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Immobilization of Phosphines on Silica: Identification of Byproducts via ^{31}P CP/MAS Studies of Model Alkyl-, Aryl-, and Ethoxyphosphonium Salts

J. Sommer, Y. Yang, D. Rambow, and J. Blümel*

*Organisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270,
69120 Heidelberg, Germany*

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Immobilizing bifunctional phosphines with ethoxysilane groups on silica often leads predominantly, and sometimes quantitatively, to P(V) side products that occupy space on the surface but cannot bind metal complexes. Although this side reaction is well-known, and dreaded because it leads to leaching of adsorbed catalysts that are not bound covalently, the exact nature of the surface-bound side product was not yet known. With the help of polycrystalline model compounds of the types $[R_3PEt]^+X^-$ and $[R_3POEt]^+X^-$ (R = alkyl, aryl; X = Cl^-, Br^-, I^-, BF_4^-) and their solid-state NMR characteristics [$\delta(^{31}P)$, CSA], it is demonstrated that the side product is an ethylphosphonium salt bound to the surface by a siloxide anion, $[R_3PEt]^+[Si–O]^-$.

Surface-bound species are of established importance in a variety of different areas, such as combinatorial chemistry,[1] solid-phase synthesis,[2] chromatography,[3] and catalysis.[4] We have been active in the latter field, improving the recyclability and lifetimes of homogeneous catalysts by binding them to oxidic supports.[5] In this capability, solid-state NMR spectroscopy[6] has proved to be an indispensable analytical method. We recently optimized the cross-polarization (CP) process at higher magic angle spinning (MAS) frequencies[7] in order to improve the signal-to-noise ratio (S/N) and added suspension NMR spectrocopy[8] to our repertoire that allows us to study mobilities and to quantitatively distinguish between adsorbed and covalently bound species.

Being thus equipped, we found that immobilizing metal complexes via bifunctional phosphines, such as $Ph_2P(CH_2)_3Si(OEt)_3$, involves many problems that can lead to the well-known leaching of catalysts. Most importantly, the proper choice of the support is crucial. For example, the ethoxysilane group cannot bind irreversibly to TiO_2, so that the linker is detached from the support even by washing the material with organic solvents.[8] Silica and $Si(OEt)_3$ groups turn out to be the optimal team, forming robust Si−O−Si bonds.[8] Then, metal complexes with two monodentate linkers are not necessarily bound in a chelating manner,[9a] again making them vulnerable to leaching.[9b] This problem can be solved by using chelating linkers.[5,9b,c] The greatest challenge, however, arises when side products are formed on the silica surface during the immobilization process. They occupy space on the surface, but they cannot bind metal complexes. Such a scenario was presented earlier,[10a] and with every new linker/support combination, this sort of side reaction can again take place.[10b] Although it was obvious long ago[10a] that the side reaction, taking place by the combined action of $Si(OEt)_3$ groups and the silica surface, led to a phosphonium-type P(V) surface species, the exact nature of the latter remained unclear. From the results presented earlier, it could be either

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* Corresponding author: Prof. Dr. J. Blümel. Tel.: (+49)6221-548470. Fax: (+49)6221-544904. E-mail: J.Bluemel@urz.uni-heidelberg.de.

(1) (a) Nicolaou, K. C., Hanko, R., Hartwig, W., Eds. *Handbook of Combinatorial Chemistry*; Wiley-VCH: Weinheim, Germany, 2002; Vols. 1 and 2. (b) Bannworth, W., Felder, E., Eds. *Combinatorial Chemistry*; Wiley-VCH: Weinheim, Germany, 2000.

(2) (a) Seneci, P. *Solid-Phase Synthesis and Combinatorial Technologies*; John Wiley & Sons: New York, 2000. (b) Zaragoza Dörwald, F. *Organic Synthesis on Solid Phase*; Wiley-VCH: Weinheim, Germany, 2000.

(3) (a) Vansant, E. F.; VanDer Voort, P.; Vrancken, K. C. *Characterization and Chemical Modification of the Silica Surface*; Elsevier: Amsterdam, 1995. (b) Scott, R. P. W. *Silica Gel and Bonded Phases*; John Wiley and Sons: New York, 1993.

(4) (a) Hartley, F. R. *Supported Metal Complexes*; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985. (b) DeVos, D. E., Vankelecom, I. F. J., Jacobs, P. A., Eds. *Chiral Catalyst Immobilization and Recycling*; Wiley-VCH: Weinheim, Germany, 2000.

(5) (a) Merckle, C.; Haubrich, S.; Blümel, J. *J. Organomet. Chem.* **2001**, *627*, 44. (b) Reinhard, S.; Soba, P.; Rominger, F.; Blümel, J. *Adv. Synth. Catal.* **2003**, *345*, 589. (c) Merckle, C.; Blümel, J. *Adv. Synth. Catal.* **2003**, *345*, 584. (d) Merckle, C.; Blümel, J. *Topics Catal.* **2004**, in press.

(6) (a) Bell, A. T., Pines, A., Eds. *NMR Techniques in Catalysis*; Marcel Dekker: New York, 1994. (b) Fyfe, C. A. *Solid-State NMR for Chemists*; C. F. C. Press: Guelph, Canada, 1983. (c) Stejskal, E. O.; Memory, J. D. *High-Resolution NMR in the Solid State*; Oxford University Press: New York, 1994. (d) Fitzgerald, J. J., Ed. *Solid-State NMR Spectroscopy of Inorganic Materials*; American Chemical Society: Washington, DC, 1999.

(7) Reinhard, S.; Blümel, J. *Magn. Reson. Chem.* **2003**, *41*, 406.

(8) Merckle, C.; Blümel, J. *Chem. Mater.* **2001**, *13*, 3617.

(9) Behringer, K. D.; Blümel, J. *Chem. Commun.* **1996**, 653. (b) Reinhard, S.; Behringer, K. D.; Blümel, J. *New J. Chem.* **2003**, *27*, 776. (c) Tsiavaliaris, G.; Haubrich, S.; Merckle, C.; Blümel, J. *Synlett* **2001**, 391.

(10) (a) Blümel, J. *Inorg. Chem.* **1994**, *33*, 5050. (b) Posset, T.; Rominger, F.; Blümel, J. *Chem. Mater.*, manuscript submitted.

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Table 1. Isotropic Chemical Shifts δ_{iso},[a] Principal CSA Components δ_{ii},[b] and CSA Values $^3/_2|\delta_{33} - \delta_{iso}|$ of Selected Polycrystalline Phosphonium Salts, as Derived from ^{31}P CP/MAS Measurements

compound	no.	δ_{iso}	δ_{11}	δ_{22}	δ_{33}	CSA[18]
$[Ph_3P(OEt)]BF_4$	**1**	48.2	80	69	-1^c	74
$[Ph_2P(OEt)CH_2]_2[BF_4]_2$	**2**	56.4/52.0	100	$82/64^d$	-13^d	104/98
$[Ph_2PMe(OEt)]BF_4$	**3**	53.3/51.5	104^c	77	-26^c	119/116
$[Cy_3POEt]BF_4$	**4**	69.6	107	91	8^c	92
$[Cy_3PEt]BF_4$	**5**	33.4	44	37	21	19
$[Ph_3PCH_2OMe]Cl$	**6**	19.6	36	23	1	28
$[Ph_3PMe]Cl$	**7**	18.9	34	23	−1	30
$[Ph_3PEt]BF_4$	**8**	25.8/23.6	38	25	16	$18/22^e$
$[Ph_3PEt]Cl$	**9**	28.4	46	31	9	29
$[Ph_3PEt]Br$	**10**	27.9	45	30	8	30
$[Ph_3PEt]I$	**11**	26.8	44	17	10	26^e
$[Ph_3P^nPr]Br$	**12**	25.5	45	28	5	30
$[Ph_2MePEt]BF_4$	**13**	28.0	46	23	16	27^e
$[Ph_2PEt_2]BF_4$	**14**	29.6	54	25	10^d	37^e
$[(Ph_2PEt)_2CH_2][BF_4]_2$	**15**	26.0	51	24	8	38^e
$[(Ph_2EtPCH_2)_2][BF_4]_2$	**16**	30.9	45^d	28	16	22
$[Ph_4P]Br$	**17**	19.0	38	16	0^c	29

[a] Values are ±0.2 ppm. [b] Values are generally ±1 ppm. [c] Values are ±3 ppm. [d] Values are ±2 ppm. [e] $^3/_2|\delta_{11} - \delta_{iso}|$.[18]

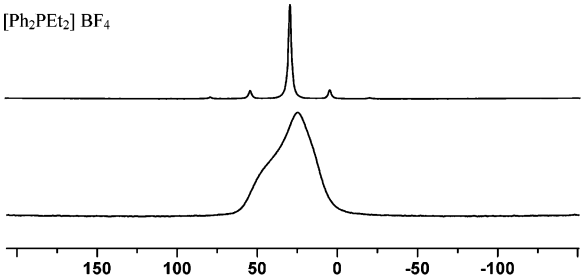

Figure 1. ^{31}P CP/MAS spectra of polycrystalline $[Ph_2PEt_2]BF_4$ (**14**) at 4 kHz (top) and 0 kHz (bottom) spinning speeds.

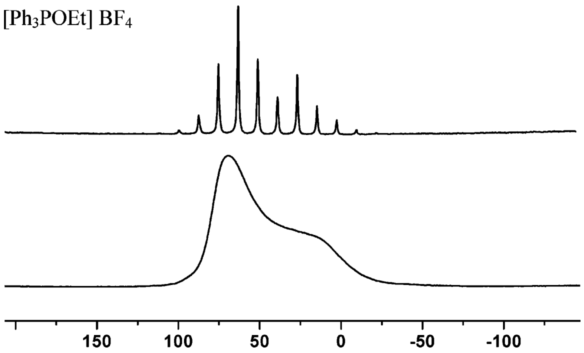

Figure 2. ^{31}P CP/MAS spectra of polycrystalline $[Ph_3POEt]BF_4$ (**1**) at 2 kHz (top) and 0 kHz (bottom) spinning speeds.

$[R_3POEt]^+[SiO]^-$ or $[R_3PEt]^+[SiO]^-$.[10a] Here, we demonstrate with model compounds and solid-state NMR spectroscopy[7] that the latter is correct.

Unfortunately, the side products have $\delta(^{31}P) = 20-34$ ppm, a spectral region that is fairly uncharacteristic because it is also frequented by other phosphorus compounds, e.g., phosphine oxides and phosphonic and phosphinic acids.[10a] Fortunately, solid-state NMR spectroscopy provides one more diagnostically valuable parameter, the chemical shift anisotropy (CSA), along with its principal components δ_{11}, δ_{22}, and δ_{33}.[11] In the following discussion, we apply the CSA definition described by Duncan.[11] As demonstrated previously,[10a] phosphine oxides and phosphonic and phosphinic acids could be ruled out as the side product. Although phosphonium salts of the type $[R_4P]^+$ were synthesized long ago with different counterions and substituents R,[12] we could not find their ^{31}P CSA values in the literature. This is astonishing, because phosphonium salts have ample applications as ionic liquids and polymerization initiators. The same is true for $[R_3POR]^+$-type salts.[13] Therefore, using $[Et_3O]^+[BF_4]^-$, we prepared various aryl and alkyl, as well as alkoxy, phosphonium salts of mono- and bidentate phosphines with different counterions (Table 1). The dppm- and dppe-type chelate phosphines could easily be doubly quaternized. However, as dppn-type bisphosphines,[14] dppp could not be doubly quaternized and was therefore omitted. The isotropic chemical shifts, $\delta_{iso}(^{31}P)$ (Table 1), correspond very well to the $\delta(^{31}P)$ values in solution and to literature data.[12,13] The spectra were usually obtained in less than 1 h, so δ_{11}, δ_{22}, and δ_{33} could be taken from the wide-line patterns recorded without sample spinning. For the salts **2**, **3**, and **8**, two isotropic signals are obtained at high spinning speeds even after recrystallization, rendering polymorphs unlikely and thus indicating that there are at least two magnetically inequivalent P nuclei in the unit cell. In the case of **2**, the CSA difference of the two signals is large enough to give even two δ_{22} maxima in the wide-line spectrum.

It is obvious (Table 1, Figures 1 and 2) that alkyl and alkoxy phosphonium salts have very different CSA ranges ($\delta_{11}-\delta_{33}$), the latter displaying wide-line spectra that span from 81 (**1**) to 130 (**3**) ppm, whereas the former result in rather narrow signals that are, even without spinning, merely between 20 (**13**) and 44 (**14**) ppm in width.

Furthermore, the $\delta_{iso}(^{31}P)$ values of the alkoxy phosphonium salts are between 50 and 70 ppm, whereas the values for the aryl and alkyl phosphonium salts can be observed within a range from 19 to 34 ppm. This matches the $\delta_{iso}(^{31}P)$ region for the side products found on silica. Therefore, we conclude that the unknown species on the surface must be of the type displayed in Scheme 1.

However, the phosphonium moiety does not necessarily have to be part of a linker. Even phosphines without ethoxysilane groups can be bound to silica by adding any other $Si(OEt)_3$-containing compound. This is demonstrated by the binding of Ph_3P, which normally does not react with silica, as a phosphonium salt to the surface. Figure 3 shows a comparison of the spectrum of the resulting $[Ph_3PEt]^+[SiO]^-$ (**18**) with that of $[Ph_3PEt]I$ (**11**).

As Figure 3 indicates, the counteranion of the phosphonium cations does not play a major role for $\delta_{iso}(^{31}P)$ or the CSA patterns. This is shown in Table 1 for the compounds

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(11) Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; Farragut Press: Chicago, IL, 1990.

(12) (a) Grim, S. O.; Davidoff, E. F.; Marks, T. J. *Z. Naturforsch.* **1971**, *26B*, 184. (b) Grim, S.; Yankowsky, A. W. *J. Org. Chem.* **1977**, *42*, 1236. (c) Olah, G. A.; McFarland, C. W. *J. Org. Chem.* **1969**, *34*, 1832.

(13) (a) Maeda, H.; Koide, T.; Maki, T.; Ohmori, H. *Chem. Pharm. Bull.* **1995**, *43*, 1076. (b) Crich, D.; Dyker, H. *Tetrahedron Lett.* **1989**, *30*, 475. (c) Denney, D. B.; Denney, D. Z.; Wilson, L. A. *Tetrahedron Lett.* **1968**, *1*, 85.

(14) Karacar, A.; Klaukien, V.; Freytag, M.; Thönnessen, H.; Omelanczuk, J.; Jones, P. G.; Bartsch, R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2589.

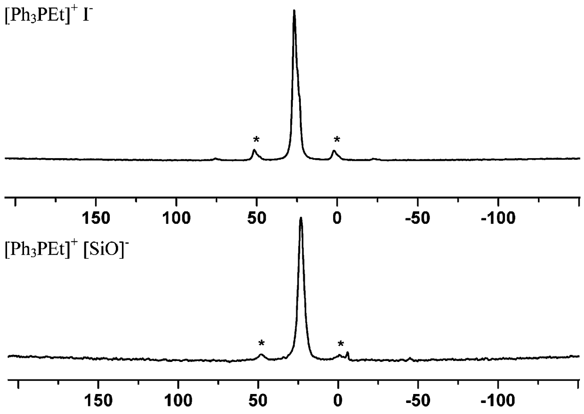
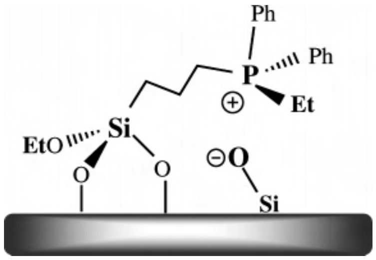


Figure 3. ^{31}P CP/MAS spectra of amorphous $[Ph_3PEt]^+[SiO]^-$ (**18**) and polycrystalline $[Ph_3PEt]I$ (**11**) at 4 kHz. Rotational sidebands are denoted by stars.

Scheme 1. Typical Side Product from the Immobilization of a Phosphine on Silica



8−11 with the same phosphonium moiety $[Ph_3PEt]^+$ and counterions varying from BF_4^- to Cl^-, Br^-, and I^-. Thus, changing the counterion to a surface siloxide anion $[Si{-}O]^-$ also should make no difference in the NMR characteristics.

Furthermore, it is known from previous work[10a] that aryl or alkyl substituents at ^{31}P do not change the $\delta_{iso}(^{31}P)$ value or the CSA patterns of the side products substantially. This is also found for the model compounds in Table 1. Going in a stepwise manner from the all-alkyl phosphonium salt **5** via diphenyl (**13−16**) and triphenyl (**6−12**) compounds to $[Ph_4P]^+Br^-$ (**17**) results in no major differences in the δ_{iso} or δ_{ii} values. Although the differences are greater, the same accounts for the alkoxy phosphonium salts **1−4**, another observation supporting the applicability of the model compounds and thus our assumption. Furthermore, comparing the practically identical data sets of **6** and **7** shows that substitution at the methyl group bound to phosphorus by a $-CH_2OCH_3$ group does not substantially alter the electronic symmetry around the P nucleus. To produce major differences in the $\delta_{iso}(^{31}P)$ and δ_{ii} values, the direct bonding of an alkoxy group to phosphorus is needed. This demonstrates that our criterion for distinguishing alkyl/aryl phosphonium salts from alkoxy phosphonium compounds is robust and generally applicable.

Initially, the quaternization of phosphines by ethyl groups from $Si(OEt)_3$ moieties on silica surfaces seems rather unlikely. However, the same process has recently been found by ^{13}C solid-state NMR spectral data: Tertiary amines treated with alcohols on zeolites at moderate temperatures of 200 °C could be transformed into ammonium salts on the surface.[15a] Furthermore, the selective *N*-methylation of amines with methanol could be achieved on oxidic supports.[15b] The proposed siloxide counterion $[Si{-}O]^-$ of the phosphonium cations is well-known, and the discrete siloxide−cation interactions on surfaces have, for example, just been studied in detail.[16]

Finally, the origin of the ethyl groups has to be addressed. It is known from earlier work[17] that the binding of ethoxysilyl groups to silica always results in surface-bound ethoxy groups, but also unreacted ethoxy groups at the silane moiety.[17b] Therefore, the ethyl groups quaternizing the phosphines could stem from either surface-bound ethoxy groups or from residual ethoxy groups from the $Si(OEt)_3$ functionalities. However, when ethoxy-modified silica[17a] was refluxed with Ph_3P in toluene, none of the phosphonium species formed. Therefore, we conclude that the quaternizing ethyl groups must stem from residual ethoxy groups bound to the silane functionality.

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(15) Wang, W.; Buchholz, A.; Ivanova, I. I.; Weitkamp, J.; Hunger, M. *Chem. Commun*. **2003**, 2600. (b) Oku, T.; Arita, Y.; Tsuneki, H.; Ikariya, T. *J. Am. Chem. Soc*. **2004**, *126*, 7368.

(16) Mammen, M.; Carbeck, J. D.; Simanek, E. E.; Whitesides, G. M. *J. Am. Chem. Soc*. **1997**, *119*, 3469.

(17) (a) Blümel, J. *J. Am. Chem. Soc*. **1995**, *117*, 2112. (b) Behringer, K. D.; Blümel, J. *J. Liq. Chromatogr*. **1996**, *19*, 2753.