamyl ethyl carbonate lead to the following comments:

The SAP methodology is well-adapted to the heterogeneization of truly biphasic water/nitrile systems such as H_2O/PhCN: the activity of the SAP catalyst is then superior to that of the biphasic homogeneous system through an increased interphase surface area. With H_2O/CH_3CN, the SAP catalyst always has a lower activity than the same system under homogeneous monophasic conditions.

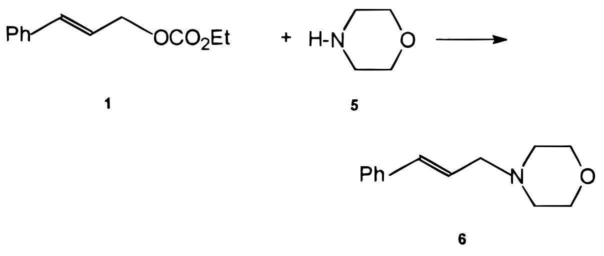
The activity of the SAP catalyst in PhCN is optimum when the water content of the solid is comprised between 30 and 50 wt %; this corresponds, formally, for the silica used, to the amount of water necessary to achieve one-half and full pore filling. Above these quantities of water, non-negligible palladium leaching is observed, hampering recycling of the catalyst.

The selectivity of the catalyst under SAP conditions is much higher than under biphasic (H_2O/PhCN) or monophasic (H_2O/CH_3CN) homogeneous conditions. In the latter case, 50% cinnamyl alcohol is produced by hydrolysis of the carbonate, a reaction favored by the temperature used in these experiments (80 °C) and the presence of large amounts of water (H_2O/nitrile = 1/1).

Although we did not perform, at this stage, any recycling tests of the SAP catalyst, one must mention that the catalytically active species $Pd(tppts)_n$ is more stable when supported on silica than in solution; black particles precipitate under the latter conditions during the course of the catalytic test, while we never observed this on the solid.

Finally, no major differences were oberved between solids **SAP25P** and **SAP50P**, for which we suspected that the initial degree of reduction of Pd(II) to Pd(0) might have been different.

b. Alkylation of Morpholine by (*E*)-Cinnamyl Ethyl Carbonate. With morpholine as the nucleophile (eq 2), we introduce two new parameters which may influence the catalytic properties of the palladium SAP catalysts described here: solubility of one reactant in water and possible interaction of this reactant with the surface of silica. Indeed, adsorption of morpholine, in the gas phase, was successfully used to determine the silanol surface concentration of different silicas: adsorption occurs through hydrogen bonding between the NH moiety of morpholine and the surface hydroxyl groups.[25]



(2)

Influence of the Water Content of SAP25P. Preliminary tests, using CH_3CN as the organic solvent, show clearly a very high activity of **SAP25P** (3 wt % H_2O) catalyst for reaction 2: thus, at 50 °C, with a molar

---

(25) Ettlinger, M.; Ferch, H.; Mathias, J. *Arch. Pharm.* **1987**, *320*, 1.

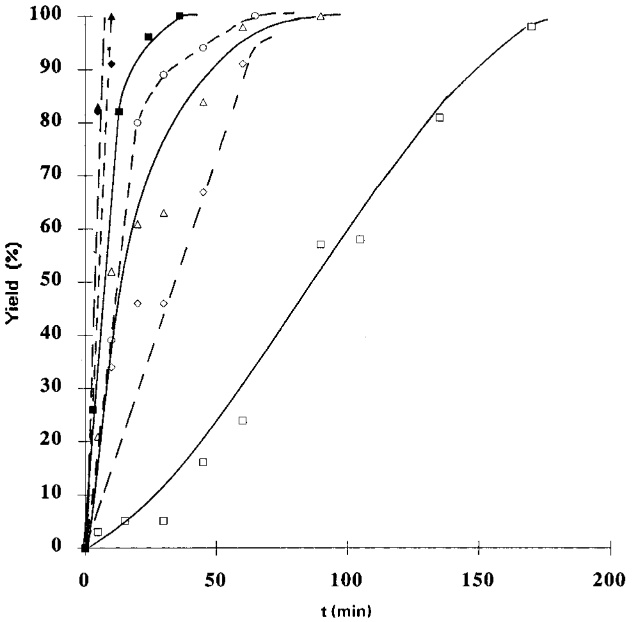


Figure 4. Influence of the water content of solid **SAP25P** (0.76% Pd) on its catalytic properties for the allylic alkylation of morpholine with (*E*)-cinnamyl ethyl carbonate. Evolution with time of the yield of product **6**. Experimental conditions: $m_{\text{cat.}} \approx 200$ mg; $T = 50$ °C, solvent CH_3CN. Water content (wt %): (□) 3; (◇) 13; (△) 22; (○) 31; (■) 51; (◆) 65; (▲) 90.

ratio of [Pd]/[carbonate]/[morpholine] equal to 1/25/30 and a carbonate concentration close to 4.3×10^{-2} mol/L, total carbonate conversion is achieved within 3 h. Although these conditions were not optimized, we used them throughout the whole study. The activity of **SAP25P** is sharply dependent upon the water content of the solid (Figure 4): it increases continuously with increasing amounts of water and reaches the activity of the monophasic CH_3CN/H_2O system for water contents above *ca.* 50 wt %.

The partial solubility of morpholine in water can explain these results: a higher activity overall of both catalytic systems (SAP and homogeneous) for reaction 2 when compared to reaction 1 i.e., lower activity of **SAP25P** when compared to the H_2O/CH_3CN homogeneous system and increased activity with increasing water content of **SAP25P**. It is worth mentioning that with both systems, we observe 100% selectivity for the desired product **6**: no cinnamyl alcohol is formed, a probable result of the lower temperature used (50 °C) in these experiments.

The advantage of the **SAP** catalysts resides in the possibility to recycle them very easily by simple filtration. This assumes, among other criteria, no metal leaching. At the end of the catalytic test performed with **SAP25P** (65 wt % H_2O), the supernatant solution is colorless. The absence of significant leaching of palladium as an active entity is further suggested by the inactivity of this solution toward a new dose of reactants (no detectable transformation after 2 h) and confirmed by analysis of the solution (only *ca.* 0.4% of the introduced palladium was extracted from the solid). The solid itself, after filtration and washing with CH_3CN, was engaged in a second catalytic run. Its activity is significantly lower (Figure 5). This may originate either from a partial degradation of the catalytically active species or from a partial loss of water during the first reaction test and/or during the washing procedure. When considering the latter hypothesis, the activity loss is such that the recycled solid behaves as a solid with a water content comprised of between 3 and 13 wt % water. This latter hypothesis was confirmed on other samples (*vide infra*).

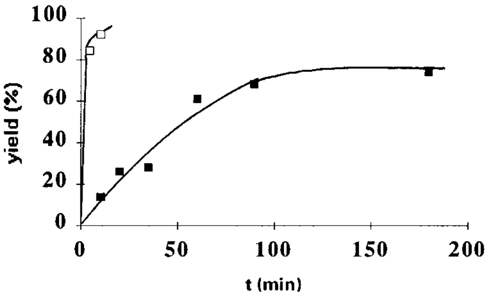


Figure 5. Recycling test for solid **SAP25P** (0.75% Pd, 65 wt % H_2O). Test reaction: alkylation of morpholine with (*E*)-cinnamyl ethyl carbonate. Experimental conditions: $m_{\text{cat.}} \approx 200$ mg, $T = 50$ °C, solvent CH_3CN. (□) first run; (■) second run.

With **SAP25P** (90 wt % H_2O), it is clear from the yellow color of the liquid phase that most of the palladium complex is extracted from the solid. The active palladium species is leaching, and this is confirmed by the catalytic activity of the solution (after the solid had been filtered off): reactants added at the same concentration are totally converted within 35 min. This activity, which is lower than that of the initial solid, may be the result either of only a partial extraction of the catalyst from the solid or of a partial decomposition of the active species.

These data, when taken all together, show that as long as the water content of the **SAP25P** catalyst is below 65 wt %, it is an efficient catalyst for reaction 2; there is no significant palladium leaching. However, a significant drop of the activity is observed after recycling which may be explained by partial leaching of water in acetonitrile.

Influence of the Nature of the Nitrile. If water leaching is the source of catalyst deactivation, then one may expect the phenomenon to be less important with benzonitrile as the solvent. Figure 6 represents the evolution with time of the yield of **6** for solid **SAP25P**, using benzonitrile as the organic phase. It is noteworthy that whatever its water content, **SAP25P** is more active than the same catalytic system under biphasic conditions, despite the solubility of morpholine in water. Remarkably, the activity of **SAP25P** increases continuously with its water content, up to an optimal value of *ca.* 50 wt % H_2O. Above this content, the activity of **SAP25P** decreases significantly. Figure 7 more clearly shows the differences in the catalytic properties of **SAP25P** for reaction 2 induced by the nature of the nitrile.

Preliminary tests of recycling of **SAP25P** (49 wt % H_2O) in PhCN show, nevertheless, that the activity decreases continuously with the number of runs (Table 1). So, after two recyclings, the carbonate conversion has decreased from 100% (after 5 min of reaction) to 33% (after 10 min of reaction). This can be due either to a progressive leaching of palladium in the solution, which is certainly low if one considers that the solution

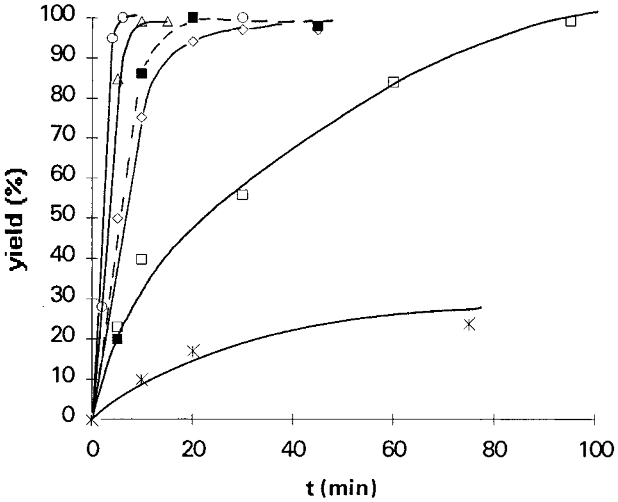


Figure 6. Influence of the water content of solid **SAP25P** (0.76% Pd) on its catalytic properties for the allylic alkylation of morpholine with (*E*)-cinnamyl ethyl carbonate. Evolution with time of the yield of product **6**. Experimental conditions: $m_{cat.} \approx 200$ mg, $T = 50$ °C, solvent PhCN. (□) 2.9%; (◇) 12; (△) 20; (○) 49; (■) 62; (X) under biphasic conditions (H_2O/PhCN = 1/1).

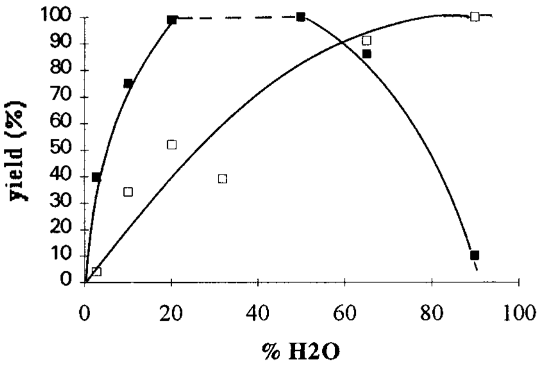


Figure 7. Effect of the nature of the nitrile on the influence of the water content of the solid **SAP25P**. Yield of product **6** after 10 min of reaction. Experimental conditions: $m_{cat.} \approx 200$ mg, $T = 50$ °C. (□) CH_3CN; (■) PhCN.

Table 1. Recycling Tests of Solid SAP25P (49 wt % H_2O) for Reaction 2[a]

run	conv. of **5** (%)	conv. of **1** (%)	yield of **6** (%)	% H_2O[d]
1	95	100	100	0.66
2	61	68	52	0.17
3[b]	33	45	32	0.17
4[c]	90	100	95	n.d.

[a] Experimental conditions: $m_{cat.} = 284$ mg (0.74% Pd), solvent PhCN (anhydrous, 14 mL); [carbonate] = 3.1×10^{-2} mol/L; [morpholine] = 3.7×10^{-2} mol/L; $T = 50$ °C, $t_R = 5$ min, except where indicated. [b] $t_R = 10$ min; [c]256 μL of H_2O added. [d] Water content of the catalytic solution at the end of the catalytic test.

remains colorless, or a progressive degradation of the active species, and/or a progressive loss of water. Analysis of the water content of the catalytic solution at the end of the catalytic test (run 1) clearly shows that water loss is one of the reasons for the progressive catalyst deactivation. This is further confirmed by complete recovery of the activity by simple addition of water (in the solution of reactants) (run 4, Table 1).

Although the activity of the same solid **SAP25P** is much lower when it has a low water content, we though it might be easier to recycle. Table 2 shows the results obtained with **SAP25P** (2.3 wt % H_2O). Clearly, the drop in activity is less important with this low water-containing solid. Nevertheless, it is still too high to be viable. We then attempted to introduce water *via* the solvent at each step of the recycling process; we used nonanhydrous PhCN (wt % H_2O = 0.05). Interestingly, the solid **SAP25P** (2.3 wt % H_2O) is more active already for the first run; thus, total carbonate conversion is reached after 1 h of reaction (Table 3) *versus* 1.5 h when anhydrous PhCN was used (Table 2), suggesting that water is transferred from the solvent onto silica. Yet activity decreases run after run, suggesting that the water concentration in PhCN is not optimum.

Table 2. Recycling Tests for Catalyst SAP25P (2.3 wt % H_2O)[a]

run	conv. of **5** (%)	conv. of **1** (%)	yield of **6** (%)
1	100	100	97
2	100	92	100
4	70	68	65
5[b]	89	97	100
6	77	68	73

[a] Experimental conditions: $m_{cat.} = 358$ mg (0.76% Pd), solvent PhCN (anhydrous, 18 mL), $t_R = 90$ min; [carbonate] = 3.09×10^{-2} mol/L; [morpholine] = 3.72×10^{-2} mol/L; $T = 50$ °C. Between two runs, the solid is filtered and washed twice with 6 mL of anhydrous PhCN. [b] Addition of 10 μL of H_2O.

Table 3. Recycling Tests for SAP25P (2.3 wt % H_2O). Influence of the Water Content of the Solvent[a]

run	conv. of **5** (%)	conv. of **1** (%)	yield of **6** (%)
1	100	98	100
2	89	83	85
3	81	78	77
4	73	71	65

[a] Experimental conditions: $m_{cat.} = 384$ mg (0.76% Pd), solvent PhCN (18 mL, 0.05% H_2O); [carbonate] = 3.24×10^{-2} mol/L, [morpholine] = 3.85×10^{-2} mol/L, $T = 50$ °C, $t_R = 60$ min. Between two runs, the solid is filtered and washed twice with 6 mL of PhCN.

In conclusion, the major problem encountered with the SAP catalysts is not the palladium leaching but the water leaching, a problem which can only be solved by an extensive study of the partition function of water between the silica-supported palladium catalyst and benzonitrile. This study is currently under investigation. One cannot totally discard some loss of solid during the recycling procedure itself, which would also lead to a drop of activity.

Influence of the Porosity of Silica. Figure 8 allows for a comparison of the catalytic properties of two **SAP25** catalysts prepared using either a porous silica, **SAP25P**, or a nonporous silica, **SAP25NP**, as a support. Both silicas have similar specific surfaces. The test reaction is the alkylation of morpholine with (*E*)-cinnamyl ethyl carbonate using benzonitrile as the solvent. The influence of the water content of these solids on their activity is very similar: the yield of product **6** (the only product obtained) increases with the water content until a value of 32 wt % H_2O. A difference in the behavior of the two catalysts is only detected for water contents above 50 wt %. This amount corresponds to that necessary for achieving full pore filling of silica P. For the nonporous silica, the activity decreases only slightly above this value (Figure 8). It is, thus, not obvious that porosity is the effective

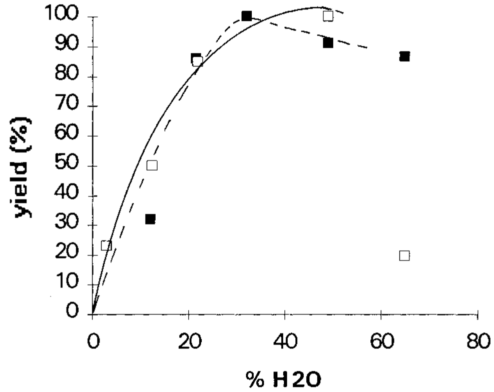


Figure 8. Influence of the nature of the silica support on the behavior of **SAP25** catalysts with different water contents. Test reaction: allylic alkylation of morpholine with (*E*)-cinnamyl ethyl carbonate. Experimental conditions: $m_{\mathrm{cat.}} \approx 200$ mg, $T = 50$ °C, solvent PhCN. (□) porous silica; (■) non porous silica.

working parameter; it may simply be the wetting volume. Similarly, the analysis of the catalytic solution at the end of the first catalytic run performed with solids **SAP25NP** ($3 <$ wt % $H_2O < 65$) evidences water leaching, in quantities close to those observed with **SAP25P**. Simultaneously, no significant palladium leaching could be detected (<0.06% of palladium introduced). These data suggest that when the water content is below *ca.* 50 wt %, no major effect of the porosity of the silica can be detected. Above this content, a number of problems arise which lead to an overall decrease of the activity and to nonrecyclable catalysts (water and Pd leaching).

Conclusions. The supported aqueous phase catalysts described here were synthesized by immobilization on silica of the *in-situ*-generated catalyst $Pd(OAc)_2$/5tppts. They are active for nucleophilic allylic substitution. Their performance clearly depends upon the water content of the solid, a parameter which may *a priori* intervene at different levels, such as the rate of the reaction of reduction of Pd(II) to Pd(0) and the nature of the interaction between the complex(es) and the silica. We have, therefore, attempted to characterize the surface species.

2. Characterization of the Catalysts by ^{31}P NMR Spectroscopy. The different supported catalysts were prepared from aqueous solutions of the precursors ($Pd(OAc)_2$ and tppts) kept at 25 or 50 °C for a given time before contact with silica. The nature of the initial surface species may, thus, differ from one sample to the other; this and the possible evolution of these species in the presence of different amounts of water and/or of the organic solvent may influence the catalytic properties of the SAP solids. ^{31}P NMR spectroscopy was used for the identification of the different species present during the course of the synthesis of the catalysts.

Reaction of $Pd(OAc)_2$ with tppts in Water. From cyclic voltammetry and/or ^{31}P NMR spectroscopic data,[24,26,27] it was shown that the reduction of Pd(II), in $Pd(OAc)_2$ or $PdCl_2$, to Pd(0) occurred in a two-step process involving the fast formation of a Pd(II) adduct, $Pd(OAc)_2L_2$, followed by the intramolecular reduction of Pd(II) to Pd(0) stabilized by phosphine ligands, with concomitant formation of phosphine oxide; the reduction step is the rate-determining step. The same mechanism is certainly operating when the phosphine is water soluble, such as tppts.[28-30] The precise nature of the Pd(0) complex is dependent on the L/Pd ratio and the kinetics of the reduction on the reaction medium (acetonitrile/water or water).

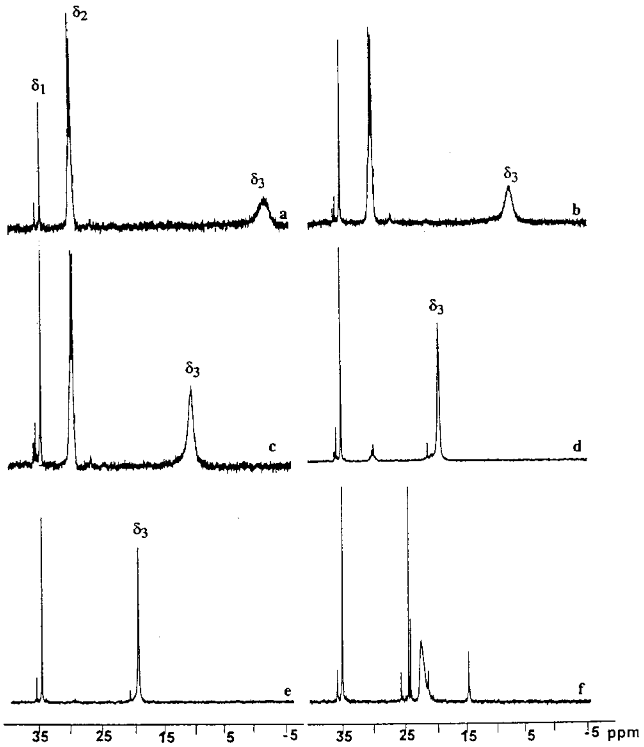


Figure 9. Evolution with time of the ^{31}P NMR spectrum of $Pd(OAc)_2$/5tppts in D_2O at 25 °C. (a) 3 min; (b) 45 min; (c) 85 min; (d) 48 h; (e) 1 week; (f) 1 week + PhI.

The different SAP catalysts were prepared from aqueous solutions kept either at 25 or at 50 °C for *ca.* 1 h before impregnation of silica. Figure 9 represents the evolution with time of the ^{31}P spectrum of a solution $Pd(OAc)_2$/5tppts in D_2O at room temperature. In agreement with the previously reported data,[30] the immediate formation of tppts oxide (Otppts), characterized by a single sharp peak at δ_1 34.6 ppm, and of $Pd(OAc)_2(tppts)_2$, characterized by a broad signal centered at δ_2 29.5 ppm, is detected. Simultaneously, a broad weak signal is observed at δ_3 *ca.* −2 ppm, but no peak corresponding to free tppts at δ −5.6 ppm is observed. This spectrum changes with time; the main features are the intensity decrease of δ_2 and increase of δ_1 and δ_3. This latter peak is simultaneously shifted to lower fields and becomes sharper (Figure 9, a−e). After 24 h, this δ_3 peak is at 18.6 ppm and δ_2 has vanished. No significant evolution is detected over 1 week, suggesting that the complex characterized by δ_3 is stable in water under N_2. It is a complex of Pd(0): indeed, addition of an excess of PhI suppresses δ_3 and new peaks appear

---

(26) Amatore, Ch.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009.

(27) Ozawa, F.; Kubo, A.; Hayashi, T. *Chem. Lett.* **1992**, 2177.

(28) Monteil, F.; Kalck, Ph. *J. Organomet. Chem.* **1994**, *482*, 45.

(29) Papadogianakis, G.; Peters, J. A.; Maat, L.; Sheldon, R. A. *J. Chem. Soc. Chem. Commun.* **1995**, 1105.

(30) Amatore, C.; Blart, E.; Genêt, J. P.; Jutand, A.; Lemaire-Audoire, S.; Savignac, M. *J. Org. Chem.* **1995**, *60*, 6829.

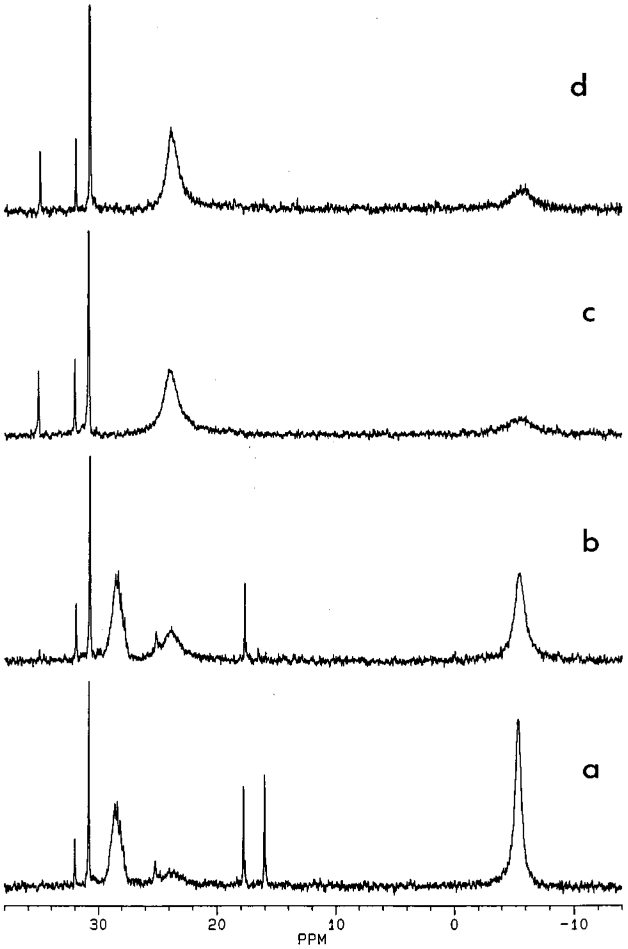


Figure 10. Evolution with time and temperature of the ^{31}P NMR spectrum of $Pd(OAc)_2/5tppts$ in ethylene glycol. (a) 10 min at 20 °C; (b) 1 h at 20 °C; (c) 1.5 h at 20 °C then 15 min at 25 °C and 10 min at 20 °C; (d) 15 °C.

at δ 23.7, 23.4, 21.6, 20.5, and 14.0 ppm. By comparison with published data,[26,28] the peak at δ 23.7 ppm may be attributed to the formation of the complex $PhPdI(tppts)_2$ resulting from the oxidative addition of PhI on a Pd(0) complex $Pd(tppts)_n$. Substitution of the iodide ligand by an acetate ligand would lead to $PhPd(OAc)(tppts)_2$.

The time-dependent behavior of the δ_3 peak has been attributed to a fast exchange between PdL_3, PdL_2, and free L.[26,28,30] In order to check this hypothesis, we replaced D_2O by a more viscous solvent, ethylene glycol; this considerably slows down the rate of the exchange process (Figure 10). Interestingly, one can now observe two broad signals at δ 23.4 and −5.6 ppm, attributed to $Pd(tppts)_3$ and free tppts (from the spectra of authentic samples), along with the signals at δ 28.5 ($Pd(OAc)_2(tppts)_2$) and 30.8 ppm (Otppts). With time, only the relative intensity of these peak changes but not their chemical shift (Figure 10, a and b). As expected, the reduction process is accelerated at higher temperatures; thus, after 15 min at 45 °C, total reduction is achieved (no peak at δ 28.4 ppm); the integrated intensity ratio of the peaks at δ 23.5 and −5.6 ppm is close to 3/1, in agreement with the occurrence of reaction 3. When the

$$Pd(OAc)_2 \xrightarrow{tppts} Pd(OAc)_2(tppts)_2$$

solution is cooled down to 15 °C (Figure 10c), the two

$$Pd(OAc)_2(tppts)_2 \xrightarrow{tppts} Pd(tppts)_3 + Otppts \quad (3)$$

signals at δ 23.8 and −5.6 ppm become sharper, in agreement with a lower exchange rate. These data are strongly in favor of a process of exchange between free tppts and tppts coordinated to Pd(0) (in $Pd(tppts)_3$). This process is much faster in water than in ethylene glycol, as evidenced by the coalescence at room temperature of the two related signals in the former solvent. The displacement of the δ_3 signal to lower fields indicates the progressive increase of the concentration of tppts coordinated to Pd(0) relative to that of free tppts and, thus, the progressive reduction of Pd(II) to Pd(0) (yet more clearly evidenced by the intensity decrease of the δ_2 peak, $Pd(OAc)_2(tppts)_2$).

In conclusion, the reduction of $Pd(OAc)_2$ with *ca.* 5 equiv of tppts in water is a slow reaction at room temperature: after 24 h, the reduction of Pd(II) to Pd(0) is achieved to an extent of *ca.* 80%. Among the 4.6 equiv of tppts introduced per 1 equiv of Pd, *ca.* 1 equiv is oxidized to Otppts, 0.3 equiv are free, and the remaining are coordinated to Pd(0) and Pd(II).[31] A fast exchange between free and Pd(0)-coordinated tppts is observed, which explains the time-dependent shift of the δ_3 peak from −2 to 19 ppm as the concentration of $Pd(tppts)_3$ increases. Thus, under the conditions of the synthesis of solid **SAP25**, $Pd(OAc)_2(tppts)_2$ is the major species present in solution just before contact with silica: roughly 20% of the palladium is reduced to Pd(0).

When the same reaction is performed at 50 °C, the reduction of Pd(II) to Pd(0) is as expected, much faster: the reaction is completed after *ca.* 40 min (Figure 11). Qualitatively, the spectrum of the solution changes, as observed at room temperature, and the final spectrum presents two peaks at δ 34.6 (δ_1) and 17.8 ppm (δ_3). The broadness of the signal and the value of the chemical shift of the latter when compared to the peak of pure $Pd(tppts)_3$ in D_2O (δ 22.6 ppm) are in agreeement with a fast exchange between palladium-coordinated tppts and free tppts. Roughly, among the 4.6 equiv of tppts introduced per palladium, 1.3 equiv is oxidized to Otppts, 3 equiv is coordinated to Pd(0) (all Pd(II) is reduced), and 0.25 equiv remain free in solution. The conditions of the synthesis of **SAP50** are, thus, such that $Pd(0)(tppts)_3$ is the major Pd species deposited on the surface of silica.

In light of these experiments, it is, thus, clear that the two solids **SAP25P** and **SAP50P** may differ strongly by their initial concentration of reduced palladium Pd(0). In order to understand the effect of parameters such as the water content on their catalytic properties, we analyzed them by solid-state ^{31}P MAS NMR spectroscopy.

Influence of the Water Content on the ^{31}P MAS NMR Spectrum of SAP25 Solids. Preliminary ex-

---

(31) The relative amount of each type of phosphine L present in the sample, i.e., oxidized, coordinated to Pd(0), and free is deduced from the integrated peak intensities in the ^{31}P NMR spectrum. We assume that Pd is present in solution only as $Pd(OAc)_2L_2$ and PdL_3. The quality of the fit (agreement between % Pd(0) deduced from the peak at 29 ppm and that deduced from PdL_3) gives a rough estimation of the validity of this assumption. The amount of free L is calculated by considering that the chemical shift of the peak δ_3 is the weighted average of the peak characteristic of PdL_3 at δ 23.5 ppm and the peak characteristic of free L at δ −5.6 ppm.

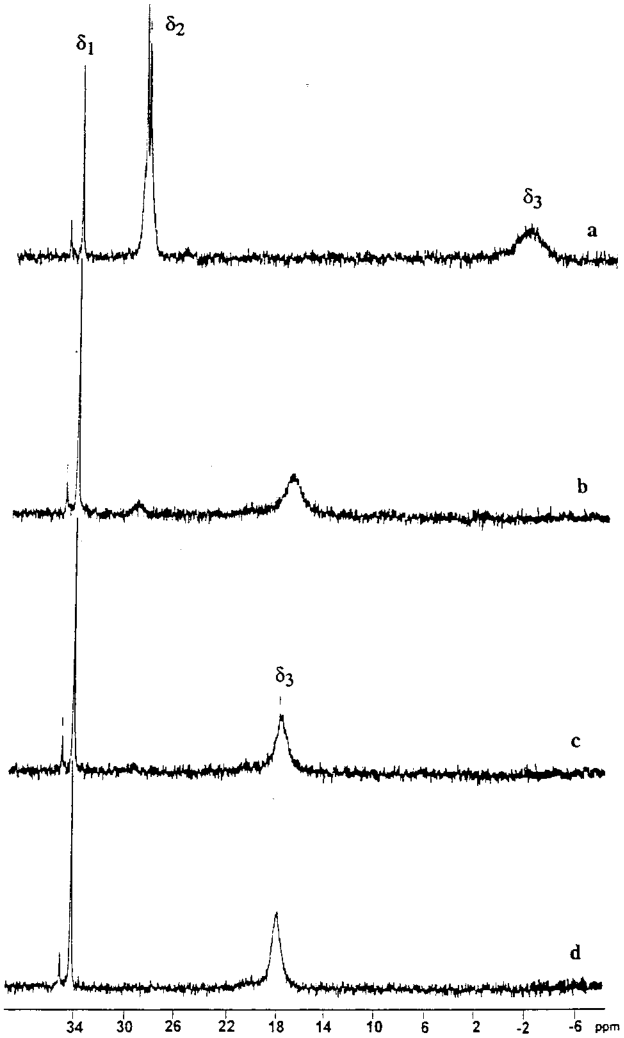


Figure 11. Evolution with time of the ^{31}P NMR spectrum of Pd(OAc)$_2$/5tppts in D_2O at 50 °C. (a) 3 min at 25 °C, then heating at 50 °C for (b) 23 min, (c) 41 min, and (d) 1.5 h.

periments performed on three **SAP25P** solids, differing by their water content, clearly show the increased mobility of the phosphinated surface complexes with increasing water amount. Thus, with water contents lower than 15 wt %, the spectra are very broad (Figure 12), avoiding identification of the surface phosphinated species. With a H_2O content of 23 wt %, the spectrum is very close to the solution spectra (Figure 12c).

When this latter sample of **SAP25P** (23 wt % H_2O) is heated at 80 °C, one observes a sharp decrease of the intensity of the δ_2 peak at 29 ppm and a low-field shift of the δ_3 (Figure 13). Within less than 15 h, almost all Pd(II) is reduced to Pd(0) and the peak characterizing the rapidly exchanging system (Pd(tppts)$_3$ + tppts) is at δ 19.9 ppm. The presence of a weak shoulder near δ 23 ppm and of a small peak near δ 0 ppm suggests that a small fraction of tppts is not concerned by the exchange process.

When a **SAP25P** (3 wt % H_2O) is heated at 80 °C (Figure 14A, a−d), no evolution of the spectrum can be detected due to the broadness of the signals. The broad signal near δ 0.5 ppm could be identified as tppts interacting directly with the surface of silica (Figure 15). The interaction is a weak one, most probably a hydrogen-type bonding either with the sulfonyl group or directly

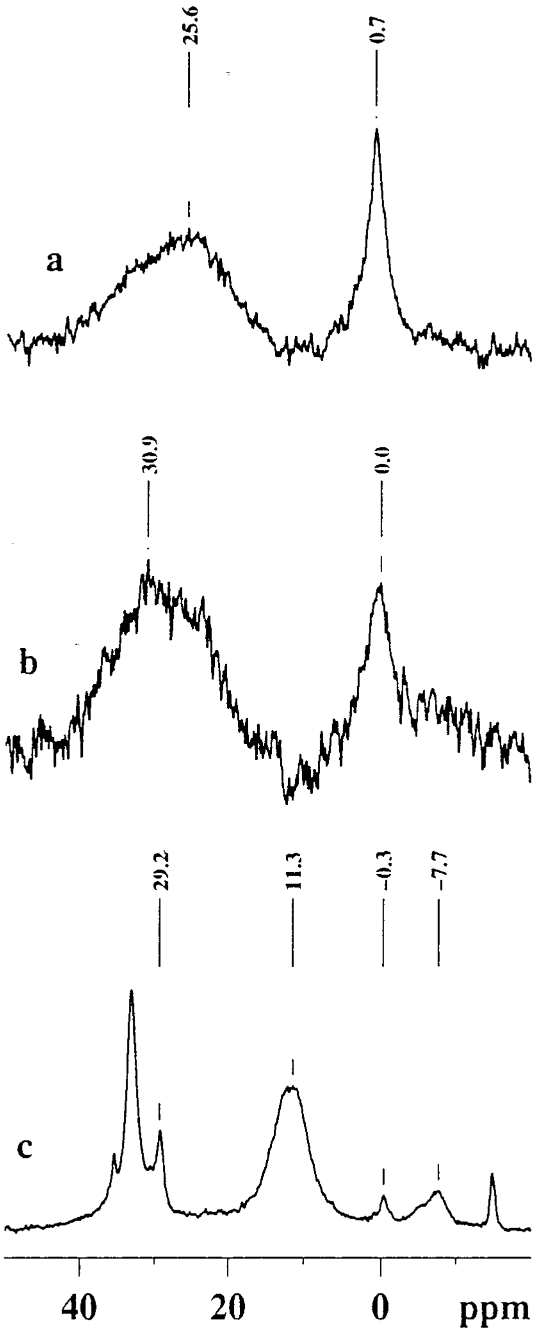


Figure 12. Influence of the water content (wt %) of solid **SAP25P** on the ^{31}P MAS NMR spectrum. (a) 3%; (b) 13%; (c) 23%.

with the phosphorus atom. It is broken by water (Figure 15b). In order to get some insight into the "kinetics" of the surface chemistry, we introduced, directly in the rotor and just before recording the spectrum, a small amount of water to the sample so as to render the species mobile enough for observation of sharper signals; we have checked that this procedure does not significantly disturb the kinetics of the reduction of Pd(II) into Pd(0) species. Figure 14B corresponds to the spectra shown in Figure 14A with added water (heating is performed on the 3.3 wt % H_2O sample). Reduction of Pd(II) to Pd(0) is clearly a slow process. Thus, initially, *ca.* 70% of Pd is reduced while among the 5 equiv of tppts per Pd introduced, 1.7 equiv is oxidized to Otppts and 0.3 equiv is free. After 24 h at

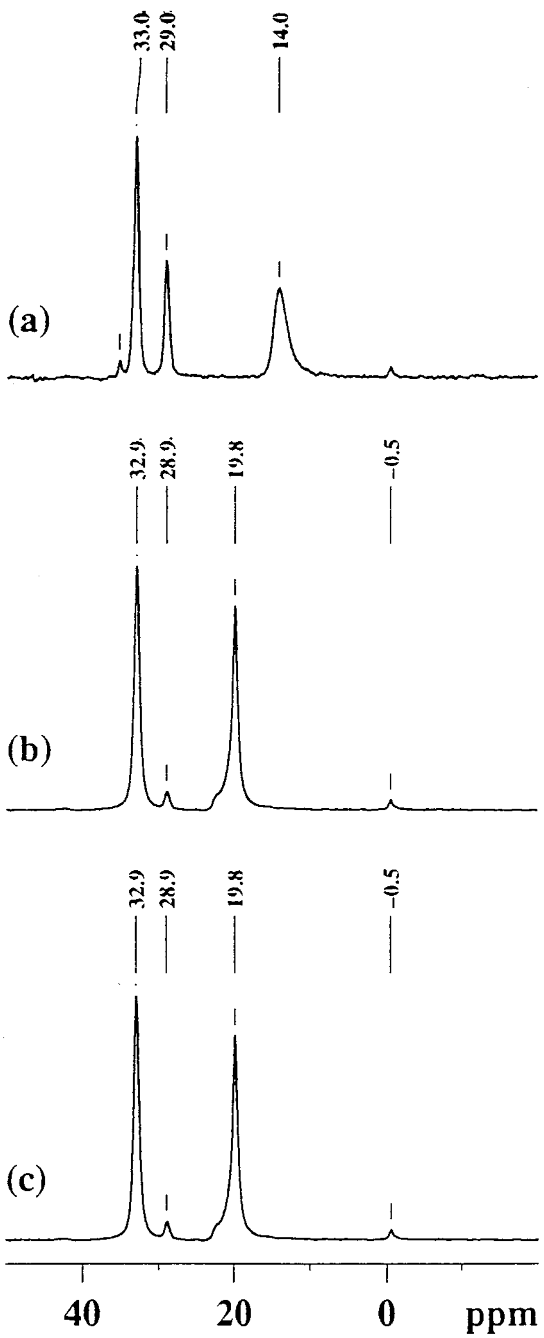


Figure 13. Evolution with time of the ^{31}P MAS NMR spectrum of solid **SAP25P** (23 wt % H_2O) maintained at 80 °C for (a) 2h; (b) 15 h; (c) 62 h.

90 °C, 80% of the Pd(II) is reduced while 1.9 equiv of tppts is oxidized and 0.3 equiv remain free.

Clearly, when the solid has a low water content, the degree of reduction of palladium does not change and is close to 80%. Thus, during the time the solution [Pd(OAc)$_2$/5tppts/H_2O] is prepared and then poured onto silica and the water removed, the degree of reduction gets close to 80%. Thus, when the catalytic test is started, most of the Pd is present as complex Pd(tppts)$_3$, the species generally accepted as the active species.

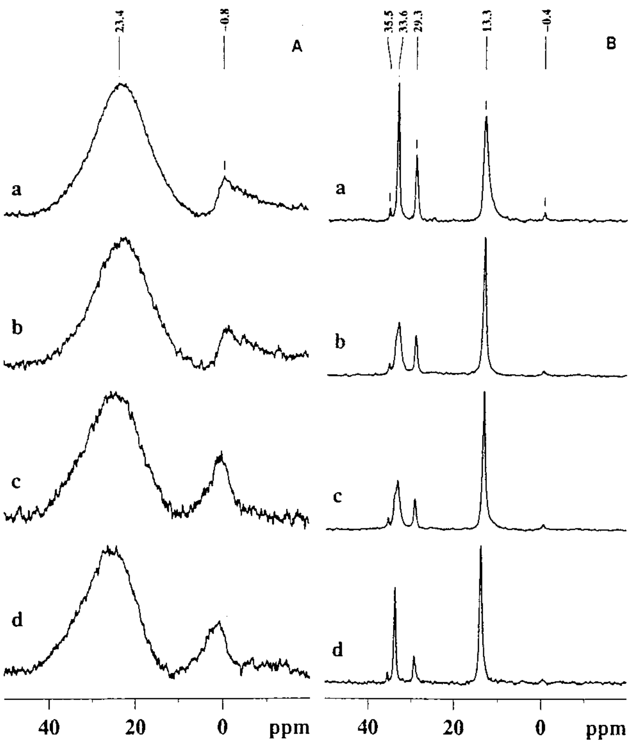


Figure 14. Evolution with time of the ^{31}P MAS NMR spectrum of solid **SAP25P** (3 wt % H_2O) maintained at 80 °C for (a) 0 h; (b) 3 h; (c) 6 h; (d) 24 h. (A) without added water; (B) after addition of water prior to spectrum recording.

Treatment of solid **SAP25** (3 wt % H_2O), suspended in acetonitrile at 80 °C for 3 h, has no significant effect on the degree of reduction but favors oxidation of tppts to an extent, in some cases, that no free tppts is present: then one observes a peak δ_3 at δ 22.2 ppm, characteristic of pure Pd(tppts)$_3$.

When the catalyst is synthesized by contacting silica with an aqueous solution of Pd(OAc)$_2$/5tppts preheated at 50 °C for 1 h (**SAP50P**), the surface complex is, as expected, essentially Pd(tppts)$_3$ (Figure 16), even when the water content of the solid is low (spectrum b is recorded after the addition of water prior to spectrum recording). Roughly 80% of Pd is reduced. Again, the amount of Otppts is larger than expected from eq 3 so that under the conditions used no tppts remains free on the solid.

Discussion. Under the operating conditions i.e., impregnation of silica with an aqueous solution of Pd(OAc)$_2$ and 5 equiv of tppts prepared at 25 °C, despite the low rate of reduction of Pd(II) by tppts, most of the palladium introduced as Pd(II) is reduced at the beginning of the catalytic test (≥80%). This explains *inter alia* the observation of only negligible differences between the catalytic properties of solids **SAP25** and **SAP50**. The complex formed, Pd(tppts)$_3$, is characterized by a peak whose chemical shift depends on the amount of free tppts present; an exchange occurs between free and coordinated tppts in aqueous solution and on the surface of the solids with more than *ca.* 20% H_2O. This exchange process does not involve the intermediate complex Pd(OAc)$_2$(tppts)$_2$ nor any other species such as Pd(0)(tppts)$_n$ ($n = 2, 4$). On silica with low water content, the mobility of the Pd complex is restricted but no specific interaction could be evidenced by ^{31}P NMR spectroscopy. The free phosphine interacts with the surface under these latter conditions, likely through hydrogen bonds between the surface silanol

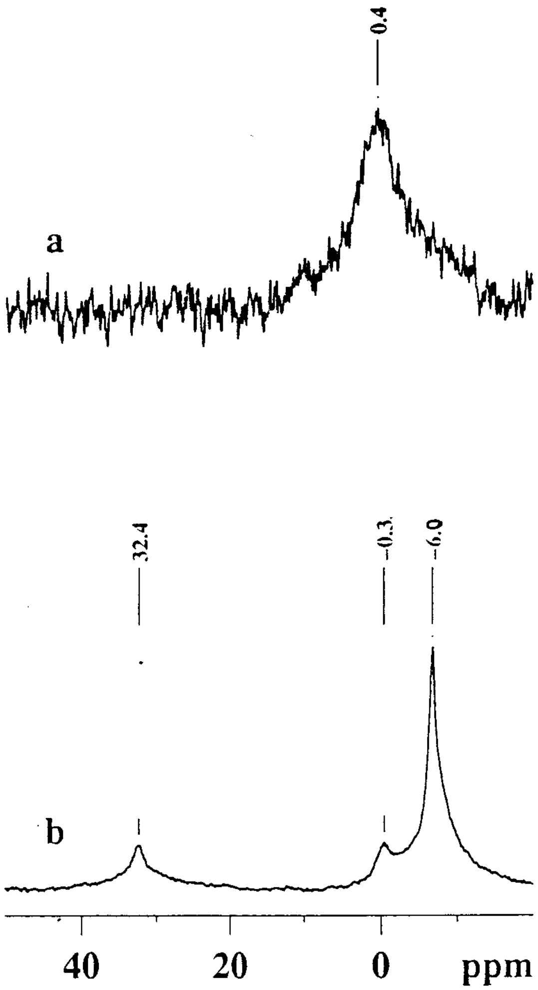


Figure 15. ^{31}P MAS NMR spectra of tppts/silica P (3% D_2O) (a) kept under dry N_2; (b) left under air for 1 h.

groups and either oxygen from the sulfonyl groups or directly with phosphorus.

Conclusions

The deposition of the *in-situ*-generated catalyst Pd-$(OAc)_2$/tppts on silica *via* the wet impregnation method using water as the solvent led us to obtain a molecular heterogeneous catalyst, which is active for allylic alkylation (Trost−Tsuji reaction). A number of parameters which govern the catalytic properties and the recyclability of this catalytic system were identified: water content of the solid, degree of miscibility of water and nitrile, and solubility of the reactants in water. For this reaction, mesoporosity of silica is not required but the optimum amount of water seems to be a subtle compromise between the mobility of the complex, solubilization of the reactants, and leaching (of water essentially) into the organic phase. Chemical engineering studies are currently under way in order to more precisely estimate the potential of this method of heterogeneization of homogeneous catalysts for future industrial applications.

Experimental Section

Reagents. Acetonitrile and benzonitrile were purchased anhydrous from Aldrich and used without further purification.

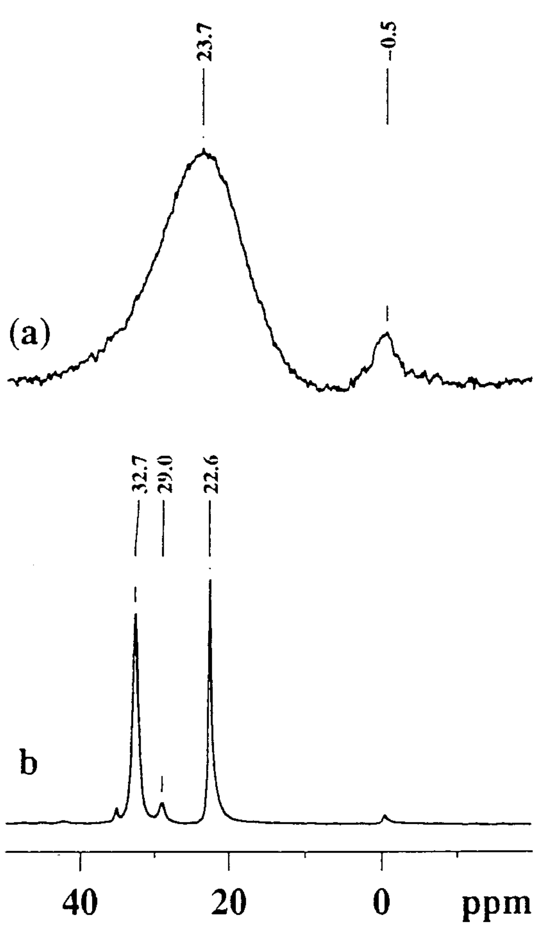


Figure 16. ^{31}P MAS NMR spectrum of solid **SAP50P** (3 wt % H_2O) (a) as such; (b) after addition of water prior to spectrum recording.

Morpholine was purchased from Fluka, purified by distillation, and stored over molecular sieves. Ethyl acetoacetate was purchased from Fluka and used as received.

(*E*)-Cinnamyl ethyl carbonate, (*E*)-2-acetyl-5-phenylpent-4-enoic acid ethyl ester, and *N*-cinnamylmorpholine were synthesized according to published methods[32−34] and characterized by their IR and ^1H NMR spectra.

Silica P (generous gift from GRACE) is a high surface area (S_{BET} = 185 m^2/g), hydrophilic mesoporous silica, with a narrow pore size distribution (∅ = 24 nm). The pore volume, as determined by adsorption of N_2 at 77 K, is equal to 1.2 mL/g. The wetting volume is 3 mL/g. Silica NP is a nonporous Aerosil silica from Degussa (S_{BET} = 200 m^2/g)

Synthesis of the SAP Catalysts. The SAP catalysts are synthesized by the incipient wetness method. In a typical experiment, $Pd(OAc)_2$ (21 mg, 0.094 mmol) and tppts·$3H_2O$ (293 mg, 0.47 mmol) are degassed by freeze-thaw cycles and then dissolved in deaerated H_2O (3 mL) in a Schlenk tube under argon; the solution is stirred for 1.5 h at ambient temperature. Silica (1 g), pretreated under vacuum (250 °C, 10^{-4} Torr, 6 h), is then added to this solution, and the wet solid is stirred for 2 h. Water is then evacuated (10^{-1} Torr, 30 min, then until a vacuum of *ca.* 10^{-4} Torr is obtained). A dry, yellow powder is obtained. This solid is kept under Ar prior to use. This procedure allows one to obtain, in a reproducible way, a solid with a water content close to 3 wt % (as determined by TGA). Elemental analysis of the solid: Pd = 0.76 wt %.

---

(32) Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341.
(33) Cuvigny, T.; Julia, M. *J. Organomet. Chem.* **1987**, *331*, 121.
(34) Bergbreiter, D. E.; Weatherford, D. A. *J. Org. Chem.* **1989**, *54*, 2726.

SAP25 and **SAP50** catalysts differ by the temperature at which the solution of $Pd(OAc)_2/5tppts$ in water is maintained before impregnating silica; for the first one, the solution is kept at 25 °C for 1.5 h; for the second, it is maintained at 50 °C for 1 h.

These preparations were carried out with either the porous silica from Grace (the solids are then referred to as **SAP25P** and **SAP50P**) or the nonporous silica from Degussa (the solids are then referred to as **SAP25NP** or **SAP50NP**).

Catalytic Tests. All catalytic tests were performed under N_2 (passed over molecular sieves and a deoxo catalyst).

Tests in Biphasic Medium, Water/Nitrile. In a typical experiment, $Pd(OAc)_2$ (8.2 mg, 3.66×10^{-2} mmol) and tppts·$3H_2O$ (114 mg, 0.18 mmol) are placed in a two-necked round-bottomed flask equipped with a condenser and a septum and degassed by successsive freeze−thaw cycles. Degassed water (15 mL) is then added, and the solution is magnetically stirred at ambient temperature for 1 h. (*E*)-cinnamyl ethyl carbonate (175 μL, 0.91 mmol), and ethyl acetoacetate (140 μL, 1.1 mmol) in CH_3CN (15 mL) are then added *via* a syringe to the aqueous solution. The solution is then brought to 80 °C. The course of the reaction is followed by GPC for the time necessary to reach full reactant conversion (or 24 h).

Test under SAP Conditions. Typically, the "dry" catalytic solid (200 mg) is transferred in a two-necked round-bottomed flask equipped with a condenser and a septum. The water content of the solid is adjusted by introduction of deaerated water via a syringe on the solid: magnetic stirring is maintained for 0.5 h in order to disperse water homogeneously on the solid. Typically, 22 (10 wt %) to 365 μL (65 wt %) of water is introduced. Simultaneously, the nucleophile (3.6 mmol, 30 equiv) and (*E*)-cinnamyl ethyl carbonate (3 mmol, 25 equiv) are dissolved in the nitrile (6 mL) in a Schlenk tube under argon. This solution is then transferred onto silica *via* a syringe, and the reaction mixture is brought to the desired temperature (preheated oil bath) under mechanical stirring, maintained at the same speed for all experiments.

Analytical samples (0.2 mL) are removed during the course of the reaction. When the reaction was performed at 80 °C, the reactor was first rapidly cooled in a water/ice bath in order to condense the solvent in the flask. The samples were analyzed by GPC after addition of an internal standard (geraniol, 1 μL). The reactant conversion and product yield were determined from standard curves established using authentic samples. The nucleophile conversion is given taking into account the stoichiometry of the reaction.

Physical Techniques. Thermal Differential Analysis. The solids were analyzed by DTA−TGA on a SETARAM TGA 92 apparatus: the water content of the SAP catalysts was deduced from analysis of the weight loss between 25 and 130 °C (5 °C/min) under N_2, in this temperature range, only water is eliminated.

Elemental Analysis. The Pd content of the solids was determined by ICP, after acid attack of the solid with HF, followed by HCl. The Pd content in the organic solutions was determined after evaporation of the solvent to dryness, calcination of the residue, and dissolution in aqueous HCl.

Gas-Phase Chromatography. The catalytic reaction solutions were analyzed by GPC on a INTERSMAT IGC 120FL, equipped with a capillary column, Quadrex Q2 ($l = 15$ m, i.d. = 0.32 mm). Conditions: $p(N_2) = 0.6$ bar, $p(H_2) = 1.2$ bar; $T_{inj} = T_{det} = 210$ °C; $T_{oven} = 70-250$ °C.

NMR Spectroscopy. Liquid-phase ^{31}P NMR spectroscopy was performed on a Bruker AC 200 spectrometer (81 MHz) calibrated with H_3PO_4 as the external standard. Solid-state ^{31}P NMR spectra were recorded at room temperature on a Bruker DSX 400 spectrometer equipped with a commercial 5 mm MAS probe. The working frequency was 161.99 MHz, and without specific indications, the spinning rate of the sample was 12 kHz. The repetition rate was 0.2 Hz, and the line broadening was set to be 30 MHz. H_3PO_4 was used as the external standard. The samples were transferred in the rotor in a dry glovebox under N_2.

OM970729P