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# Bifunctional Phosphines Immobilized on Inorganic Oxides

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The bifunctional phosphine $Ph_2P(CH_2)_3Si(OEt)_3$ has been immobilized on MgO, $TiO_2$, $Al_2O_3$, and $SiO_2$ surfaces. The materials were studied by $^{27}$Al MAS, $^{29}$Si CP/MAS, $^{31}$P CP/MAS, and $^{31}$P suspension NMR spectroscopy. MgO and $TiO_2$ cannot bind the phosphine strongly, so persistent leaching occurs. $Al_2O_3$ was applied in the basic, neutral, and acidic versions. All of them needed extensive washing, and leaching of the phosphine was found for acidic $Al_2O_3$. With alumina and silica as the supports, the half-widths and chemical shifts of the $^{31}$P suspension NMR signals of the phosphine have been determined in order to investigate the mobilities of the phosphine moieties. Hereby the surface coverages, suspension media, acidities, and pore diameters have been varied. While the pore diameters (40−100 Å) and acidities have practically no influence on the signal line widths, increasing surface coverage leads to narrower lines for all supports. This was interpreted as the result of brush-type rather than blanket-type arrangement of the phosphine molecules, when their packing on the surface gets denser. With respect to leaching and convenience of handling, $SiO_2$ turned out to be the most favorable support for immobilizing phosphines.

## Introduction

Bifunctional phosphines are very important ligands for immobilizing catalysts on oxidic inorganic supports.[1−3] Immobilized catalysts, in turn, are of commercial as well as academic interest, because they can combine the advantages of homogeneous and heterogeneous catalysts.[4−7] The classical analytical method for studying these amorphous materials is solid-state NMR.[1−3,7−9] Herewith, for example, the immobilization process could be studied[10−12] and optimized,[8] and the formation of side products prevented.[1] However, based on Yesinowski's pioneering work on suspension NMR of modified hydroxyapatite powders,[13] this easy and practical method[14] becomes more and more popular among chemists in various fields of surface chemistry: It is applicable for example to mineral lyotropic liquid crystals such as $V_2O_5$ aqueous suspensions[15] or to clay suspensions.[16,17] Recently, it has also successfully been used for studying glycidoxypropyltrimethoxysilane-modified colloidal silica coatings[18] and stationary phases for reversed phase chromatography.[14] Even silica-immobilized phosphines and catalysts can now be investigated under realistic conditions in the presence of solvents by suspension NMR.[14,19] In the work presented here, we investigate the properties of various inorganic oxides as support materials. Using multinuclear CP/MAS and $^{31}$P suspension NMR spectroscopy as analytical tools, we investigated whether the bifunctional phosphine $Ph_2P(CH_2)_3$-$Si(OEt)_3$ (**1**) can be immobilized cleanly and how strong the covalent bonding to the corresponding support is. Since one of our future goals will be to correlate the mobility of the surface species with catalytic activity, we studied the line widths of the $^{31}$P suspension NMR signals. As could be shown previously,[14] the narrower the lines, the more mobile is, for example, the phosphine moiety of an immobilized phosphine, because anisotropic linebroadening effects such as chemical shift anisotropy or dipolar interactions are averaged out more efficiently. In the case of $Al_2O_3$, the surface acidity has been varied, as well as the surface coverage and the solvent. For silica, additionally the effect of changing the pore diameter has been studied.

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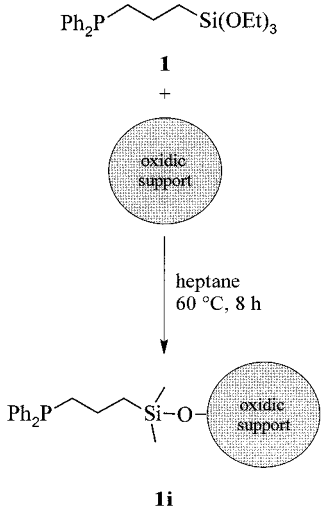
**Scheme 1. Immobilization of 1 on the Oxidic Supports MgO, $TiO_2$, $Al_2O_3$, and $SiO_2$ to give 1i**



## Results and Discussion

**1. What is the Best Oxidic Support?** Heterogeneous catalysis makes use of all sorts of inorganic oxides and ceramic materials. However, for immobilized catalysts the most popular support materials are polymers on one hand and silica as an oxidic support on the other. As compared to polymers, silica has the advantage that in organic solvents it is chemically and thermally inert, mechanically stable and robust, and inexpensive, and suppliers offer a large variety of silica with different pore diameter and particle size distributions. The question, however, is now why other oxidic materials such as titania, magnesia, or alumina have never become as popular with immobilized catalysts as with heterogeneous ones. Therefore, we took a closer look at phosphine **1**, immobilized on MgO, $TiO_2$, and $Al_2O_3$ and compared it with **1** on $SiO_2$ (Scheme 1).

*(a) Immobilization on Alumina.* Like silica, alumina is already well-characterized by the supplier (e.g., Merck) and available in a large variety of pore diameters, particle sizes, and activities. In addition, one can choose the acidity of the surface from very acidic (pH of a 10% aqueous suspension, 4.0) to basic (pH 9.0) and also the degree of activation, corresponding to the amount of water added to the dried alumina. For our studies we chose a material that comes close to our favorite silica support: alumina with a pore size of 90 Å, a particle size distribution of 0.063–0.200 mm, and without water addition after drying in vacuo at 600 °C, that is, alumina with minimal activity. The surface properties "basic", "neutral" (pH 7.0), and "acidic" as defined above have been chosen for comparison.

Although linker **1** can be immobilized on all three alumina materials without oxidation, decomposition, or protonation, as is demonstrated with $^{31}$P CP/MAS NMR, one encounters the first drawback of alumina when trying to record solid-state NMR spectra of the support. Solid-state $^{27}$Al NMR spectroscopy has been applied for some time for the characterization of solids. Recently, for example, interesting results on minerals[20] and molecular sieves[21] could be obtained. However, while $^{29}$Si CP/MAS NMR of the support is straightforward for silica,[8] $^{27}$Al is a quadrupolar nucleus (nuclear spin $I = {}^5/_2$) and shows a huge quadrupolar interaction of higher order in the $^{27}$Al MAS NMR spectrum of **1** immobilized on $Al_2O_3$ (see Figure 1). This interaction manifests itself in a plethora of rotational sidebands spanning more than 10.000 ppm overall and being folded in at both spectral boundaries. Although the isotropic lines of octahedrally and tetrahedrally coordinated aluminum nuclei can be distinguished (see expanded region in Figure 1), no additional lines due to aluminum nuclei with neighboring bound **1** can be seen. The $^{27}$Al MAS spectra for starting $Al_2O_3$ and ligand modified $Al_2O_3$ are identical. For improving the resolution in $^{27}$Al solid-state NMR spectra, there are nowadays 2D experiments[22] available, as well as sophisticated multiquantum techniques (MQMAS).[23] Unfortunately, despite some progress with "faster MQMAS" [24] these methods still reduce the sensitivity of the measurement. However, our interest is not so much in enhancing the spectral resolution but detecting besides the $Al_2O_3$ bulk resonances the signals of Al nuclei close to surface-bound phosphines, and these are intrinsically of low abundance. Therefore, we tried to enhance them with $^{27}$Al CP/MAS according to classical[25] and successful recent studies.[26,27] Although, in analogy to Ellis' work[25] the CP/MAS spectra differed from the MAS ones, the CP/MAS spectra of $Al_2O_3$ with

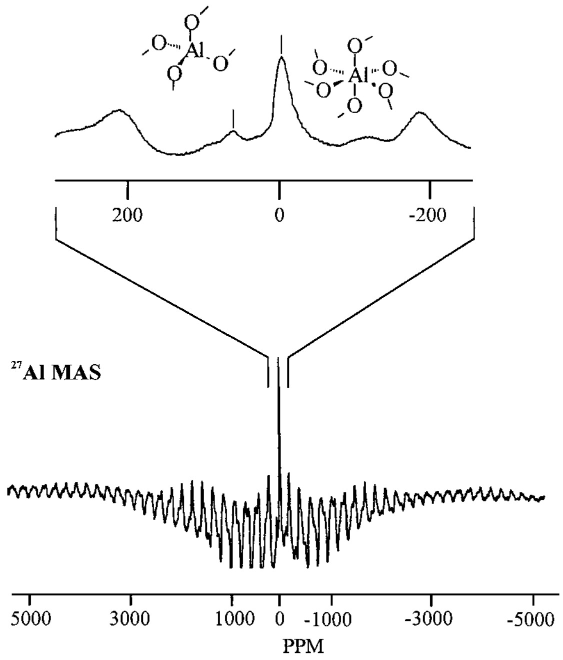


**Figure 1.** 78.17 MHz $^{27}$Al MAS spectrum of $Al_2O_3$ (neutral), modified with **1**. Rotational speed, 15 kHz. The isotropic lines are displayed in the expanded region.

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**Table 1. $^{31}$P Toluene Suspension NMR Signal Half-Widths ($\nu_{1/2}$) and Chemical Shifts [$\delta(^{31}P)$] of 1i Immobilized on Acidic, Basic, and Neutral Alumina Supports with the Given Surface Coverages**

| $Al_2O_3$[a] | surface coverage[b] | mg of **1**/g of $Al_2O_3$ | $\delta(^{31}P)$[c] | $\nu_{1/2}$[c] (kHz) |
|---|---|---|---|---|
| acidic | *m* | 75 | −20.8 (−21.2) | 4.99 (5.04) |
| | *m*/2 | 38 | −20.9 | 5.31 |
| | *m*/4 | 19 | −20.4 | 5.68 |
| | *m*/10 | 8 | −20.9 | 6.60 |
| basic | *m* | 82 | −20.1 (−20.5) | 4.90 (4.95) |
| | *m*/2 | 41 | −19.7 | 5.30 |
| | *m*/4 | 21 | −19.8 | 5.49 |
| | *m*/10 | 8 | −19.7 | 5.63 |
| neutral | *m* | 109 | −19.8 (−21.3) | 4.52 (4.61) |
| | *m*/2 | 55 | −20.6 | 5.25 |
| | *m*/4 | 27 | −20.2 | 5.34 |
| | *m*/10 | 11 | −20.4 | 5.51 |

[a] Average pore diameter of all 90 Å; all predried at 600 °C in vacuo. [b] *m* denotes maximal surface coverage. [c] Values for THF as solvent in brackets.

and without surface-bound phosphines were identical. Obviously, the magnetization transfer from linker protons to the few $^{27}$Al surface nuclei was overruled by the one from OH protons to the bulk $^{27}$Al nuclei.

One more analytical drawback of alumina as the support is that it even affects the $^{29}$Si CP/MAS spectra of the silane groups of immobilized **1** negatively: The resolution of the signals of silanes bound by one, two, or three siloxane groups to the support is lost, and in contrast to the well-resolved signals of **1i** with silica (see Figure 5 or ref. 8), only one broad $^{29}$Si resonance at about −68 ppm can be recorded with alumina as the support. This might be due both to the even less homogeneous surface of alumina with $AlO_4$ and $AlO_6$ units present, in contrast to all $SiO_4$, or to the quadrupolar broadening of $^{27}$Al, affecting even the bound $^{29}$Si nuclei via the Al−O−Si bridges.

As far as the surface coverage with **1** is concerned, there is no noteworthy difference with silica (see Table 1). Interestingly, the maximal surface coverage is obtained with neutral alumina, supporting the hypothesis that acid- or base-catalyzed hydrolysis of the ethoxy groups is not needed prior to the formation of the Si−O−Al bridge, in analogy to the formation of siloxane bridges.[8,10] However, the handling of alumina is less pleasant than that of silica, because it needs substantially more time to settle down from suspensions. Of course, on the laboratory scale a centrifuge would help; however, in a possible later industrial application this centrifugation would mean an additional work process, rendering the use of, for example, immobilized catalysts less attractive. Furthermore, both neutral and basic alumina supports need more extended washing operations than silica. Acidic alumina additionally has a tendency to strongly adsorb **1**, so the washing procedures have to be repeated more often than with silica (see also the section on $TiO_2$ below). Perhaps the acidity of the alumina support also leads to hydrolysis of the Si−O−Al bonds with time. Merely adsorbed or even free **1** in solution can easily be distinguished in the $^{31}$P suspension NMR spectrum of **1i** on alumina (Figure 2) as a narrow line sitting on the broader signal of the covalently bound **1i**. This phenomenon has been described before for both suspension[14] and solid-state NMR spectra with adsorbed versus polycrystalline[22] or surface-bound[10] species. For the discussion of the $^{31}$P suspension NMR line width characteristics as compared to those of phosphines immobilized on silica, see section 2.

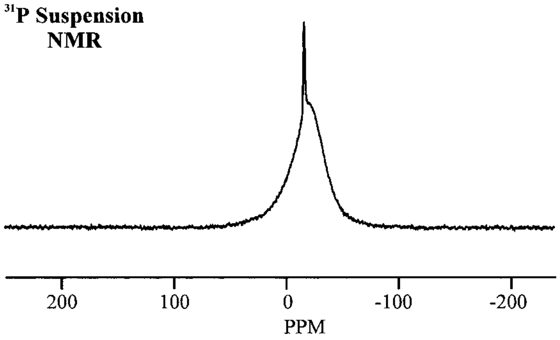

**Figure 2.** 161.9 MHz $^{31}$P suspension NMR spectrum (THF) of **1** immobilized on acidic $Al_2O_3$. The narrow line shows **1** in solution or adsorbed (see text), and the broad resonance corresponds to surface-bound **1i**.

*(b) Immobilization on Magnesia.* Magnesium oxide is a ubiquitous material in any laboratory. It is available commercially not only as a powder but also as a mechanically highly stable material pressed into different shapes and sizes (rods and columns). With respect to a later application in continuous flow catalysis with immobilized catalysts using for example a column-shaped support, we thought it would be worthwhile to test magnesia. However, the results were rather disappointing: First of all, MgO, even as a powder, has a comparably small specific surface area of 60−80 m$^2$/g, and therefore, the amount of immobilized **1** was 45 mg per 1 g of MgO (9 molecules of **1i** on 100 nm$^2$ of surface) at best. If little rod-shaped MgO pieces are used, as they are common in any analytical laboratory, the surface coverage is even less (16 mg/g of MgO). But the biggest problem for all immobilizations on magnesia was leaching of the phosphines, as described for $TiO_2$ (see below).

*(c) Immobilization on Titania.* In contrast to magnesia, the $TiO_2$ surface with a specific surface area of 8−10 m$^2$/g allowed the immobilization of **1** with a reasonable surface coverage of 21 mg of **1** per gram of $TiO_2$ (5 molecules of **1i** per 100 nm$^2$). From a practical point of view, $TiO_2$ is a favorable support, because it leads to well-dispersed homogeneous suspensions while it is stirred in toluene and settles down readily afterward. However, the $^{31}$P suspension NMR signal was very broad (10.7 kHz). Furthermore, no matter how often the material was washed, a very narrow resonance always showed up in the spectrum (see Figure 3) on top of the broad hump, corresponding to merely adsorbed or even dissolved but not chemically bound phosphine,[10,14,28] which would give a broad signal due to unreduced CSA.[29]

Quantitative investigation of repeated washing cycles gave the results displayed in Figure 4: With washing alone, even without any catalytic reaction, the phosphine linker is detached from the support. Clearly, titania could represent the showcase example for ligand

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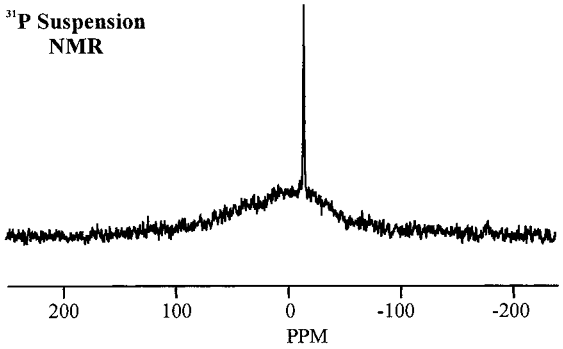

**Figure 3.** 161.9 MHz $^{31}$P suspension NMR spectrum (THF) of **1** immobilized on $TiO_2$. The narrow line shows **1** in solution or adsorbed (see text), and the broad resonance corresponds to surface-bound **1i**.

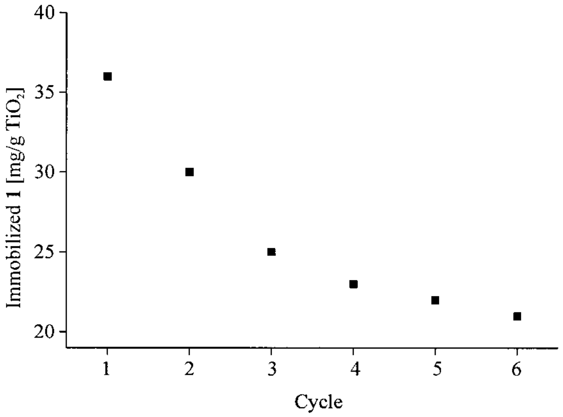

**Figure 4.** Decrease of $TiO_2$ surface coverage with immobilized **1i** after repeated washing cycles with THF.

leaching during catalysis, if it was used as support material.

Although the mechanism of detachment cannot yet be explained in detail, the mass spectra of the intact detached phosphines, recorded after each washing, did not show any traces of dimers or higher oligomers. Cross-linking, therefore, should not play a role in here. Reversible reaction, i.e., alcoholysis, should be excluded because after four or five washing cycles there should be no more ethanol. Hydrolysis can be excluded by mass spectrometry. Therefore, we assume that **1** is not bound to $TiO_2$ covalently. This is in accord with our finding that under standard $^{13}$C CP/MAS conditions (short contact time of 5 ms) for covalently bound species only signals of poor signal-to-noise ratio could be obtained.

*(d) Immobilization on Silica.* Silica offers the greatest variety of commercially available materials with different pore diameters and particle sizes. This is due to its application for column chromatography,[30] but this variety might be useful for fine-tuning of immobilized catalysts, too. The specific surface area can amount up to 750 $m^2$ per g of silica, while the material still remains pleasant to handle on the laboratory bench under nitrogen or in the glovebox, because of the big particle size of 0.063−0.200 mm. The latter constitutes a noteworthy advantage as compared to, for example, aerosils, which cannot easily be "tamed" in a Schlenk flask and pose a silicose risk. Silica settles down quickly in a suspension after turning off the stirrer and is optimally accessible to solid-state NMR spectroscopy, in contrast, for example, to alumina (see above). The reaction of

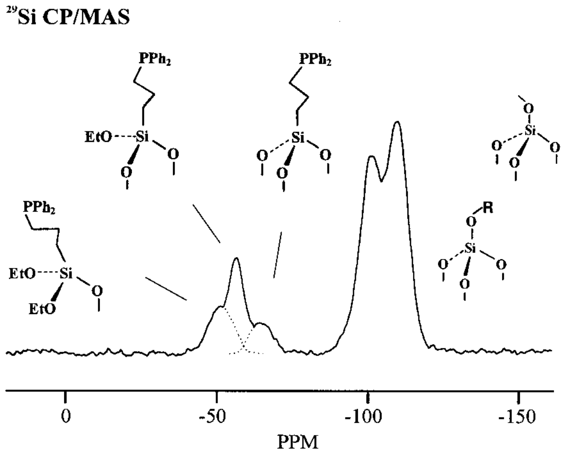

**Figure 5.** 59.6 MHz $^{29}$Si CP/MAS spectrum of **1i** on silica. Rotational speed, 4 kHz; contact time, 6 ms; pulse repetition time, 10 s.

ethoxysilanes with the silica surface is already well-explored,[1,8,10] and the optimal conditions for immobilization of bifunctional ligands such as **1** are known.[1,8] The analytical access to the bonding pattern with $^{29}$Si CP/MAS NMR is straightforward, and with **1**, as with other molecules with triethoxysilane groups, a distribution of species bound via one, two, or three siloxane bridges to the support is typically obtained.[8] This can be seen in the well-resolved silane region of the spectrum of **1i** on silica, displayed in Figure 5. Recently, even chelating phosphines containing the ethoxysilane group could successfully be bound to silica,[3] and silica-supported rhodium hydrogenation catalysts have been shown to be active and recycleable.[7]

*Résumé of Section 1.* To sum up the results of section 1, it is obvious that silica presents the optimal oxidic support material for immobilizing bifunctional phosphines such as **1**. The advantages are of an analytical as well as a practical and chemical nature: The linker **1i** on silica does not show any signs of leaching (see also section 3). At the same time, both solid-state CP/MAS NMR and suspension NMR can be used as analytical tools. Additionally, silica is available in greater variety than any of the other oxides discussed above, and especially material with greater specific surface area is commercially available. Therefore, in our next step we focused on silica-supported **1i** and studied its characteristics with suspension NMR.

**2. Suspension NMR Spectroscopy of 1i.** Immobilized catalysts are usually applied using a solvent. Therefore, performing classical $^{31}$P CP/MAS experiments on immobilized ligands or catalysts is not quite realistic, because the dry material is required for this. Some recent developments also use fast rotation of materials with adsorbed solvents, for example, for monitoring solid-phase organic reactions.[31] However, in these cases the goal is getting the lines as narrow as possible. The information contents with respect to mobility of the species is reduced along with the anisotropic interactions. Suspension NMR without fast sample spinning can fruitfully be applied to questions of mobility, because here all reduction of anisotropic

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linebroadening interactions results from the movement of the immobilized species itself.[14] Our ultimate goal will be to find out whether there is a correlation between the catalytic activity of a surface-bound complex and its mobility. Perhaps this way the effects of solvents or surface coverages on immobilized catalysts could be better understood. As a first step toward this direction, we studied the dependence of the line width of the $^{31}P$ suspension NMR signals from the solvent and the surface coverage of **1i** on various alumina and silica supports.

*(a) Suspension NMR of Alumina-Supported* **1**. The maximal surface coverage of **1** on alumina is dependent on the surface properties of $Al_2O_3$: Maximal surface coverage (109 mg of **1**/g of $Al_2O_3$) is obtained with neutral alumina, followed by basic and acidic (82 and 75 mg of **1**/g of $Al_2O_3$) alumina. Table 1 displays the results of the $^{31}P$ suspension NMR measurements with toluene and THF as the suspension media for all samples. Although the $^{31}P$ NMR chemical shifts differ a little bit with the samples and solvents, this variation does not go beyond the usual solvent and surface dependences of $\delta(^{31}P)$.

However, toluene gives narrower lines than THF for all samples. This might reflect the better solubility of the $Ph_2P$ moiety of **1** in toluene as compared to THF. With respect to surface coverage, the trend is the same as with **1** on silica (see below also for more detailed discussion): The higher the surface coverage, the smaller the half-widths of the signals. This accounts for every category of material (basic, acidic, and neutral) in itself, when decreasing the surface coverage from maximally *m* to *m*/10 in a stepwise manner. For example, for neutral alumina the $^{31}P$ suspension NMR signal half-width in toluene is 4.52 kHz for *m*, and 5.34 kHz for *m*/4. But even comparing the surfaces with different pH, this is a general trend. For example, basic alumina with a maximal surface coverage *m* of 82 mg of **1**/g of $Al_2O_3$ gives a half-width of 4.90 kHz, which increases to 4.99 kHz for acidic alumina with a smaller *m* value of 75 mg of **1**/g of $Al_2O_3$ (Table 1). Therefore, with alumina as the support, as with all the other oxidic supports, we conclude that the surface coverage is the determining factor rather than the acidity of the surface.

*(b) Suspension NMR of Silica-Supported* **1**. The influence of surface coverage with **1i**, average pore diameter of $SiO_2$, and solvent effects on the $^{31}P$ suspension NMR signal half-widths has been studied. The full set of data is displayed in Table 2. For every surface coverage and silica material, toluene always leads to narrower suspension NMR signals than THF. Again, as in the case of alumina, this might be due to the better $Ph_2P$-solvating powers of toluene as compared to THF.

For the study of the surface coverage with **1i**, we again varied the amount of ligand **1**; for example, for silica with average pore diameter of 40 Å, ligand amount varied from 156 mg (maximal coverage, *m*) to 16 mg (*m*/10)/g of silica. As shown in Table 2 and Figure 6, with toluene as the suspension medium the half-widths of the resulting $^{31}P$ suspension NMR signals increased from 2.48 to 2.99 kHz with stepwise decreasing surface coverage. This is in accord with earlier assumptions[30] that only a dense, brush-type arrangement of alkylphosphines on the surface allows good mobility of the phosphine moieties. When the surface coverage becomes thin, the phosphine moieties might bend down to the silica surface in a blanket-type fashion,[30] so that they might be less well mobilized by the solvent. The dependence of the signal half-widths on the surface coverages shows the same trends also for silica with greater values of 60 and 100 Å for the average pore diameters (Table 2), when toluene is used as the suspension medium.

**Table 2. Dependence of the $^{31}P$ Toluene Suspension NMR Signal Half-Widths ($\nu_{1/2}$) and Chemical Shifts from the Surface Coverage of Silica**

| $SiO_2$[a] | surface coverage[b] | mg of 1/g of $SiO_2$ | **1i**/100 $nm^2$ | $\delta(^{31}P)$[c] | $\nu_{1/2}$[c] (kHz) |
|---|---|---|---|---|---|
| 40[d] (750) | *m* | 169 | 35 | −17.1 (−17.2) | 2.18 (2.54) |
| 40 (750) | *m* | 156 | 32 | −17.6 (−17.5) | 2.48 (2.76) |
| | *m*/2 | 78 | 16 | −17.7 (−17.2) | 2.52 (3.84) |
| | *m*/4 | 39 | 8 | −17.8 (−17.1) | 2.72 (2.82) |
| | *m*/6 | 26 | 5 | −17.9 (−17.2) | 2.89 (3.32) |
| | *m*/10 | 16 | 3 | −17.8 (−17.2) | 2.99 (3.54) |
| 60 (480−540) | *m* | 108 | 33 | −16.8 (−16.8) | 2.33 (2.81) |
| | *m*/2 | 54 | 17 | −17.3 | 2.48 |
| | *m*/4 | 27 | 8 | −17.2 | 3.14 |
| | *m*/10 | 11 | 3 | −17.8 | 3.33 |
| 100 (270−370) | *m* | 79 | 38 | −17.7 (−16.8) | 2.22 (2.70) |
| | *m*/2 | 40 | 19 | −17.6 | 2.36 |
| | *m*/4 | 20 | 10 | −17.4 | 2.52 |
| | *m*/10 | 8 | 4 | −17.3 | 3.04 |

[a] Predried at 600 °C in vacuo with the given average pore diameters (40, 60, and 100 Å) and specific surface areas ($m^2$/g of $SiO_2$). [b] *m* denotes maximal surface coverage. [c] Values for THF as solvent in brackets. [d] Predried at room temperature.

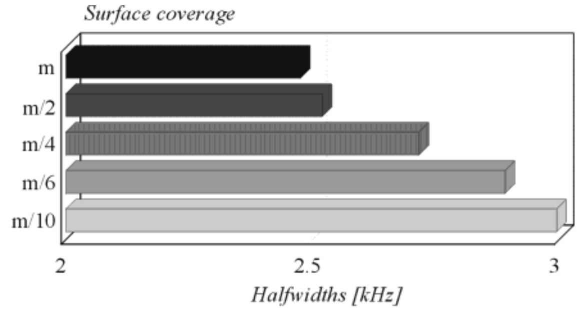

**Figure 6.** Graphical display of $^{31}P$ suspension NMR signal half-widths in toluene depending on surface coverage. Support material, predried $SiO_2$ with 40 Å average pore diameter (see Table 2).

However, there is no visible trend in the line widths when THF is used as the solvent. They vary irregularly over the whole range from 2.70 to 3.84 kHz. Obviously with the polar THF other effects such as competing adsorption on the silica surface have to be considered, too.

The dependence of the $^{31}P$ suspension NMR signal half-widths of **1i** on the average pore diameter, as well as the degree of dryness of the silica surface, was also studied within the range of 40−100 Å (Table 2), using again toluene and THF as solvents. The number of immobilized phosphines per 100 $nm^2$ of silica surface was kept about equal (32−38 molecules of **1i** per 100 $nm^2$ of surface area), while the overall amount of **1** in mg/g of silica had to decrease along with the specific surface area. In contrast to our anticipation, no substantial change in the half-widths of the signals could be seen when going from 40 to 100 Å. Obviously, 40 Å average pore diameter already provides enough space

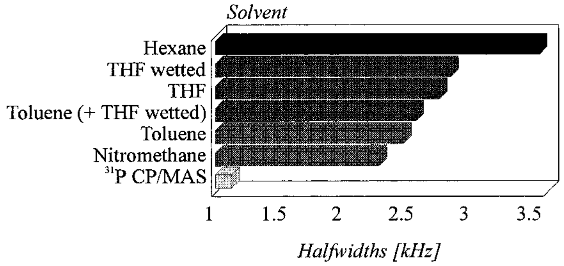

**Figure 7.** Dependence of $^{31}$P suspension NMR signal half-widths $\nu_{1/2}$ (kHz) of **1i** on silica 40 described in Table 2 with maximal surface coverage *m*, from the given solvents. The polarities of hexane, THF, toluene, and nitromethane, given as dielectric constants $\epsilon$ (°C) are 1.89 (20), 7.52 (22), 2.38 (24), and 37.27 (20), respectively. The viscosities $\eta$ (mPa·s) at 25 °C are 0.300, 0.456, 0.560, and 0.630, respectively.[32]

to ensure complete mobilization of the phosphine moieties. Again, it is the surface area per molecule that determines the line widths, as above. In addition, more important than the pore diameter seems to be the surface properties themselves: Immobilization of **1** on silica dried at room temperature with more surface silanol groups[8,10] leads to the narrowest signals for both toluene and THF. Of course this might also be due to a higher degree of cross-linking of the ethoxysilane groups and, therewith, longer, surface-detached, and more mobile chains in contrast to strictly surface-bound **1i**.[14]

Finally, the dependence of the $^{31}$P suspension NMR signal half-widths $\nu_{1/2}$ on the suspension media has been studied using hexane, THF, toluene, and nitromethane as the solvents (see Figure 7) for silica 40 with maximal **1i** surface coverage *m* (see Table 2). As already given in the Tables 1 and 2, toluene always leads to narrower signals than THF. This is surprising, since THF is more polar and less viscous and according to an earlier study[14] it should therefore be better in mobilizing the phosphine moieties of **1i**. Nitromethane, however, with its high polarity follows the expected trend (Figure 7), and the same accounts for hexane.[14]

Finally we wanted to investigate, whether the solvent is needed to detach the phosphine moieties from the silica surface or whether it is more important to mobilize the more or less freely dangling phosphine group. Therefore, we measured the modified silica with a maximal surface coverage of **1i** (see Table 2) wetted with THF, but not fully suspended. Interestingly, the line width herewith increases from 2.76 to 2.85 kHz. So, a thin layer of solvent on the silica surface is not enough to fully mobilize the phosphine moieties, as in the suspension material. However, we also did another experiment: The THF-wetted silica was fully suspended in toluene. The resulting half-width of the $^{31}$P suspension NMR signal has an increased value of 2.57 kHz as compared to 2.48 kHz in pure toluene. This shows on one hand that THF is still adsorbed on the silica surface, despite the excess of toluene. Furthermore, it demonstrates that the environment close to the silica surface is important for the mobilization of the phosphine moieties. To sum it up, the solvent dependence of the $^{31}$P suspension NMR signal line widths in our preliminary experiments already shows that for optimal mobility and therewith removal of anisotropic solid-state interactions, both the surface detachment and the solvation of the phosphine moieties of **1i** are important.

**Table 3. Data for the Detachment of Linker 1 from the Silica Support**

| solvent | ligand:$NaOC_2H_5$ | recovery of **1**[a] |
|---|---|---|
| acetone | - | 5 [7] |
| acetonitrile | - | 0 [0] |
| acetonitrile/ethanol (1:1) | - | 17 [27] |
| ethyl ethanoate | - | 0 [0] |
| ethanol | - | 15 [23] |
| ethanol | 1:1.6 | 9 [15] |
| ethanol | 1:2.5 | 15 [22] |
| ethanol | 1:6 | 20 [22] |
| ethanol | 1:1 | 18 [26] |
| ethanol | 1:1 | 23 [151] |
| ethanol | 1:0.8 | 14 [24] |
| ethanol | 1:100 | 9 [16] |
| ethanol/water | - | 16 [27] |
| tetrahydrofuran | - | 3 [5] |

[a] Recovery of detached **1** in % with respect to immobilized ligand **1i** and in [mg]. For details see the Experimental Section and text.

**3. Detaching 1 from 1i.** One of the main drawbacks of immobilized catalysts is leaching from the support. It is generally assumed that this detachment of the catalysts happens because the bonding of the ligand to the support is not strong enough. Our investigations on $TiO_2$ (see above) are a good example. With polymer supports, there might be additional reasons for leaching, since these are often not chemically inert toward the substrates and solvents used during the catalytic reaction.[33]

To check how robust the bonding of the ethoxysilane group to the silica support is, we carried out quantitative studies: The modified silica was stirred with the solvents given in Table 3, and afterward, the supernatant solution was stripped of all volatiles and the residue weighed. The integrity of the phosphine moieties in every case could be seen in $^{31}$P NMR spectra of the solutions. The residues were checked either with $^{31}$P suspension or $^{31}$P CP/MAS NMR, and no oxidic or other new species could be detected. At room temperature none of the solvents or solvent mixtures, even after the prolonged stirring period of 17 h, was able to detach substantial amounts of ligand. Especially solvents that are popular in catalysis, like toluene, THF, or acetone, did not lead to ligand leaching, even when the modified silica was refluxed in them. More polar and protic solvents were then applied: After boiling the suspensions for 5 h maximally 17 % of ligand could be regained with using a 1:1 mixture of acetonitrile and wet (96 %) ethanol. About the same amount of detached ligand was found, when a mixture of 1:1 of ethanol and water was boiled with silica for 5 h. Although by no means realistic conditions for catalysis, we forcefully tried to remove the ligand from the support with adding sodium ethylate to the solvents. Interestingly, the amount of detached linker did not correlate with the amount of NaOEt applied. After boiling the support for 3 days with a 6-fold excess of sodium ethylate with respect to the linker in ethanol a maximum of merely 20% of detached ligand could be regained.

Therefore, we conclude that the bonding of the linker to the support is very strong even under the conditions

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of catalysis, and leaching is more a problem of complex detachment from the bound phosphines, as it will be demonstrated in a later publication.[34]

## Experimental Section

Ligand **1** was synthesized and immobilized as described previously.[1,2,8] The surface coverages have been determined by weighing back the residual dissolved phosphines in the supernatant solutions after solvent removal. All the $^{31}P$ suspension and $^{31}P$ CP/MAS NMR spectra were recorded on a Bruker Avance 400 instrument, the $^{27}Al$ MAS, $^{13}C$ and $^{29}Si$ CP/MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer. For details on measurements see refs 1, 8, and 14.

Detaching **1** from **1i**: In a representative procedure, 1 g of silica, containing 156 mg (0.399 mmol) of immobilized ligand **1**, were suspended in 50 mL of ethanol. After addition of 68 mg (0.998 mmol, 2.5 equivalents) of NaOEt, the suspension was stirred at 80 °C for 24 h. Then, all volatiles were removed from the supernatant solution and the resulting oil (**1** or cross-linked species of **1**) was weighed (22 mg, 0.056 mmol, 15% with respect to **1i**). In a check experiment we made sure that no NaOEt was present in the supernatant solution after treatment of silica.

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