

## Surfaces and Interfaces

## Structures and Unexpected Dynamic Properties of Phosphine Oxides Adsorbed on Silica Surfaces

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**Abstract:** Solid-state NMR spectroscopy of selected phosphine oxides adsorbed on silica surfaces establishes the surface mobilities, even of phosphine oxides with high melting points. Crystal structures of the adducts  $\text{Ph}_3\text{PO}\cdot\text{HOSiPh}_3$  and  $\text{Cy}_3\text{PO}\cdot\text{H}_2\text{O}$  indicate that the interactions with silica involve hydrogen bonding of the  $\text{P}=\text{O}$  group to adsorbed water and surface silanol groups.

Phosphine oxides represent an immensely important class of compounds.<sup>[1]</sup> They are by-products of phosphine chemistry, and are generated as stoichiometric co-products of the Wittig, Appel, and other reactions. They are also indispensable probes for surface acidities of oxides<sup>[2]</sup> and recently received attention in the decomposition of warfare agents.<sup>[3]</sup> Another long-standing question in the field of immobilized catalysts<sup>[4]</sup> is whether adsorbed phosphine oxides mimic the  $^{31}\text{P}$  MAS (magic angle spinning) NMR signals of phosphine linkers quaternized to form phosphonium salts.<sup>[5]</sup> Despite their importance, the surface chemistry of phosphine oxides is not well documented. Herein, we prove using solid-state NMR techniques that even phosphine oxides with high melting points possess heretofore unappreciated surface mobilities in the absence of solvents. The silica-adsorption process of phosphine oxides proceeds at ambient temperature by co-grinding the dry components. Crystal structures of model compounds show that interactions with surface silanol groups and adsorbed water mediate the adsorption and mobility, which correlates with leaching data in various solvents.

The  $^{31}\text{P}$  CP/MAS (cross-polarization with MAS) spectrum of polycrystalline, adduct-free<sup>[1]</sup>  $\text{Ph}_3\text{PO}$  shows that the chemical shift anisotropy (CSA)<sup>[6]</sup> is large, and the span ( $\delta_{11}-\delta_{33}$ )<sup>[6a]</sup> of the wideline signal amounts to  $\delta=200.6$  ppm (Figure 1, bottom).<sup>[1]</sup> However, when  $\text{Ph}_3\text{PO}$  is adsorbed on  $\text{SiO}_2$ <sup>[7]</sup> as a monolayer,<sup>[8]</sup> the CSA vanishes (Figure 2) and comparatively narrow, unstructured signals result even without sample spinning (Figure 2, bottom). The absence of a CSA of the  $^{31}\text{P}$  MAS signals compared to the polycrystalline  $\text{Ph}_3\text{PO}$  proves that the crystal lattice is no longer present and that the adsorbed phosphine

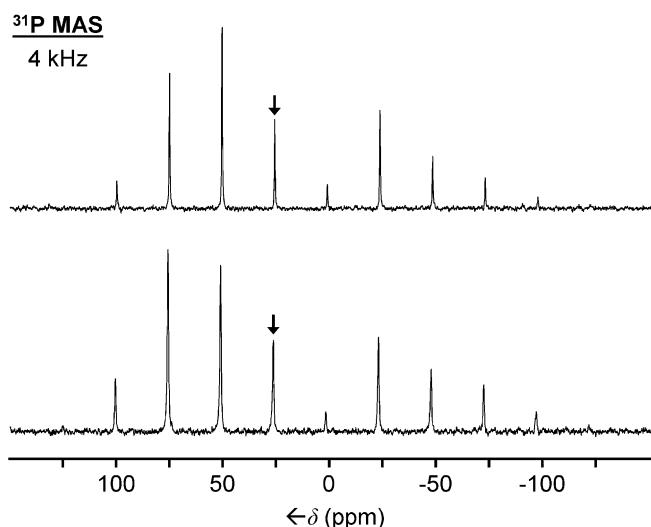


Figure 1.  $^{31}\text{P}$  MAS NMR spectra of polycrystalline  $\text{Ph}_3\text{PO}$  (bottom) and  $\text{Ph}_3\text{PO}\cdot\text{HOSiPh}_3$  (top). The arrows indicate the isotropic lines.

oxides are very mobile on the surface. The Lorentzian line-shape implies that an isotropic reorientation of the molecules occurs, which indicates a translational mobility of the molecules, spiraling along the walls inside the silica pores. This phenomenon has recently been described for the  $^{13}\text{C}$  MAS NMR signals of adsorbed metallocenes.<sup>[9]</sup>

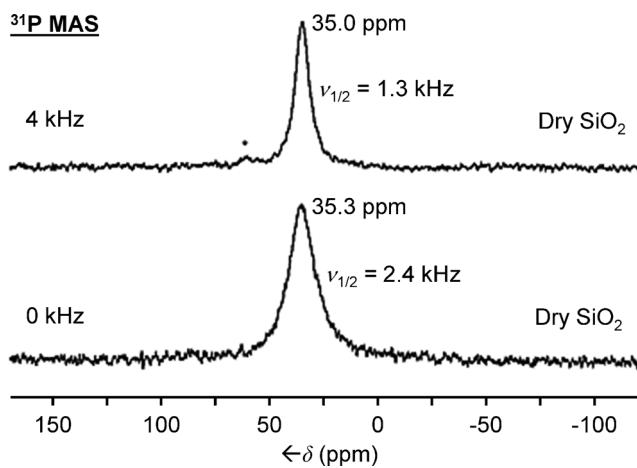


Figure 2.  $^{31}\text{P}$  MAS (top) and  $^{31}\text{P}$  wideline (bottom) NMR spectra of  $\text{Ph}_3\text{PO}$  adsorbed<sup>[8]</sup> on dry  $\text{SiO}_2$ .<sup>[7]</sup>

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The residual linewidth is smallest (1.3 kHz) when  $\text{Ph}_3\text{PO}$  is adsorbed on dry  $\text{SiO}_2$ <sup>[7]</sup> (Figure 2).  $\text{Ph}_3\text{PO}$  is more strongly bound on wet  $\text{SiO}_2$ <sup>[7]</sup> leading to slightly reduced mobility and a broader line (1.5 kHz). The sample spinning is not responsible for the removal of the CSA, because even the wideline signal is only 2.4 kHz broad (Figure 2, bottom).

Further proof of the translational mobility of  $\text{Ph}_3\text{PO}$  on  $\text{SiO}_2$  is realized by applying it to the surface by co-grinding with the dry  $\text{SiO}_2$ <sup>[7]</sup>. Although the melting point of  $\text{Ph}_3\text{PO}$  is high (157 °C),<sup>[11]</sup> the crystal lattice disintegrates within a few days, and a monolayer of adsorbed phosphine oxide forms. For this process to proceed to completion, the individual molecules have to move away from the contact points of  $\text{Ph}_3\text{PO}$  with  $\text{SiO}_2$  in a translational motion to make space for successors.

Further proof for the translational mobility of surface-adsorbed  $\text{Ph}_3\text{PO}$  is provided by variable-temperature  $^{31}\text{P}$  MAS measurements. At higher temperatures, narrower lines are obtained, whereas at low temperatures, the signals broaden.<sup>[10]</sup> Within the range of 20 to 50 °C, a linear correlation is found between the linewidth values and the temperatures.<sup>[10]</sup> Furthermore, the linewidth changes are reversible, which excludes any reaction of the phosphine oxide with the silica.

Besides signal intensity changes resulting from contact time variation,<sup>[11]</sup>  $T_1$  relaxation times are important indicators for mobilities.<sup>[6b]</sup> In the solid state, the shorter the  $T_1$  times, the more mobile molecules or functional groups are.<sup>[6b]</sup> While crystalline, immobile triaryl phosphine species have  $^{31}\text{P}$   $T_1$  relaxation times in the range of minutes,<sup>[12]</sup> the values obtained by measurements of adsorbed  $\text{Ph}_3\text{PO}$  performed as described earlier are only seconds.<sup>[13]</sup> For a monolayer of  $\text{Ph}_3\text{PO}$  adsorbed on silica (206 molecules per 100 nm<sup>2</sup>), a  $T_1$  relaxation time of about 4 s results. A sub-monolayer of  $\text{Ph}_3\text{PO}$  on the surface (27 molecules per 100 nm<sup>2</sup>) gives a  $T_1$  value of only about 2 s. This proves that the surface-adsorbed phosphine oxide is mobile, and that the mobility increases when there are fewer molecules on the surface that impede this mobility. The  $T_1$  values being a function of the surface coverage again corroborates the translational mobility of the adsorbed phosphine oxides.

To obtain additional quantitative information about the surface mobility of phosphine oxides,  $^2\text{H}$  MAS NMR of adsorbed  $([\text{D}_5\text{Ph}]\text{Ph}_2\text{PO})$  was utilized. The polycrystalline material gives a Pake pattern with a quadrupolar coupling constant  $Q_{\text{cc}}$  of 175.2 kHz.<sup>[14]</sup> The Pake pattern collapses upon adsorption and an unstructured signal with a halfwidth of 5.4 kHz results (Figure 3). This phenomenon has been described for deuterated polycrystalline and adsorbed ferrocene,<sup>[9]</sup> and was also found for mobile components in polymer networks.<sup>[15]</sup>

For averaging out a Pake pattern completely, an isotropic reorientation is needed. For example,  $^2\text{H}$  MAS gives a Pake pattern for solid poly( $[\text{D}_3]$ methyl methacrylate) (PMMA),<sup>[16]</sup> although the  $\text{CD}_3$  groups rotate rapidly around a  $C_{3v}$  axis.<sup>[6b]</sup> Similarly, solid  $([\text{D}_1]\text{Cp})_2\text{Fe}$  gives a Pake pattern<sup>[9]</sup> despite fast Cp ring rotation,<sup>[6b]</sup> and also confined, but rotating benzene.<sup>[17]</sup> The gradual collapse of Pake patterns and their resulting shapes have been visualized for angle-dependent movements.<sup>[18]</sup> Comparing the  $^2\text{H}$  MAS signal of adsorbed  $([\text{D}_5\text{Ph}]\text{Ph}_2\text{PO})$  with the calculated Pake pattern shapes<sup>[18]</sup> leads

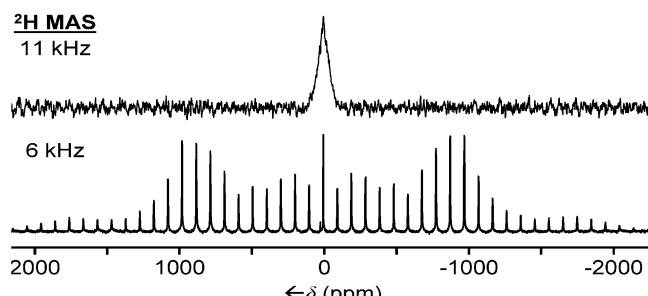


Figure 3.  $^2\text{H}$  MAS NMR spectra of polycrystalline (bottom) and adsorbed (top)  $([\text{D}_5\text{Ph}]\text{Ph}_2\text{PO})$ .

to the conclusion that there has to be isotropic mobility with a reorientation time of the molecules close to 300 ns. This means that the adsorbed  $([\text{D}_5\text{Ph}]\text{Ph}_2\text{PO})$  migrates over surface silanol groups and reorients isotropically by spiraling in a translational motion across the inner walls of the pores.<sup>[9]</sup>

Additional proof for isotropic translational mobility comes from variable-temperature  $^2\text{H}$  MAS measurements. As for  $^{31}\text{P}$ , the residual linewidths of the  $^2\text{H}$  MAS signals show a linear correlation with the temperature.<sup>[19]</sup> For example, at 77 °C the linewidth is only 1.1 kHz, whereas at 17 °C, it is 6.7 kHz. The linewidth changes are reversible, indicating a dynamic scenario and excluding any reaction of  $([\text{D}_5\text{Ph}]\text{Ph}_2\text{PO})$  with the surface.

Regarding how phosphine oxides attach to the  $\text{SiO}_2$  surface, the P=O groups could either bind covalently, or interact with the protons of surface silanol groups.<sup>[2,3]</sup> The mobility of the adsorbed phosphine oxides on the surface excludes a covalent bond, but we have demonstrated recently that phosphine oxides form rather stable hydrogen-bonded adducts with  $\text{H}_2\text{O}_2$ .<sup>[1]</sup> The downfield shift of the  $^{31}\text{P}$  signal when transitioning from the polycrystalline to the adsorbed  $\text{Ph}_3\text{PO}$  ( $\delta = 26.3$  to 36.4 ppm) suggests the formation of hydrogen bridges. There is also a  $\delta$  difference of 1.4 ppm between the signals of  $\text{Ph}_3\text{PO}$  adsorbed on wet and dry  $\text{SiO}_2$  (36.4 and 35.0 ppm). Therefore, hydrogen bonding to two different surface species is likely, presumably to  $\text{H}_2\text{O}$ , being abundant on the surface of wet  $\text{SiO}_2$ , and to surface silanol groups, which represent the dominant functional groups on dry  $\text{SiO}_2$  apart from surface siloxane groups.<sup>[20]</sup>

Indeed, when  $\text{H}_2\text{O}$  was added to  $\text{Cy}_3\text{PO}$  in a stoichiometric amount, crystals of a 1:1 hydrogen-bonded adduct were obtained (Figure 4).<sup>[21]</sup> The  $\text{H}_2\text{O}$  molecule is bound to the P=O group through a single hydrogen atom. The strength of the interaction is reflected in the lengthening of the P=O bond from 1.490 Å in pure  $\text{Cy}_3\text{PO}$ <sup>[22]</sup> to 1.501/1.499 Å (two independent molecules) in the  $\text{H}_2\text{O}$  adduct.

Next, we sought to mimic the  $\text{SiO}_2$  surface by using a silanol as molecular model. When  $\text{Ph}_3\text{SiOH}$  was added to phosphine oxides in stoichiometric amounts, large single crystals of 1:1 hydrogen-bonded adducts were formed, for example,  $\text{Ph}_3\text{PO}\cdot\text{HOSiPh}_3$  (Figure 5).<sup>[23]</sup> The strength of the interaction of the P=O group with the hydrogen atom is indicated by the lengthening of the P=O bond from 1.479 Å in pure  $\text{Ph}_3\text{PO}$ <sup>[24]</sup> to 1.503 Å (1.493 Å in the second molecule) in the silanol adduct.

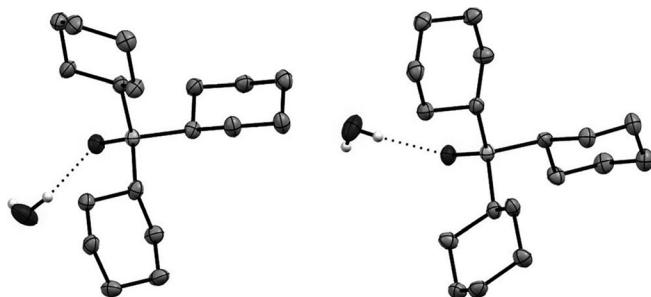


Figure 4. X-ray crystal structure of  $\text{Cy}_3\text{PO}\text{-HOH}$  (two independent adduct molecules);<sup>[21]</sup> O...H distances: 2.038/2.058 Å; O-H...O angles: 158.32/169.50°.

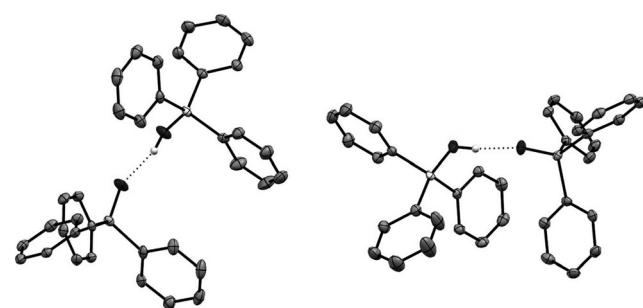


Figure 5. X-ray crystal structure of  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  (two independent adduct molecules);<sup>[23]</sup> O...H distances: 1.793/1.827 Å; O-H...O angles: 152.51/173.16°.

The melting point of the silanol adduct (123 °C) is high enough for recording the  $^{31}\text{P}$  MAS spectrum (Figure 1, top). The  $\delta(^{31}\text{P})$  of the isotropic line of  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  decreased to 25.6 ppm compared to 26.3 ppm for  $\text{Ph}_3\text{PO}$  (Figure 1, bottom). The CSA of  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  was reduced by about 20 ppm to 180.3 ppm ( $\delta_{11}=91.0$ ,  $\delta_{22}=74.9$ ,  $\delta_{33}=-89.3$  ppm) compared to 200.6 ppm for  $\text{Ph}_3\text{PO}$  ( $\delta_{11}=98.0$ ,  $\delta_{22}=83.4$ ,  $\delta_{33}=-102.5$  ppm).<sup>[1]</sup> Therefore, we conclude that the  $^{31}\text{P}$  signals of adsorbed phosphine oxides lack a CSA mainly because of their surface mobility, and only a small CSA reduction is due to hydrogen bonding to silanol groups.

The silanol adduct exhibits four  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  assemblies per unit cell (Figure 6). Therefore, theoretically there could be four lines in each  $^{31}\text{P}$  NMR spectrum of a single crystal (Figure 7).<sup>[6b,25]</sup> However, only two orientations of the P=O groups differ significantly from each other (Figure 6), and only two lines are distinguishable in the  $^{31}\text{P}$  single crystal NMR spectra.

The adsorption phenomena are also reflected in the IR data of  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$ . The  $\nu(\text{OH})$  band of neat  $\text{Ph}_3\text{SiOH}$  at 3244  $\text{cm}^{-1}$  becomes narrower upon adduct formation. The weakened O-H bond manifests itself in a decreased  $\nu(\text{OH})$  value in neat  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  (3224  $\text{cm}^{-1}$ ). Analogously,  $\nu(\text{P=O})$  decreases from 1188  $\text{cm}^{-1}$  for neat  $\text{Ph}_3\text{PO}$ <sup>[1]</sup> to 1179  $\text{cm}^{-1}$  for neat  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$ . The  $\nu(\text{P=O})$  IR band of the adduct is very narrow, indicating the well-defined nature of the hydrogen bond.

Next, attention was turned to practical issues. Thus, the maximal monolayer surface coverages<sup>[8]</sup> after the standard immobilization procedure<sup>[8]</sup> and leaching<sup>[26]</sup> with different solvents have been studied (Figure 8). Because there are more  $\text{H}_2\text{O}$  mol-

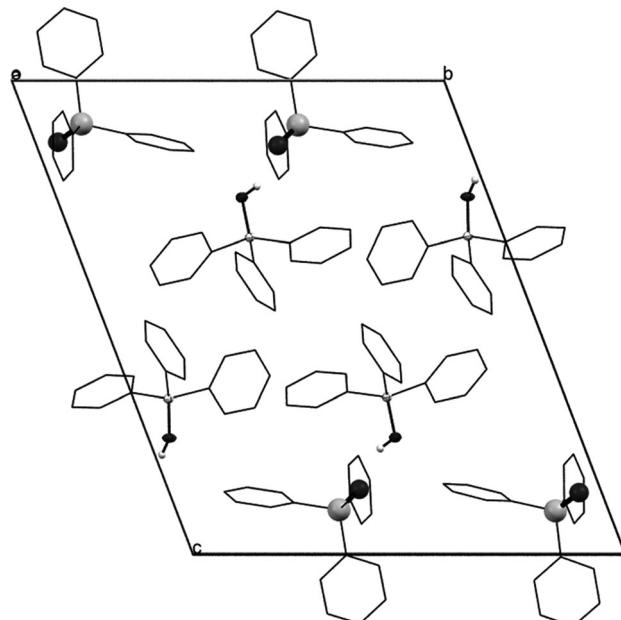


Figure 6. Unit cell of  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  viewed along the  $a$  axis.<sup>[23]</sup>

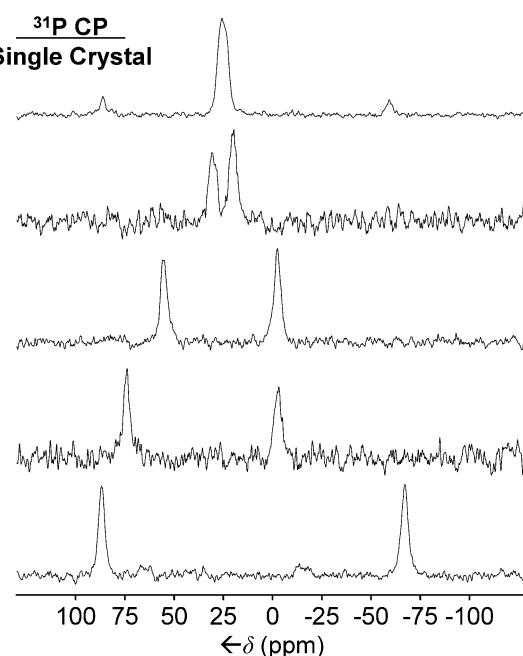


Figure 7.  $^{31}\text{P}$  CP NMR spectra of  $\text{Ph}_3\text{PO}\text{-HOSiPh}_3$  at different single-crystal orientations.

ecules and silanol groups available for hydrogen bonding on wet  $\text{SiO}_2$ ,<sup>[20]</sup> for each phosphine oxide the surface coverages are in general higher than on dry  $\text{SiO}_2$ .<sup>[8]</sup> Comparing different phosphine oxides, increasing steric bulk correlates to a decrease of the monolayer surface coverage.<sup>[8]</sup>

Figure 8 shows that protic and highly polar solvents detach adsorbed phosphine oxides from the support. Nonpolar and non-protic solvents, such as pentane and toluene, promote only modest leaching. This speaks again for the strong hydrogen bonding of the phosphine oxides with the  $\text{SiO}_2$  surface.

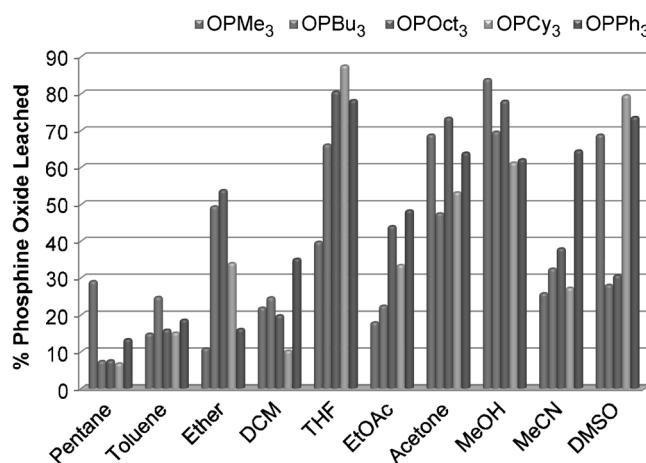


Figure 8. Leaching of phosphine oxides<sup>[26]</sup> from wet SiO<sub>2</sub><sup>[7]</sup>

The leaching characteristic can be used to remove phosphine oxides from reaction mixtures or to purify them by adsorption (Figure 8).

In conclusion, it has been demonstrated that the predominant interaction of phosphine oxides with SiO<sub>2</sub> surfaces is hydrogen bonding with silanol groups and adsorbed water. These interactions involve a single hydrogen bond, which mediates dynamic processes and can be transferred to solvents for rapid purification procedures.

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**Keywords:** adsorbed phosphine oxides • silica • solid-state NMR spectroscopy • surface chemistry

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[7] Merck silica (average pore diameter 40 Å, particle size 0.06–0.20 mm, specific surface area 750 m<sup>2</sup> g<sup>-1</sup>), dried 4 d in vacuo at 300 °C (dry SiO<sub>2</sub>), or used as received (wet SiO<sub>2</sub>).

[8] Typically, 4.0 g of SiO<sub>2</sub> is suspended in 120 mL of toluene in a Schlenk flask. After adding an excess of phosphine oxide (ca. 0.5 g), dissolved in 80 mL of toluene, the mixture is stirred at 90 °C overnight. Then the silica is allowed to settle at RT. The supernatant is decanted, and the silica is washed with toluene. After removing the solvent from the combined supernatant and wash phase, the residue is weighed. The amount of adsorbed phosphine oxide is determined from the difference between the recovered phosphine oxide and the original amount. Maximal surface coverages of phosphine oxides on wet/dry<sup>[7]</sup> SiO<sub>2</sub> (molecules per 100 nm<sup>2</sup>): Me<sub>3</sub>PO (65/53), nBu<sub>3</sub>PO (43/29), nOct<sub>3</sub>PO (29/25), Cy<sub>3</sub>PO (45/37), Ph<sub>3</sub>PO (33/26). Alternatively, after dry grinding of the pure phosphine oxides with silica, the adsorption proceeds while the mixture is allowed to stand for a few days.

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[19] <sup>2</sup>H MAS NMR signal linewidths [kHz] of ([D<sub>5</sub>]Ph)Ph<sub>2</sub>PO adsorbed<sup>[8]</sup> on dry silica<sup>[7]</sup> (T [°C]): 6.7 (17), 6.5 (27), 5.3 (37), 4.0 (47), 1.8 (67), 1.1 kHz (77).

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[26] In a representative experiment, 0.40 g of SiO<sub>2</sub> with adsorbed phosphine oxide<sup>[8]</sup> was stirred with 8 mL of solvent at RT overnight. After settling, the supernatant was filtered through filter paper, and the SiO<sub>2</sub> was rinsed twice with 4 mL of solvent. Removing the solvent from the combined liquid phases gave the weight of the residue and therewith the leached amount of phosphine oxide.

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