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Review

Linkers and catalysts immobilized on oxide supports: New insights by solid-state NMR spectroscopy

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Contents

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ABSTRACT

This review article describes classical and modern solid-state NMR methods that allow to gain insight into catalyst systems where one or two metal complexes are bound to oxide supports via bifunctional phosphine linkers, such as $(EtO)_3Si(CH_2)_3PPh_2$. Many aspects of the immobilized molecular catalysts can be elucidated with the corresponding NMR technique. The bulk of the support can be studied, as well as the interface of the support with the ethoxysilane. With respect to the linkers, their structural integrity and mobility are as easy to investigate by classical CP/MAS and high-resolution magic angle spinning (HRMAS) NMR techniques, as their adsorption behavior. Even electrostatic bonding to the support via phosphonium

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Ethoxysilanes
Silica support
HRMAS NMR

groups can be proven by solid-state NMR. For the immobilized catalysts, leaching, and even "horizontal" translational mobility effects, as probed by HRMAS NMR under "realistic conditions" in the presence of solvents, are described.

1. Introduction

Immobilized species are important in such diverse areas as combinatorial chemistry [1], solid-phase synthesis [2], chromatography [3], or catalysis [4]. This review article will deal with catalysts bound covalently and by electrostatic interactions to oxide supports via bifunctional linkers, as seen from a solid-state NMR [5] perspective. Oxides as supports provide many advantages as compared to polymers. For example, their pore size in different solvents is constant, while it is not well controllable for swelling polymers. Oxides are chemically and thermally rather stable in organic solvents, and their thermal conductivity prevents local overheating effects. From a practical point of view, it is favorable that oxides, especially with large particle diameters, settle down quickly after the catalytic reaction, and the supernatant can easily be decanted without filtration or centrifugation. Because of these obvious advantages of oxide supports, and for reasons of brevity, the scope of this review will be limited to species immobilized on oxide supports. Furthermore, only immobilizations on preformed and well characterized oxide particles will be discussed, since these allow better control of the distance of the metal centers or linkers from one another, and also because sol–gel materials have been described in detail elsewhere previously [2a,3a,b,d,e], also by solid-state NMR methods [3d,e].

Many groups, including us, have tried to improve the recyclability and lifetime of immobilized catalysts by tethering them on oxide supports by linkers. Asking the modern oracle Scifinder about "immobilized catalysts" (not checking different expressions such as "tethered" or "surface-bound" catalysts), it tells one that there are about 9700 hits using that concept. However, probing this literature search program with "immobilized catalysts and solid-state NMR", the number of hits is diminished to about 60, albeit with increasing tendency over the years. The first classical publications on studying complexes immobilized via linkers with solid-state NMR by Fyfe and co-workers [6] remained monolithic stand-alones for many years. Some more recent representative publications from other groups with a deeper emphasis on solid-state NMR are given in reference [7]. From these 60 publications, over the years ca. 20 have assembled in this field from my group, and therefore, most of the instructive examples in this review article stem from our research. It is my hope that in the future more groups will include solid-state NMR, optimally classical as well as high-resolution magic angle spinning (HRMAS) methods, into their usual repertoire of analytical methods for studying immobilized catalysts. There is more information to be gained than the essential "making sure that the immobilization worked", and it is time that this field of immobilized catalysts, studied by NMR, goes beyond the "checking" phase, and materials and their functions are investigated more thoroughly and basically.

2. Phosphine linkers for immobilizing metal complexes

2.1. Synthesis and characterization of bifunctional phosphines

Since most transition metals form stable complexes with phosphine ligands, the most common linkers are bifunctional phosphines. While the phosphine function coordinates the metal center, alkoxysilane groups bind to the oxide supports. Among the alkoxysilanes, the ethoxysilanes are most popular, followed by methoxysilanes. The number of alkoxy groups per silane can be one, two, or three without major difference in the binding performance (see Section 3.3.1 below). Chlorosilanes are more reactive than alkoxysilanes, but this advantage with respect to surface binding makes them also unpleasant to handle, because they notoriously make glass stoppers of Schlenk flasks get stuck. Additionally, they suffer from the disadvantage that HCl is formed during the reaction with surface silanol groups, which takes a long time to remove from the surface. Residual traces of HCl, however, might have adverse consequences with respect to linker detachment from the support (see Section 3.3.1), or the lifetime of sensitive catalysts. This is also why we try to avoid chlorosilanes for end-capping and use Me_3SiOEt instead, if needed [8]. The reaction of alcohols with oxide surfaces is sluggish [9], and the C–O–Si bridge for example can easily be hydrolyzed [10]. Therefore, the classical linkers are phosphines containing intramolecular ethoxysilane groups. Scheme 1 presents a compilation of representative linkers that have been synthesized in our group [11,12,14,18] over the years.

Diphenylphosphine groups are most often used for linkers, because triaryl or diarylalkyl phosphines are not as oxygen sensitive as trialkylphosphines for example. One should point out, however, that oxide supports, which are evacuated at elevated temperatures and then kept strictly under nitrogen or argon as inert gas, do not oxidize phosphines *per se*. Even for sensitive secondary phosphines oxidation only happens due to the presence of molecular oxygen in the system, and not due to some magic "ever-present", surface-adsorbed oxygen, or any "surface peroxide". More information on phosphine oxidation on supports is given in Section 4.1.

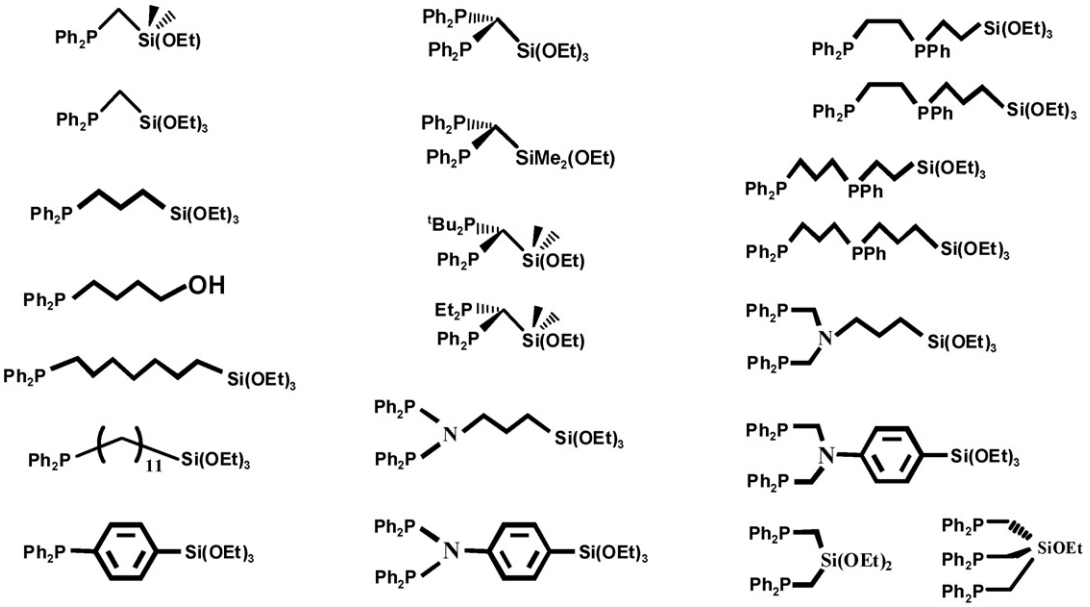
While the syntheses of the monodentate linkers are straightforward, each type of chelate linker needs its specific approach. Dppm-type linkers, for example, can be synthesized according to Scheme 2.

Luckily, although most of the bifunctional linkers presented in Scheme 1 are viscous liquids or low-melting solids, large single crystals could be obtained from $(Ph_2P)_2CHSiMe_2OEt$. They can serve as a textbook example of single crystal measurements without MAS, because at the proper orientation of the single crystal in the rotor all eight lines, as expected from the unit cell of the crystal, are visible (Fig. 1) [12].

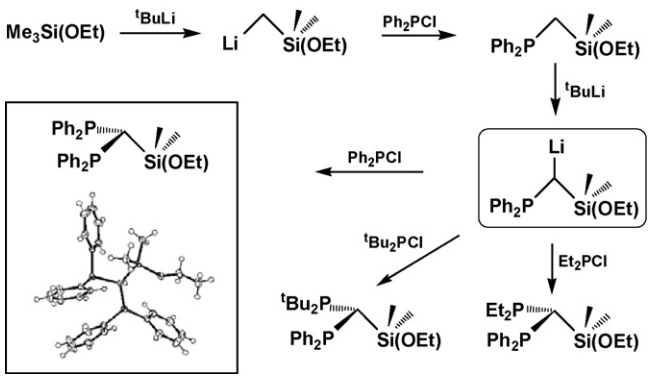
Most interesting from a liquids NMR point of view is that one can frequently observe virtual couplings [13] in the ^{13}C spectra of the chelate phosphine linkers [12,14,15]. Some of such classical patterns are shown in Fig. 2.

2.2. Complexation of the phosphine linkers

All the phosphine linkers displayed in Scheme 1 (Section 2.1) show the expected behavior, when coordinating them to transition metal complexes. This has been demonstrated multiple times with nickel complexes [10,12,16], dppe- and dppp-type rhodium complexes [17], palladium and copper complexes [15,18] or tungsten tricarbonyl complexes [14]. While decomposition of the linker-complex system on silica is not too unusual (see Section 3.3.2 below), it is rarely seen without the presence of silica. One formidable exception is the rearrangement of the tripod-type linker $(Ph_2PCH_2CH_2)_3SiOEt$ in the coordination sphere of rhodium due to its insertion into one C–Si bond, which happens already at ambient temperature in solution [19].



Scheme 1. Some classical and representative linkers for immobilizing metal complexes on oxide supports [11,12,14,18].



Scheme 2. Synthesis of dppm-type chelate linkers [12].

3. Classical immobilization of phosphine linkers

3.1. Reactions of ethoxysilanes with oxide surfaces

Chlorosilanes most probably react with surface silanol groups under formation of HCl, which has an adverse effect on the long-term stability of the Si–O–Si bridge and the lifetime of the catalysts (see Section 2.1 above). In contrast to this, ethoxysilane groups lead to the comparatively benign and easy to remove ethanol after a hydrolysis/condensation reaction with surface silanol groups, which is why they are preferred as linkers. However, early work already showed that besides this reaction path, the addition reaction of ethoxysilanes to strained surface siloxane groups can take place [8,20]. With silica that has been rigorously dried at 600 °C in oil pump vacuum for 12 h, this is even the preferred reaction pathway, and the ^{13}C CP/MAS spectra of silica modified with Me_3SiOEt show that the ethoxy group is retained on the surface quantitatively [8]. With more than one ethoxy function per silane the scenario becomes more complicated, because there are always residual ethoxy groups at the silanes, as the spectrum of an immobilized phosphinopropyltriethoxysilane indicates [21]. The number of residual ethoxy groups is independent of the substituent at the triethoxysilane group, as the example of the ^{29}Si CP/MAS spectrum of immobilized vinyltriethoxysilane in Fig. 3 shows [20].

Disregarding the chemical shift, the spectrum shows a typical 1:2:1 pattern of silane signals besides the bulk silicon resonances of the material. The same pattern is usually obtained for phosphine or other linkers with triethoxysilane groups after immobilization

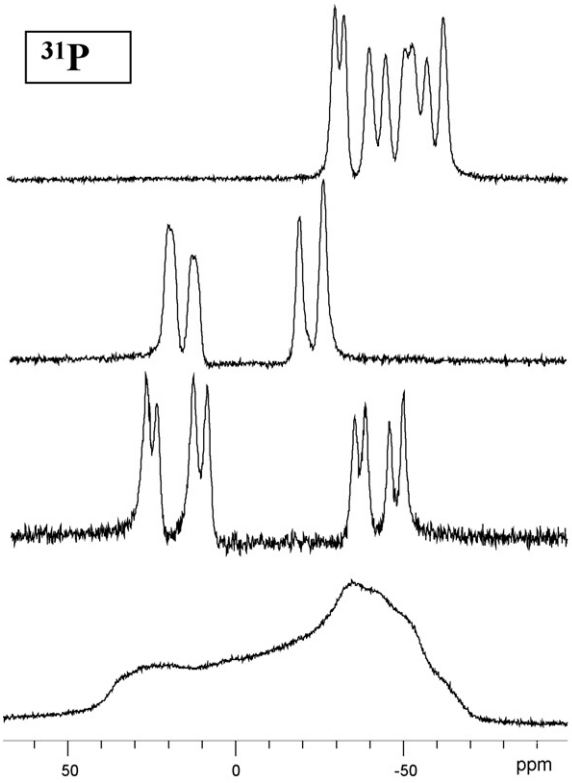


Fig. 1. Single crystal ^{31}P CP measurements of $(Ph_2P)_2CHSiMe_2OEt$ at different random orientations of the crystal in the rotor (top traces), and powder spectrum (due to the low melting point no thorough grinding of the single crystal was possible, hence the "bumpy" look of the wideline resonance) of the compound (bottom) [12].

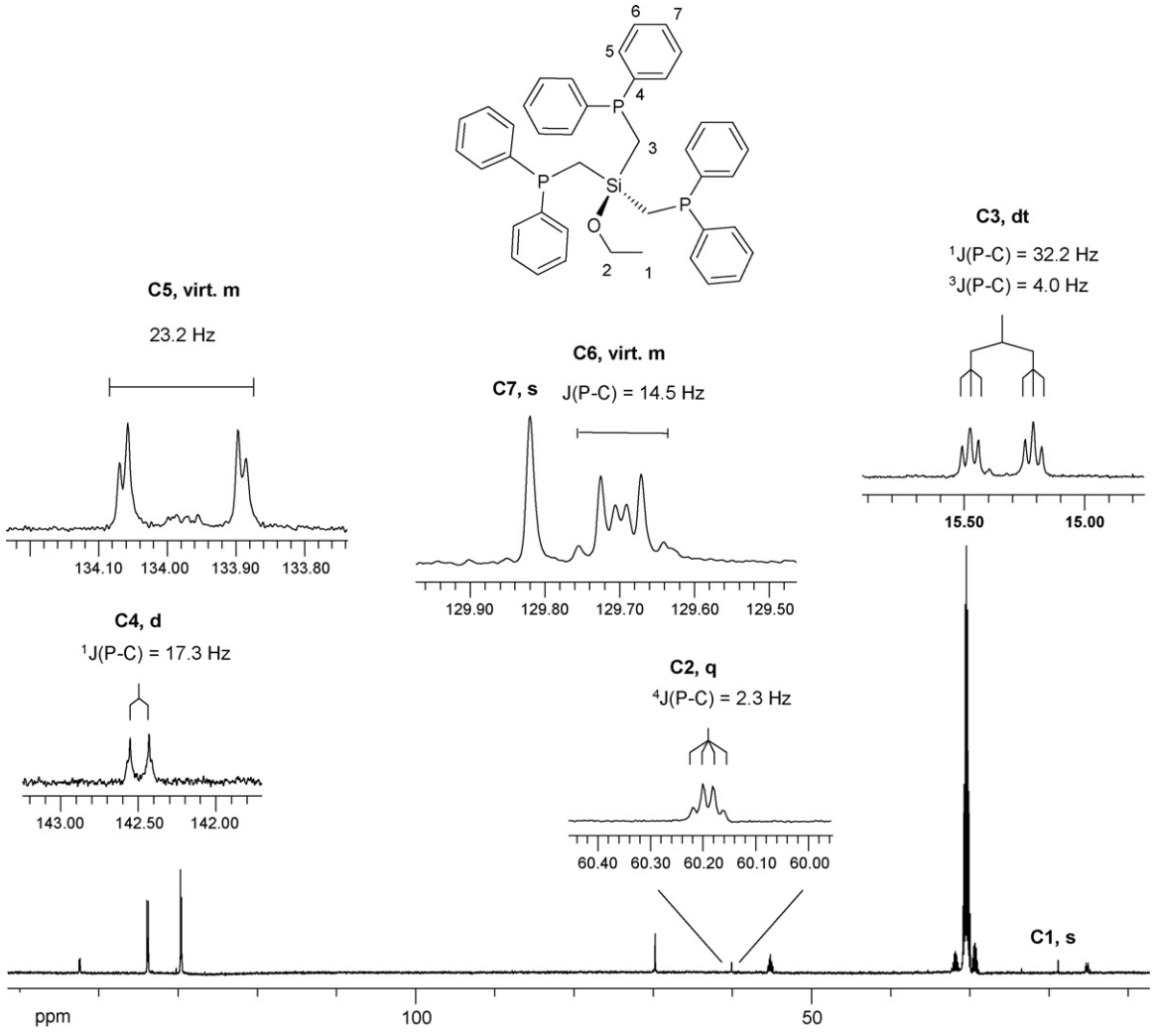


Fig. 2. $^{13}C\{^1H\}$ NMR spectrum of the shown linker in acetone-d_6. An example of virtual couplings in the tripod-type linker $(Ph_2PCH_2)_3SiOEt$ [14].

on silica [21]. This is an important piece of knowledge, because it implies that without ^{29}Si and ^{13}C CP/MAS the amount of ethoxy groups is unknown, and thus the surface coverage of the linkers or their complexes cannot be determined by elemental analysis. The latter is hampered by the surplus of silica in the samples, which leads to silicon carbide formation and thus too low carbon values, anyway.

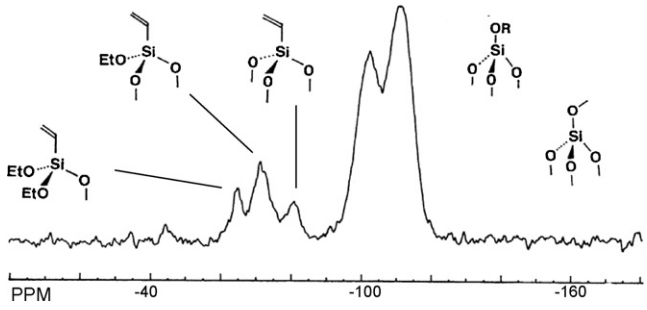


Fig. 3. ^{29}Si CP/MAS spectrum of immobilized vinyltriethoxysilane [20]. The signal assignment follows the sequence of the structures.

The bulk ^{29}Si CP/MAS signals (Fig. 3) at about −103 and −112 ppm give, for example, valuable information about the degree of dryness and surface modification of the silica, in case these signal intensities are studied varying the contact time [5b]. The silica we use routinely for catalysis is dried at about 600 °C in vacuo, so that surface-adsorbed water is removed, and most of the silanol groups are transformed into surface siloxane groups. The signal intensities of the bulk resonances are diminished with respect to the intensities of the silane resonances, because the bulk material contains fewer protons that could serve for the magnetization transfer required for CP pulse sequences. For the silanes the magnetization transfer mostly occurs from the alpha alkyl- or alkene-protons to the Si nuclei [20].

Another insight gained by ^{29}Si CP/MAS is that the solvent is extremely important for the immobilization process. In case the solvent is too polar, it covers the oxide surface and does not allow any contact with the ethoxysilanes. Therefore, in solvents such as ethanol, ether, ethyl acetate, ethylene glycol, etc., the surface coverage with ethoxysilane linker according to the usual immobilization procedure will be zero, even at elevated reaction temperatures [20]. The total failure of immobilization in these cases cannot be due to detachment of the ethoxysilanes after the covalent binding, because esters, ethers, and especially alcohols are not capable of

doing this [8,20]. The optimal solvents for immobilizing linkers via ethoxysilane groups are nonpolar ones such as heptane, or toluene [20].

3.2. Mobility of immobilized linkers in the presence of solvents

3.2.1. Static samples

This section will describe the NMR properties of surface-bound species in the presence of a solvent, while the samples are not rotated, but static. In this case, the samples can be measured in a conventional liquids NMR spectrometer, because no MAS or high power are needed. Tethering metal complexes to oxide supports via linkers incorporating alkyl chains has the advantage that they gain at least some degree of mobility, when a solvent is added [21]. This mobility is not unlimited and random as it is for free molecules in solution. Nevertheless, with respect to later catalysis, which is done like homogeneous catalysis in the presence of a solvent, the increased mobility and the solvent itself creates more realistic conditions for the measurements. The most visual picture is probably provided by the analogy with the kelp forest of the Californian coast, where one end of the plants is rooted at the ocean floor and immobile, while the upper parts of the plants move with the waves. Regarding immobilized linkers, one should point out that the mobility in the presence of a solvent does not originate from the whole support particles moving, but from the mobility of the linker chain itself. In fact, the support particles usually settle down quickly after adding the solvent, an effect that does not influence the resulting NMR signals at all. Fortunately, for most of the linkers shown in Scheme 1 their increased mobility in solvents as compared to dry samples translates into favorable T_1 relaxation times between 0.5 and 2 s. This means that spectra can be recorded quickly, because the relaxation delays can be short. While the lines of ^{1}H and ^{13}C NMR spectra are too broad in case the sample is not rotated, the ^{31}P resonances of suspensions compare favorably with those of corresponding ^{31}P CP/MAS spectra of the same dry materials (Fig. 4). The halfwidths usually have about double the values for the static samples.

Although for analytical quests with respect to the structure of surface-bound species, recording suspension NMR spectra is nowadays better done with HRMAS (see next chapter), the measurement without sample rotation still provides some crucial and singular insights. Most importantly, one can distinguish between covalently bound linkers and linkers that are merely adsorbed or even in solution. Leached linkers might still be merely adsorbed, before they are washed totally from the support and can be found in solution. The linewidths of covalently bound phosphine linkers is in the kHz region, while the halfwidths of adsorbed linkers range between 50 and 100 Hz. Fig. 5 shows a typical example of a covalently bound linker, which leaches from the support and gives a narrow line sitting on top of the broad signal. In contrast to this, with CP/MAS NMR adsorbed species are difficult to detect [8], and often their signals are even invisible, because the magnetization transfer is impeded by the mobility. Investigating leaching of the linkers is, however, crucial for identifying the proper linkers/support system for immobilizing catalysts (see Section 3.3 below).

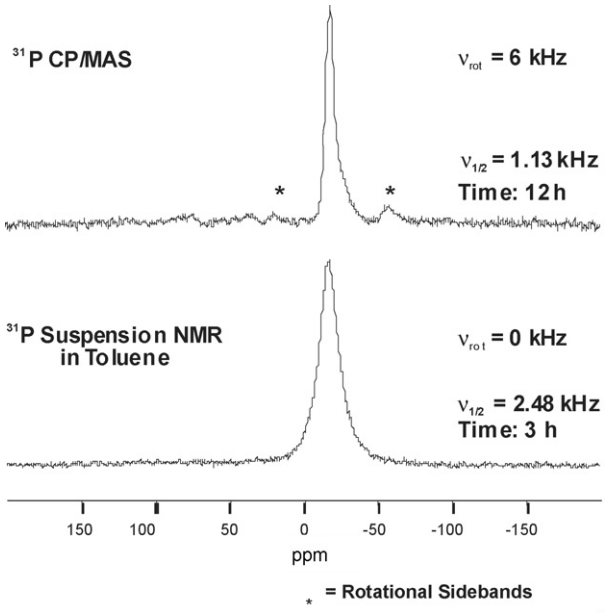


Fig. 4. ^{31}P CP/MAS (top, 6 kHz) and ^{31}P suspension NMR (toluene, no sample rotation) of the surface-bound linker $Ph_2P(CH_2)_3Si–\{SiO_2\}$ [21].

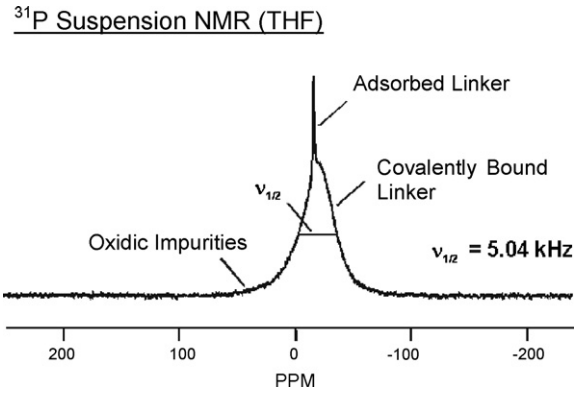


Fig. 5. ^{31}P NMR spectrum of a suspension of $Ph_2P(CH_2)_3Si–\{Al_2O_3\}$ in THF [21].

Furthermore, measuring suspension NMR spectra without sample rotation also allows one to study more subtle effects, such as interactions of the phosphine moieties with the support surface. Polar solvents for example compete with the phosphines for surface adsorption sites, remove the latter from the surface, and in this way lead to their increased mobility and thus to narrower lines. Nonpolar solvents, on the other hand, leave the phosphine groups adsorbed on the surface, and due to their immobility, their ^{31}P NMR signals can be broadened out of existence [21] (see also Section 5.2.3). As anticipated, the less viscous solvents allow higher mobility of the linkers and therefore lead to narrower lines. In the same way the nature of the oxide support and its "adsorptive power" with respect to the phosphines can be probed, and in this respect, too, silica turns out to be the optimal support among the available oxides, leading to the smallest linewidths [21]. Interestingly, even the density of the linker packing on the surface can be correlated with the suspension NMR linewidth: the denser the phosphine "lawn", the more mobile they are, because the adsorption of their phosphine groups is hindered.

3.2.2. Multinuclear HRMAS NMR of surface-bound linkers

High-resolution magic angle spinning NMR combines the mobilizing influence of the solvent (see previous chapter) with the line-narrowing effect of MAS. In this way, spectra of unprecedented resolution can be obtained from surface-bound linkers and catalysts [11b,15,16,18,19,22]. Fig. 6 shows a typical example. No special equipment is needed for HRMAS, except the rotors, which are equipped with spacers and a screw with a tiny hole to remove surplus solvent (Fig. 7).

The advantage of a HRMAS versus a ^{31}P CP/MAS measurement, besides the narrower lines, is that no Hartmann Hahn optimization is necessary. On the contrary, simple high-power decoupling

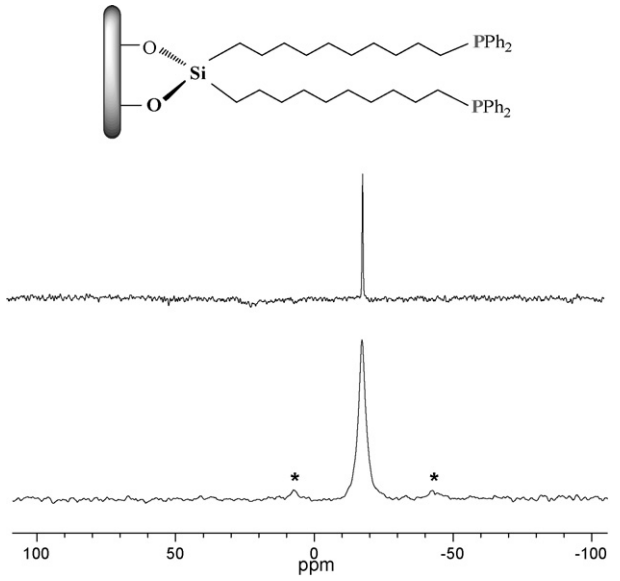


Fig. 6. ^{31}P CP/MAS (bottom, 4 kHz) and ^{31}P HRMAS NMR (top, 2 kHz, toluene) of the shown surface-bound linker [11b].

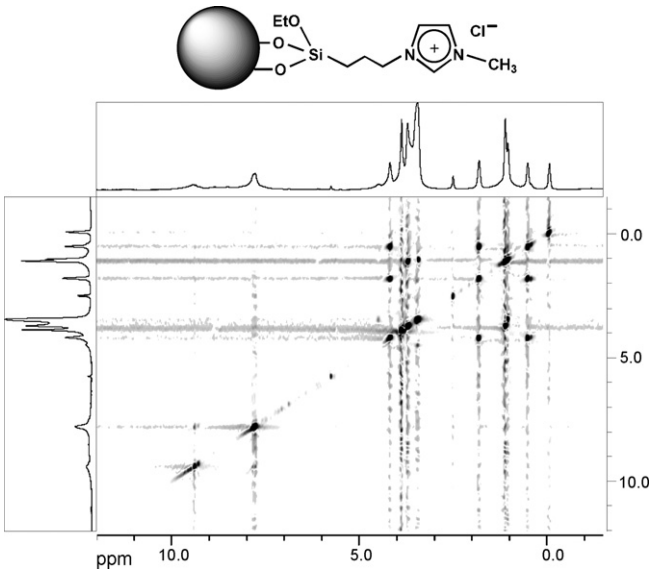


Fig. 8. ^{1}H,^{1}H DQF-COSY spectrum of the shown surface-bound ionic liquid at 2 kHz rotational speed in DMSO as the suspension medium [23].

in a single pulse sequence gives the best results in 1D measurements, because then one does not have to take complications due to the reduced magnetization transfer in mobile species into account [15]. Using HRMAS even ^{1}H and ^{13}C spectra with high resolution can be recorded of surface-bound linkers mobilized by the proper solvent [23], and one is not limited to ^{31}P any more, as it is the case with static measurements. Therefore, HRMAS is the method of choice for any sort of mobile, but not homogeneous species. Even the 2D correlation spectra known from liquids NMR can be obtained from surface-bound linkers and metal complexes, given the proper spectral resolution [18,23]. This is demonstrated for example with surface-bound ionic liquids (Fig. 8) [23]. Of course, as in the case of static suspension measurements (see previous chapter), the solvent has to be optimized. The surface-bound ionic liquids, for example, needed a very polar solvent, DMSO (dimethylsulfoxide), to be sufficiently mobilized.

The limitation of this method is that there needs to be at least a minimum mobility of the surface-bound species. The ^{29}Si HRMAS signal of surface-bound ethoxysilane groups is invisible, only the bulk of the silica support shows up. However, one can use this fact in order to distinguish surface-bound from unbound or cross-linked silane groups, or even silicon grease impurities, because these, again, lead to narrow signals [24] with the corresponding chemical shifts. This is an important piece of information, because especially for monodentate linkers it is not a given thing that both linkers are attached covalently to the support [24,25].

3.3. Linker leaching

3.3.1. Linker detachment from the support

The most obvious reason for leaching is the hydrolysis of the Si–O–X bond, where X is for example Si, Al, or Ti, that connects an ethoxysilane linker with the oxide surfaces of SiO_2, Al_2O_3, or TiO_2. This hydrolysis is facilitated by the presence of surplus water on the oxide surface, which is one reason why we pre-dry our oxide supports thoroughly prior to use, but also acids or bases. Therefore, intrinsically acidic supports, such as acidic alumina, will always be problematic as support material in combination with ethoxysilane linkers. This can be seen in the static ^{31}P NMR spectrum (Fig. 5) shown above, where, besides the covalently bound linker, large amounts of merely adsorbed linker can always be found, no matter how often the support is washed [21]. The same holds true for titania supports, where one meets the additional challenge that the Si—O—Ti bond is not as strong as the Si—O—Si bond, and the

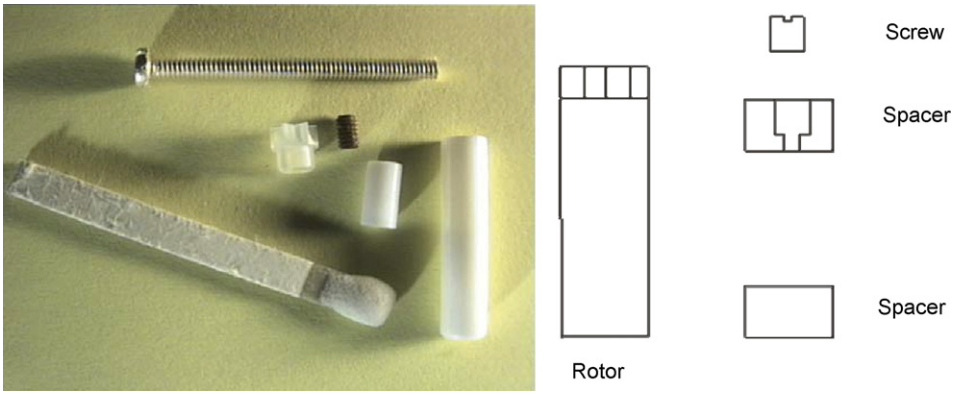


Fig. 7. *Left*: Commercially available 4 mm HRMAS rotor with top spacer, screw, and KelF cap. Photo by Bruker Biospin. *Right*: The schematic drawing shows on the left the empty rotor with the cap, and on the right the spacers that go on the bottom and top of the rotor inside. The support and solvent are added between the two spacers. The top spacer is sealed by the screw, so that the solvent does not leak during spinning.

^{31}P resonance of a covalently bound linker in the static suspension NMR spectrum is very broad [21]. From a practical point of view it should be mentioned that alumina and titania do not settle down from suspensions in organic solvents as rapidly and readily as silica, and ^{27}Al NMR spectra of the alumina support are hampered by the quadrupolar nature ($I = 5/2$) of the ^{27}Al nucleus and the many rotational sidebands resulting [21]. Luckily, the bonding of linkers to silica via Si—O—Si bridges is rather robust, even if there is only one of them. Detaching such linkers from silica needs harsh conditions and strong acids or bases, as we determined in a qualitative and quantitative manner [21].

Interestingly, linkers bound via phosphonium groups (see Section 4 below) cannot be detached from the surface by any means [26]. The electrostatic interactions of the linker with the surface anions therefore is strong and chemically robust, and withstands the impact of strong acids and bases, or offerings of various other, even soluble, counter anions in large excess. In order to set such phosphonium linkers free, for example from a silica support, one has to dissolve the silica [26].

3.3.2. *Leaching due to linker decomposition*

Binding the phosphine linkers to oxide surfaces in a clean and well-defined manner is crucial for the next step, coordinating catalysts to them. If the linkers are not intact on the surface, the catalysts will not stick to them, and either leach from the support, or they are bound to the surface in a different, ill-defined manner, and both scenarios are not desirable in the later quest for reliable catalysis data. Surprisingly, checking the integrity of the linker on the surface is not in the focus of many groups working with immobilized catalysts. However, over the years we had to experience many cases, where phosphine linkers containing ethoxysilane groups decomposed on oxide surfaces unexpectedly, or formed side-products during the immobilization step. One such case with a side-product, a phosphonium salt, will be detailed later in Section 4.1. Luckily, in this case, the knowledge of the side reaction could at the end be turned into a new immobilization strategy. In general, however, a decomposed linker molecule just blocks a binding site on the surface and prevents the proper characterization of the immobilized catalyst.

One drastic case of total linker decomposition on silica surfaces concerns bisphosphinoamine linkers with a propyl chain, or a phenyl group between the ethoxysilane and phosphinoamine functions [15,16]. The bisphosphinoamine linkers $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ and $(Ph_2P)_2N(p\text{-}C_6H_4)Si(OEt)_3$ are easy to synthesize, they could be obtained in crystals of sufficient quality for X-ray analysis, and they were chemically robust in solution, displaying only moderate air-sensitivity, and they readily coordinated to various metal centers [15,16]. However, oxide surfaces are different "worlds", and one cannot extrapolate from the solution behavior of linkers to their immobilization characteristics on silica. When these linkers were immobilized using our standard procedure, both decomposed entirely [16]. This was already evident in the ^{31}P CP/MAS spectra of the materials, but the HRMAS measurements with their enhanced signal resolution allowed us to identify the products of the decomposition, and thus finally its mechanisms (Fig. 9). One side-reaction of the linker immobilization is the well-known formation of the corresponding ethylphosphonium salt. But another, at first sight more surprising byproduct was $Ph_2P(O)PPh_2$, with its $^1J(^{31}P–^{31}P)$ coupling well visible, as indicated by the arrow in Fig. 9 [16]. Having detected this key compound by HRMAS, it was easy to figure out that the bisphosphinoamine linkers are in equilibrium with the corresponding phosphinimines. The latter are not visible in solutions of the linkers. However, when the phosphinimines are removed from the equilibrium by hydrolysis due to water on the surface, the linkers can be used up quantitatively. Syntheses of model compounds and following their destiny on silica surfaces with ^{31}P CP/MAS and HRMAS flanked this investigation [16]. Using the easier to dry surface of alumina helped the bisphosphinoamine linkers to survive better, but finally we decided to use less troubled linkers for immobilizing the precious catalysts.

Another interesting case of linker decomposition is that the tripod-type phosphine ligand, shown in Scheme 3, loses one "phosphine twig" as CH_3PPh_2, when the silica support is not dried rigorously prior to the immobilization [14]. The final product is the surface-bound diphosphine species $(Ph_2PCH_2)_2Si[O–SiO_2]_2$, as could be proven by the synthesis and immobilization of the corresponding diphosphine (Scheme 3). Again, solid-state NMR, here

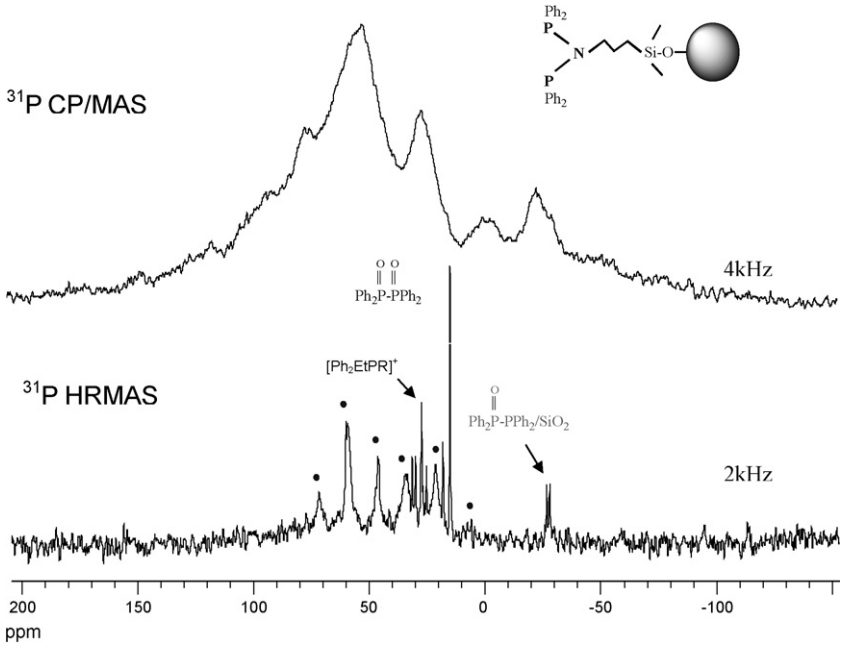
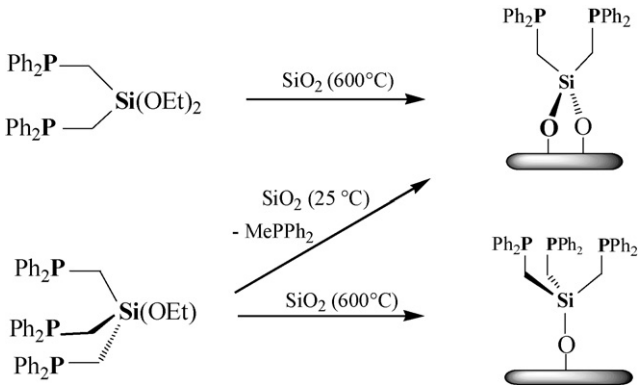


Fig. 9. ^{31}P CP/MAS and HRMAS measurement of silica reacted with $(Ph_2P)_2N(CH_2)_3Si(OEt)_3$ [16]. The dots denote the signal of the intact linker and its rotational sidebands. The most intense signal corresponds to the dioxide, which stems from the oxidation of the diphosphine monoxide.



Scheme 3. Decomposition of a tripod-type linker by traces of water on silica [14].

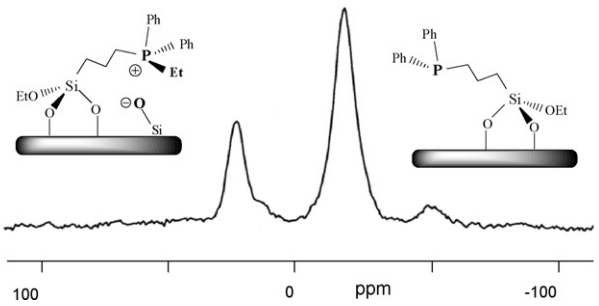


Fig. 10. ^{31}P CP/MAS signals of silica-bound phosphine and the phosphonium salt as the side-product [27]. The spectrum was obtained after stirring silica with an excess of $Ph_2P(CH_2)_3Si(OEt)_3$ in toluene at 80 °C for 14 h.

^{29}Si CP/MAS is the only method, which provides unequivocal evidence about the outcome of the immobilization. Happily, when the silica is dried rigorously prior to the immobilization, the tripod-type linker retains its three phosphine moieties.

To sum up this chapter, phosphine linkers have to be tested whether they can be immobilized in a well-defined manner prior to their coordination to metal complexes. Even when they are not sensitive towards water or other reagents in homogeneous phase, they might be so in the presence of oxide surfaces. An additional challenge arises, when the linkers decompose due to the impact of the metal complex to be coordinated. For example, we had to learn that the dppm-type linker $(Ph_2P)_2CHSiMe_2OEt$ [12] loses its silyl group when reacted with the Si–C activating Wilkinson's catalyst $ClRh(PPh_3)_3$. So, instead of the target molecule $ClRh(PPh_3)[(Ph_2P)_2CHSiMe_2OEt]$, $ClRh(PPh_3)[(Ph_2P)_2CH_2]$ was obtained [24]. This also happens with the surface-bound linker, $(Ph_2P)_2CHSiMe_2O–SiO_2$, so that the catalyst leaches already during the immobilization step [24]. Since the dppm-type diphosphine $(Ph_2P)_2CHSiMe_2OEt$ is on its own also vulnerable with respect to phosphonium formation (see Section 4) during the immobilization step, we prefer not to use it any longer. There is ample choice of other, well-behaved and robust chelate phosphine linkers (see Section 2.1 above).

4. Immobilization of phosphine linkers by electrostatic interactions

4.1. Phosphonium salts as side-products of immobilizations

The most often used, traditional phosphine linkers are attached to oxide supports via alkoxysilane functions. In solution, alkoxysilane groups do not react with phosphines even at high temperatures (160 °C) over a prolonged period of time. However, when phosphines containing ethoxysilane groups are reacted with silica at elevated temperatures, a side-product forms in variable amounts, and sometimes even quantitatively. The spectrum in Fig. 10 shows a typical scenario (and already betrays the nature of the side-product to the reader).

The side-product cannot bind metal complexes later, and therefore only uses up surface sites and the precious phosphine linker. Our first task in the field of immobilized catalysts was to determine the nature of this side-product with indicative chemical experiments, and by solid-state NMR [27]. The main results of the latter investigation are described in the following: the chemical shift of the side-product is rather uncharacteristic with about 25 ppm, since phosphonic and phosphinic acids, phosphine oxides, and phosphonium salts all display signals in this region. However, looking at the CSA (chemical shift anisotropy) [28], phosphonic and phosphinic acids, as well as phosphine oxides could be ruled out due to their large CSA values. In contrast to this, the CSA of the side-product is rather small. The ^{31}P CP/MAS after immobilizing the phosphine linker without using an inert atmosphere shows that the side-product at 25 ppm is different from the phosphine oxide. Treating this silica batch with H_2O_2 transforms all the phosphine into its oxide, and proves that the side-product cannot be further oxidized. Other classical solid-state NMR measurements helped to determine the nature of the side-product already at this time: dipolar dephasing [29] that negatively discriminates P atoms with directly bound protons for example showed that the side-product was not due to simple protonation of the phosphines by acidic surface silanol groups. The side-product can be prevented by keeping the immobilization temperature low, at about 50 °C, and these clean materials are ready for use in catalysis.

The structure of the side-product has been determined by using molecular polycrystalline model compounds [30]. Based on the chemical shifts and CSA values, the side-products must be ethyl phosphonium salts (Fig. 10), with the silica surface or a siloxy anion of the ethoxysilane group as the counteranion. The latter does not play a big role for the appearance of the phosphonium ^{31}P CP/MAS signal, as Fig. 11 shows.

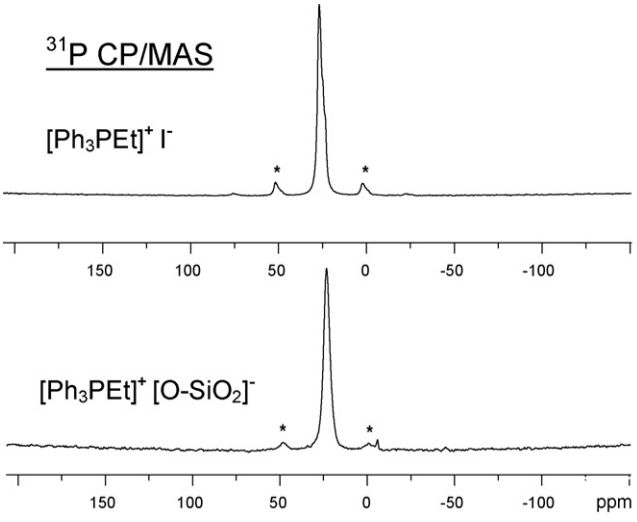


Fig. 11. ^{31}P CP/MAS signals of surface-bound triphenylethyl phosphonium salt and its corresponding polycrystalline model compound with an iodide counter anion [30].

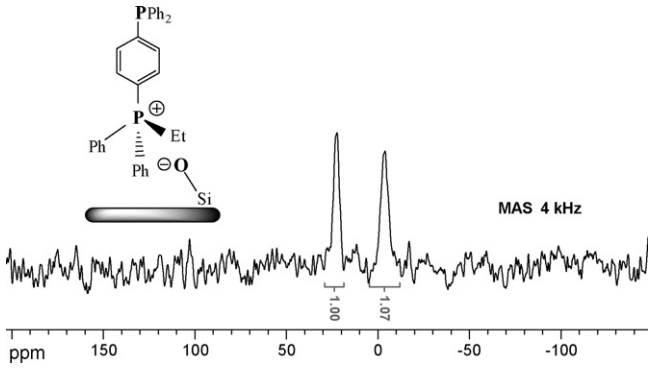


Fig. 12. ^{31}P MAS of $Ph_2P(p\text{-}C_6H_4)PPh_2$ after immobilization on silica/ethoxysilane [26]. The resonance at about 23 ppm belongs to the phosphonium group, the signal at ca. −6 ppm to the phosphine moiety.

4.2. Phosphonium moieties as linker functions for immobilizations

The knowledge of the nature of the surface-bound phosphonium salts led to several important findings: (a) Not only phosphines with intramolecular ethoxysilane groups can be bound to silica as ethylphosphonium salts, but also unmodified phosphines, as long as ethoxysilanes are added to the silica either prior to or during the phosphine immobilization [27,30]. (b) Phosphine oxides can be bound covalently to silica as the corresponding ethoxyphosphonium salts [30]. The fact that both phosphines and phosphine oxides can be bound to silica by stirring it with ethoxysilanes can be exploited to remove both species in one step from reaction mixtures. Regarding point (a), it is possible to immobilize phosphines without intramolecular ethoxysilane groups, that can still function as linkers on silica, when only one of several phosphine groups can be bound to the support due to steric reasons. This is for example realized with rigid tetra- or diphosphines of the type shown in Fig. 12 [26], where only one phosphonium group per linker is bound to the support, while the second one is still unchanged and can coordinate to metal complexes.

Here, one has to take care with integrating the different ^{31}P signals: since the ethylphosphonium moiety has many more protons in the vicinity of the P nucleus, its signal is enhanced as compared to the triarylphosphine signal, when measuring with CP. The correct intensity ratio of the signals is only obtained, if the spectrum is measured with MAS alone, using a long relaxation delay. This type of immobilization will be exploited in our next generation of linkers, since phosphines without intramolecular ethoxysilane groups are easier to synthesize, and the electrostatic interactions of the phosphonium groups with the surface are stronger and chemically more robust than the covalent Si—O—Si bridges. In fact, when trying to detach the phosphonium species from the support, we found that one needs such drastic acidic or basic measures that the support is dissolved along with the phosphonium salt.

5. Immobilization of metal complexes

5.1. Different strategies

As it is outlined in Scheme 4 for a Pd complex, there are two different strategies for binding metal complexes to oxide supports via linkers. One option is to synthesize the molecular complex from a proper precursor and the linker, and then immobilizing the whole assembly on silica. Alternatively, the silica can be modified with the linker first, and the precursor of the targeted metal complex is added in the final step. The first strategy has the advantage that the metal complex can be fully characterized prior to the immobilization. From an NMR point of view, the most interesting aspect is that for chelating phosphines and their metal complexes virtual couplings with characteristic signal patterns [13] are found frequently [12,14,15]. But also the standard *J* couplings to the metal nuclei, which can only occasionally be obtained for the immobilized complexes due to the increased linewidths, can be measured for the molecular species, e.g. in the case of Rh complexes [17]. Sometimes even NMR spectrocopy of the metal nucleus, e.g. ^{61}Ni NMR [31] is feasible. Finally, pursuing the first strategy, the catalytic activity of the molecular complexes in homogeneous runs can be compared to their activity after binding them to the oxide surface.

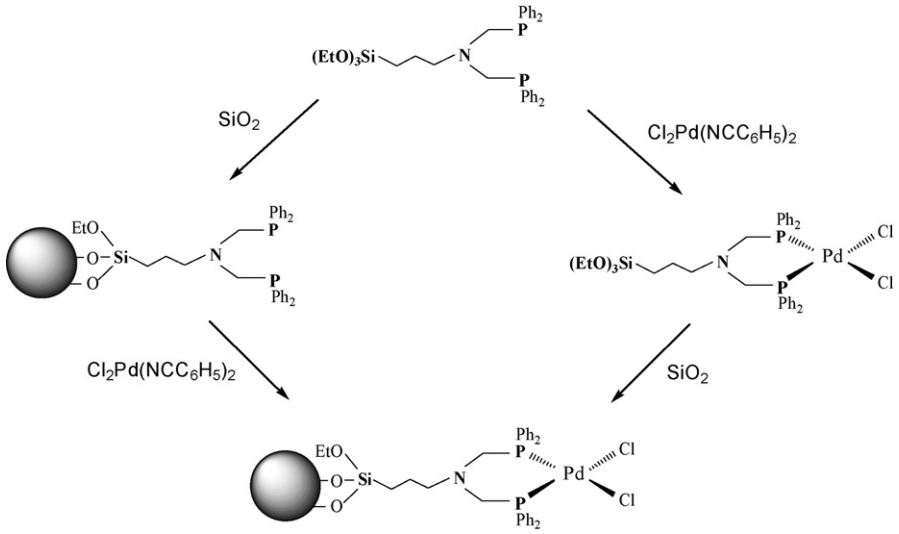
The second strategy offers the advantage that phosphine-modified silica can be prepared in larger quantities, and then smaller batches thereof are used for immobilizing different catalysts. Furthermore, in this way the phosphine-modified silica only has to be characterized once. But besides these practical advantages, the main reason for reacting a precursor metal complex with modified silica is to prevent its decomposition. Metal complexes, even when they carry coordinated linkers always run the risk that they hit the bare, reactive oxide surface “with the wrong end ahead”, and not with the linkers first. Many metal complexes, such as $(COD)_2Ni$ or Cp_2Cr, however, react quickly with oxide surfaces, turning them black due to formation of Ni(0) or CpCr(III) species, which have been investigated by paramagnetic solid-state NMR [32]. Preparing a dense “lawn” of phosphine linkers on the surface prior to the addition of the metal complexes affords a “soft landing” and reduces the chances for decomposition. In cases where the linkers have to be applied dilute on the surface, the surplus binding sites are best end-capped using Me_3SiOEt (see Section 3.1 above) prior to the application of the metal complex precursor [8].

In some cases, where the precursor complex is not soluble, one can also generate the immobilized metal complex on the surface. One such example is described for an immobilized Cu(I) species that has been immobilized by a surface-bound chelate phosphine linker starting from a mixture of $(CH_3CN)_4CuBF_4$ with PPh_3 [18].

5.2. Characterization of immobilized catalysts

5.2.1. Classical ^{31}P CP/MAS measurements

Catalysts immobilized on oxide supports are amorphous materials, which can be characterized by a variety of analytical methods [33]. The most versatile, however, for metal complexes bound to oxide supports via linkers is solid-state NMR in its different facets. Especially phosphine complexes allow easy analytical access to the catalysts via ^{31}P CP/MAS. Since immobilized catalysts represent amorphous materials and are less homogeneous and well defined than polycrystalline samples of the corresponding molecular complexes, their residual linewidths are always larger. This can be seen for example in Fig. 13 for an immobilized Wilkinson-type catalyst [17]. While the spectrum of the polycrystalline sample even shows all the P–P and Rh–P *J*-couplings, the signals of the surface-bound complex are rather broad, swallowing the indirect couplings. It is also obvious from Fig. 13 that in most cases with chelate ligands, the intensity ratios of the different phosphine signals are not correct in the ^{31}P CP/MAS spectra. This is not surprising, although it is unusual for polycrystalline complexes, because the ^{31}P nuclei might have different surroundings with respect to close-by protons, and thus different relaxation times. The change of the signal intensity ratios on going from the polycrystalline molecular to the surface-bound complexes is less understandable, since the immediate surroundings of the ^{31}P nuclei does not change upon tethering. Obviously the magnetization transfer is sensitive towards small differences in mobility, or the surface changes the situation. Both points need a more detailed investigation in the future. This is also true with



Scheme 4. Different strategies for immobilizing the shown Pd complex.

respect to the changed CSA (e.g. Fig. 13). When going from the molecular to the tethered complex, in most cases the CSA becomes substantially smaller [17b,c]. Again, this can only happen, when the immediate surroundings or mobility of the ^{31}P nuclei changes. This effect of diminished CSA is for example known for polycrystalline and surface-adsorbed PPh_3 [26]. In order to investigate whether the interaction of the metal complex with the surface is responsible for the diminished CSA of immobilized complexes, linkers that prevent any contact of the catalyst with the surface will be applied in future projects (see also Section 4.2).

However, when comparing only immobilized complexes with one another, the CSA is reliable and reproducible, sensitive even towards small changes of the molecular structure, and characteristic for these complexes. For example, one can distinguish surface-bound dicarbonyl- from tricarbonylnickel complexes as well with ^{31}P CP/MAS due to their slightly different CSA, as with IR [34].

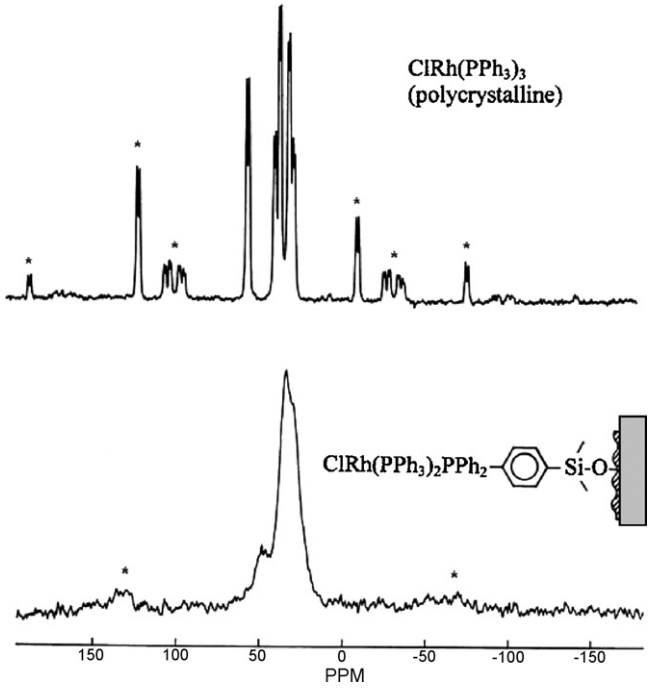


Fig. 13. ^{31}P CP/MAS of polycrystalline Wilkinson's catalyst (top) and its immobilized version (bottom) [17b].

5.2.2. *Improving the S/N for ^{31}P CP/MAS at higher rotational frequencies*

As compared to molecular species, immobilized catalysts suffer from one major disadvantage: most of the matter that is packaged into the rotor consists of bulk material due to the silica support. The catalyst is very dilute, because it only sits on the surface of silica, albeit also on the surface within the pores. Typically, about 50 mg of catalyst are immobilized on 1 g of silica. In cases where a diminished surface coverage of the metal complexes is desirable in order to prevent deactivation of the catalyst by dimerization, as it is the case for rhodium catalysts [17], the catalyst/silica ratio is even smaller. Since solid-state NMR is, at least for heteronuclei, a comparatively insensitive technique, low surface coverages can create problems with getting a sufficient S/N ratio within a reasonable time period even for ^{31}P.

This problem is aggravated at higher rotational frequencies, that are, however, desirable because of the larger CSAs of phosphine resonances of metal complexes: at higher MAS frequencies, the Hartmann Hahn (HH) matching profile splits into a center band and sidebands, as shown for the standard $NH_4H_2PO_4$ in Fig. 14 [35]. The positions of the latter change with the spinning speed, and therefore the HH matching condition most often changes with the rotational frequency. Fig. 14 shows a typical scenario. This splitting of the HH matching profile means that the uncritical HH match obtained at lower spinning speeds might lead to zero signal intensity at higher speeds, because one might then be in the position of a matching "valley". The fewer protons there are around the ^{31}P nucleus in the sample, the more pronounced is the splitting of the HH profile already at moderate spinning frequencies. For example, at 4 kHz the HH matching profile of the chelate complex $Cl_2Ni(dppe)$ with its ligand rich in alkyl protons (dppe = $Ph_2PCH_2CH_2PPh_2$) is smooth and has a broad plateau, while the similar complex $Cl_2Ni(PPh_3)_2$, which has only aryl protons, already shows substantial signs of the splitting [35]. Additionally, the matching profiles of different substance classes look very different. What is a good match for a standard sample, might not be a match at all for a metal complex sample. Speaking in practical terms, one might achieve the perfect HH match with the standard sample $(NH_4)H_2PO_4$, and nevertheless, even at a moderate spin-

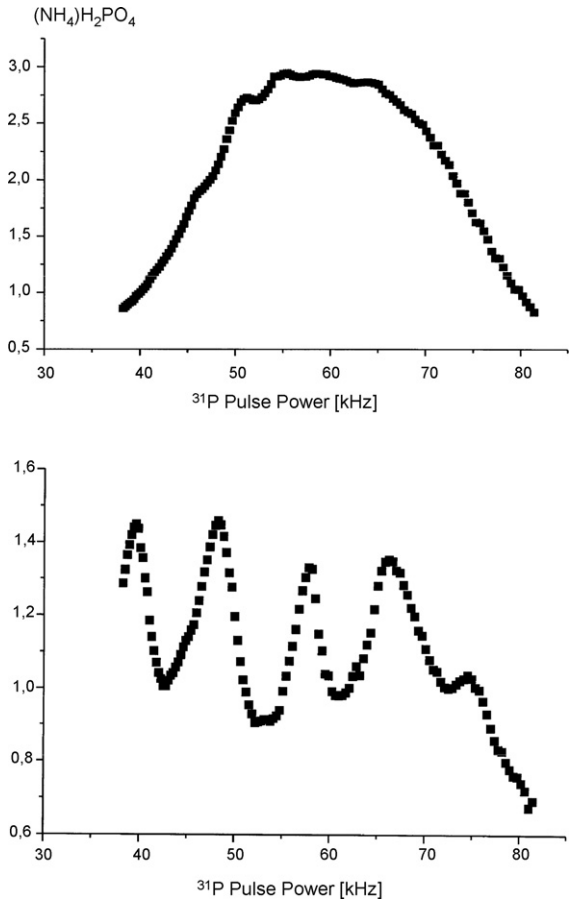


Fig. 14. Hartmann Hahn matching profile for $(NH_4)H_2PO_4$ at different spinning frequencies (top: 4 kHz, bottom: 8 kHz) [35]. The ^1H pulse power was kept constant, while the intensity of the FIDs in arbitrary units, depending on the ^{31}P pulse powers, was recorded [35].

ning speed of 8 kHz, end up with only the baseline after one night of measuring an immobilized catalyst.

Ramp techniques [35], that gradually change the ^1H or ^{31}P irradiation power during the contact time, in order to catch at least part of some HH matching band for the magnetization transfer, do not offer a reliable and robust solution. In the real life cases of immobilized catalysts, we had to experience that the results were of variable quality with respect to the obtainable S/N ratio [35].

The best way to solve this problem turned out to be first synthesizing molecular model complexes with similar structures as compared to the targeted immobilized catalysts [35], for example $Cl_2Ni[(Ph_2CH_2)_2CHOH]$ for the silica-bound $Cl_2Ni[(Ph_2CH_2)_2CH–O–SiO_2]$. Then the HH matching profile for the model compound is recorded, a procedure that can be done in an automatic mode in about an hour. Subsequently, the ^1H and ^{31}P pulse powers that give the highest signal intensity for the model compound are applied to the sample of the immobilized analog. In this way, ^{31}P CP/MAS signals of the surface-bound catalysts can be obtained reliably, and with good S/N ratios even at high spinning speeds. Since the matching profiles of the model complexes do not change within a period of at least six months, and one can use always the same HH matching pulse powers, the overall procedure is less time consuming than optimizing the HH match for a standard sample each time prior to the measurement of a real sample. Luckily, the matching profiles do not change substantially with the length of the contact pulses, so the latter can be optimized along with them [35]. Finally one should mention that in case quantitative information is needed, MAS with long relaxation delays, but without CP is still the method of choice. Such measurements of course take a long time, but the only alternative would be to look at a series of CP spectra recorded with different contact times (and longer relaxation delays) in order to obtain reliable quantitative data.

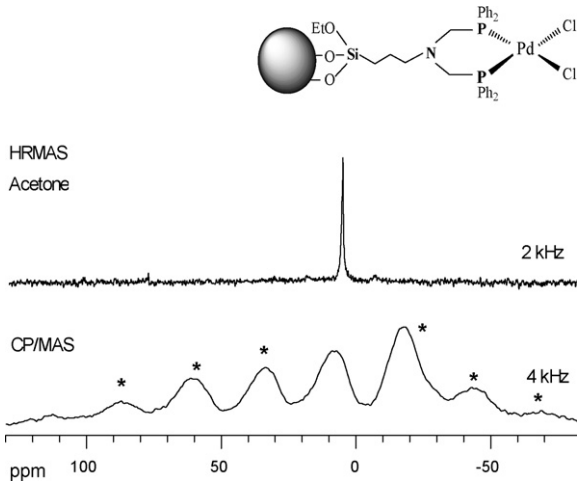


Fig. 15. ^{31}P CP/MAS (bottom) of the dry sample of silica-bound complex, and ^{31}P HRMAS spectrum (top) of the identical sample in the presence of acetone [15,18].

5.2.3. *^{31}P HRMAS of immobilized catalysts*

For surface-bound transition metal complexes with comparatively small CSA, as for example carbonylnickel complexes, it is possible to obtain ^{31}P signals with moderate linewidths in the presence of a solvent, but without MAS [36]. Without sample rotation, however, in general the suspension NMR method is not competitive with the classical ^{31}P CP/MAS of dry samples. Fortunately, the HRMAS technique that has already been described under Section 3.2.2, is extremely useful for surface-bound transition metal complexes. Here, the gain in signal resolution is even more dramatic than for uncoordinated linkers, because the CSA of transition metal coordinated phosphines in dry samples is much larger. One example of drastically reduced residual linewidth and CSA is shown in Fig. 15.

The biggest drawback of this method is that the solvent used has to mobilize the surface-bound complex sufficiently for providing a signal [15,18]. Fig. 16 shows, how different the spectra for the same immobilized Pd complex as in Fig. 15 can be, when other solvents than acetone are used.

Since one solvent does not necessarily mobilize all species on the surface in the same way, the integration of signals from different species might be problematic in some cases. If quantitative information is needed, several spectra of the same material in different solvents have to be evaluated. Fortunately, in this respect acetone seems to be a good choice for most species that can occur on the surface. However, the next question one has to ask in case one targets *in situ* investigations is whether the solvents chosen are also the ones that have to be used for the actual catalytic reaction. The use of solvent mixtures has not been fully explored for immobilized catalysts at present.

In spite of all the research that is still needed in this area, comparing classical solid-state NMR methods with the HRMAS technique, it is obvious that the latter provides the optimal means for characterizing surface-bound complexes with respect to their structural nature, but also their “behavior” on the surface (see below). Perhaps in the future HRMAS will even provide some more direct or indirect insight into catalytic mechanisms.

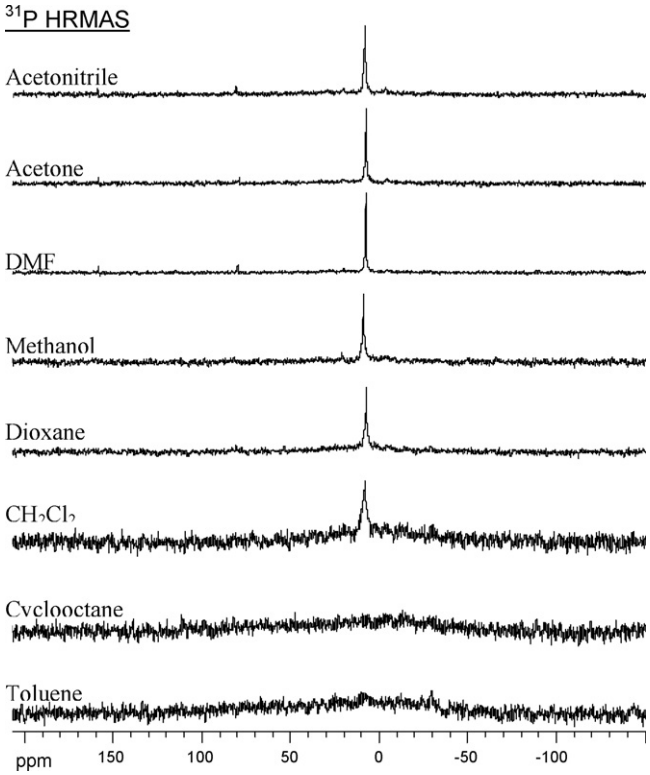


Fig. 16. ^{31}P HRMAS spectra of the immobilized Pd complex shown in Fig. 15, with different solvents as suspension media at 2 kHz rotational frequency and 2000 transients each [15,18].

6. Immobilized catalysts

6.1. Leaching of the metal complexes prior to catalysis

At first sight the leaching of catalysts even before the actual catalytic reaction starts seems to be unlikely. However, as described in a previous chapter, the linkers themselves might leach or suffer oxidation or total decomposition during the immobilization step. Whenever that happens, the metal complexes lose their tether to the support and get detached from it. Furthermore, one has to take into account that especially monodentate phosphines are not always bound firmly to a metal center. The complex formation constant has to be taken into account. For example, even with a chelate phosphine linker, the $PdCl_2$ fragment is obviously not bound firmly, because with AAS a Pd content of 1–2% with respect to surface-bound complex can be detected in the supernatant solution after stirring the silica in acetone at ambient temperature [15]. Leaching at this low level cannot reliably be detected with any solid-state NMR method, and of course not with liquids NMR, since the linkers stay tethered to the support. In the course of several catalytic runs, the loss of metal might, however, be substantial. The problem is aggravated, whenever the catalytic reaction needs (a) additives, or (b) substrates, which compete with the linker phosphines for coordination sites at the metal center. For example, (a) some catalytic reactions might need an excess of base or molecular phosphines. The latter, e.g. PMe_3, has been demonstrated in the case of surface-bound carbonylnickel complexes to replace the linkers from the metal center, leading to the dissolved nickel complex $(CO)_2Ni(PMe_3)_2$, which can be detected by NMR in solution, while the uncoordinated linker remains on the support and shows up in the ^{31}P CP/MAS spectrum of the support [25,37]. As an example for (b), we recently had to learn that a common substrate for

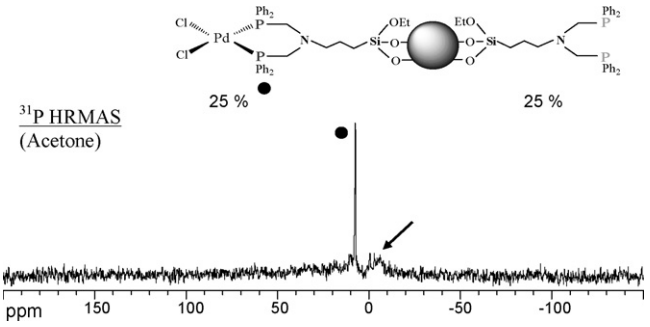


Fig. 17. ^{31}P HRMAS of the shown material suspended in acetone at 2 kHz rotational frequency. The indicated surface coverages are with respect to maximal (100%) surface coverage.

Sonogashira cross-coupling reactions, PhI, in combination with the solvent dioxane, detaches the $PdCl_2$ moiety from the support quantitatively, even when a chelate phosphine is used, and at ambient temperature [15,18]. Therefore, one has to conclude that using classical linkers as shown in Scheme 1, not every catalyst can be firmly and irreversibly immobilized. Our future goal will be to synthesize and test a new generation of linkers, which can prevent any leaching due to their structural characteristics.

6.2. Translational surface mobility of immobilized catalysts

Besides the "vertical" leaching of metal complexes from the surface into solution, we recently detected another form of "horizontal" linker-metal lability with ^{31}P HRMAS [15,18]. In case the $PdCl_2$ moiety is bound to a silica support as shown in Scheme 4, i.e. the Pd and the chelate phosphine linker are present in a ratio of 1:1, the ^{31}P HRMAS spectra of the material feature a narrow signal at 7.4 ppm, as Figs. 15 and 16 show [15,18]. However, if a surplus of uncoordinated silica-bound phosphine linkers is present on the surface, with a Pd complex to uncoordinated phosphine ratio of 1:1, the scenario changes. Now, only traces of the Pd complex resonance remain, while no signal of the uncoordinated phosphine can be detected in the ^{31}P HRMAS spectrum (Fig. 17).

However, an additional, broad signal emerges at about −7 ppm. We interpret this broad signal at about half the distance between the expected chemical shifts of the Pd complex and the uncoordinated linker as a dynamic effect, with Pd "hopping" over the lawn of phosphine linkers on the surface. The "vertical" leaching of 1–2% of the Pd complex into solution cannot be responsible for the observation, because it takes place also in case all surface-bound phosphine linkers are coordinated to Pd (see previous chapter), and it does not disturb the ^{31}P HRMAS signal. "Blocking" the uncoordinated phosphine linkers with BH_3 stops the "hopping" of the Pd moieties, as the narrow signals in Fig. 18 show [15,18]. So, obviously, enough "empty" phosphine linkers have to be present in order to allow the fast one-by-one hopping process of practically all the Pd centers. One should point out that with classical ^{31}P CP/MAS of the dry materials such "horizontal" mobility scenarios are not visible, and in the absence of the solvent most probably also do not take place.

6.3. Immobilized catalyst systems with two different metals

When a catalyst with only one metal center is immobilized on an oxide support, one has the choice of tethering the linker first, and then coordinating the metal moiety, or synthesizing the molecular catalyst and immobilizing it subsequently (see Section 5.1 above). With two different metal complexes that are needed for a catalytic reaction, additional options emerge. Only one of them might be

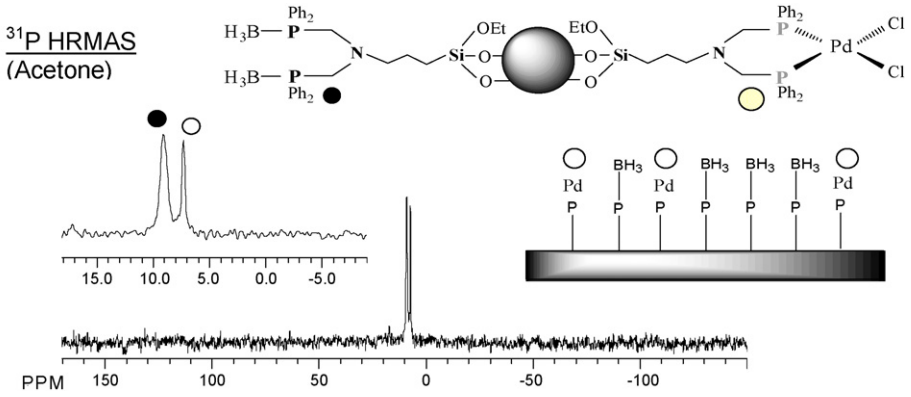


Fig. 18. ^{31}P HRMAS spectrum of the same material as shown in Fig. 17, after protecting the uncoordinated phosphines with BH_3 groups.

immobilized, while the other metal component acts as a homogeneous catalyst, or both catalysts are immobilized. Which approach is finally pursued, depends on the catalytic reaction and the metal complexes needed for it. Although at first sight immobilization seems to make the situation more complicated as compared to entirely homogeneous catalysis, in fact it provides more insight into the catalytic mechanisms. The potential of this aspect of immobilization, in combination with solid-state NMR analytics does not seem to be well explored at the moment.

One illustrative example, however, of the Sonogashira catalyst system will be discussed here [15,18]. The first surprise was that no matter what the immobilization sequence was, the Pd complex reacted with the Cu complex already during the immobilization step. This could be seen in the presence of unassignable ^{31}P HRMAS signals, or even their total absence, suggesting the formation of Pd–Cu aggregates or nanoparticles. The material obtained was, however, highly active with respect to the Sonogashira coupling. Therefore, even with unsatisfactory solid-state NMR spectra at hand, one can conclude that the mechanism for this reaction requires both metal complexes to react with each other and form an agglomerate irreversibly, which is the actual catalytically active species. This is corroborated by the following observation: when the Pd and Cu components are immobilized on different batches, which are combined for catalysis, or when they are both tethered to silica cleanly by protecting the Cu component first, one can obtain the separate and well-defined ^{31}P HRMAS signals for both immobilized species [18]. However, after the catalytic reaction, only ill-defined signals, if any at all, can be observed [15]. The observation of translational surface mobility of the Pd component, described above in Section 6.2 suggests that the latter "goes to find the Cu component" on the surface, and binds to it irreversibly. With adding the substrates phenyliodide and phenyl acetylene, or only different solvents, such as dioxane and piperidine, the picture becomes even more complicated, and an excess of PPh_3 might even allow translational mobility of the Cu component. From a practical point of view, with these NMR insights we could obtain a well recyclable and highly active Sonogashira catalyst system with immobilizing the Cu component only and optimizing the solvent used [18].

So, these preliminary investigations [15] already demonstrate that immobilized catalyst systems with two different metal complexes feature complicated scenarios, but also that they are a large, unexplored playground that can only be investigated by HRMAS methods. The insights obtained allow one to optimize immobilized catalyst systems quickly. Furthermore, what can be learned from immobilizations, however, should bring forward the research of such systems in homogeneous phase, too.

7. Following the destiny of immobilized metal complexes during catalysis

Molecular catalysts tethered to an oxide support via a linker have, to the best of my and (Scifinder's) knowledge, not yet been studied by *in situ* by NMR. However, many spectra before and after catalysis [17c,22,37], and a series of spectra from the immobilized catalyst material taken from the reaction mixture at regular intervals have been recorded [37]. In repeated batchwise catalytic runs, for example the cyclotrimerization of phenylacetylene with an immobilized dicarbonylnickel complex [37], or the hydrogenation of alkenes with Wilkinson-type rhodium catalysts [17c], the most prominent destruction and therewith leaching mechanism of the catalysts is the oxidation of the phosphines. This has the simple reason that traces of oxygen enter the Schlenk flask each time it is opened and new substrate is added. For continuous catalysis, or at least repeated catalysis runs in a closed system such as a soxhlet extractor [37], much less of the phosphine oxide is found in the spectrum. While the destiny of the linker is known in such cases, it remains unclear whether the metal precipitates and clings to the support surface, or whether metal "nanoparticles" or aggregates form, that stay suspended in solution. The color of the support, turning progressively darker greyish or black, often speaks for the latter [37], while sometimes larger amounts of metal can be found in a clear solution by AAS of the colorless supernatant [15]. Besides oxidation of the phosphine linkers, the unprovoked detachment of the metal centers especially from monodentate linkers can be observed [37]. As mentioned in the previous chapter, in the case of the immobilized Pd/Cu Sonogashira catalyst system neither before, nor after the reaction could a ^{31}P HRMAS signal be obtained. We tentatively attribute this to the formation of Pd/Cu metal aggregates, which shield the linker from the radio frequency irradiation [18].

8. Conclusion

NMR in its various facettes and applications is the ideal analytical method to study molecular, as well as immobilized catalysts. Each part of the latter system can be investigated independently. One can take a look at the bulk of the support, and its surface, especially after improving the S/N of CP/MAS spectra even at higher rotational frequencies. The binding sites can be probed by ^{29}Si or ^{31}P CP/MAS, depending on whether ethoxysilanes or phosphonium moieties are used for the tethering process. The linker can be characterized with respect to its structure and mobility in different solvents. In cases where the structural integrity of the linker is not retained, its pathways of decomposition can be fully described.

HRMAS techniques, that combine the line-narrowing effects of MAS with those of a mobilizing solvent present, allow one to observe interesting new behavior with respect to migration of metal centers over phosphine-modified surfaces. This might give crucial clues with respect to catalytic activity and lifetime in particular for heterobimetallic surface-bound catalyst systems, such as the Sonogashira Pd/Cu couple. Overall, the insights obtained especially by the new HRMAS techniques should propel the progress in the field of immobilized catalysts. On the other hand, empirically investigating immobilized species only with respect to their catalytic activity, but without solid-state NMR as the analytical method might not bring the field forward as fast as it would be possible with NMR.

Acknowledgments

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