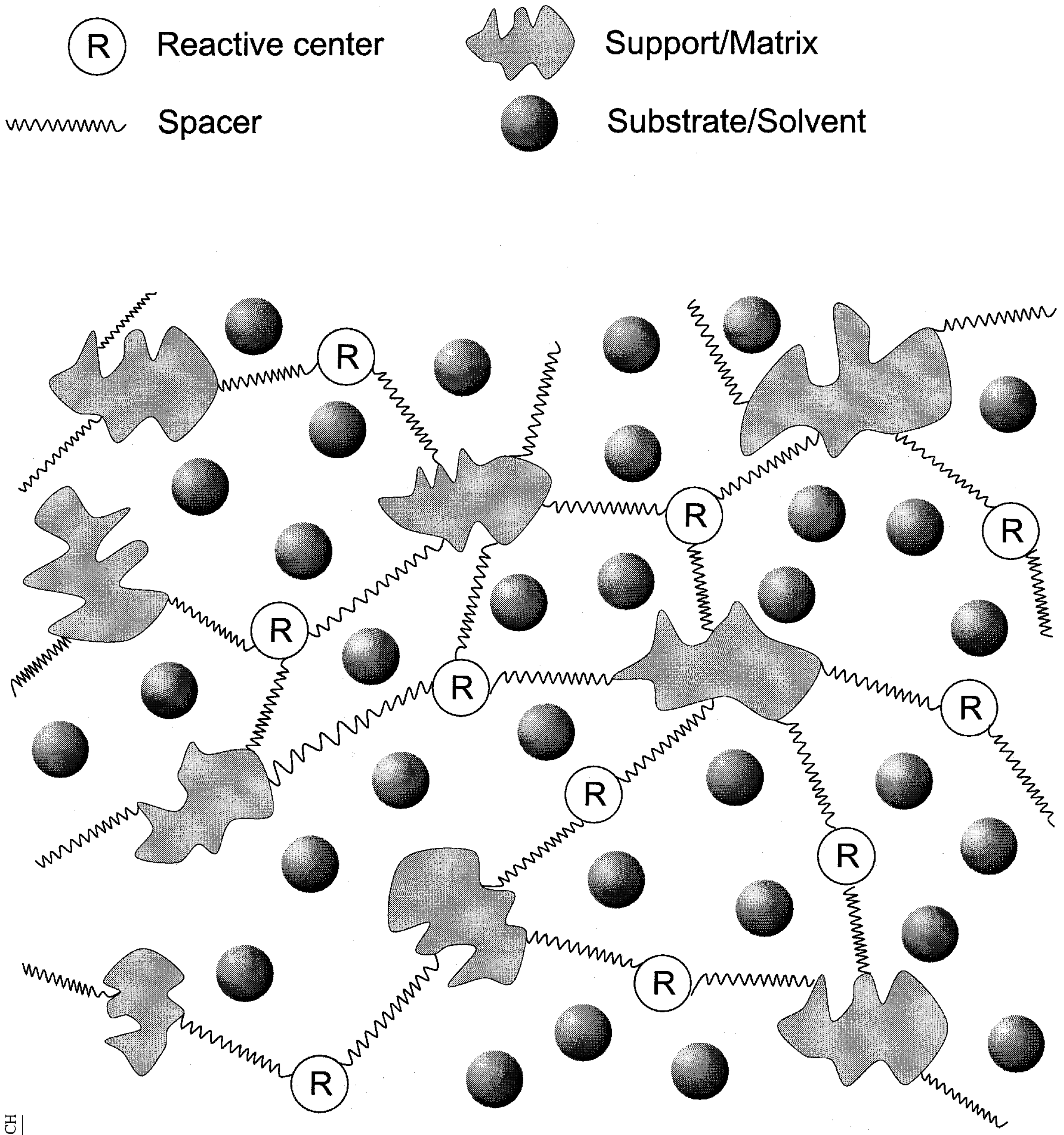
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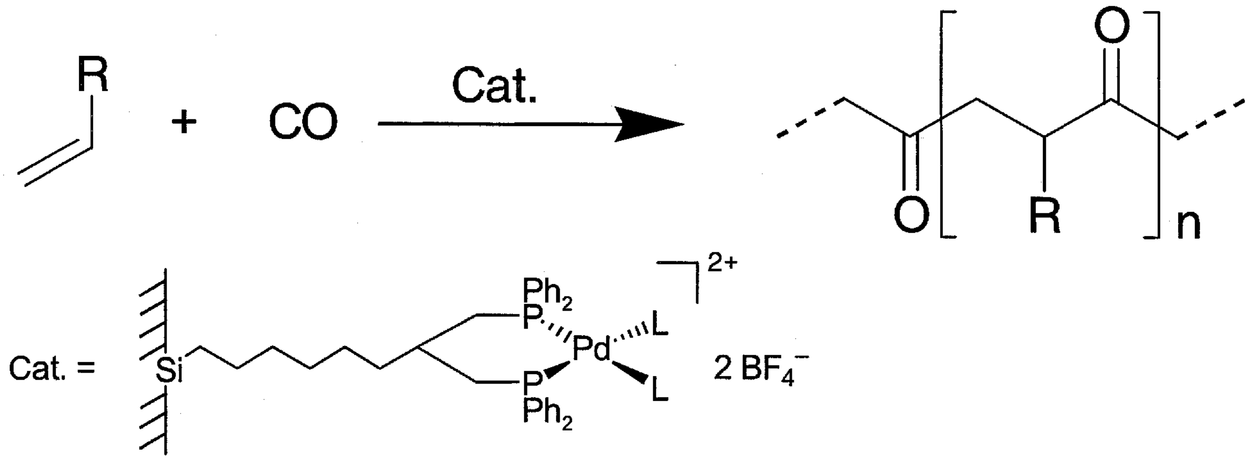
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# Chemistry in Interphases—A New Approach to Organometallic Syntheses and Catalysis

**Ekkehard Lindner,* Theodor Schneller, Friedrich Auer, and Hermann A. Mayer***

*Dedicated to Professor Helmut Werner on the occasion of his 65th birthday*

Processes in which a stationary and a mobile component penetrate each other on a molecular level exist in many fields of current chemical research such as chromatography or solid-phase syntheses. Such systems are designated as *interphases* and constitute a large area of interdisciplinary research. They connect inorganic, organic, and physicochemical disciplines with many aspects in applied and experimental physics. Modern developments in microscopic and spectroscopic methods (e.g. solid-state NMR spectroscopy) offer a unique possibility to get detailed insight into the structures, properties, and chemistry of new polymeric materials. Concomitantly they stimulate the development of advanced materials for optimized interphases. In the past three decades transition metal complexes bound to polymeric supports have attracted great interest, since they promise to combine the advantages of homogeneous catalysis with the easy separability of heterogeneous systems. However, such immobilized catalysts hardly ever met the expectations, mostly due to the high degree of metal loss during the reaction ("leaching"). Moreover, the optimization of such systems was often limited to trial-and-error methods due to the lack of knowledge of the structure and environment of the reactive centers and the polymers. Chemistry in interphases offers a new approach to organometallic syntheses and catalysis, since a subtle design of the hybrid-polymer matrix allows to suppress the detrimental influence of the support. An interphase represents a state which, in an extreme case, may be similar to that of a solution. Thus catalysts are available which provide favorable activities in the hydrogenation and hydroformylation of unsaturated substrates and the copolymerization of alkenes with carbon monoxide without any marked leaching of the catalytic active transition metal centers.

**Keywords:** heterogeneous catalysis · organic–inorganic hybrid composites · NMR spectroscopy · sol–gel processes · supported transition metal complexes

## 1. Introduction

Reactions of polymer-bound reagents were introduced in peptide synthesis three decades ago by Merrifield.[1] Since then this technique has been continuously improved up to the routinely applied automatic solid-supported synthesis of polypeptides,[2] oligo- and polynucleotides,[3] and oligosaccharides.[4] Nowadays organic chemistry on solid support is a promising approach for the expeditious and simultaneous multiple synthesis of nonpolymeric molecules.[5] The performance of all these solid-phase reactions is based on filtration since this is the fastest and simplest method of isolating a substance from a liquid, such as a solution of reactants. This ease of intermediate product isolation brings benefits to any type of synthesis.[6] Moreover, solid-phase synthesis permits the use of an excess of reagents to drive reactions to completion, since excess reagents can be washed away from the polymer beads very easily afterward. Besides the economical interest in the anchored reagents, the significance of their ecological aspects will steadily increase.

Efforts to transfer these principles to transition metal complexes were already performed more than 20 years ago in order to overcome the greatest drawback of homogeneous catalysis, the difficulty of separating the catalyst from the reaction mixture.[7] Basically the anchoring of a homogeneous catalyst to a matrix is achieved in different ways. Most frequently applied is the fixation through donor ligands covalently bound to the support, usually an organic polymer like polystyrene.[8, 9] In contrast to organic polymers inorganic supports show advantages such as mechanical stability and resistance against aging, solvents, and higher temperatures.[10] Supports like silica allow functionalization with surface hydroxyl groups in analogy to materials for reverse-phase

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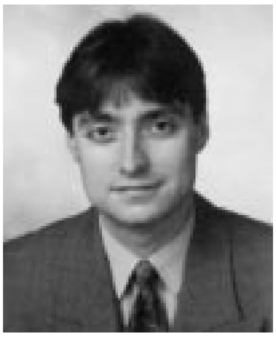
chromatography.[11] To a certain extent, fixation to a support by ionic bonds and by chemi- and physisorption has been accomplished.[12] Furthermore, anchoring has been carried out by the impregnation of a solid support with a liquid medium containing a dissolved homogeneous catalyst.[13]

If no solid phase but rather a second immiscible liquid is employed, a liquid–liquid biphase system is realized. The most popular biphase systems are those employing water and organic solvents.[14] Recently Horváth and Rábai developed fluorous phases as an interesting variant of the liquid–liquid biphase systems.[15]

Another route for the heterogenization of homogeneous catalysts involves the polycondensation of appropriately modified monomeric metal complexes.[10] The hydrolysis and polycondensation of alkoxysilyl-functionalized organometallic precursors and the simultaneous cocondensation of these materials with various types of alkoxysilanes offers a versatile alternative for the preparation of polymer-bound transition metal complexes. Thus hybrid polymers with tailored properties are accessible.

In the present article the concept of interphases is introduced, which is mainly focused on organic–inorganic hybrid materials. Interphases are defined as particular regions within a material in which a stationary and a mobile component penetrate each other on a molecular level without formation of a homogeneous mixture (Figure 1). In these regions a reactive center becomes highly mobile, thus simulating the properties of a solution. An interphase should not be confused with the term interface, which is described as the area of contact between two phases (e.g. solid/solid, liquid/liquid, solid/liquid, solid/gas, liquid/gas) that do not penetrate one another. These common boundaries form sharp thin layers in the nanometer range and are considered as a two-dimensional geometric interface.[16] The penetration of a mobile phase into the network of a stationary phase as discussed above generates a three-dimensional interphase.


E. Lindner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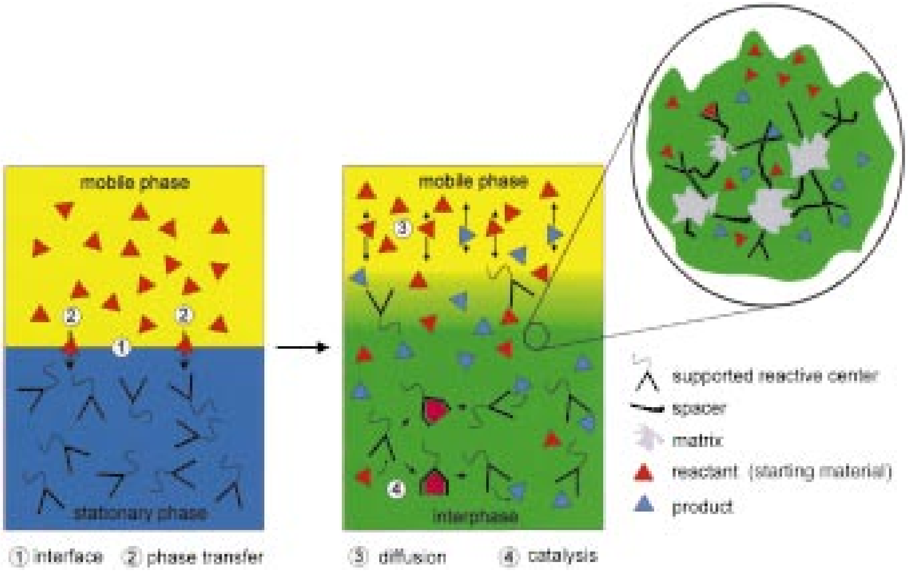
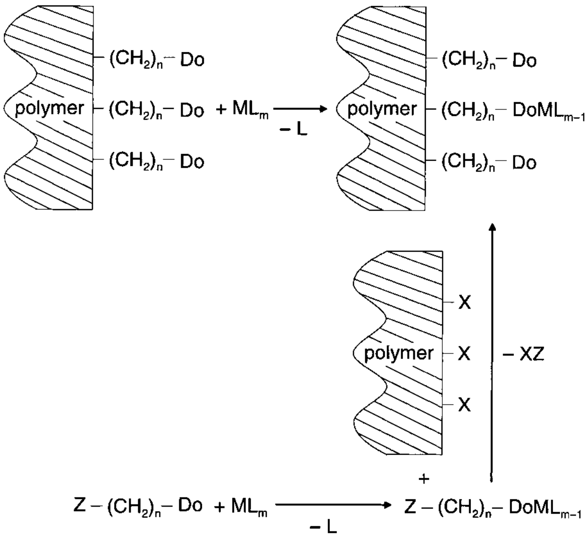


Figure 1. Schematic representation of an interphase.

## 2. Historical Background

Already in the late 1960s Acres et al.[7a] and Rony[7b] dissolved rhodium complexes in nonvolatile liquids and dispersed these solutions within porous silica.[17, 18] With such *s*upported *l*iquid-*p*hase *c*atalysts (SLPCs) vapor-phase reactions were performed in the manner of gas-liquid chromatography.[19, 20] Compared to the conventional homogeneous catalysis in solution, the SLPC conditions reduce the contact time of the reactants with the catalyst dramatically. As a consequence a catalyst suitable for SLPC must exhibit a very high activity to obtain a sufficient space-time yield. Moreover these systems are less useful for liquid-phase systems owing to the loss of catalyst by elution from the support. In 1989 Davis et al.[13] described *s*upported *a*queous-*p*hase *c*atalysts (SAPCs) as a new family of heterogeneous catalysts using water as the liquid phase to overcome the above-mentioned problems. Within this process a high surface area hydrophilic solid was impregnated with an aqueous solution of a rhodium complex. This system was employed in the hydroformylation of hydrophobic olefins dissolved in organic solvents.[21] With either catalyst system the reaction itself takes place at the interface between the liquid phase and the vapor phase (SLPC) or organic phase (SAPC). Consequently the reaction rates are proportional to the interfacial area. Moreover, conversions and selectivities are highly influenced by the liquid loading of the support. Ethylene glycol as a nonvolatile hydrophilic liquid replaced water to circumvent problems associated with hydrolysis of metal–ligand bonds.[22] The low molecular weight polymeric congeners like polyethylene glycol containing water-soluble hydroformylation catalysts were utilized as a nonvolatile liquid phase with SLPCs.[23, 24] These polymer films have a low solubility in aldehyde-rich solutions and therefore can be used to solve the problems of classical SLPCs. Very recently a further improvement of this approach has been reported, in which the polyether phase is covalently bound to silica.[25] This concept reduces the loss of the liquid phase to a minimum. The described polyoxometalate systems are rather complexed than simply dissolved in the polyether phase. Thus no leaching was found.[25]

Besides these developments most of the published work over the period of nearly three decades deals with the covalent anchoring of transition metal complexes.[10] In the first attempts transition metal carbonyls were directly connected with unmodified organic polymers like poly-2-vinylpyridine.[26a,b] However, this kind of anchoring is not available for a great variety of complexes and therefore not universally applicable. Hence most frequently the polymers were functionalized with donor groups (Do; Scheme 1, top).[26c,d, 27–31a, 32] Mainly the displacement of ligands in suitable precursors by anchored donors gave the corresponding immobilized metal complexes. In principle, appropriately functionalized metal complexes are likewise prepared prior to the reaction with the support (Scheme 1, bottom). In this way the preformed complexes may be characterized in solution before immobilization. Although this method should result in defined supported complexes, it was less commonly used because sensitive transition metal complexes tend to decompose during the polymerization.[33]



Scheme 1. Possible pathways for the fixation of a metal complex to a polymer. Do = donor group (e.g. $PR_2$, $NR_2$, SR).

In the beginning of the research on polymer-bound catalyst complexes, polystyrene and styrene/divinylbenzene copolymers (Merrifield resins) were by far the most widely studied organic supports.[8] In the following years other organic polymers like polyvinyls,[26] polyacrylates,[31] and cellulose[34] have been used. In addition, the classical Merrifield resins were connected with hydrophilic polyethylene glycol chains (TentaGel)[35, 36] as linkers.[37] Preferably diphenylphosphane groups were grafted onto the polymeric supports.[8] The ligands were predominantly bound to the organic support either directly or through one methylene group ($n = 0$, 1 in Scheme 1). This kind of fixation restricts the mobilities and reduces the activities of the anchored complexes. Principal disadvantages of organic supports are their limited thermal and mechanical stability.[10] Therefore in the early 1970s attempts have been made to attach the above-mentioned donor groups to inorganic supports by the reaction between surface hydroxyl groups and a readily hydrolyzable moiety.[18] For this purpose a wide range of bifunctional compounds of the type $\mathrm{Do{-}(CH_2)_n{-}SiX_3}$ (X = hydrolyzable group) are available (see Section 5.2). Allum et al. pioneered the use of this technique with their study of silica treated with [2-(diphenylphosphanyl)ethyl]triethoxysilane or related compounds.[28a, 38] Shortly after, Capka and Hetflejs functionalized other inorganic materials with surface hydroxyl groups like $\gamma$-alumina, molecular sieves (zeolites), and glass with several ligands.[39] Until now silica is the most popular matrix among the inorganic materials[28a, 40] because it is neutral and its surface properties[41] and possibilities to be modified[42, 43] are well explored. Owing to the rigidity of the inorganic supports the donor groups were mainly bound through a flexible hydrocarbon chain ($n \geq 2$ in Scheme 1) to introduce sufficient mobility of the ligands and finally of the complexes. Although often highly desirable, flexibility is not always an asset. In particular, if catalyst deactivation occurs by dimerization, long spacers should be avoided or the density of complex centers should be reduced.[9, 33, 44] Intolerably high degrees of leaching have yet prevented the commercial breakthrough of any of the described techniques of covalent catalyst anchoring.

Other fixation techniques such as ionic bonding, physisorption, and chemisorption are discussed in the literature[45] and will not be further considered in the present article.

## 3. Recent Developments

Organometallic catalysis in biphasic media is of growing interest in present academic and industrial work.[14, 46, 47] Most of the research activities are dedicated to biphasic processes in which water serves as "liquid support". For this purpose phosphane ligands are modified with hydrophilic groups to make them soluble in water.[47] In 1984 this approach was successfully installed in the Ruhrchemie/Rhône-Poulenc (RCH/RP) oxo process,[48] which uses the water-soluble catalyst $[\mathrm{HRh(CO)\{P(\mathit{m}\text{-}NaO_3S\text{-}C_6H_4)_3\}_3}]$ to produce butyraldehydes.[49] With the RCH/RP process the loss of catalyst by leaching was reduced to the ppb range. However, the efficient hydroformylation of higher olefins like octene is still an unresolved problem of biphasic-aqueous media catalysis, due to the low solubility of the olefin in water. The *S*hell *h*igher *o*lefin *p*olymerization (SHOP) process, in which the generated olefins separate from the polar reaction solution, is a further example of a biphasic catalytic reaction with industrial significance.[50]

A different concept of biphasic catalysis employs fluorocarbons.[51] The resulting *f*luorous *b*iphasic *s*ystem (FBS) is based on the limited miscibility of partially or fully fluorinated compounds with most common organic solvents. When the two phases mix above ambient temperature, single-phase catalysis with biphasic separation of products and catalysts is possible. To achieve a high solubility of the catalysts in the fluorous phase, perfluoroalkyl segments ("ponytails") are appended to the ligands. For example, this "immobilization principle" was successfully applied in reactions like hydroformylation,[15] hydroboration,[52] and oxidation.[53] A major disadvantage of this method may be the ozone depletion potential being associated with the employment of fluorocarbons on an industrial scale.

An alternative approach to separate product and catalyst from the solvent is the application of supercritical fluids. They have become popular in chromatography[54] and as extraction media,[55] and a number of polymerization reactions have been practiced for decades.[56] Supercritical fluids like $\mathrm{scCO_2}$ and $\mathrm{scH_2O}$ are increasingly investigated in order to replace organic solvents owing to their environmentally friendly character, low cost and toxicity, easy solvent removal, and recycling. Moreover, the miscibility with gaseous reaction partners is rather high, and limitation of the reaction rate by diffusion processes is avoided.[57, 58] Typical examples are the rhodium-catalyzed hydrogenation of $\mathrm{CO_2}$ to formic acid,[59] the generation of tetraethylpyrone from 3-hexyne and $\mathrm{CO_2}$,[60] methyl formate synthesis,[59c, 61] the copolymerization of $\mathrm{CO_2}$ with propylene oxide,[56] and the conversion of $\mathrm{CO_2}$, $\mathrm{H_2}$, and $\mathrm{Me_2NH}$ into *N,N*-dimethylformamide.[62] It is noteworthy that in the latter case sol–gel-processed hybrid materials have been used as heterogeneous catalysts. The drawback of the poor solubility of ionic catalysts in supercritical media is overcome by modification of either the anion or the ligand backbone of the cationic complex with fluorinated functions.[63]

Photochemical activation of C–H bonds,[64] hydroformylation,[65] hydrogenation[59b,c, 66] as well as organometallic chemistry of the type normally performed with matrix isolation techniques is possible in supercritical fluids at room temperature. Thus dinitrogen and dihydrogen half-sandwich complexes of transition metals of Groups 6, 7, and 8 were generated which were only detected in cryogenic solvents.[67] Furthermore, it was demonstrated that supercritical water can act as a benign solvent for traditional synthetic organometallic chemistry.[68]

A further approach to bind catalysts in a liquid phase is the application of ionic liquids.[69] Such systems enable an easy separation of the products from the catalyst, since most organic substances are insoluble in very polar media.

The idea to apply soluble polymers in catalysis instead of the more common insoluble ones dates back to the mid 1970s.[70a,b] Bayer[70] and Bergbreiter[71] applied soluble polymers as complex ligands of high molecular weight. With such systems catalysis is carried out under homogeneous reaction conditions. Catalyst recovery and separation from reaction products is accomplished by membrane filtration or precipitation. In spite of these advantages research activities remained low for years. However, a renaissance of soluble polymers in the field of immobilized reagents has been reported.[72] In the early 1990s new efforts have been undertaken to attach transition metal catalysts to soluble polymers.[73] Owing to the excellent solubility of PEG in water it has been suggested to employ PEG-functionalized phosphane ligands in aqueous biphasic catalysis.[74, 75] These systems may be capable of overcoming the above-mentioned mass transfer limitations of higher olefins. The inverse phase–temperature dependence of the solubility of polyalkylene oxide oligomers in water[76] leads to a single-phase system at higher temperatures. Upon cooling of the system, the catalyst is recovered by simple separation of the aqueous phase. Very recently the asymmetric dihydroxylation of olefins with MEO-PEG-bound cinchona alkaloid ligands was described.[77] Janda et al.[77b] transferred the principle of the already known multipolymer reaction[78] to the asymmetric dihydroxylation (AD) reaction. One component, the catalyst in the present case, is attached to a soluble polymer, and the other component, the substrate (*trans*-cinnamic acid), is bound to an insoluble support. This procedure enables the easy separation of both starting materials (ligands, catalysts) and products from the solvent and from side products. In addition, the product is directly applicable in reactions with other substrates.

Dendrimers[79] may also be considered as soluble supports. They have the advantage of a nanoscale, precise molecular architecture and are suitable to quantitative modification with donor groups like amines[80] or phosphanes[81d] at their periphery. With dendritic amine ligands supported transition metal catalysts were synthesized. Van Koten et al.[80] developed this approach and employed a dendrimer-bound (diaminoaryl)nickel catalyst in the Kharasch addition of polyhalogenoalkanes to carbon–carbon double bonds. Since then dendrimers are generating growing interest as support materials for transition metal catalysts.[81]

## 4. Concept of Interphases

Homogeneous catalysts have uniform and well-defined reactive centers, which lead to high and reproducible selectivities.[82] The activity as well as the efficiency of these catalysts are generally high. A drawback of supported catalysts is the loss of this homogeneity due to minor changes in the structure which many reactive centers suffer. This leads to a reduced reactivity and selectivity of the immobilized catalysts.[33] In many cases the influence of the matrix on the final outcome of the reactivity and selectivity is not known. This is due to the lack of structural knowledge about both the reactive centers and the polymer matrix.

The application of surface-modified inorganic and organic materials (Figure 2) has been less successful because of 1) the short lifetimes of these catalysts caused by the leaching of the reactive centers (poor anchoring), 2) reduced accessibility of the catalysts, 3) steric effects of the matrix, 4) inhomogeneity of the reactive centers, and 5) difficulties in controlling the density of the reactive centers on the surface.[33, 83]

The idea to establish a concept that lies between the homogeneous phase (including classical homogeneous catalysts and soluble polymer-supported catalysts) and the heterogeneous phase gave the impetus for the methodology “chemistry in interphases”. The term interphase was first introduced in reverse-phase chromatography.[84, 85] In 1995 the transfer of this concept to the area of supported transition metal complexes was presented.[86] For the application of interphases in chromatography, catalysis, and organic synthesis, the same rationale is inherent.[87]

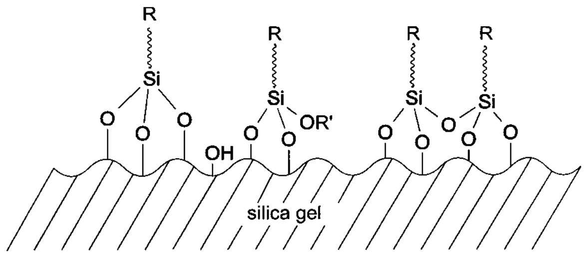


Figure 2. Surface coverage of modified silica gel. R = reactive or interaction center; OR′ = alkoxy group.

### 4.1. Definition

Optimal results in the performance of anchored homogeneous catalysts should be obtained if the reactive center is in a state that is able to simulate homogeneous reaction conditions. In this context, an interphase is defined as a region within a material in which a stationary and a mobile component penetrate each other on a molecular level (see Section 1, Figure 1). The stationary phase is composed of an inert matrix, a flexible spacer, and a reactive center, whereas the mobile phase consists of a solvent or a gaseous, liquid, or dissolved reactant. Organic–inorganic hybrid polymers[43, 88] fulfill the required preconditions for stationary phases (see Section 7). Rigid, porous materials can as well serve as supporting matrix provided that sufficiently long spacers lead to a satisfactory mobility of the reactive centers.

### 4.2. Matrix

The matrix is that part of the stationary phase that effects the cross-linking and therefore the insolubility of the support. Mainly element-oxygen-element (e.g. Si-O-Si, Si-O-Al) and carbon–carbon bonds form the polymer backbone. In particular the type of the matrix and therefore the properties of the resulting interphase can be tailored in the case of sol–gel-processed materials. By the simultaneous cocondensation of suitable modified hydrolyzable precursors (cocondensation agents), the stationary phases are modulated from rigid to highly flexible materials. In addition the porosity and the swelling ability are adjustable. The aim is to achieve a compromise between two—basically contradictive—ideals: A high degree of cross-linking should provide efficient anchoring of the functional groups. At the same time sufficient swelling abilities have to maintain the mobility of the reactive centers. The resulting advantages of interphases are 1) accessibilities of the reactive centers in the interphase that are comparable to that in the homogeneous phase, 2) tuneable densities and distances of the reactive centers and therefore adjustable reactivities in the interphase, 3) reduced leaching of functional groups due to the high degrees of cross-linkage (the stability of the anchored complexes largely depends on the transition metal–ligand bond strengths, like in the homogeneous case), and 4) easy and complete separation of the reaction products from the polymer by a simple filtration or centrifugation process.

### 4.3. Spacer

The linkage between the matrix and the reactive center is designated as the "spacer". It usually consists of a hydrocarbon chain of variable length, ensuring sufficient mobility of the reactive center. Linkers with heteroatoms incorporated in the hydrocarbon chain (e.g. PEG) are also utilized.[37] In this context particularly TentaGel[35, 36] has to be mentioned.[89] A recent study reports on the use of TentaGel as a support in enantioselective interphase catalysis.[37]

### 4.4. Reactive Center

For the performance of organometallic chemistry in interphases, transition metal complexes serve as reactive centers. They are bound to the spacer through a suitable linker which has to ensure stable covalent bonding of the substrate. In the case of catalysis the variety of structurally well defined metal complexes acting as catalysts is merely limited by the stability of the complex under the heterogenization conditions (e.g. sol–gel process). Hence most of the typical homogeneous catalysts can be embedded into stationary phases through suitable functionalized ligands (Figure 3; see also Section 5).

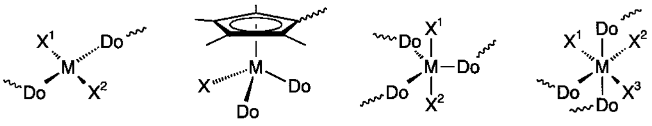


Figure 3. Different possibilities for the connection of the reactive center with the support.

### 4.5. Mobile Phase

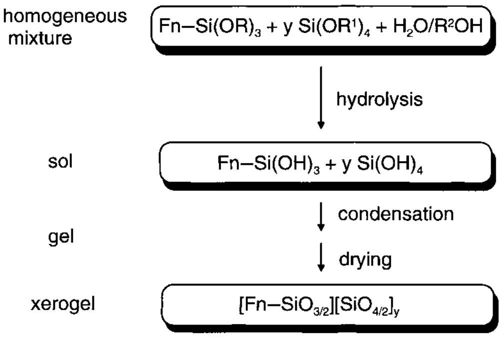
Solvents, gaseous, liquid, or soluted reactants which are able to penetrate the stationary phase represent the mobile phase. Suitable combinations of the two phases have to be chosen to provide sufficient accessibility of the reactive center within the polymer.

## 5. Synthesis of Stationary Phases

### 5.1. Sol–Gel Process in Organometallic Chemistry

Sol–gel processes are well explored and established in material sciences and technologies owing to their diversity.[90, 91] Besides the access to ceramics and glasses of high purity, high homogeneity, and direct molding, the sol–gel route has been shown to be an excellent tool for the preparation of suitable stationary phases. The ease of modification of sol–gel precursors enables tailoring of the properties of the matrix (rigid/mobile, hydrophilic/hydrophobic) by the simultaneous cocondensation of two or more monomers. Even biocatalysts are suitable for entrapment in sol–gel materials.[92] In the present work only the most important aspects of the sol–gel process relating to the synthesis of stationary phases are described.

In Scheme 2 the main steps of an idealized sol–gel reaction are exemplarily summarized. The hydrolysis is performed by mixing alkoxysilanes with water and homogenizing the emulsion with a minimum amount of a solubilizer. Since the hydrolysis is very slow under normal conditions, catalysts are necessary to accelerate and complete the reaction.[91] The resulting silanols condense to generate siloxane bonds. Condensation reactions give rise to a solution of growing polysiloxane. Branching and cross-linking in the solution continues until the network is sufficiently large for the gel transition to occur. The resulting gel consists of a solid polymer network interspersed with solvent. In a subsequent drying step, the network shrinks with loss of the supporting solvent to afford a polysiloxane xerogel.[93]



Scheme 2. The sol–gel process for the cocondensation of a functionalized trialkoxysilane with a tetraalkoxysilane (idealizd polycondensation). Fn = functionality (see Scheme 5.1)

The monomeric alkoxysilyl-functionalized molecules are formally distinguished in functional groups (mostly metal complexes) and in cocondensation agents (network modifiers). Among the different alkoxysilanes each of the components plays a specific role (Figure 4):

1) Monofunctional alkoxides ($R^1R^2R^3SiOR$, not shown in Figure 4) serve as end-capping reagents to remove the remaining hydroxyl groups after the sol–gel reaction or to hydrophobize surfaces of silica and glass.[90b]
2) Dialkoxysilanes ($R^1R^2Si(OR)_2$) cannot act as network formers. However, their tendency to form chains is currently used to provide some flexibility to the oxide network.[91] The most common $R^1$ (or $R^2$) substituents for these precursors are methyl or phenyl groups.
3) Trialkoxysilanes ($R^1Si(OR)_3$) are usual precursors to introduce organic groups into an inorganic network.[91] If they are ideally polycondensed without any cocondensation agent a two-dimensional "pleated sheet" structure is built up.[90b] Such silanes are commercially available in a

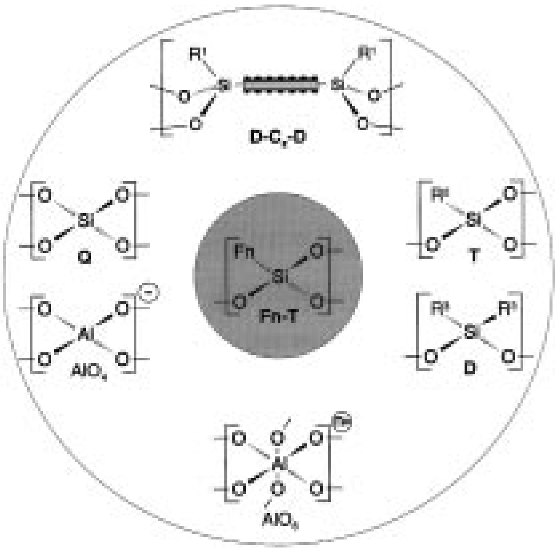


Figure 4. Selected structural units in transition metal functionalized polysiloxanes and polyalumosiloxanes. For an explanation of the nomenclature see Figure 5 and Section 5.3.

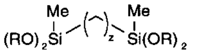
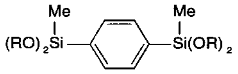
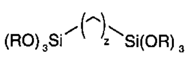
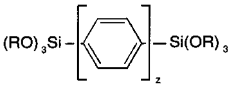
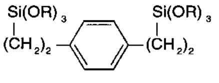
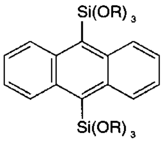
large variety. Careful control of polymerization reactions would lead to a homogeneous distribution of organic $R^1$ groups within the organic–inorganic network. If $R^1$ contains donor groups like $PR_2$ or $NR_2$ the designation Fn (functionality, see Section 5.3) is chosen.

4) Metal alkoxides are typical inorganic network formers.[90, 91, 94] They act as cross-linking agents between organosilicon units in order to increase the hardness of the materials. The most popular representatives are tetraalkoxysilanes $Si(OEt)_4$ (TEOS) and $Si(OMe)_4$ (TMOS), but aluminium alkoxides ($Al(OR)_3$; $R = i$Pr, etc.) have also been employed (see Section 5.2). In addition transition metal alkoxides $M(OR)_4$, ($M = $Ti, Zr, etc.) are also considered.[91]

In Table 1 selected and partly well investigated cocondensation agents are presented. Some of them are commercially available. Besides the classical sol–gel precursors (entries 1-3), bisilylated or possibly polysilylated organic molecules with various shapes and structures allow a general and easy preparation of hybrid organic–inorganic gels. This novel class of materials, which is called bridged polysilsesquioxanes, forms three-dimensional networks with an organic fragment as an integral component.[95] The intimate association of the organic and inorganic phase, a true "molecular composite", coupled with the variability of the organic component permits engineering of both chemical and physical properties of the material.[96] These properties combined with their high possibility for cross-linking are of increasing interest for the preparation of stationary phases. Thus two types of hydrocarbon-bridged alkoxysilanes (Table 1, entries 4–6) have been applied as cocondensation agents for the sol–gel process of trimethoxysilyl-functionalized transition metal complexes (see Scheme 8 and Section 7.1). Other bisilylated precursors displayed in Table 1 have not yet been utilized as cocondensation agents, but have a great potential.

Trialkoxysilyl-functionalized donors (Do) are most suitable for the synthesis of metal complexes compatible for sol–gel chemistry, since they can easily be prepared in a great variety. In addition they provide a maximum of three Si-O-Si bonds which ensure a stable connection to the siloxane backbone (Table 2).

Table 1. Selected network modifiers for the sol–gel process of trialkoxysilyl-functionalized transition metal complexes.

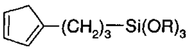
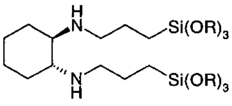
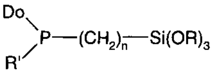
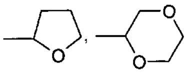
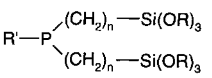
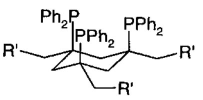
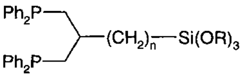
| Entry | Cocondensation agent | $z$ | Properties, remarks | Ref. |
|---|---|---|---|---|
| 1 | $(R^1)_2Si(OR)_2$ | | introduces flexibility, metal complex density not controllable | [97] |
| 2 | $R^1Si(OR)_3$ | | modifies matrices more mobile than TEOS (entry 3), metal complex density controllable | [97] |
| 3 | $Si(OR)_4$ | | produces rather rigid silica gel like matrices, complex density controllable | [98] |
| 4 |  | 6 | highly cross-linked matrices, complex density controllable, flexibility range between that of entries 1 and 2 | [44, 99] |
| 5 | | 8 | | |
| 6 | | 14 | | |
| 7 |  | | have not yet been used for the sol–gel process of metal complexes | [100] |
| 8 |  | 2 | only the hexylene-bridged derivative (entry 10) has been used for a sol–gel process with metal complexes, higher cross-linkage than in entries 4–6 expected | [101] |
| 9 | | 4 | | |
| 10 | | 6 | | |
| 11 | | 8 | | |
| 12 | | 9 | | |
| 13 | | 10 | | |
| 14 | | 14 | | |
| 15 |  | 1 | have not yet been used for a sol–gel process with metal catalysts | [102, 103] |
| 16 | | 2 | | |
| 17 | | 3 | | |
| 18 |  | | introduces more flexibility than in entries 15–17 | [104] |
| 19 |  | | has not yet been used for a sol–gel process with catalysts, should introduce minor flexibility | [102] |
| 20 | $Al(OR^2)_3$ | | well separable due to the introduction of ionic charges, highly cross-linked matrices, rigid material | [105] |

## 5.2. Synthesis of Polysiloxane-Bound Transition Metal Complexes

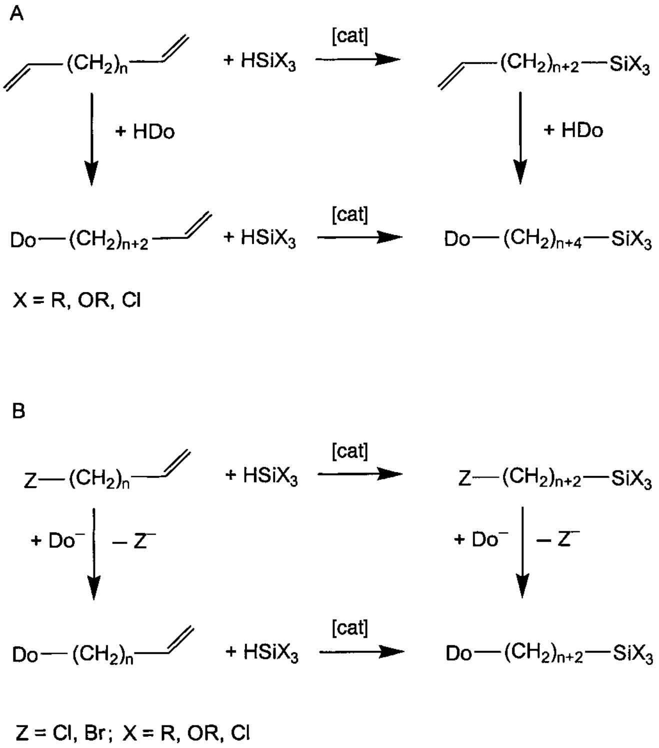
The generation of stationary phases may be performed in three steps: 1) synthesis of silyl-functionalized donor ligands, 2) synthesis of silyl-functionalized metal complexes, and 3) sol–gel condensation of the monomeric precursors.

Silyl-functionalized donor ligands are most conveniently accessible starting with an $\alpha,\omega$-diene or an $\alpha,\omega$-halogenoalkene (Scheme 3). In the presence of catalysts such as

Table 2. Selected organofunctionalized silanes.[106]

| Entry | Ligand[a] | Properties, remarks | Ref. |
|---|---|---|---|
| 1 | $S[-(CH_2)_3-Si(OR)_3]_2$ | | [107] |
| 2 | $H_2N-(CH_2)_3-Si(OR)_3$ | | [108] |
| 3 |  | | [109] |
| 4 | $(H_5C_6)_2P-(CH_2)_n-Si(OR)_3$ | $n = 2$<br>$n = 3, 6$<br>$n = 8, 14$ | [28a, 110]<br>[111]<br>[112] |
| 5 |  | chiral | [113] |
| 6 |  | $n = 3, 6, 8$ for $R' = Ph$,<br>$n = 3$ for $R' = Cy$,<br>$Do = CH_2CH_2OCH_3$,<br> | [98a, 105a] |
| 7 |  | $n = 3, 6, 8, 14$ for $R' = CH_2CH_2OCH_3$<br>$n = 3$ for $R' = Ph$ | [114]<br>[115] |
| 8 |  | $R' = (OCH_2CH_2)_xO-(CH_2)_3Si(OR)_3$,<br>$x = 15-60$ | [116] |
| 9 |  | | [117] |

[a] $R = CH_3, C_2H_5$.



Scheme 3. Synthesis of silyl-functionalized donor ligands from $\alpha,\omega$-dienes (A) and $\alpha,\omega$-haloalkenes (B). [cat] = catalyst, Do = donor group (e.g. $PR_2$).

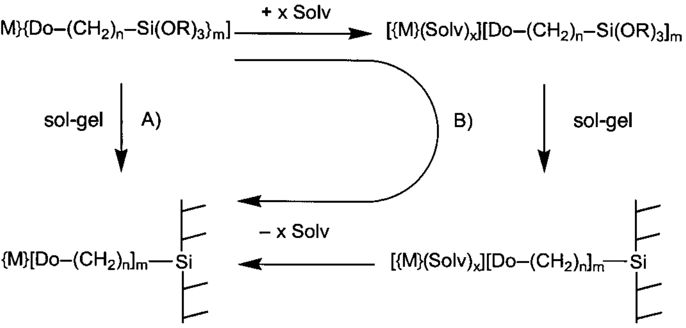
$H_2[PtCl_6]$ or $RhCl_3$, a tertiary silane is added in a stereoselective anti-Markovnikov manner to one of the two terminal double bonds.[118] Chlorosilanes react more readily than alkoxysilanes, but the chlorine atoms have to be replaced by alkoxy groups prior to the subsequent reaction step. The resulting $\omega$-silylalkenes are then transformed to the desired donor ligands by the photochemical addition of a secondary phosphane (HDo) to the remaining terminal double bond (Scheme 3 A). The $\alpha$-halo-$\omega$-silylalkane intermediates react with the corresponding anion of the donor group ($Do^-$) in a nucleophilic substitution (Scheme 3 B). The described reaction sequence is generally favorable over a pathway via an $\omega$-alkenylphosphane ($Do-(CH_2)_n-CH{=}CH_2$, Scheme 3), since strongly binding donor groups like phosphanes prevent the hydrosilylation by poisoning the catalyst.

A generally applicable route to metal complexes with SiOR groups is the combination of silyl-functionalized donor ligands with suitable transition metal precursors in which the metal already has the necessary oxidation state and the participating ligands (Scheme 4). Easily replaceable ligands such as alkenes or triphenylphosphane are quantitatively substituted for the more basic (alkoxysilylalkyl)phosphanes. In contrast to syntheses starting from a metal halide and employing an excess of phosphane which concomitantly acts as a ligand and as a reducing agent, this method allows stoichiometric addition of the ligand and working in neutral, aprotic media under mild conditions. Thus, problems to separate excess ligand from the product, wasting of the precious bifunctional ligands, and premature hydrolysis of the silyl groups are avoided.

$$[\{M\}L_m] + m\,Do{-}(CH_2)_n{-}Si(OR)_3 \xrightarrow{-m\,L} [\{M\}\{Do{-}(CH_2)_n{-}Si(OR)_3\}_m]$$

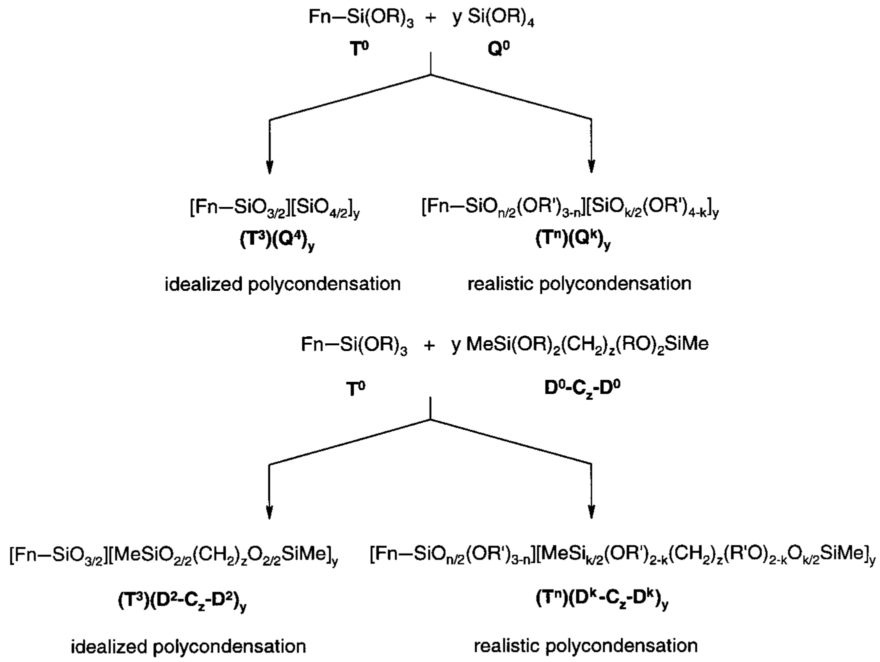
Scheme 4. Synthesis of **T**-silyl-functionalized transition metal complexes as monomeric precursors for a stationary phase. {M} = transition metal complex fragment; L = easily replaceable donor ligand; $Do-(CH_2)_n-Si(OR)_3$ = silyl-functionalized donor ligand.

After addition of water, cocondensation agent, and condensation catalyst, the silyl-functionalized complexes are subjected to the sol–gel process.[10, 90c] In the case of complexes insensitive to water this method leads directly to the aspired stationary phases (route A in Scheme 5).[98a] Particularly square-planar ether–phosphane chelate complexes of palladium(II) or rhodium(I) show a strong affinity to water, forming hydroxide complexes which tend to decom-



Scheme 5. Direct (A) and indirect synthesis (B) of stationary phases consisting of polysiloxane-bound transition metal complexes. Solv = coordinating solvent; Do = donor group (e.g. $PR_2$); R = Me, Et.

pose.[44, 119] This undesirable process is circumvented by performing the sol–gel procedure in a coordinating solvent, which is subsequently removed in vacuo (route B in Scheme 5). The coordinating solvent has to meet several requirements: It has to bind substantially stronger to the metal than to water to avoid the formation of hydroxide complexes. On the other hand, it should coordinate weaker to the metal than the silyl-functionalized ligands to evade their displacement and to ensure the reversibility of their coordination. Finally, they must be volatile enough to be evaporated quantitatively after polycondensation. Pyridine for rhodium systems[44] and acetonitrile for palladium systems[119] have proven most useful in this method.



Scheme 6. Idealized and realistic composition of stationary phases. Fn = ligand, transition metal complex fragment; R = alkyl; R′ = H, alkyl; **Q**, **T**, **D** = quadruply, triply, and doubly functionalized silane; *k*, *n* = number of Si-O-Si bonds.

### 5.3. Nomenclature

As mentioned in Section 5.1., the polycondensation of the silanol groups generally does not proceed quantitatively, and the different monomeric silyl species are not always incorporated in the polysiloxane network in the ratio given by the stoichiometry.[40a, 90] This deviation from the idealized composition is expressed by a nomenclature which is based on that developed by Engelhardt et al.[120] and is demonstrated here by means of two examples.

The designation of the silicon species refers to reactive, hydrolyzable groups (e.g. the number of Si–OR functions) rather than to the valence of the silicon atom. A *mono*functional silicon is labeled as **M**, a *di*functional silicon as **D**, a *tri*functional silicon as **T**, and a *quadri*functional silicon as **Q**. The functionality attached to silicon is described with superscripted numbers designating the degree of condensation (Scheme 6). A survey of the different silicon species and their labeling is given in Figure 5. The subscripted number indicates the stoichiometry of the silicon species.

For the two examples in Scheme 6 the silane monomer is designated as $\mathbf{T^0}$, and the cocondensation agents are denoted as $\mathbf{Q^0}$ and $\mathbf{D^0\text{-}C_z\text{-}D^0}$. The labeling $\mathbf{(T^3)(Q^4)_y}$ and $\mathbf{(T^3)(D^2\text{-}C_z\text{-}D^2)_y}$ is based on a complete polycondensation and implies that in the polysiloxane networks three and four, and three and each two Si-O-Si bonds, respectively, are present. In fact the degree of polycondensation is usually expected in the range between 75 and 95%.[40a, 95b, 98a] The realistic compositions are delineated as $\mathbf{(T^n)(Q^k)_y}$ and $\mathbf{(T^n)(D^k\text{-}C_z\text{-}D^k)_y}$, where *n* and *k* vary between 1–3 and 1–4, and 1–3 and 0–2, respectively. The individual silyl species $\mathbf{Q^0}$, $\mathbf{Q^1}$, $\mathbf{Q^2}$, $\mathbf{Q^3}$, $\mathbf{Q^4}$, $\mathbf{T^0}$, $\mathbf{T^1}$, $\mathbf{T^2}$, $\mathbf{T^3}$, and $\mathbf{D^0}$, $\mathbf{D^1}$, $\mathbf{D^2}$, which show different chemical shifts, are quantified by $^{29}$Si CP/MAS NMR spectroscopy.

## 6. Characterization

A variety of different methods is available for the investigation of organic–inorganic hybrid polymers (stationary phases) and interphases.[121] Each of these techniques affords an access to different regions and aspects of the sol–gel derived materials.

### 6.1. IR Spectroscopy

IR spectroscopy is a simple and fast method for the characterization of the reactive centers within a stationary phase. Functional groups like carbonyls, nitriles, isonitriles, thiocarbonyls, sulfonyls, hydrides, and halides are easily recognized.[122] Besides structural subunits, the stereochemical environment of a coordination center can be elucidated as well.

### 6.2. EXAFS and EDX Spectroscopy

Since sol–gel-processed materials have an amorphous character, structural informations cannot be obtained by conventional X-ray diffraction methods. However, the application of *e*xtended *X*-ray *a*bsorption *f*ine *s*tructure (EXAFS) spectroscopy provides a possibility to get insight into the coordination sphere of reactive centers.[123] A comparison of structural data obtained for similar homogeneous and hybrid catalysts investigated by X-ray structural analyses and EXAFS shows an excellent agreement of their bond lengths.[124]

A combination of several methods is employed for the quantitative analysis of sol–gel-derived materials: *e*nergy *d*ispersive *X*-ray analysis (EDX),[125] elemental analysis, and solid-state NMR spectroscopy. Since the stationary phases generally do not reveal an ideal stoichiometry it is necessary to ascertain their realistic composition. This is performed by determining the degree of condensation by $^{29}$Si CP/MAS

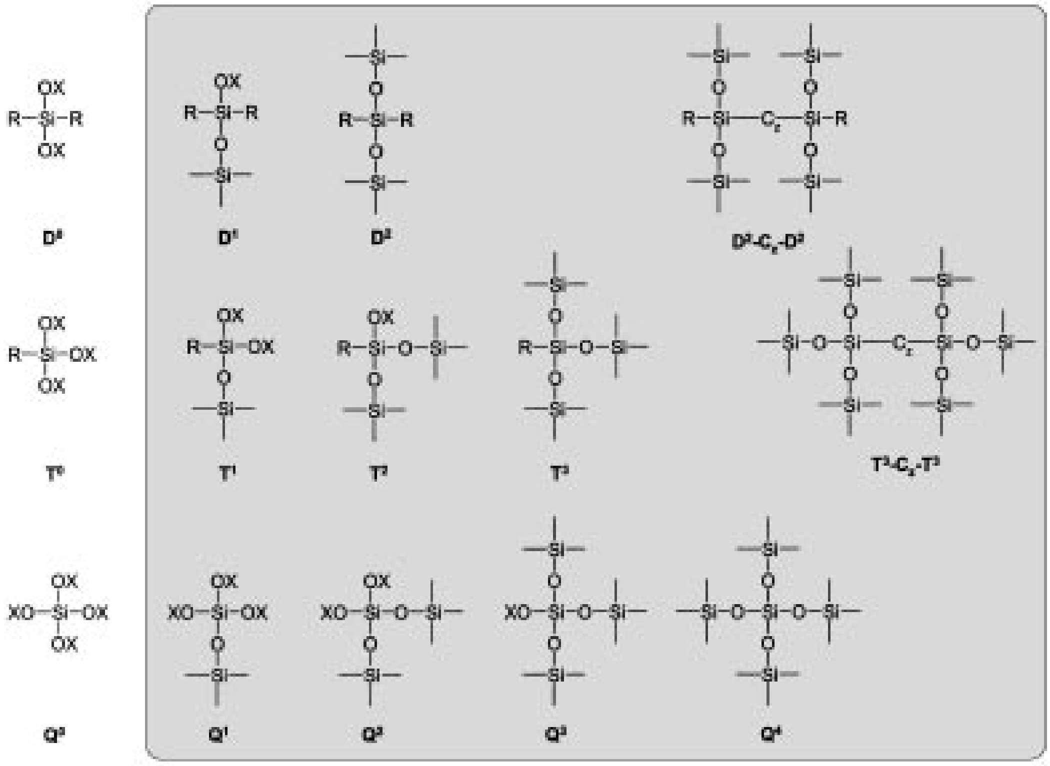


Figure 5. Nomenclature of **Q**, **T**, and **D** polysiloxanes. The cross-linking increases from left to right, and the flexibility increases from the bottom to the top.

NMR spectroscopy. A comparison of these results with those obtained from elemental analyses show sufficient agreement.[105] Elements which cannot easily be determined by elemental analyses are candidates for semiquantitative analysis by EDX.

### 6.3. Scanning Electron Microscopy

*S*canning *e*lectron *m*icroscopy (SEM) affords microscopic information about the average corn size, the distribution of the corn sizes, and the morphology of the particles.[126] The backscattering technique allows the detection of transition metal particles on the polymer surface generated by complex decomposition. SEM also enables a first clue about the surface, while BET measurements[127] offer an accurate characterization of the surface area of the polymers.

### 6.4. Solid-State NMR Spectroscopy

As a selective technique, NMR spectroscopy allows the observation of one signal per magnetically inequivalent nucleus. Therefore the structure and dynamic behavior of each part of a heterogeneous material like organic–inorganic hybrid catalysts can be investigated independently.[128, 129] The various NMR-active nuclei at different sites of the material are ideal for a multinuclear, multiparameter approach. This allows the design of experiments to gain information about the various local environments such as the structure of the inorganic matrix, the spacer, and the catalytically active site as well as the dynamics of the matrix, spacer, and the metal complex. The method is also useful to determine connectivities and the degree of hydrolysis and condensation of the network.[41a, 97, 98a, 119] Moreover, the question of the distribution of the reactive centers within the matrix is adressed as well. Thus the formation of domain structures is discernible from homogeneously dispersed reactive centers in the material. This is valuable information with respect to the performance of an anchored catalyst system.

#### *6.4.1. Characterization of Stationary Phases*

Structural information about the inorganic part of the matrix is derived from $^{29}Si$ NMR chemical shifts. For silicate-related systems many empirical relationships between isotropic $^{29}Si$ NMR chemical shifts and structural features have been established.[41a, 130] Of significance is the finding that the formation of a Si-O-Si connection at a given $SiO_{4-n}(OSi)_n$ environment ($\mathbf{Q}^k$) causes a high-field shift of approximately 10 ppm.[41a] In amorphous samples with highly disordered structures broad and overlapping resonances are observed which still allow the distinction between different $\mathbf{M}^l$ (see Section 5.3), $\mathbf{D}^i$, $\mathbf{T}^n$, and $\mathbf{Q}^k$ environments (Figure 6),[120] but prevent the exact determination of the number of chemically and/or crystallographically inequivalent silicon sites. In general it is possible to analyze the spectra by deconvolution and line-fitting procedures, and careful considerations of the cross-polarization dynamics in CP/MAS experiments[131, 132] or time-consuming MAS spectra allow the evaluation of the relative populations (quantification) of the different silicon groups.[41b,c] In this way a number of stationary

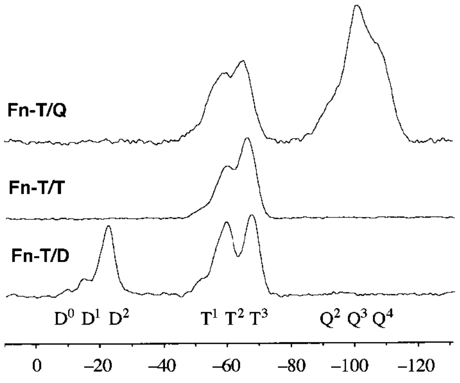


Figure 6. Typical $^{29}Si$ CP/MAS NMR spectra of **Fn-T/Q**, **Fn-T/T**, and **Fn-T/D** copolymers. **Fn** = transition metal complex.

phases have been characterized. It was found that the degree of condensation increases from $\mathbf{D} < \mathbf{T} \approx \mathbf{Fn\text{-}T} < \mathbf{Q}$ groups and depends on the stoichiometry of the **Fn-T** and cocondensation agent and on the sol–gel technique used.[97b, 98a, 119] The determination of the ratio between **Fn-T** and the cocondensation agent revealed that **D** groups are unsuitable for building blocks of metal-functionalized stationary phases.[97a] In contrast to the case of **Fn-T/T** and **Fn-T/Q** polymers, it is impossible to vary the stoichiometry over a broad range and thus control the complex density of the polymer.

$^{31}$P and $^{13}$C CP/MAS NMR spectroscopy give insight into the structure of the spacer and the coordination sphere of the metal complex within a stationary phase. This is illustrated in Figure 7 for a series of supported rhodium complexes.[44] Two resonances for the two different phosphorus sites are characteristic for the chelate complex. A dimeric form is responsible for the broad high-field signal (A, left). After treatment of this material with carbon monoxide only one signal in the $^{31}$P NMR spectrum caused by the two equivalent phosphane ligands is observed (B, left). The reaction of the sterically more demanding tolan is incomplete, as demonstrated by the small residual peaks of the starting complex. Apparently there are regions within the material with less accessible reactive centers (C, left).

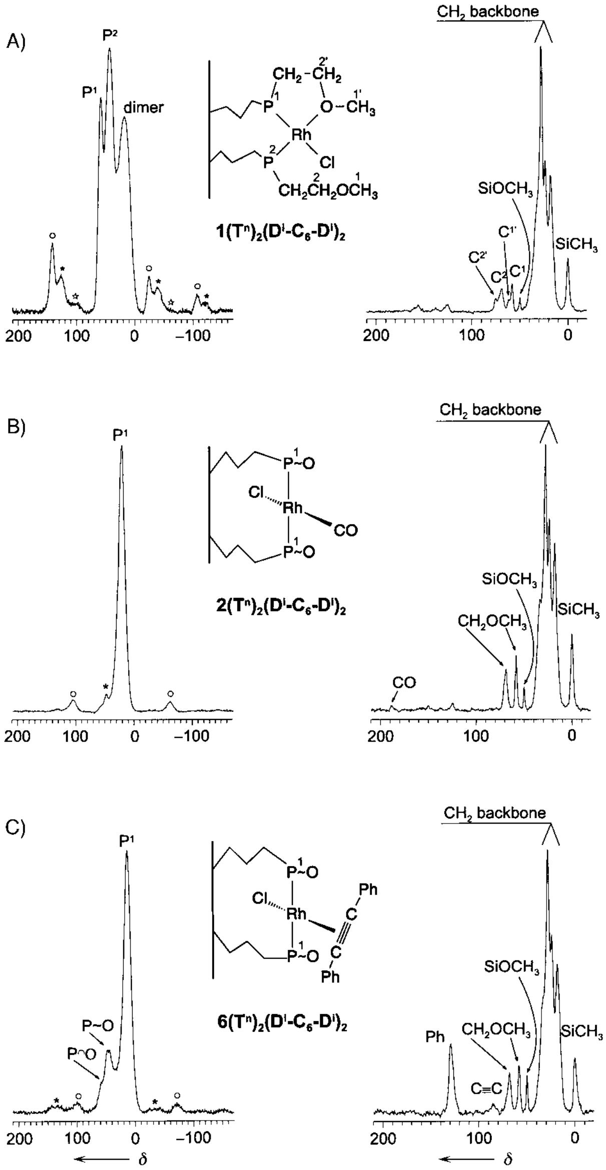


Figure 7. Selected $^{31}$P (left) and $^{13}$C CP/MAS NMR spectra of stationary phases (right). P∼O: $\eta^1$-(P)-coordinated ether–phosphane; P⌒O: $\eta^2$-(P,O)-coordinated ether–phosphane.

The spacer and the ligand backbone carbon atoms give rise to broad peaks in the alkane region of the $^{13}$C CP/MAS NMR spectra (right-hand side of Figure 7). The high-field singlet of the $SiCH_3$ function indicates an intact cocondensation agent, whereas the characteristic $SiOCH_3$ signal allows the estimation of the degree of hydrolysis and condensation. Important features in the $^{13}$C CP/MAS NMR spectra are the resonances of the participating ligands such as the carbonyl group and tolan, which establish the structure and the integrity of the metal complexes in the matrix. The spectral information is limited to the chemical shift of the inequivalent nuclei since the linewidth prevents the evaluation of the homo- and heteronuclear coupling constants ($J_{RhP}$, $J_{PP}$, $J_{PC}$).

As a volume property, the proton relaxation times in the rotating frame ($T_{1\rho H}$, see Section 6.4.2) provide information about the distribution of the reactive centers within the material. Stationary phases in which the reactive centers are completely mixed with the cocondensate are preferred over matrices with local domains of either cocondensate or **Fn-T** groups. If the $T_{1\rho H}$ values detected with $^{29}$Si and $^{31}$P NMR spectroscopy are compatible and if both display a monoexponential behavior, a homogeneous matrix has been formed. Investigations in this direction reveal a homogenous distribution of the reactive centers when in $\mathbf{Fn\text{-}T/T}_y$ matrices $y$ is not larger than 48 and in $\mathbf{Fn\text{-}T/Q}_y$ materials $y$ is smaller than 30. If $y$ exceeds 48 or 30, respectively, domain structures are formed.[86, 98a]

### *6.4.2. Mobility Studies of Stationary Phases*

Detailed knowledge of the dynamic behavior of the stationary phases is a precondition to optimize the reactivity of the catalytic centers. Below the glass-transition temperature the linewidths in solid-state NMR spectra of spin ½ nuclei are governed by the chemical shift dispersion, owing to small conformational differences, *c*hemical *s*hift *a*nisotropy (CSA), dipolar interactions, and relaxation processes.[128c, 133] The NMR parameters $T_{XH}$, $T_{1X}$, $T_2$, $T_{1\rho H}$ and the linewidths of the signals in the CP/MAS NMR spectra and of the protons in two-dimensional *wi*deline *se*paration (WISE) NMR spectra are sensitive toward motions on different times scales.[129b, 134, 135] It is difficult to interpret the relaxation times in terms of the correlation times, as has been performed for polymers in solution.[136] Information about mobilities of molecules or molecule fragments from $T_{1X}$ or $T_{1\rho H}$ data is only unambiguous if the corresponding correlation times $\tau_R$ are known.[129b, 134, 136] If certain assumptions are made and if different NMR parameters are compared, one is able to draw a good qualitative picture about the dynamics of the stationary phases which correlates well with the chemistry of the materials (see Section 7).

The discussion about the dynamics of the stationary phases is restricted to those examples for which detailed temperature-dependent NMR investigations exist.[97, 98a] The phosphorus nucleus was selected as a probe since the local environments of the phosphorus atoms in the ligands and complexes of the different copolymers are comparable. Thus the changes in the linewidths of the $^{31}$P signals in CP/MAS NMR spectra reflect to some extent the variable flexibilities of the materials.

Also the cross-polarization constants $T_{PH}$ are solely determined by the mobilitiy of the stationary phases. Fast motions in the kHz region lead to inefficient cross-polarization and therefore to higher $T_{PH}$ values.[137] The relaxation time of the protons in the rotating frame, $T_{1\rho H}$, is an averaged quantity within domains that are 1–2 nm in diameter, provided sufficient dipolar coupling among the protons provides spin diffusion.[138] In cases with enhanced mobilities in the kHz region dipolar coupling among protons becomes inefficient, and specific $T_{1\rho H}$ values for certain parts of the material are obtained. The spin-lattice relaxation times $T_{1P}$ represent characteristic values for each species and are sensitive toward motions in the MHz region.[128c, 134]

The mobilities of the polymer-bound ligands depend on the type of cocondensate and increase in the order **Fn-T/Q** < **Fn-T/T** ≪ **Fn-T/D-C$_z$-D** < **Fn-T/D** (see Figure 5). The extension of the spacer from *n*-propyl through *n*-hexyl to *n*-octyl results in a marked rise in the flexibilities of the phosphorus atoms. The same order was established for P-coordinated phosphane-metal complexes, but much less pronounced. This was interpreted by an increase of cross-linking when two or three ligands coordinate to a metal fragment. It should be emphasized that the hydrocarbon-bridged dimethoxymethylsilanes are so far the ideal cocondensation agents since they combine high cross-linking with high flexibility.

Two-dimensional WISE NMR spectroscopy has been applied to obtain more detailed information about the mobilities of different parts within the polymer.[139] The pulse sequence of the WISE experiment correlates the high-resolution $^{13}$C or $^{31}$P NMR spectrum with the wide-line $^{1}$H NMR spectrum. The linewidths in the *F*1 (proton) dimension are determined by $^{1}$H–$^{1}$H dipole interactions, which are reduced by molecular motion and magic angle spinning. Thus the experiment allows one to distinguish between carbon or phosphorus atoms attached to protons in a mobile and in a rigid environment. The WISE experiments support the conclusions about the dynamic behavior of the stationary phases drawn from relaxation data and cross-polarization constants.

Figures 8 displays the application of this experiment to polysiloxane-bound ligands and complexes.[97b] The narrow linewidths of about 5 kHz in the *F*1 dimension indicate high mobilities in the region of several 10 kHz for the **Fn-T/D** polysiloxane-bound ligand (Figure 8, left). This ligand behaves like a polymer above the glass-transition temperature $T_g$.[139] The **Fn-T/T** blend shows broader linewidths of the $^{13}$C resonances at $\delta = 30$ and 0. This was explained with a much more rigid polysiloxane backbone. *D*ifferential *s*canning *c*alorimetric (DSC) measurements confirm this interpretation. The glass transition temperatures $T_g$ increase in the order **Fn-T/D** < **Fn-T/T** ≪ **Fn-T/Q**. The resonances of the aromatic region and the ether moiety of **Fn-T/T** are broader than those of the methylene groups in the alkyl chain, which is in agreement with an increase of the mobility along the spacer (Figure 8, right). This observation could not be established for corresponding polysiloxane-bound complexes. Their linewidths are approximately twice as large, confirming the findings that the polysiloxane-bound complexes are more rigid than the corresponding polysiloxane-bound ligands.

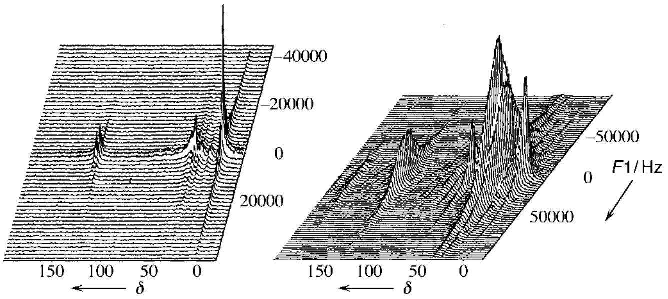


Figure 8. 2D ($^{13}$C, $^{1}$H) WISE spectrum of the stationary phase **Fn-T$^n$/D$^i$** (left) and **Fn-T$^n$/T$^n$** (right). **Fn** = phosphane ligand.

Figure 9 shows the 2D ($^{1}$H, $^{31}$P) WISE NMR spectra of a stationary phase synthesized by cocondensation of a phos-

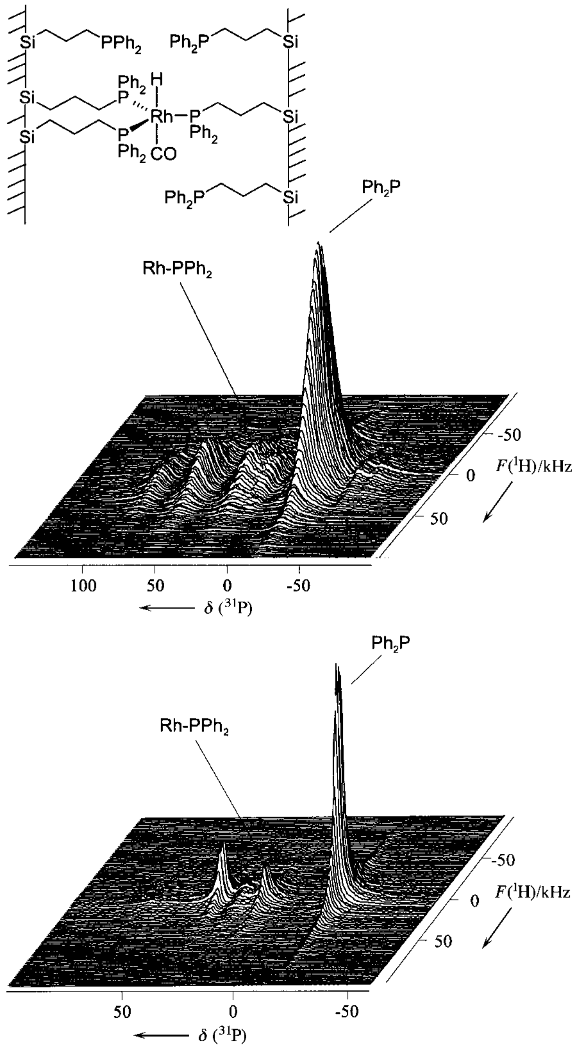


Figure 9. 2D ($^{31}$P, $^{1}$H) WISE spectrum of a system made up of a polysiloxane whose phosphanyl group is partially bound to a rhodium(I) complex in the dry state (top, stationary phase) and swollen in ethanol (bottom, interphase). Rh–PPh$_2$ = coordinated phosphanyl group; PPh$_2$ = noncoordinated phosphanyl group.

phanerhodium complex with its corresponding non-coordinated phosphane ligand.[101b] A comparison of the spectrum of the dry polymer (Figure 9, top) with that of the polymer treated with ethanol (Figure 9, bottom) reveals an increase in mobility in the swollen gel (interphase). The substantial decrease of the linewidths in the $^1$H dimension of the wet polymer is again more pronounced for the noncoordinated ligand than for the complex.

### 6.4.3. Chemical Exchange in Interphases

As a further example of the increased mobility in the interphase, the chemical exchange of three ether–phosphane ligands in the coordination sphere of a ruthenium complex[86] is discussed (Figure 10 and Scheme 7). The stereochemistry of the polysiloxane-bound ruthenium complex **7(T$^n$)$_3$** generates three different phosphorus sites, two of which are resolved in the solid-state $^{31}$P CP/MAS NMR spectrum (Figure 10 A). Treatment of this stationary phase with methanol as the mobile phase forms a highly swollen gel with regions of high mobility. In the $^{31}$P CP/MAS NMR spectrum of the swollen gel a signal with a very small linewidth is observed (Figure 10 B). Its resonance frequency corresponds to the weighted average of the resonances of all three phosphorus nuclei in the dry polymer, which indicates that a chemical exchange process is responsible for the equivalence of the three phosphorus sites. As a further consequence, the spinning side bands are strongly reduced. The exchange process of the ether–phosphane ligands in the interphase is suppressed by lowering the temperature (Figure 10 C) and by removing the mobile phase (methanol).

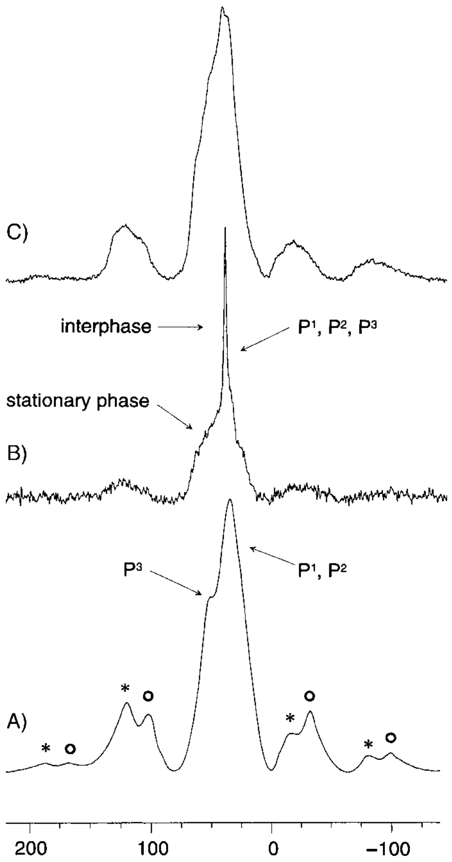
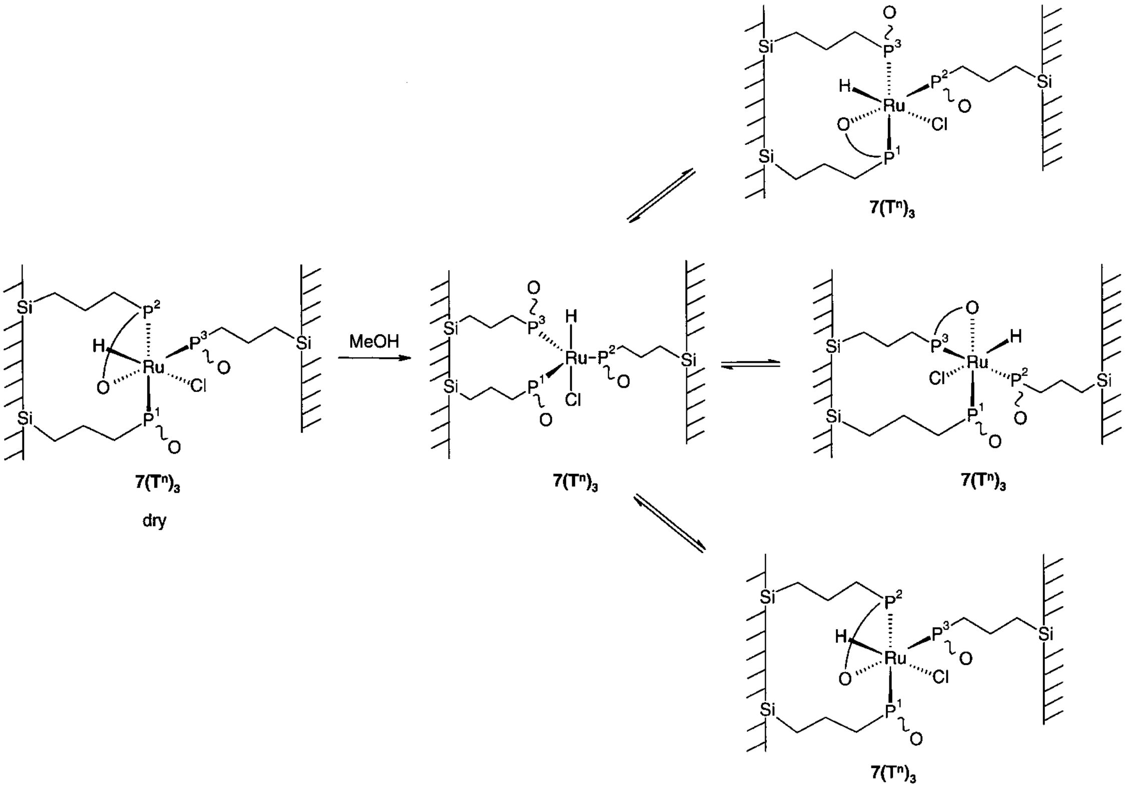


Figure 10. $^{31}$P CP/MAS NMR spectra of **7(T$^n$)$_3$**. A) Stationary phase (○ and *: rotation side bands for the signals from P$^1$, P$^2$ and P$^3$, respectively). B) Interphase (swollen in MeOH). C) Interphase at –70 °C. For definitions of P$^1$, P$^2$, and P$^3$, see Scheme 7.



Scheme 7. Mechanism of a chemical exchange in the interphase.

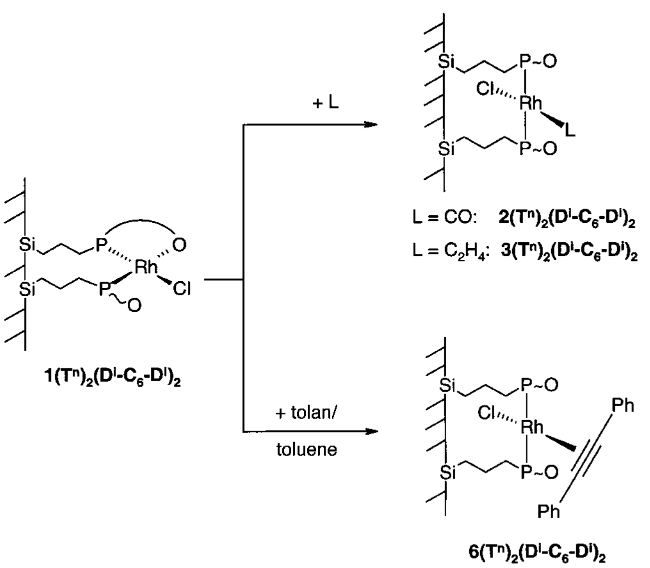
## 7. Examples for Reactions in Interphases

### 7.1. Organometallic Model Reactions in Interphases

To prove that transition metal catalyzed processes are possible in interphases, several model reactions have been performed with stationary phases containing platinum group complex fragments. The feasibility of reactions such as oxidative additions, carbon monoxide insertions, or the activation of molecules demonstrates that diffusion problems are restrained by the generation of a solutionlike state in appropriate interphases.

### *7.1.1. Reactions in Gaseous/Solid Interphases*

When the stationary phase $\mathbf{1(T^{n})_2(D^{i}\text{-}C_6\text{-}D^{i})_2}$ containing a rhodium(I) complex as an active center is exposed to an atmosphere of carbon monoxide or ethene (mobile phase) at ambient temperature, a facile cleavage of the weak Rh-O bond takes place and the adducts $\mathbf{2(T^{n})_2(D^{i}\text{-}C_6\text{-}D^{i})_2}$ and $\mathbf{3(T^{n})_2(D^{i}\text{-}C_6\text{-}D^{i})_2}$ are quantitatively formed (Scheme 8). The latter is only stable in an atmosphere of ethene.[44]

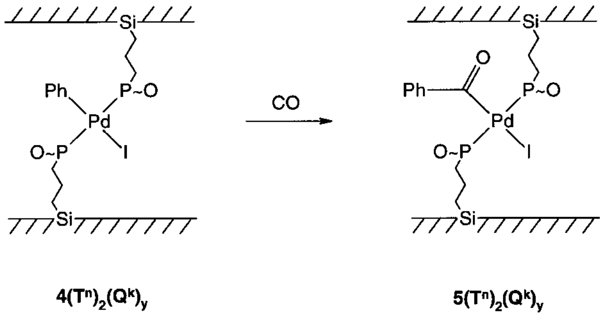


Scheme 8. Examples for reactions of a rhodium(I) complex in the interphase.

Arylpalladium complexes are known to undergo CO insertion reactions under very mild conditions. It was shown that this insertion is also possible in the interphase: IR spectra prove the formation of the benzoyl complexes $\mathbf{5(T^{n})_2(Q^{k})_y}$ in quantitative yields when the polysiloxane-bound arylpalladium complexes $\mathbf{4(T^{n})_2(Q^{k})_y}$ are exposed to carbon monoxide (20 bar, 40 °C, Scheme 9).[119]

### *7.1.2. Reactions in Liquid/Solid Interphases*

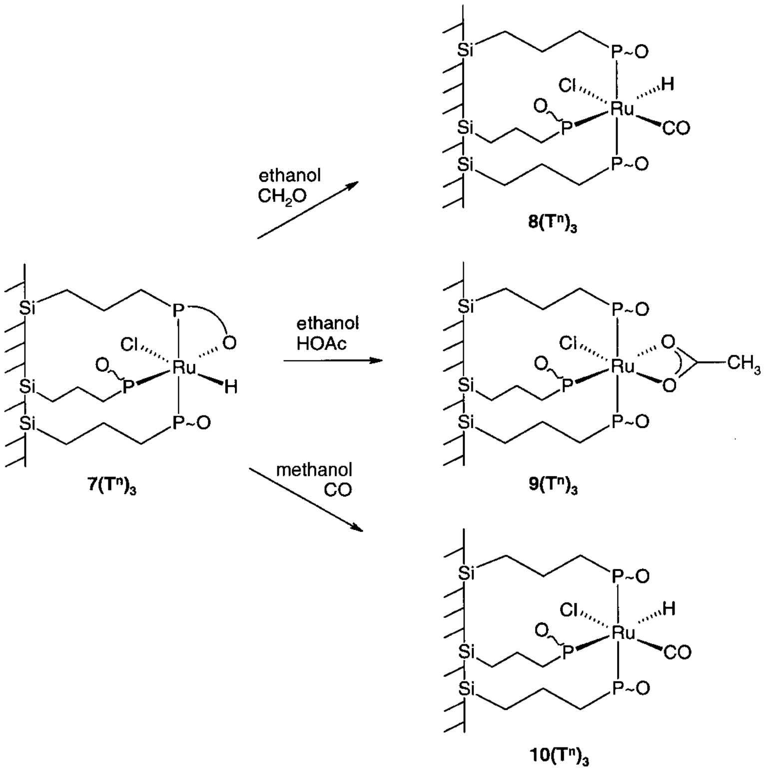
Interphases based on liquid/solid systems benefit from the swelling abilities of the polymers or copolymers, making the reactive centers also accessible for larger molecules. This was demonstrated in the case of the reaction of the rhodium(I) complex $\mathbf{1(T^{n})_2(D^{i}\text{-}C_6\text{-}D^{i})_2}$ with tolan in toluene, resulting in the formation of the $\eta^2$-diphenylacetylene complex $\mathbf{6(T^{n})_2(D^{i}\text{-}C_6\text{-}D^{i})_2}$ (Scheme 8).[99] The stationary phase contains the component **D-C$_6$-D**, which is responsible for the swelling ability of the resulting polymer. The accessibility of the rhodium atoms within the matrix is improved by increasing the reaction temperature or the amount of the cocondensation agent **D-C$_6$-D**, since both effect an increase in the mobility of the material. In a similar fashion a suspension of $\mathbf{1(T^{n})_2(D^{i}\text{-}C_6\text{-}D^{i})_2}$ in *n*-hexane and ethanol/pyridine reacts readily with carbon disulfide and dihydrogen in the interphase, to give $CS_2$ and dihydride complexes, respectively.[44]



Scheme 9. Example for a CO insertion into a palladium–aryl bond in the interphase. P ~ O = PhP(CH$_2$(Do))(CH$_2$CH$_2$CH$_2$SiO$_{3/2}$); Do = CH$_2$OCH$_3$, CH$_2$C$_4$H$_7$O (tetrahydrofuryl).

The polysiloxane-supported ruthenium(II) complex $\mathbf{7(T^{n})_3}$ presents three ether–phosphane ligands in its coordination sphere, one of which is $\eta^2$-(O,P)-bound. If the gel of $\mathbf{7(T^{n})_3}$ is swollen in ethanol and treated with methanal at 60 °C, a smooth reaction in the interphase takes place with formation of the carbonyl(hydrido)ruthenium complex(II) $\mathbf{8(T^{n})_3}$ (Scheme 10).[140]

To obtain further evidence for the chemical exchange process in $\mathbf{7(T^{n})_3}$ (see Scheme 7) the gel swollen with ethanol or methanol was treated with acetic acid and carbon monoxide, respectively (Scheme 10). The reaction of acetic acid with the fluxional ruthenium complex $\mathbf{7(T^{n})_3}$ results in liberation of hydrogen to give the acetato complex $\mathbf{9(T^{n})_3}$ in the interphase (Scheme 10), as was shown by IR spectroscopy.[86] In a carbon monoxide atmosphere the Ru–O bond in $\mathbf{7(T^{n})_3}$ is cleaved, forming the corresponding carbonyl complex $\mathbf{10(T^{n})_3}$.[140] This reaction has been monitored by $^{31}$P CP/MAS NMR spectroscopy. In Figure 11 spectrum A displays the exchange signal of the highly swollen gel of $\mathbf{7(T^{n})_3}$. Spectrum B was obtained within a few minutes after a partial reaction of $\mathbf{7(T^{n})_3}$ + $CH_3OH$ with CO directly in the NMR rotor. Besides the nonconverted, fluxional species $\mathbf{7(T^{n})_3}$ the carbonyl complex $\mathbf{10(T^{n})_3}$ is observed, which generates two broad signals owing to two different environments of the phosphorus sites. In the acetato and carbonyl complexes $\mathbf{9(T^{n})_3}$ and $\mathbf{10(T^{n})_3}$ the weakly coordinated oxygen atom is replaced by the stronger ligands $MeCO_2^-$ and CO, respectively. Since the formation of (O,P)-coordinated chelate complexes is prevented by blocking of the easily accessible coordination site, the exchange process is suppressed (see Section 4.3).



Scheme 10. Examples for reactions of a ruthenium(II) complex in the interphase. P ~ O = PhP(CH$_2$CH$_2$OCH$_3$)(CH$_2$CH$_2$CH$_2$SiO$_{3/2}$).

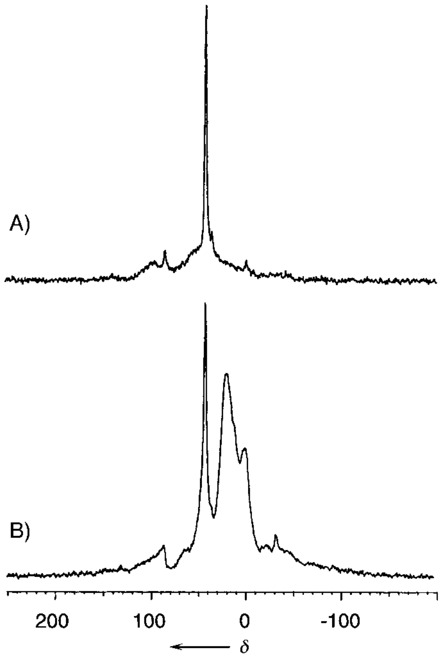
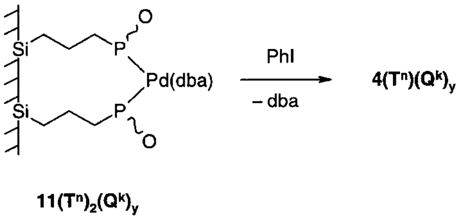


Figure 11. $^{31}$P CP/MAS NMR spectra of the interphases **7(T$^n$)$_3$**/MeOH (A) and **7(T$^n$)$_3$** + **10(T$^n$)$_3$**/MeOH (B).

Even an oxidative addition of iodobenzene to a palladium(0) complex is possible in an interphase. If a suspension of the palladium(0) complex **11(T$^n$)$_2$(Q$^k$)$_4$** in toluene is treated with PhI the arylpalladium(II) complex **4(T$^n$)$_2$(Q$^k$)$_4$** is generated in quantitative yields (Scheme 11),[119] as can be concluded from the $^{13}$C CP/MAS NMR spectra.



Scheme 11. Example for an oxidative addition to a palladium(0) complex in the interphase. dba = dibenzylideneacetone.

## 7.2. Catalysis in Interphases

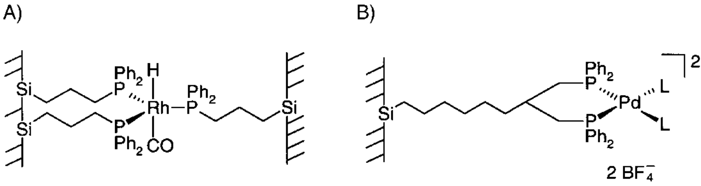
Having demonstrated that organometallic model reactions are performable in interphases, in the following chapter we transfer the concept of interphases to catalysis.

### 7.2.1. Hydrogenation

In several studies on the hydrogenation of *n*-butanal[98a] and 2-butenal,[105, 141] ruthenium(II) hybrid complexes proved to be efficient catalysts. A more detailed investigation on the hydrogenation of tolan under mild conditions with the rhodium(I) complex [ClRh(P ~ O)(P$\frown$O)] **[1(T$^n$)$_2$(D$^i$-C$_6$-D$^i$)$_y$]** ($y = 2$, 8; see Section 7.1) bound to an excellently swellable polysiloxane copolymer resulted in high selectivities toward *cis*-stilbene.[44] The catalytic behavior is highly dependent on the polarity of the applied solvent: A significant increase in the reaction rate with increasing polarity is observed, whereas selectivities achieved an optimum for medium polarities. The influence of the hydrogen pressure and of the temperature on the conversion was found to be much less pronounced than the solvent effect. Therefore, the diffusion of the rather rigid and bulky tolan molecules across the interphase to the reactive centers is considered to be the rate-determining step. This assumption is supported by the fact that the turnover frequency increases at higher substrate concentration as well as by a more flexible polysiloxane framework. Despite the hampering diffusion effect, the polysiloxane-bound rhodium complex **1(T$^n$)$_2$(D$^i$-C$_6$-D$^i$)$_y$** features a higher catalytic activity than its monomeric precursor **1(T$^0$)$_2$** under homogeneous conditions. This surprising observation is explained by the generation of catalytically less active dimeric rhodium species in solution under hydrogen pressure.[142] In an interphase, however, this dimerization process is prevented or at least impeded, as the monomeric rhodium(I) complex centers are spatially isolated in the stationary phase **[1(T$^n$)$_2$(D$^i$-C$_6$-D$^i$)$_y$]**.

### 7.2.2. Hydroformylation

The rhodium complex **12(T$^n$)$_3$(T$^n$-C$_6$-T$^n$)$_y$** (Figure 12 A) polycondensed with the bifunctional cocondensation agent **T$^0$-C$_6$-T$^0$** (Table 1, entry 10) catalyzes the hydroformylation of 1-hexene in the presence of a wide variety of solvents from toluene to water.[101b] As for the hydrogenation of tolan



**12(T$^n$)$_3$(T$^n$-C$_6$-T$^n$)$_y$**

**13(T$^n$)**

**13(T$^n$)(D$^i$-C$_6$-D$^i$)$_y$**

Figure 12. Examples of transition metal complexes active in hydroformylation (A) and copolymerization (B) in the interphase.

(Section 7.2.1) the selectivity of the catalyst is best for solvents of medium polarity (acetone and ethanol), while the conversion achieved its maximum for the more polar methanol.

Addition of excess **T**-silyl-functionalized phosphane $(MeO)_3Si(CH_2)_zPPh_2$ (**T$^0$**; $z = 3, 6$) to the monomeric complex $[HRhCO\{PPh_2(CH_2)_zSi(OMe)_3\}_3]$ (**12(T$^0$)$_3$**) prior to the sol–gel process affords a catalyst with considerably enhanced selectivity: The amount of total aldehyde rises from 85 to 93%, and the *n*:*iso* ratio is improved from 6:1 to 14:1. A stationary phase provided with a hexamethylene spacer instead of a trimethylene spacer between the polymer and the phosphorus donor atom is less selective in the hydroformylation of 1-hexene. However, this material accomplishes higher turnover frequencies and selectivities in the oxo reaction of the higher alkenes 1-decene and 1-tetradecene.

The observation that the highest selectivities are obtained for solvents of medium polarity is rationalized by the fact that these solvents give rise to optimal swelling of the stationary phase. In these interphases the state of the reactive centers is similar to that in solution. The local environment around the catalytically active sites is more uniform in such systems, because the reactive centers are rather affected by the ligand sphere than by the polymer matrix.

Provided that the substrate is not a solid under the existing reaction conditions, the employment of a solvent can be avoided. In such cases the mobile phase is formed only by the gaseous or liquid substrate and its reaction products. If 1-hexene as the mobile phase is subjected to hydroformylation with the stationary phase **12(T$^n$)$_3$(T$^n$-C$_6$-T$^n$)$_y$**, higher turnover frequencies resulted compared to the employment of an additional solvent.[101b] This outcome is traced back to the higher substrate concentration around the reactive centers, while the decrease of selectivities is attributable to the poor swelling abilities of the polysiloxane matrix in an olefin environment.

The possibility that the catalytically active species in the described hydrogenation and hydroformylation is a dissolved rhodium complex generated by leaching was ruled out experimentally: The mobile phases did not show any further reaction under identical conditions after being separated from the stationary phase.

### *7.2.3. Copolymerization*

A recent achievement in transition metal catalysis is the alternating copolymerization of ethene and carbon monoxide,[143] which was developed on an industrial scale at SHELL. It was demonstrated that such an ethene/carbon monoxide copolymerization is also possible in the interphase if the mentioned palladium(II) complexes were bound to a polysiloxane matrix. For this the monomeric complex **13(T$^0$)** was polycondensed with and without the cocondensation agent **D$^0$-C$_6$-D$^0$** to give the stationary phases **13(T$^n$)(D$^i$-C$_6$-D$^i$)$_y$** and **13(T$^n$)** (Figure 12B). The resulting hybrid palladium catalysts showed a polyketone productivity comparable with catalysis in a homogeneous phase. High molecular weights of the resulting polyketones in the range of $6 \times 10^5\,g\,mol^{-1}$ were obtained. A further enhancement of the catalytic activity is achieved by rising the temperature from 25 to 50 °C.[112]

## 8. Summary and Outlook

The present article emphasizes that chemistry in interphases offers a novel and valuable approach to combine the advantages of homogeneous and heterogeneous catalysis. Comprehensive spectroscopic studies on the structures of stationary phases and investigations of their reactive behavior resulted in an optimization of their catalytic properties. Thus major drawbacks of conventional supported catalyst complexes like leaching, poor selectivity, and restricted accessibility of the reactive centers can be overcome. Detailed insights into the dynamics of interphases are also stimulating for current research in organic chemistry such as solid-phase syntheses and chromatography. These and other examples illustrate that chemistry in interphases is not restricted to organometallic chemistry, but represents a growing field of interdisciplinary research that connects other areas like organic, inorganic, solid-state, physical, and technical chemistry, spectroscopy, and physics.

To further optimize the accessibility of the reactive centers for an improved catalytic activity the swelling abilities of stationary phases have to be ameliorated by the variation of the polysiloxane matrix. A valuable possibility to meet this requirement is the introduction of adequate cocondensation agents. A great variety of these organo-functionalized materials is already known from other applications of sol–gel chemistry.[91, 95] The introduction of geometrically defined building blocks—for example adamantane, phenylene groups, or fused aromatic systems—offers a way to tune selectivities. It is anticipated that they allow one to adjust the size of the cavities within the polymer to select molecules of different size and shape on their way to the reactive centers. In contrast to crystalline materials like zeolites, such noncrystalline species should preserve their advantageous flexibility.

An alternative to gain control of diffusion problems of starting materials and products is the adaption of the polarity of the matrix to the requisitions of the respective catalytic reaction. To achieve a higher polarity of the polymer with maintenance of a sufficient flexibility, hydrocarbon-based cocondensation agents containing different polar groups (e.g. ethers and amines) can be introduced into the polymer. Furthermore, the polarity and swelling behavior of the support is modulatable by the incorporation of oxide network building elements other than silicon (e.g. boron, aluminum, yttrium, or titanium). However, the choice of such heteroatoms is restricted to elements with stable oxidation states insensitive to redox processes.

The generation of stationary phases with an excellent swelling capacity enables the performance of ambitious catalytic processes that need a high uniformity of the reactive centers, in particular asymmetric hydrogenation and the selective hydrogenation of polyunsaturated substrates. Moreover, the application of interphases in the carbon monoxide/alkene copolymerization will also be extended to terpolymerization, an important industrial process.

A major goal in the future will be detailed knowledge of all the interactions present in the interphase for the design of new stationary phases with a variety of catalytic properties. Up to now solid-state NMR spectroscopy has been the dominant tool for structure elucidation and dynamic studies of the materials. There is still a wealth of encouraging pulse experiments available which have not yet been applied, but which should yield information, for example, about interatomic distances (*r*otational *e*cho *do*uble *r*esonance, REDOR)[144] and segmental mobilities (dipolar filter).[139, 145] An important method for the investigation of amorphous systems is X-ray absorption spectroscopy (EXAFS). The structure of some metal complexes have already been successfully determined by this method. Since EXAFS is independent of the aggregation state, an extension to the interphase should be possible. Therefore, EXAFS is especially promising for studying reaction mechanisms of catalytic processes in interphases. A further development in this direction is XANES.[123] There is a number of other important spectroscopic techniques based, for example, on photo emission and light and electron scattering[146] which still have to be looked at for structure elucidation in stationary and interphases.

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