Inorg. Chem. 1994, 33, 5050−5056

Reactions of Phosphines with Silica: A Solid-State NMR Study

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Received November 10, 1993⊗

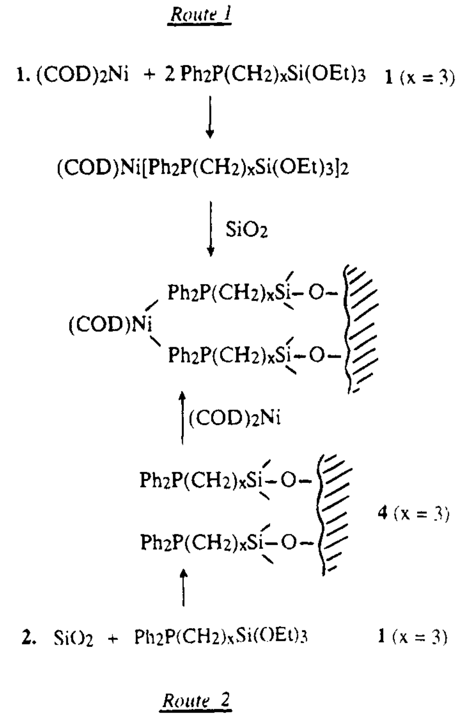
The bifunctional phosphines $Ph_2P(CH_2)_3Si(OEt)_3$ and $Ph_2P(CH_2)_2Si(OEt)_3$ are commonly used in order to bind metal complexes to support materials. When these phosphines are grafted on the silica surface, a side reaction takes place and a P(V) species is generated in considerable amount, which is no longer able to bind transition metal catalysts. This P(V) species is not the immobilized phosphine oxide, in contrast to a widespread belief. Instead, it has a cyclic, surface-attached, oxyphosphorane type structure with a pentacoordinated P(V) atom. This assumption is corroborated mainly by (a) ^{31}P NMR spectroscopic comparison with surface-bound phosphine oxides and phosphonium salts, as well as dipolar dephasing ^{31}P NMR experiments, and (b) independent synthesis and ^{31}P and ^{13}C NMR spectroscopic characterization of a surface-attached model compound. A pseudo-Wittig type reaction mechanism for the formation of the P(V) species is proposed, on the basis of the observation that both, OEt groups and silica surface, are indispensable prerequisites for this side reaction to take place. The reaction can either be used to attach any monofunctional phosphine to the silica surface as a P(V) species or avoided by mild reaction conditions or application of bifunctional phosphines without $Si(OEt)_3$ groups like $Ph_2P(CH_2)_4OH$.

I. Introduction

The interest in immobilized catalysts is growing steadily, because they should, in principle, combine all the advantages of heterogeneous and homogeneous catalysis:[1−10] They are easily removed from the reaction mixtures, and the reactions themselves are of a homogeneous nature, thus providing high selectivity and yield. Furthermore, the reaction centers are well defined and the lifetime of the catalysts should be greater than that of heterogeneous catalysts due to the strong chemical bonding to the support. Very popular supports are inorganic oxides, because they are cheap and inert against most chemicals and elevated temperatures. The most common support is silica, because its surface properties are well explored.[11−14]

Since most transition metals form stable complexes with phosphines, bifunctional phosphines like $Ph_2P(CH_2)_3Si(OEt)_3$ (**1**) and $Ph_2P(CH_2)_2Si(OEt)_3$ (**2**) (Scheme 1) are often used as linkers. They are synthesized easily in good yields from inexpensive starting materials[15] and should provide a strong anchor to the support by condensation via up to three ethoxy groups.[16]

Scheme 1. Two Possible Strategies in Order to Immobilize a Transition Metal Complex[a]



[a] COD = 1,5-cyclooctadiene; Ph = phenyl; Et = ethyl; x = 3 (**1**) or 2 (**2**).

There are two possible ways that allow one to attach a transition metal fragment to the support[17] (Scheme 1). First, the phosphine complexes can be prepared prior to the reaction with silica (route 1). In this way, the metal/phosphine ratio is

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⊗ Abstract published in *Advance ACS Abstracts*, October 1, 1994.

(1) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.

(2) Bemi, L.; Clark, H. C.; Davies, J. A.; Fyfe, C. A.; Wasylishen, R. E. *J. Am. Chem. Soc.* **1982**, *104*, 438.

(3) Finch, W. C.; Gillespie, R. D.; Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 6221.

(4) Allum, K. G.; Hancock, R. D.; Howell, I. V.; McKenzie, S.; Pitkethly, R. C.; Robinson, P. J. *J. Organomet. Chem.* **1975**, *87*, 203.

(5) Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* **1989**, *55*, 330.

(6) Lindner, E.; Glaser, E.; Mayer, H. A.; Wegner, P. *J. Organomet. Chem.* **1990**, *398*, 325.

(7) Capka, M.; Czakoová, M.; Wlodzimierz, U.; Schubert, U. *J. Mol. Catal.* **1992**, *74*, 335.

(8) Lindner, E.; Kemmler, M.; Mayer, H. A. *Chem. Ber.* **1992**, *125*, 2385.

(9) Alexiev, V. D.; Clayden, N. J.; Cook, S. L.; Dobson, C. M.; Evans, J.; Smith, D. J. *J. Chem. Soc., Chem. Commun.* **1986**, 938.

(10) Liu, D. K.; Wrighton, M. S.; McKay D. R.; Maciel, G. E. *Inorg. Chem.* **1984**, *23*, 212.

(11) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley: Chichester, U. K., 1987; and literature cited therein.

(12) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208.

(13) Rocha, J.; Welch, M. D.; Klinowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 7100.

(14) Iler, K. R. *The Chemistry of Silica*; John Wiley: New York, 1979.

(15) Capka, M. *Syn. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 347.

(16) Albert, K.; Bayer, E. *J. Chromatogr.* **1991**, *544*, 345.

(17) Bemi, L.; Clark, H. C.; Davies, J. A.; Drexler, D.; Fyfe, C. A.; Wasylishen, R. *J. Organomet. Chem.* **1982**, *224*, C5.

0020-1669/94/1333-5050$04.50/0

controlled easily, and the metal complex can, in principle, be purified prior to the immobilization step. But very often this is not an easy task, since the complexes cannot be chromatographed, sublimation does not work for heavier species, and successful crystallization is often prevented by the long alkyl chains of the phosphine ligands.[18] A further disadvantage of route 1 is that sensitive transition metal complexes like the one depicted in Scheme 1 might undergo decomposition when they hit the bare silica surface with the wrong end, which is, in this case, the COD moiety of the complex. This does not happen when a suitable precursor reacts with a previously modified silica surface (route 2).

Furthermore, the surface coverage with phosphines can be maximized independently and therefore a later "bleeding" of the catalyst is reduced. Route 2 also offers the option of a rational synthesis of a bigger batch of starting material for the immobilization of different catalysts.

Therefore route 2 (Scheme 1) was studied in more detail in this contribution. The analytical method of choice is ^{31}P solid-state NMR spectroscopy, because of the great natural abundance (100%) and large chemical shift dispersion of this spin $^1/_2$ nucleus. The quality of the spectra is improved by magic angle spinning (MAS)[11,19] and cross polarization (CP)[20] techniques.

When phosphines like $Ph_2P(CH_2)_3Si(OEt)_3$ (**1**) or $Ph_2P(CH_2)_2Si(OEt)_3$ (**2**) are reacted with silica, a surface-bound phosphine **4** is formed together with a side product **3** in variable amounts.[2] Since **1** and **2** react in exactly the same way, out of reasons of clarity, the rest of the paper will deal with **1** only.

Formation of **3** can be seen in the ^{31}P CP/MAS NMR spectrum as an additional resonance at 25.9 ppm besides the one of the surface-bound phosphine **4** at -16.3 ppm. The side product **3** is usually called the "phosphine oxide",[21] on the basis of its ^{31}P NMR signal shift value, which is, however, somewhat low at about 26 ppm.[17,22]

This contribution sheds some light on the true nature of the byproduct **3** and shows how it can be avoided easily, which is extremely important considering the fact that **3** occupies space on the surface but is unable to bind transition metal complexes and thus reduces the actual surface coverage with phosphines and enhances bleeding effects.

II. Results

1. Immobilization of Diphenylphosphinic acid and Phenylphosphonic acid. When silica $[SiO_2]-OH$ is treated with diphenylphosphinic acid, a simple condensation reaction with surface silanol groups takes place to form $[SiO_2]-O-P(O)-Ph_2$. The ^{31}P CP/MAS NMR spectrum of such modified silica is shown in Figure 1. A large chemical shift anisotropy (CSA) as is known for other derivatives of diphenylphosphinic acid[22] is observed. This manifests itself in a multitude of rotational sidebands at a spinning frequency of 4 kHz. An analogous result is obtained after reaction of phenylphosphonic acid with silica.

2. Role of Oxygen. Even in solution, phosphine **1** is oxidized only slowly by oxygen, over the course of days. When phosphine **1** is reacted with SiO_2 at 90 °C without exclusion of air, surface-bound phosphine oxide **5** forms as expected (Scheme 2). But there also remains a large amount of intact surface-bound phosphine **4** and of byproduct **3**.

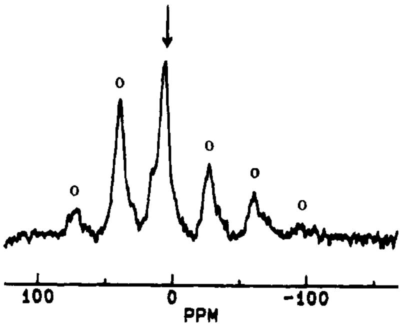

Figure 1. 121.5 MHz ^{31}P CP/MAS NMR spectrum of diphenylphosphinic acid immobilized on silica. The arrow denotes the isotropic line; the circles, rotational sidebands.

The ^{31}P CP/MAS NMR spectrum of the material is shown in Figure 2, which contains the signals of **3**–**5**. The ^{31}P NMR chemical shift value (Table 1) matches the one of free oxide, synthesized independently and measured with liquid-state NMR, very well. When phosphine-modified silica **4** containing the side product **3** is oxidized by treatment with H_2O_2,[23] the silica-bound phosphine oxide **5** is obtained quantitatively, whereas **3** does not react (Scheme 2). This is demonstrated by the ^{31}P CP/MAS NMR spectrum of the material (Figure 3).

When **1** is reacted with silica under rigorous exclusion of oxygen, some Ph_2PH is usually found in the liquid phase. Ph_2PH does not react with silica, but even traces of oxygen transform it into Ph_2PHO.

3. Role of Temperature. The influence of the reaction temperature on the formation of side product **3** (Scheme 2) was studied quantitatively by ^{31}P CP/MAS NMR spectroscopy. (It is shown below that the integrals of the signals are quantitatively reliable.) The ratio **3**/**4** as a function of the reaction temperature, is at a constant reaction time of 12 h, is given in the Experimental Section.

As it is shown in Figure 4, reaction at 50 °C gives only little **3**, while the yield of **3** increases rapidly with reaction temperature. The maximum surface coverage of about 6 weight % carbon atoms, as determined by elemental analysis, is obtained already at 25 °C with stirring overnight.

4. Protonation of Surface-Bound Phosphine 4. Treatment of phosphine-modified silica **4** containing some side product **3** with hydrochloric acid (Scheme 2) results in transformation of all the phosphine into the corresponding phosphonium salt. The byproduct **3**, however, is not altered, as can be seen in the ^{31}P CP/MAS NMR spectrum (Figure 6, bottom spectrum). The high-field signal at 5 ppm corresponds to the phosphonium salt; the smaller one stems from residual **3**.

5. A Model Compound. In contrast to tertiary phosphine oxides, diphenylphosphine oxide **7** does react with the surface silanol groups of silica (Scheme 2). The ^{31}P CP/MAS NMR spectrum of the resulting material **8** displays a signal with nearly identical chemical shift and CSA as compared to the signal of **3**. The ^{13}C CP/MAS NMR spectrum of silica, modified by reaction with **7**, demonstrates that the phenyl groups are still present (Figure 5).

The side product **3** gives an analogous ^{13}C CP/MAS spectrum with additional resonances of residual OEt groups and of the methylene groups. When diphenylphosphine oxide **7** is treated with $HOSiEt_3$ instead of SiO_2 under the same conditions, an inseparable oily mixture of several species, with ^{31}P chemical

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(18) Grobe, J.; Martin, R.; Huttner, G.; Zolnai, L. *Z. Anorg. Allg. Chem.* **1992**, *607*, 79.

(19) Fyfe, C. A. *Solid-State NMR for Chemists*; C. F. C. Press: Guelph, Canada, 1983; and literature cited therein.

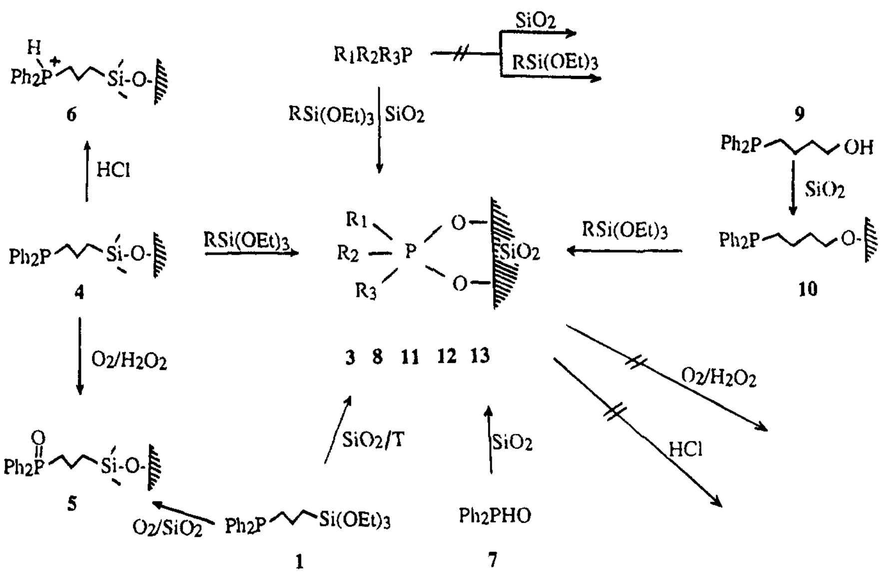
(20) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.

(21) Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; *Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987; p 473.

(22) Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; Farragut Press: Chicago, 1990; and literature cited therein.

(23) Copley, D. B.; Fairbrother, F.; Miller, J. R.; Thompson, A. *Proc. Chem. Soc.* **1964**, 300.

Scheme 2. Overview of the Main Results of Section II[a]



[a] R = 3-chloropropyl, vinyl, methyl; R_1, R_2 = Ph = C_6H_5; R_3 = H (**8**), $(CH_2)_3Si-O-[SiO_2]$ or $Si(OEt)_3$ (**3**), $(CH_2)_4-O-[SiO_2]$ or $(CH_2)_4OH$ (**11**), CH_2CH_3 (**12**), C_6H_5 (**13**). For the reaction conditions, see the Experimental Section and text.

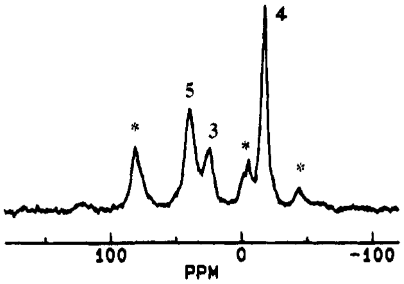


Figure 2. 121.5 MHz ^{31}P CP/MAS NMR spectrum of silica after immobilization of phosphine **1** in air: **3** = side product; **4** = immobilized phosphine; **5** = phosphine oxide. Asterisks denote rotational sidebands of signal **5**.

Table 1. ^{31}P Chemical Shifts from ^{31}P CP/MAS NMR Spectra of Surface-Bound P(III) and P(V) Species

no.	P(III) and P(V) species	$\delta(^{31}P)$
4	$Ph_2P(CH_2)_3Si{\leqslant}O-[SiO_2]$	−16.3
	$Ph_2P(O)-O-[SiO_2]$	7.5
	$PhP(O)(-O-[SiO_2])_2$	20.6
5	$Ph_2P(O)(CH_2)_3Si{\leqslant}O-[SiO_2]$	39.5
6	$Ph_2P^+H(CH_2)_3Si{\leqslant}O-[SiO_2]$	5.8
3	$Ph_2P(-O-[SiO_2])_2(CH_2)_3Si{\leqslant}O-[SiO_2]$	25.9
8	$Ph_2PH(-O-[SiO_2])_2$	26.3
10	$Ph_2P(CH_2)_4-O-[SiO_2]$	−16.8
11	$Ph_2P(-O-[SiO_2])_2(CH_2)_4-O-[SiO_2]$	26.7
12	$Ph_2P(CH_2CH_3)(-O-[SiO_2])_2$	28.2
13	$Ph_3P(-O-[SiO_2])_2$	27.0

shifts around 25 ppm, results. The P—H bond is retained in all the compounds while there is no more P═O bond, as evidenced by the ^1J(P—H) couplings and IR spectroscopy of the mixture. This mixture reacts with silica, which is shown by the ^{31}P CP/MAS NMR spectrum of the material. The latter is identical with the one of modified silica, obtained by treatment with **7**.

6. NMR Experiments. Applied without intimate knowledge of the measured system, cross polarization can lead to grossly distorted signal intensities and thus render quantification of spectral results unreliable. Therefore, phosphine-modified silica **4** containing some **3** was measured ^{31}P NMR spectroscopically with simple high-power proton decoupling. While maximum signal intensity of **4** is already obtained with a pulse delay of 10 s, the resonance of **3** requires a delay of ≥100 s in order to achieve maximum intensity. The same observation is made when a simple one-pulse sequence without proton decoupling is applied. In this case, both the ^{31}P NMR signals of **3** and **4** are broadened by about 0.4 kHz due to dipolar couplings to protons. Since relaxation delays of about 100 s render quantita-

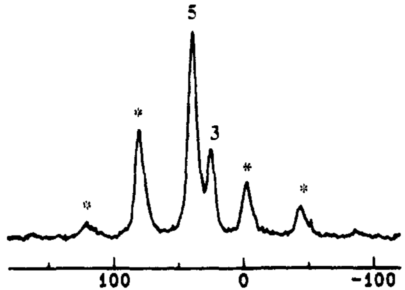


Figure 3. 121.5 MHz ^{31}P CP/MAS NMR spectrum of phosphine-modified silica **4**, containing some side product **3**, after oxidation with H_2O_2: **3** = side product; **5** = phosphine oxide. Asterisks denote rotational sidebands of signal **5**.

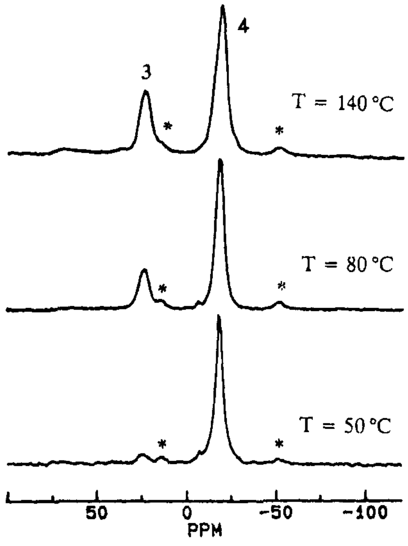


Figure 4. 121.5 MHz ^{31}P CP/MAS NMR spectrum of silica, modified with phosphine **1** at the given temperatures: **3** = side product; **4** = silica-immobilized phosphine **1**. Asterisks denote rotational sidebands of signal **4**.

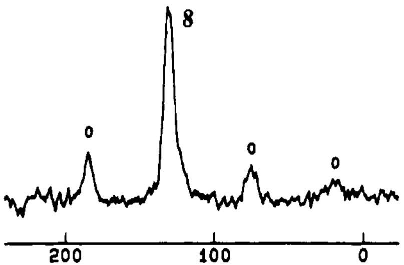


Figure 5. 75.5 MHz ^{13}C CP/MAS NMR spectrum of silica **8**, prepared by reaction of silica with diphenylphosphine oxide (**7**). Circles denote rotational sidebands of the phenyl resonance **8**.

tive routine measurements impractical, cross polarization has to be optimized with respect to correct quantification of the results.

Variation of the contact time between 0.25 and 15 ms shows that (fortunately) optimum signal intensity for both **3** and **4** is obtained with 1 ms. The signal intensities as a function of contact time are given in the Experimental Section. Using cross polarization with a contact time of 1 ms and a pulse delay of 4 s results in spectra that are identical with the ones obtained by simple high-power decoupling with a pulse delay of 100 s. The signal intensity of **4** displays only slight changes within the studied range of contact times. In contrast, the intensity of the ^{31}P NMR signal of **3** declines rapidly with longer contact times. Measurement of **3** and **4** with CP but without MAS gives a wide-line spectrum for **4** that displays a CSA typical of free and surface-bound phosphines.[2,17,22] while the ^{31}P signal of **3** shows only slight broadening (MAS, half-width 1.0 kHz; wide-line, half-width 1.2 kHz) and hence vanishing CSA.

The question, however, whether all the above mentioned surface-bound species have protons attached to their ^{31}P atoms can only be answered by dipolar dephasing experiments.[24]

Hereby, a variable delay without ^{1}H decoupling is inserted between the contact time and the acquisition of the FID. Due to dipolar interactions, the signals of ^{31}P nuclei with attached protons are shrinking as compared to those of proton-free ^{31}P nuclei when longer delays (40–80 μs) are applied. However, care must be taken because of the high mobility of all the species involved.[25,26] Therefore the surface-attached phosphonium salt **6** and phosphine **4** were used as internal intensity standards. The lower half of Figure 6 shows that the signal of the phosphonium phosphorus atom is shrinking to about half its original size, when the delay is increased to 40 μs. The signals of the side product **3** and phosphine **4**, on the other hand, are not altered in intensity by delays of up to 80 μs (upper half of Figure 6). The loss of intensity of the ^{31}P NMR signal of modified silica **8** is already quite evident with a delay of 40 μs.

7. Oxidizing Agents. In order to further elucidate the structure of the unknown species **3**, the knowledge of the phosphine-oxidizing agent(s) is essential. When secondary or tertiary phosphines like Ph_3P, Ph_2PEt, or Ph_2PH are treated with silica under conditions analogous to those applied for the immobilization of **1** (Scheme 1), no surface-attached species can be detected (Scheme 2). The solution contains only unchanged phosphines. Furthermore, the degree of hydration of the silica material or its brand does not matter at all with respect to the result of the reaction of **1** with silica. The same is true for the kind of solvents. No changes are observed when toluene is replaced by THF, ether, ethanol, diglyme, or triglyme.

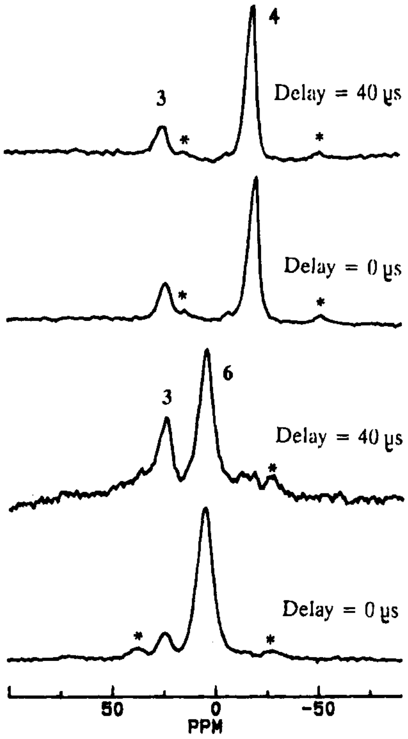


Figure 6. Dipolar dephasing experiments of original (top two spectra) and protonated (bottom two spectra) silica **4**, containing little **3**, with the given delays: **3** = side product; **4** = silica-immobilized phosphine **1**; **6** = phosphonium salt of **4**. Asterisks denote rotational sidebands of signals **4** and **6**.

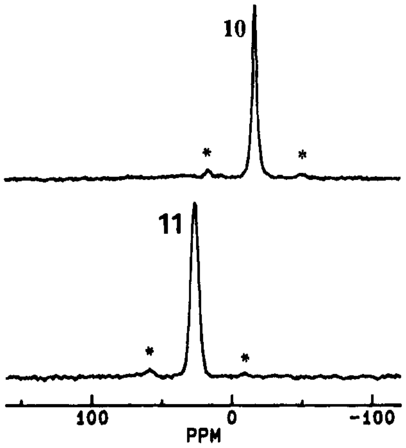


Figure 7. 121.5 MHz ^{31}P CP/MAS NMR spectra of modified silica: top trace, immobilized (4-hydroxybutyl)diphenylphosphine (**10**); bottom trace, P(V) species **11**, prepared by treatment of **10** with $RSi(OEt)_3$. Asterisks denote rotational sidebands.

When diphenyl(4-hydroxybutyl)phosphine (**9**) is attached to the silica surface via the hydroxyl group, surface-immobilized **10** is the only product (Scheme 2). Even at reaction temperatures higher than 140 °C no side product can be detected by ^{31}P CP/MAS NMR (Figure 7, top spectrum). In solution there is just residual starting phosphine, but no oxidized species and especially no Ph_2PH can be found by ^{31}P NMR spectroscopy. However, when surface-attached **10** is treated with an excess of $RSi(OEt)_3$ (R = 3-chloropropyl, vinyl, methyl; others not tested but probably equally effective), a species **11** is formed quantitatively (Scheme 2 and Figure 7, bottom spectrum). Species **11** displays ^{31}P NMR spectroscopic characteristics which are identical with those of **3**. The side product **3** can also be obtained quantitatively by treatment of surface attached **4** with $RSi(OEt)_3$ (Scheme 2).

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(24) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

(25) Pfleiderer, B.; Albert, K.; Lork, K. D. K.; Unger, K. K.; Brückner, H.; Bayer, E. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 327.

(26) Zeigler, R.; Maciel, G. E. *J. Phys. Chem.* **1991**, *95*, 7345.

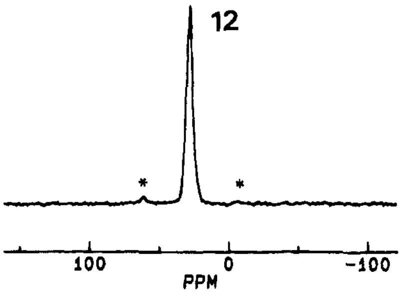

Figure 8. 121.5 MHz ^{31}P CP/MAS NMR spectrum of $Ph_2PEt/RSi(OEt)_3$-modified silica **12**. Asterisks denote rotational sidebands.

When Ph_2PEt, together with an equimolar amount of $RSi(OEt)_3$, is stirred with silica, the ^{31}P CP/MAS spectrum of the latter shows a signal of **12** at 28.2 ppm that is again analogous to the one of the side product **3** (Scheme 2 and Figure 8). Ph_2PEt does not react with $RSi(OEt)_3$ in solution even at elevated temperatures (Scheme 2). Addition of simple molecular silanols does not lead to any reaction, either.

Both the silica surface and $Si(OEt)_3$ groups are necessary for the production of species like **8**, **11**, and **12**, analogous to **3**. Not only Ph_2PEt, but all phosphines that would not react with silica alone, can easily be attached to the surface with high coverage as P(V) species by addition of $RSi(OEt)_3$ (Scheme 2).

III. Discussion

The main results of the previous section are summarized in Scheme 2 and Table 1. On the basis of these results, the presented surface-bound, oxyphosphorane type structure with a pentacoordinated P(V) atom is proposed as the common structure of the side product **3** and its analogs **8** and **11**−**13**. Hereby, an ionic structure or a cyclic structure for **3** and **11** is not excluded and both phosphorus-bound oxygen atoms might also stem from geminal silanol groups. The evidence for the suggested structure is discussed in detail in the following paragraphs. For the sake of clarity, **3** is taken as a representative, but the argumentation also accounts for its analogs **8** and **11**−**13**.

1. As compared to liquid-state NMR, solid-state NMR spectra offer the chemical shift anisotropy (CSA) as an additional piece of information. The CSA is often characteristic for the signals of one type of functional group[19,22] and manifests itself in the intensity and number of rotational sidebands at moderate spinning frequencies.[27]

The solid-state ^{31}P NMR signals of species with a P═O double bond generally show large CSA values.[17,22,28,29] This is also illustrated by the ^{31}P CP/MAS NMR spectrum of silica after treatment with diphenylphosphinic acid (Figure 1), which undergoes a condensation reaction with the P(OH) group while the P═O double bond is retained. Regarding the vanishing CSA of the ^{31}P NMR signal of the side product **3** (Figure 4), it is rather unlikely that it should originate from a phosphine oxide or another species with a P═O double bond. In particular a comparison with the spectra of surface-attached phenylphosphonic acid and diphenylphosphinic acid (Figure 1) shows that **3** cannot be a derivative of these acids.

2. The results of section II.2 show that oxygen cannot possibly be responsible for the formation of side product **3**. The presence of air-sensitive diphenylphosphine in the liquid phase when working under nitrogen indicates that oxygen can be excluded effectively. Furthermore, the ratio of **3**/**4** is not changed when oxygen is admitted to the reaction mixture. Even if the immobilization reaction (Scheme 1, route 2) is run at a high temperature in air, there still remains a large amount of intact phosphine **4** and side product **3** (Figure 2). The third signal of the spectrum shows the true phosphine oxide **5** with a ^{31}P chemical shift of 39.5 ppm which was expected from literature data[22] and liquid-state NMR of the free phosphine oxide synthesized independently. As already mentioned above, the found ^{31}P chemical shift value of 25.9 ppm for **3** would be unusual for a phosphine oxide.[22] The large chemical shift anisotropy of **5** is in accord with the CSA data of other tertiary phosphine oxides.[22] Therefore, from the chemical shift (25.9 ppm) and the vanishing CSA of **3** and from the presence of **3** besides **5** in the spectrum (Figure 2), it is obvious that **3** cannot be the phosphine oxide and in particular that it cannot contain a P═O double bond. The fact that **3** is not oxidized by hydrogen peroxide demonstrates that **3** must already be a phosphorus(V) species.

3. As shown by the results in II.3, the formation of **3** depends on the reaction temperature. Therefore, the side product **3** can be obtained quantitatively by heating phosphine-modified silica **4** for a prolonged period of time. On the other hand, with the knowledge of this temperature dependence, **3** can be avoided easily and effectively by just running the immobilization reaction at 40 °C or below. The surface coverage is not diminished by this, and there is no need for one further reduction step with trichlorosilane,[2] which might destroy sensitive transition metal complexes that are to be immobilized later.

4. Since it is known that the surfaces of inorganic supports can be fairly acidic,[30] it seemed worthwhile to test whether the side product **3** could possibly be a phosphonium salt. However, the results in II.4 show that **3** is different from a phosphonium species (Scheme 2). Furthermore they prove that **3** cannot be protonated and, therefore, most probably does not have a free electron pair at the phosphorus atom.

5. In order to further prove the structure of **3** displayed in Scheme 2, a model compound was employed. Unfortunately compounds of the type $RP(OR)_2(OR')_2$ and $R_3P(OR)_2$ are all oily liquids or low melting solids that cannot be measured with MAS NMR. However, it was found in the course of this work that diphenylphosphine oxide (**7**) reacts with silica under formation of a surface-bound species **8** analogous to **3**. As was demonstrated earlier,[31,32] the P═O double bond of **7** is very polar. Therefore, the reaction of **7** with surface silanol groups of silica is proposed to proceed via an addition reaction prior to a possible condensation step with one more silanol group according to the following:

$$\underset{\mathbf{7}}{Ph_2PHO} + HO-[SiO_2] \rightarrow$$

$$Ph_2PH(OH)-O-[SiO_2] \rightarrow \underset{\mathbf{8}}{Ph_2PH(O-[SiO_2])_2}$$

Unfortunately, when **7** is reacted with $HOSiEt_3$, a mixture of several species is obtained. However, the structural elements of these liquid species (P−H bond present but no more P═O bond) are the same as the ones proposed for **8**. The solid-state NMR characteristics (δ, CSA) of the surface-bound model **8**

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(27) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

(28) Harris, R. K.; Merwin, L. H.; Hägele, G. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1409.

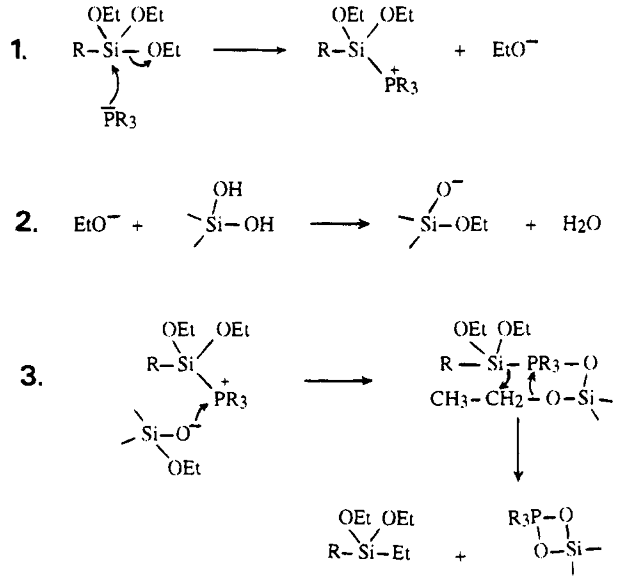
(29) Hargé, J.-C.; Abdallaoui, H. E. A. E.; Rubini, P. *Magn. Reson. Chem.* **1993**, *31*, 752.

(30) Pfeifer, H.; Freude, D.; Hunger, M. *Zeolites* **1985**, *5*, 274.

(31) Dahn, H.; Toan, V. V.; Ung-Truong, M.-N. *Magn. Reson. Chem.* **1992**, *30*, 1089.

(32) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

Scheme 3. One Possible Mechanism for the Generation of Silica-Bound Cyclic, Oxyphosphorane Type P(V) Species



are analogous to the ones of **3**. Different results are obtained with P−H discriminating NMR experiments as discussed below.

6. The different behavior of **3** and **4** toward variation of the CP time and the different ^{31}P relaxation times of **3** and **4** indicate that both species must have very different structural features. The complexity and number of different parameters like relaxation, mobility, and structure prevent a straightforward exploitation of these results. However, direct evidence for one structural element, namely the presence of a P−H bond, comes from the dipolar dephasing experiments.[24] With the use of the phosphonium salt **6** and the phosphine **4** as internal intensity standards, the absence of a P−H bond in **3** and **11**−**13** and its presence in **8** could be demonstrated unequivocally (Figure 6).

7. The results described in section II.7 (Scheme 2) show that both the silica surface and Si(OEt)$_3$ groups are necessary prerequisites for the formation of the P(V) species **3** and **11**−**13** when starting from P(III) precursors. Furthermore the oxidation reaction does not take place when the silica surface is simulated by molecular silanols. One possible mechanism for the formation of P(V) species is presented in Scheme 3. The nucleophilic addition of phosphines to atoms with a positive partial charge under the formation of phosphonium species is a quite common reaction.[33] Therefore in step 1 of the reaction mechanism, the phosphine adds to the positively polarized Si atom of RSi(OEt)$_3$. This reaction is facilitated by the removal of OEt$^-$ groups from the equilibrium by reaction with neighboring surface silanol groups of silica (step 2). These silanol groups do not necessarily have to be geminal, as illustrated in Scheme 3. In step 3 of the mechanism, a fast addition reaction takes place, which is followed by a pseudo-Wittig type rearrangement. The final product is a cyclic surface-bound P(V) species and a silane. Unfortunately the latter is most probably bound to the silica surface via the remaining two ethoxy groups and thus cannot easily be detected. Possible species containing P−OEt fragments cannot be expected in the liquid phase either, because these most probably undergo condensation reactions with surface silanol groups like the OSiEt$_3$ derivatives of **7** do (II.5). Although this mechanism must remain a hypothesis at the present stage, it supplies a plausible explanation for the formation of the oxyphosphorane type P(V) species.

In summary, the knowledge of this surface reaction is important: It helps to avoid the unwanted oxidation side reaction by using low reaction temperatures or bifunctional phosphines without Si(OEt)$_3$ groups like **10**. Additionally, it opens a new general method to prepare silica materials, modified selectively with tailored P(V) species. Among other widespread applications, they can be used as column materials for HPLC.[34]

IV. Conclusion

By using ^{31}P CP/MAS NMR spectroscopy, it could be demonstrated unequivocally that the long known side reaction that takes place when bifunctional phosphines are attached to silica by Si(OEt)$_3$ groups does not lead to the phosphine oxide. Instead a silica-bound pentacoordinated P(V) species is formed by the combined action of silica surface and Si(OEt)$_3$ groups. Analogous surface-bound species can also be generated from all monofunctional, unreactive phosphines by addition of RSi(OEt)$_3$ to the reaction mixture. From the point of view of attaching catalytically active metal complexes on silica surfaces, the side reaction should be avoided. This can easily be done by reacting the bifunctional phosphines **1** and **2** with silica at room temperature or by using phosphines like **10**.

Experimental Section

Solid-State NMR Spectroscopy. All ^{31}P solid-state NMR spectra were recorded on a Bruker MSL 300 spectrometer, equipped with a 7 mm double bearing MAS probehead. Cross polarization (CP),[20] magic angle spinning (MAS)[11,19] with rotational speeds of 4−4.5 kHz, and high-power decoupling were used. The recycle delay was 4 s, and the optimized contact time (see text, section II, and data given below in Silica-Supported Phosphines) was 1 ms. Usually 500−1000 transients gave satisfactory signal to noise ratios. The modified silica samples were filled loosely into the ZrO$_2$ rotors, and the spinning speed was enhanced slowly in order to let the material settle down symmetrically. The ratio of different phosphorus species as determined by integration of their ^{31}P solid-state NMR signals did not change when simple high-power decoupling with a relaxation delay of 100 s was used instead of CP. All spectra were recorded at room temperature (296 K) and referenced with respect to 85% H$_3$PO$_4$ (aq) by setting the ^{31}P NMR peak of solid NH$_4$H$_2$PO$_4$ to +0.81 ppm. The Hartmann−Hahn match was set by using solid NH$_4$H$_2$PO$_4$, and a typical 90° pulse width was 4 μs.

Experimental Technique. If not stated otherwise, all experiments were performed under purified inert gas by Schlenk techniques. Solvents were dried by standard methods, and oxygen was removed. The identity of molecular compounds was checked by their elemental analyses, carried out by the microanalytical laboratory of the Anorganisch-chemisches Institut, and by their solution-state ^{1}H, ^{13}C, and ^{31}P NMR spectra.

Silica. All the experiments were carried out independently with Merck silica 40 and 60, both with different degrees of hydration. The silica was either dried at room temperature or at 600 °C in vacuo (10^{-2} Pa) in order to remove adsorbed water[14] or condense surface silanol groups, respectively.[14] The results of the experiments did not change with the water content or brand of the silica material used.

Ph$_2$P(CH$_2$)$_2$Si(OEt)$_3$ (2). **2** was prepared according to the procedure given by Howell.[4]

Ph$_2$P(CH$_2$)$_3$Si(OEt)$_3$ (1). **1** was prepared from Ph$_2$PLi[35] and (3-chloropropyl)triethoxysilane according to the procedure given by Capka.[15]

Ph$_2$PHO (7). Diphenylphosphine oxide (**7**) was freshly prepared from Ph$_2$PH according to the procedure given by Rauhut[36] before use.

Ph$_2$P(CH$_2$)$_4$OH (9). Diphenyl(4-hydroxybutyl)phosphine (**9**) was synthesized using the procedure given by Garner.[37]

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(33) Kosolapov, G. M.; Maier, I. *Organic Phosphorus Compounds*; Wiley-Interscience: New York, 1972.

(34) Lukes, I.; Borbaruah, M.; Quin, L. D. *J. Am. Chem. Soc.* **1994**, *116*, 1737.

(35) Luther, G. W.; Beyerle, G. *Inorg. Synth.* **1977**, *17*, 186.

(36) Rauhut, M. M.; Currier, H. A. *J. Org. Chem.* **1961**, *26*, 4626.

(37) Garner, A. Y.; Tedeschi, A. A. *J. Am. Chem. Soc.* **1962**, *84*, 4734.

Silica-Supported Phosphines. In a typical experiment, 0.5 g of silica was slurried in about 20 mL of toluene and an excess of reagent (0.2 g) was added.[2] Then the reaction mixture was warmed to the desired reaction temperature and stirred overnight or the time given in the schemes. Then the silica was allowed to settle down at room temperature. The solution was decanted and the silica washed three times with toluene and then dried for 5 h in vacuo at room temperature. A surface coverage of about 6 weight % carbon atoms is usually obtained, as determined by elemental analysis. $\delta(^{31}P) = -16.3$ (**4**) and -16.8 (silica-supported **2**). Ratio of side product **3** to supported phosphine **4** as a function of reaction temperature (°C): 0.00 (30); 0.04 (40); 0.07 (50); 0.12 (60); 0.16 (70); 0.23 (80); 0.27 (90); 0.31 (100); 0.35 (110); 0.40 (120); 0.41 (130); 0.43 (140). Hereby the solvent for the temperature range 20−90 °C was toluene and for 100−140 °C diglyme and a constant reaction time of 12 h was applied. Intensity ratio of the ^{31}P CP/MAS signals of the side product **3** and phosphine **4** as a function of CP contact time (ms): 0.41 (0.25); 0.48 (0.5); 0.63 (1.0); 0.53 (1.5); 0.49 (2.0); 0.46 (3.0); 0.31 (4.5); 0.25 (6.0); 0.16 (8.0); 0.14 (10.0); 0.13 (12.0); 0.11 (15.0).

Reaction of Ph_2PHO (7) with Silica. Silica was treated with **7** at 90 °C in the same way as it is described for the supported phosphines above.

Silica-Supported Phosphine Oxide 5. Method a. **1** was reacted with silica at 80 °C as described above but under air. $\delta(^{31}P) = 39.5$ (**5**).

Method b. **1** was reacted with silica as described above at a temperature of 80 °C, so that the obtained ratio of **4**:**3** was about 3:1. A 0.5 g amount of this modified silica was slurried in about 10 mL of acetone and 1 mL of a 10% solution of H_2O_2 in H_2O was added[23] before stirring overnight at room temperature. Then the solution was decanted and the residue dried in vacuo. $\delta(^{31}P) = 39.7$ (**5**).

Silica-Supported Phosphonium salt 6. A 0.5 g amount of silica **4**, which was modified with **1** at 75 °C, was stirred with 10 mL of concentrated HCl at room temperature overnight. Then the solution was removed and the silica was dried in vacuo. $\delta(^{31}P) = 5.8$.

Generation of 3 and 11−13. Method a. A 0.5 g amount of **4** or **10** was slurried in 20 mL of toluene. Then an excess of $RSi(OEt)_3$ (R = 3-chloropropyl, vinyl, methyl) (0.5 g) is added and the mixture is stirred overnight at 80 °C. Workup is as described above. $\delta(^{31}P) = 25.9$ (**3**) and 26.7 (**11**).

Method b. A 0.5 g amount of silica was slurried in 20 mL of toluene, and equimolar amounts of monofunctional phosphines (e.g. Ph_2PEt, Ph_3P) and $RSi(OEt)_3$ were added. After being stirred at 80 °C overnight, the reaction mixture was worked up as described above. $\delta(^{31}P) = 28.2$ (**12**) and 27.0 (**13**).

Acknowledgment. I am especially thankful for many fruitful discussions with Prof. F. H. Köhler (TU München) and Prof. R. K. Harris (University of Durham). Furthermore I thank the Fonds der Chemischen Industrie for a Liebig fellowship and financial support. I am also grateful for financial support by the Leonhard Lorenz foundation and the Pinguin foundation.