

# Improved rhodium hydrogenation catalysts immobilized on silica\*

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Wilkinson-type rhodium catalysts with various mono and bidentate phosphine ligands have been synthesized starting from  $[(\text{COD})\text{RhCl}]_2$  and  $(\text{COD})\text{RhCl}(\text{PPh}_3)$  as the precursors. Those ligands containing an ethoxysilane group could function as linkers for immobilizing the rhodium complexes on silica and alumina. All polycrystalline and amorphous materials have been investigated by solid-state NMR spectroscopy. The catalytic activity of the complexes, both in homogeneous phase and immobilized, has been determined using the hydrogenation of 1-dodecene, 2-cyclohexen-1-one, and 4-bromostyrene. The homogeneous and immobilized rhodium catalysts with monodentate, as well as dppe- and dppp-type phosphine linkers all showed similar activity. For the immobilized catalysts larger average pore sizes of the support (100 Å) led to faster reactions as compared with smaller pores (e.g. 40 Å). The reaction times in single batchwise runs could be reduced substantially by diluting the immobilized catalysts on the support surfaces. This measure also prolonged the lifetime of the catalysts when being recycled. Their recyclability is further improved by the chelate linkers, which prevent leaching of the metal moiety. As another reason for catalyst deactivation during recycling the oxidation of the phosphine linkers has been detected by solid-state NMR.

**KEY WORDS:** alkene reduction; catalytic hydrogenation; immobilized catalysts; P ligands; rhodium; silica; solid-state NMR;  $^{31}\text{P}$ ; silica supports.

## 1. Introduction

Finding the ideal catalyst [1] is one of the most intriguing challenges in chemistry today. Interestingly, most often the strategy of empirical trial and error is applied still. This trial-and-error-process can be accelerated e.g. with combinatorial or high-throughput approaches [2] or syntheses of multiple ligand derivatives. Additionally, one can study the basic principles underlying catalysis, or improve the analytical tools. In this contribution, we will demonstrate that after analyzing the problems of a seemingly well-known catalyst system, substantial improvements in its catalytic performance and lifetime can be achieved by simple means.

The catalyst system studied here is composed of a homogeneous catalyst that is bound to oxidic supports via bifunctional phosphine ligands, as e.g.  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ . The phosphine moiety is supposed to coordinate the metal fragment, while the ethoxysilane functionality binds to the support. This way of immobilizing or anchoring homogeneous catalysts [3] is of growing interest, because in principle it allows an easy separation of the catalyst from the reaction mixture as well as its recycling [3], while the catalyst can still be “tailored”. Thus, we, like others, have pursued this idea by immobilizing homogeneous nickel and rhodium catalysts on inorganic oxidic supports via bifunctional phosphine linkers [4–7]. As in solid-phase synthesis [8], the main disadvantage of immobilized catalysts has

always been leaching, the uncontrolled detachment of the metal fragment from the support, with or without the linker. Step by step we could identify and eliminate the main sources of leaching: Most importantly, one has to prevent the quarternization of the phosphine by the combined action of the silica surface and the ethoxysilane groups during the immobilization step [9]. The ethylation of the phosphine moiety, leading to phosphonium salts that use up space on the surface but cannot bind metal complexes any more, is a severe and widespread problem for a broad range of phosphine linkers. For example, even bisphosphinoamine ligands are vulnerable to this side-reaction [9c]. In this case, even a change of the support was necessary, while usually mild immobilization conditions suffice to prevent the usual bifunctional phosphines from being quarternized [9a]. Next, it is important to recognize that e.g. two monodentate phosphines, even after being anchored on the support, do not necessarily bind the metal moiety in sort of a chelating manner by having both linkers attached to the support [10]. More realistic is the formation of a double layer with only one linker being bound to the surface [10]. The stronger coordination and less leaching is usually found with chelating phosphines of the dppe or dppp types [4b,5,7], a variety of which we have synthesized recently [9c,11]. Leaching can also happen at the anchoring point between the silane moiety and the support. Fortunately, the most popular support silica [12] forms, under moderate conditions in organic solvents, irreversibly a strong Si–O–Si connection [13]. Only acidic or basic reaction media or unfavorable supports such as titania or magnesia lead to linker leaching at this point [13]. However, even the reaction of ethoxysilanes with the

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well-known silica surface [12] deserves a closer look: If the solvent chosen for the immobilization is too polar, as it is the case for example with ether, glycol, diglyme, or ethanol, these are adsorbed strongly on the surface, and access by the ethoxysilane is blocked, preventing its binding [14]. If the silane moiety is merely adsorbed, however, the linker will be washed off the support, together with the catalyst in a catalytic reaction [13]. For analytical purposes it is also important to know that ethoxysilane groups preferentially add to surface siloxane groups [15]. This means that ethoxygroups are bound to the surface in the vicinity of the linker [15]. Furthermore, there is always a number of silane-bound residual ethoxy groups, which renders elemental analysis for the determination of the surface coverage useless, if it is not combined with  $^{29}\text{Si}$  solid-state NMR measurements (see below). The often postulated hydrolysis–condensation reaction sequence only takes place when the silica is not dried rigorously and therefore carries an abundance of silanol groups and adsorbed water on the surface [12d,15]. With respect to the subsequent catalysis, however, we found that rigorously dried silica is suited best as a support [7,13].

Most of the results described above were obtained with classical solid-state NMR techniques [16], and some with suspension NMR spectroscopy of a stationary sample [13,17]. The latter method is especially useful for detecting merely adsorbed in contrast to covalently bound species, and more generally, for studying mobilities of linkers and catalysts under realistic conditions at the solid–solvent interface. Solid-state NMR with fast rotation, magic angle spinning (MAS) [16], gives better signal resolution than suspension NMR of static samples. Cross-polarization (CP) [16], a magnetization transfer usually from protons to the hetero nuclei ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$  etc.), helps to reduce the relaxation times and enhance the signal intensities. However, CP often interferes with fast MAS, which is why we designed a strategy using different CP standard samples to improve the signal to noise ratio (S/N) of the spectra [18]. This is especially crucial for dilute species, that is molecules that are only attached to the surface of a bulk material, being responsible for about 2% of the matter in a rotor.

In this contribution, we will demonstrate that combining our experience in surface chemistry with the powerful analytical method of multinuclear solid-state NMR, the efficiency, stability, and lifetimes of immobilized catalysts can be improved substantially. We use Wilkinson-type rhodium catalysts for olefin hydrogenation that are immobilized via chelating phosphine linkers [4b,7,11], because olefin hydrogenation is one of the best developed and most important areas of catalysis [19].

## 2. Experimental section

All catalytic reactions were performed under inert gas using Schlenk techniques, prior to admitting hydrogen.

The solvents were carefully dried according to the usual procedures and stored under nitrogen. All catalysts were immobilized according to the standard procedure given in ref. [6]. The silica was purchased from Merck (Merck silica40 to 100), its characteristics and pretreatment are described in the text. The catalytic runs were followed by GC. All the spectra presented here were recorded on a digital Bruker Avance 400 NMR spectrometer equipped with an ultrashield widebore magnet, and a 4 mm multinuclear double-bearing MAS probehead. The polycrystalline molecular compounds were densely packed, modified silicas were filled loosely into the  $\text{ZrO}_2$  rotors in a glove-box. CP and MAS with rotational speeds between 0 and 15 kHz were applied, as described in the text. The  $^{31}\text{P}$  CP/MAS NMR spectra were referenced with respect to 85%  $\text{H}_3\text{PO}_4(\text{aq})$  by setting the  $^{31}\text{P}$  NMR peak of solid  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  to +0.81 ppm. The  $^{13}\text{C}$  CP/MAS spectra were referenced to external adamantane [20]. The Hartmann-Hahn matches and contact times were set as described previously [18]. For the exponential multiplication a line-broadening factor of 20–50 Hz was applied for spectra of immobilized species, no modification of the FID was needed for the polycrystalline compounds. More details of the solid-state NMR measurements are given in ref. [18].

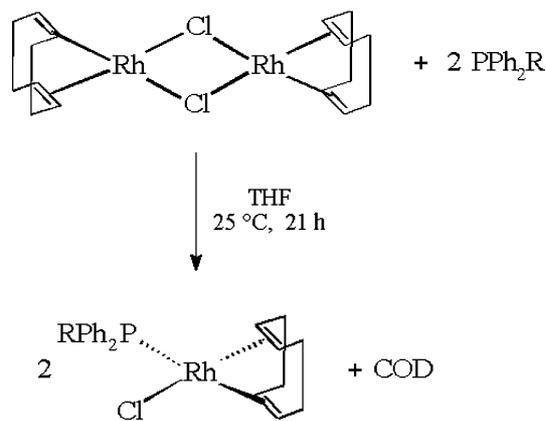
## 3. Results and discussion

### 3.1. Synthesis of rhodium catalysts and their characterization

As demonstrated previously [6,7], and used here for obtaining the Wilkinson-analog  $\text{ClRh}[\text{Ph}_2\text{P}(\text{p-C}_6\text{H}_4)\text{SiMe}_2\text{OEt}]_3$  (**1**), the dimer  $[(\text{COD})\text{RhCl}]_2$  is a good starting material for synthesizing rhodium complexes with modified phosphine ligands in a clean and stoichiometric manner. Hereby, the cleavage of the dimer and the following exchange of the COD ligand can be done in a stepwise manner. As shown in scheme 1 the complexes **2–4** with modified monodentate phosphine ligands could be synthesized and fully characterized.

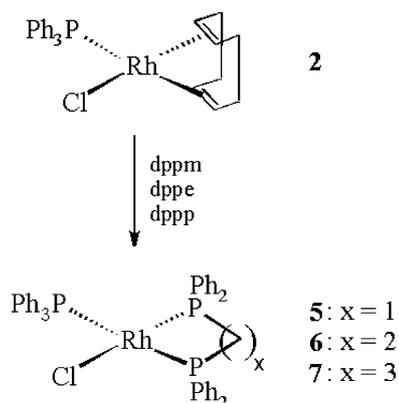
The rhodium compound **2** in turn served as the starting material for the preparation of complexes with chelate ligands, such as **5–7** containing dppm, dppe, and dppp. Complexes **5–7** are useful as standard materials for the optimization of the Hartmann–Hahn condition for solid-state NMR measurements of transition metal complexes [18]. They serve as rudimentary chelate complexes without ethoxysilyl groups, and they also present the basis for comparing the catalytic activity of chelate complexes containing modified phosphines with different bite angles in homogeneous phase (scheme 2).

When unsymmetric modified ligands are used instead of symmetric ones, such as the linkers described previously [4b,11], two inseparable isomers of the square-planar complexes are obtained in statistical ratios (scheme 3).



- 2** : R = Ph  
**3** : R =  $-(\text{CH}_2)_3\text{Si}(\text{OEt})_3$   
**4** : R =  $-(\text{p-C}_6\text{H}_4)\text{SiMe}_2\text{OEt}$

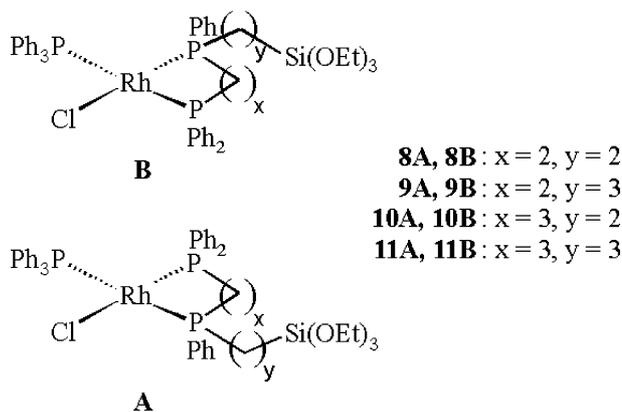
Scheme 1. Synthesis of rhodium catalysts with monodentate phosphine ligands.



Scheme 2. Synthesis of rhodium catalysts with chelating ligands.

The diarylalkylphosphine moiety of the ligand can occupy the position *trans* to the Cl substituent (series **A**), or *cis* to Cl (series **B**). This has to be taken into account when analyzing the NMR spectra of the mixtures. Figure 1 for example shows the spin systems of the  $^{31}\text{P}$  signals of a typical mixture of isomers for **9A** and **9B**. A detailed discussion of the NMR properties of such rhodium complexes will be given elsewhere soon [21]. As the small halfwidths of the signals show, there is obviously no phosphine exchange happening at ambient temperature, as it is found for triaryl phosphines in Wilkinson's catalyst or ethoxysilyl-modified triphenylphosphine derivatives thereof.

As it will be shown below, the rhodium complexes of series **A** display the same catalytic activity as those of series **B**. Therefore, for clarity and brevity in the following narrative, we will only display and discuss the representatives of series **A**.



Scheme 3. Two possible isomers of rhodium complexes with unsymmetric chelate ligands.

### 3.2. Immobilization of rhodium catalysts

The rhodium catalysts **8–11** (scheme 4) have been synthesized with unsymmetric chelating ligands [4b,11] as shown in Scheme 2, and fully characterized. They can be immobilized as described previously [4a,6,14,15], and the heterogenized catalysts **8i–11i** are obtained. If not stated otherwise, silica with 40 Å average pore diameter, 750 m<sup>2</sup>/g specific surface area, and a particle size of 0.063–0.2 mm, and dried at 600 °C in vacuo for 24 h prior to use has been applied as the support material under N<sub>2</sub>. According to previous results, other oxidic supports such as alumina are possible, but they might lead to leaching [13]. The rigorous drying of the silica prior to use prevents any crosslinking of the ethoxysilane moieties during immobilization. Furthermore, moisture sensitive metal complexes can be immobilized in the absence of water on the support surface. The pore diameter is close to optimal, as the results below show. The high value for the surface area is favorable, because it allows the dilution of metal complexes on the surface, while enough loading is still guaranteed for the intrinsically insensitive solid-state NMR spectroscopy. The large size of the particles makes them heavy enough to allow the convenient handling of the material in a stream of inert gas (in contrast to light and fluffy aerosol particles), and clogging of the particles during catalysis is prevented this way. After the catalytic runs and stirring, the large particles of the support material settle down within 5–10 min (in contrast to the aerosol particles, which stay suspended in solution, and can only be filtered off with difficulties).

In the same way as described above, the complexes **1**, **3**, and **4** can be immobilized, resulting in the surface-bound species **1i**, **3i**, and **4i**. All the immobilized catalysts, even the more sensitive COD complexes, can be studied by solid-state NMR spectroscopy [18]. Figure 2, for example, shows the  $^{31}\text{P}$  CP/MAS spectrum of immobilized **4i** (bottom trace). No oxidic or phosphonium-type byproducts [9] or uncomplexed phosphines [5] are visible in the spectrum. The latter would

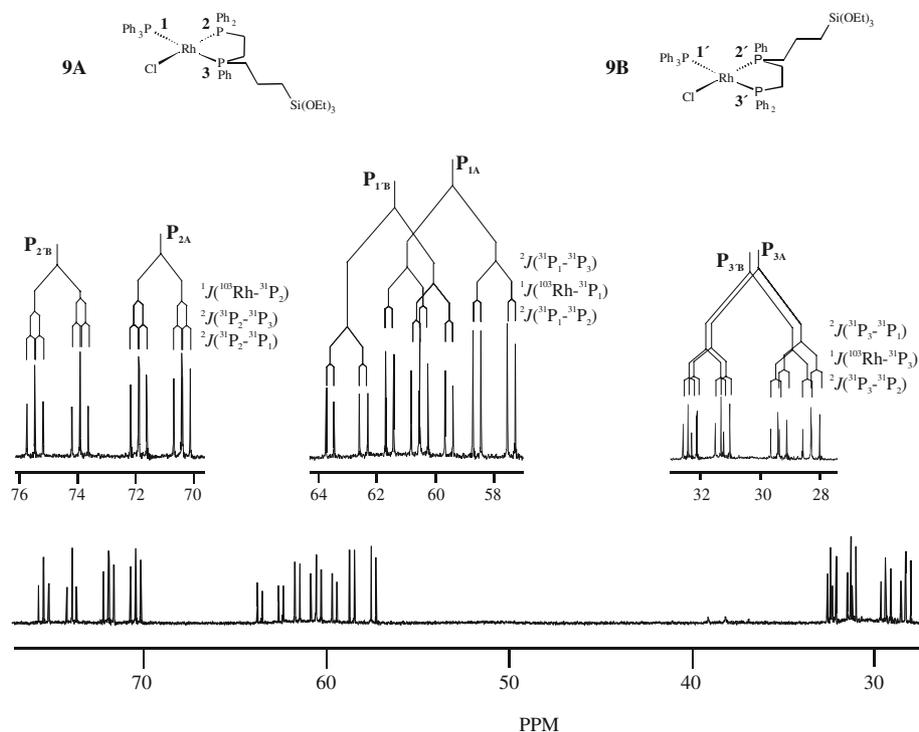
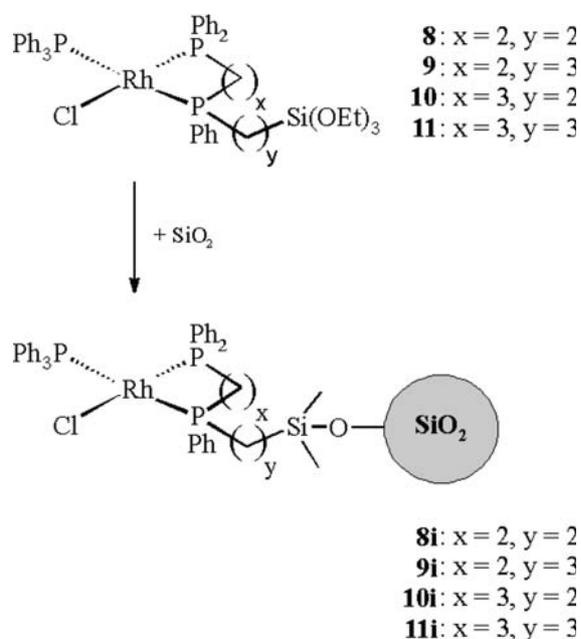


Figure 1. 121.5 MHz  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **9A** and **9B**. For a thorough analysis and detailed discussion see ref. [21].

be expected if the rhodium complex lost COD and was thus destroyed by the silica, in analogy to the findings with nickel catalysts [5].

The polycrystalline complex **2** can serve for comparison (top trace of figure 2) when checking the success of the immobilization. The isotropic lines of **2** and **4i** have approximately the same chemical shift ( $\delta(^{31}\text{P}) = 30.8$  for

**2** in  $\text{THF-d}_8$  and 30.4 for **4** in  $\text{CD}_2\text{Cl}_2$ ), because the electronic environment of the phosphorus nuclei is very similar. Due to their more inhomogeneous surroundings on the silica surface, however, the lines of **4i** are broader than those of the analogous polycrystalline complex  $\text{Cl}(\text{PPh}_3)\text{Rh}(\text{COD})$  (**2**). The resolution in the spectrum of **2** is even good enough to show the scalar coupling



Scheme 4. Immobilization of rhodium catalysts with chelate phosphine linkers.

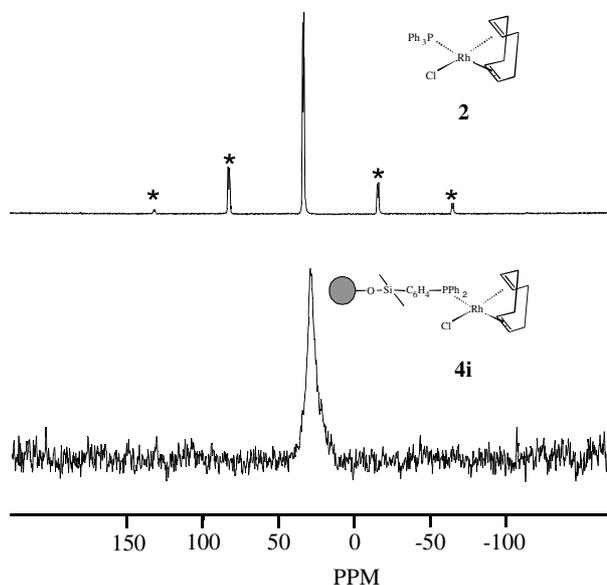


Figure 2. 161.9 MHz  $^{31}\text{P}$  CP/MAS NMR spectra of polycrystalline **2** at a rotational frequency  $\nu_{\text{rot}} = 8$  kHz (top spectrum), and immobilized complex **4i** (bottom spectrum,  $\nu_{\text{rot}} = 13$  kHz). Asterisks denote spinning sidebands. For details of measurement see ref. [18].

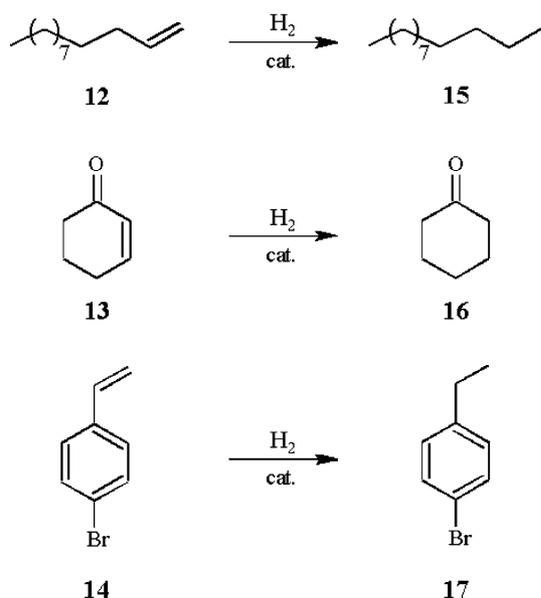
$^1J(^{103}\text{Rh}-^{31}\text{P})$  with 158.5 Hz, in good agreement with the value of 151.5 Hz found for **2** in solution (THF- $d_8$ ). A splitting of the isotropic line due to magnetically different phosphorus nuclei in the unit cell of **2** is less likely [22], because the doublet due to the scalar coupling has to appear in the spectrum, given the superb resolution. Furthermore, each magnetically different signal would have its own chemical shift anisotropy (CSA) [23], and therewith different signal intensities in the rotational sidebands, which is not the case here.

Interestingly, as observed many times before [e.g. 6,7], even taking into account the increased rotational speed for **4i**, leading to spinning sidebands of lower intensity, the CSA [23] is decreased substantially on going from polycrystalline to the corresponding immobilized species. This will be the subject of further investigation of the solid-state NMR of covalently bound and adsorbed surface species.

### 3.3. Hydrogenation of olefins

For the easy comparison of the hydrogenation characteristics with our previous results [6,7], and with those of other groups [e.g. 24], we used the standard set of substrates for the catalytic runs, 1-dodecene (**12**), 2-cyclohexen-1-one (**13**), and 4-bromostyrene (**14**). In the work presented here, all the substrates **12–14** were selectively and, under the right conditions, quantitatively hydrogenated by all homogeneous and immobilized catalysts, and dodecane (**15**), cyclohexanone (**16**), and 4-bromoethylbenzene (**17**) were the only products (scheme 5).

The rate of conversion was determined by NMR and GC analysis. For the proper comparison with earlier results [6,7] we used the glass apparatus described previously [6] for all the hydrogenations, as well as



Scheme 5. Hydrogenation of representative olefins.

standardized reaction conditions. If not stated otherwise, the solvent was toluene, the reaction temperature 25 °C, the  $\text{H}_2$  pressure 1.1 bar, and the catalyst to substrate ratio 1:100. All hydrogenation curves presented here were reproduced at least twice, with minimal changes being found for the corresponding conversions.

Our first experiment in this series addressed the question whether the ethoxysilane groups of the modified ligands would change the catalytic activity of the rhodium complexes. Therefore, we studied **1** in solution under the same conditions as  $\text{ClRh}[\text{PPh}_3]_3$  previously [6]. With the substrates **12** and **13**, the TOF (turnover frequencies) were practically identical (figure 3). Interestingly, however, for bromostyrene (**14**) the time necessary for quantitative conversion was reduced to ca. 50 h, which is about half the reaction time needed with Wilkinson's catalyst [6]. As figure 3 shows, this is partly due to the absence of the induction period, but also due to a higher TOF after the start of the reaction. So, the modification of the ligands with ethoxysilyl groups might even speed up the homogeneous hydrogenation by reducing induction periods.

The silica-immobilized version of the catalyst, **1i**, cuts down the reaction time for **14** again to one half, as figure 4 demonstrates. Even the conversions of dodecene (**12**) and cyclohexenone (**13**) are quicker with **1i** as compared to **1**. So, this is one more case in which immobilization of a homogeneous catalyst leads to a more active species, while the selectivity of the reaction is not harmed.

As we have shown previously [6,7], rhodium complexes with monodentate alkyldiarylphosphine ligands can be as active and selective as those with triarylphosphines. Since monodentate linkers cannot bind the metal fragments as firmly as chelating linkers [5], the next question was whether chelating alkyldiarylphosphines would diminish the activity of their rhodium catalysts. As shown for  $\text{Cl}(\text{PPh}_3)\text{Rh}(\text{dppe})$  (**6**) and  $\text{Cl}(\text{PPh}_3)\text{Rh}(\text{dppp})$  (**7**) in figures 5 and 6, such chelating phosphines lead to

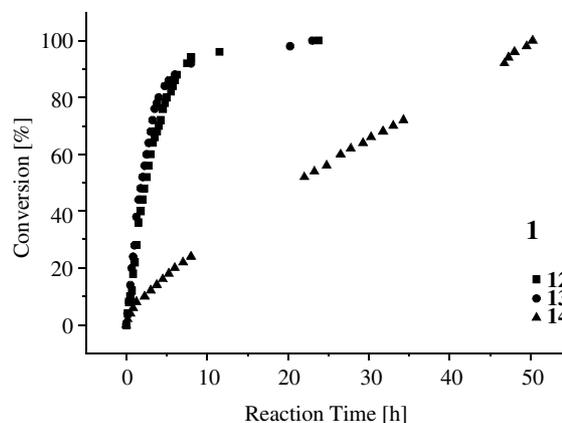


Figure 3. Hydrogenation of dodecene (**12**), cyclohexenone (**13**), and bromostyrene (**14**) with catalyst **1** in toluene at 25 °C with a catalyst to substrate ratio of 1:100.

practically unchanged activity for **12** as the substrate. The hydrogenation is, however, faster for **13** and **14**, when slightly higher temperatures of 45 and 60 °C are chosen. Regarding the bite angle, dppe is more favorable than dppp.

With unsymmetric chelate ligands, two isomers of Wilkinson-type rhodium complexes (series **A** and **B**, see above) are always present. So, the next question was, whether these isomers would display different catalytic activity, in which case using a mixture of both would not give clear results in future experiments. Therefore, two mixtures of **9A** and **9B** with the ratios 2.8:1.0 and 1.6:1.0 have been investigated with **12** and **13** as the substrates. If one of the isomers would be more active, then the mixtures should display different catalytic activity. Fortunately, as figure 7 shows, both mixtures give practically identical curves for the hydrogenation of dodecene and cyclohexenone, respectively. Therefore, we conclude that the complexes of series **A** and their isomers of series **B** have similar catalytic activity, and thus the composition of the mixtures should not have a crucial influence on the results of our investigations.

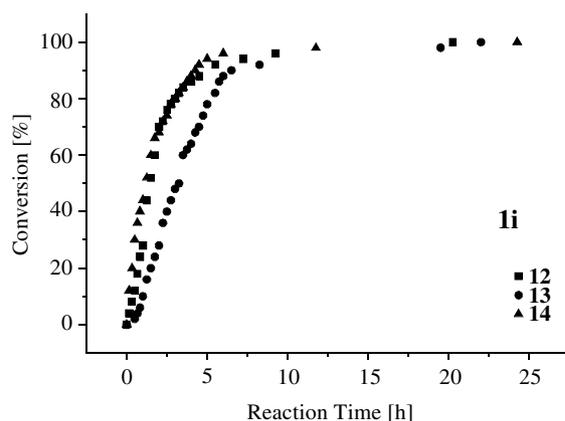


Figure 4. Hydrogenation of dodecene (**12**), cyclohexenone (**13**), and bromostyrene (**14**) with catalyst **1i** in toluene at 25 °C with a catalyst to substrate ratio of 1:100.

Comparing the catalytic activity of complexes **8–11** in the homogeneous hydrogenation of dodecene (**12**) in toluene solution, the trend seen for **6** and **7** is surprisingly not observed (figure 8). In contrast to expectation, the bite angle obviously does not determine the catalytic activity, because catalyst **9** with the dppe-type ligand performs equally well as the catalysts **10** and **11** with dppp-type chelating phosphines. Only catalyst **8** needs nearly 100 h for complete conversion of the substrate, while **9–11** are done within 30 h. This result is somewhat surprising, because earlier work showed that hydrogen adds to Wilkinson-type rhodium complexes in *cis* positions, while both phosphine moieties of chelate phosphines stay coordinated to the metal center [6]. On the other hand, it is unlikely that the length of the linker plays a major role, because catalyst **10** with the short ethyl(triethoxysilyl) substituent at phosphorus performs about as well as **11** with the longer propyl(triethoxysilyl) group. Overall, however, a large bite angle in combination with a long spacer moiety, as in **11**, seems to be more favorable than a small bite angle with short spacer, as represented in **8**. This interpretation is also corrob-

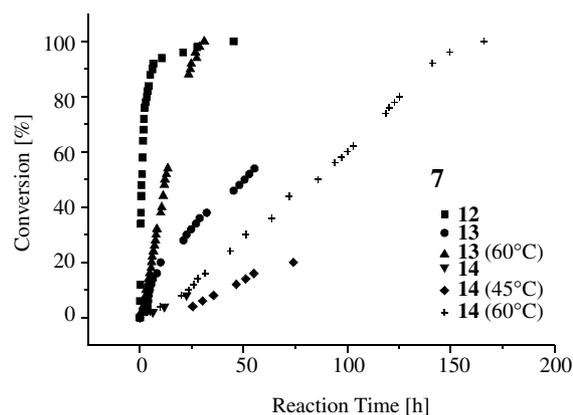


Figure 6. Hydrogenation of **12**, **13**, and **14** with catalyst **7** in toluene at the indicated temperatures.

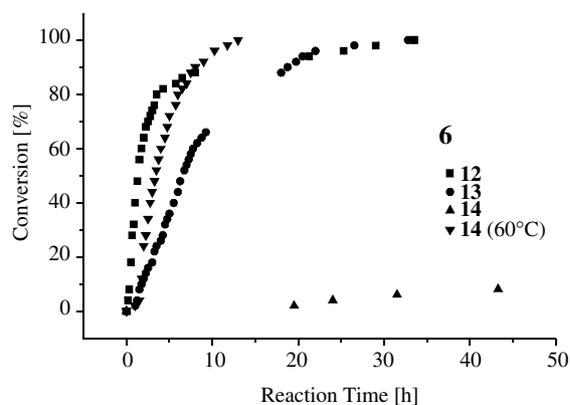


Figure 5. Hydrogenation of **12**, **13**, and **14** with catalyst **6** in toluene at 25 °C (**14** also at 60 °C) with a catalyst to substrate ratio of 1:100.

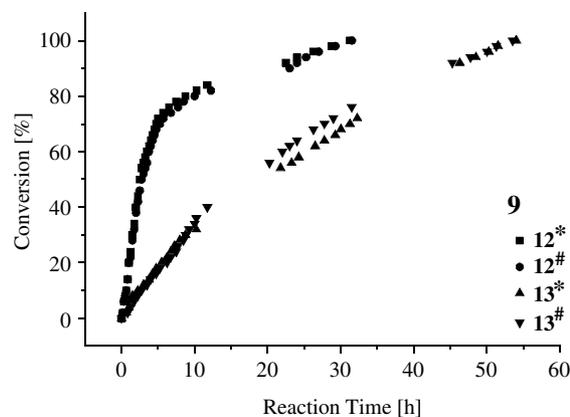


Figure 7. Hydrogenation of **12** and **13** with different mixtures of **9A** and **9B**. \*Ratio **9A:9B** = 2.8:1.0; #Ratio **9A:9B** = 1.6:1.0.

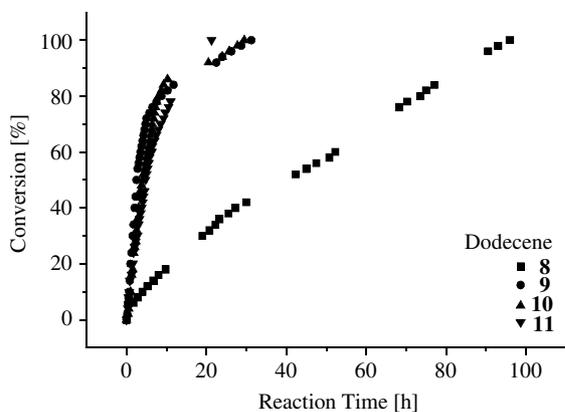


Figure 8. Hydrogenation of dodecene (**12**) with catalysts **8–11** in toluene with a catalyst to substrate ratio of 1:100.

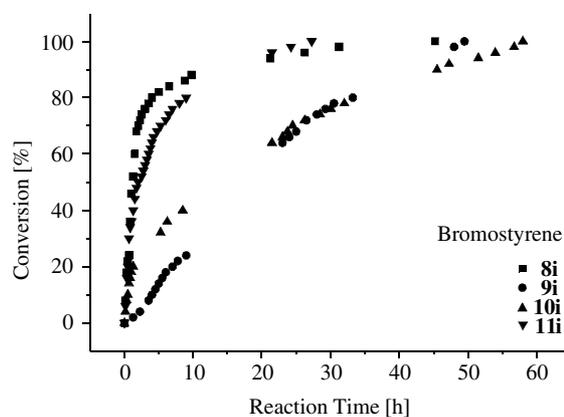


Figure 10. Hydrogenation of bromostyrene (**14**) with catalysts **8i–11i** in toluene at 60 °C with a catalyst to substrate ratio of 1:100.

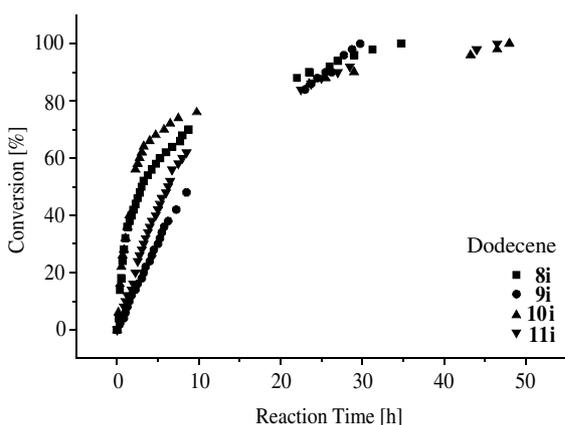


Figure 9. Hydrogenation of dodecene (**12**) with catalysts **8i–11i** in toluene at 25 °C (**8i**: 60 °C) with a catalyst to substrate ratio of 1:100.

orated by earlier results obtained from the homogeneous hydrogenation of **13** and **14** with **8–11** [7].

Next it was tested whether the efficiencies of the immobilized catalysts **8i–11i** were comparable to those of **8–11**. In contrast to earlier results with **13** as the substrate for the hydrogenation [7], with dodecene (**12**) only catalyst **8i** needs the slightly higher reaction temperature of 60 °C (figure 9).

While catalyst **9i** is even as active as **9** in solution with complete conversion of **12** within 30 h, catalysts **10i** and **11i** require longer reaction times of about 50 h. This is probably due to the fact that dodecene must adopt a linear conformation to diffuse into the pores of the support now. Again, as in the case of the homogeneous catalysis, no general statements can be made about the most favorable bite angle or spacer length. It is just the combination of dppe-type chelate and short ethylene spacer moiety in **8** that is again most unfavorable. However, the situation changes if bromostyrene (**14**) is hydrogenated by **8i–11i** (figure 10).

Here, all the catalysts need a temperature of 60 °C, and under these conditions catalyst **8i** is performing best of all. The time needed for quantitative conversion with

**8i** is below 30 h, about the same time that **8** takes in homogeneous catalysis [7]. In contrast to that, up to 60 h are needed by the catalysts **9i–11i**, while **9–11** only needed 20–22 h in homogeneous phase [7].

So, the general result at the moment is that for every substrate there is the optimum catalyst with the most favorable reaction conditions. No general trends regarding bite angle and spacer length are visible irrespective of the substrate. In order to explore the limits of the levelled impact of the bite angle, in future research we will also investigate rhodium complexes with modified dpmm-type ligands.

#### 3.4. Influence of the surface coverage on the catalytic activity

The complex  $\text{ClRh}[\text{PPh}_2(\text{CH}_2)_3\text{Si}(\text{OEt})_3]_3$  (**18**) was synthesized starting from the precursor  $[(\text{COD})\text{RhCl}]_2$ , characterized and immobilized to give **18i** as described previously [6].

Since it is known for rhodium catalysts that dimerization leads to unreactive species [25], we sought to improve our catalysts further by diluting them on the silica surface, and thus keep the reactive metal centers apart from each other—one of the additional options that immobilization offers in contrast to homogeneous catalysis. Indeed, as it can be seen in figure 11 for **18i** on silica with an average pore diameter of 60 Å, and **13** as the substrate, when the surface coverage is decreased stepwise from the maximal coverage  $m$  to half the surface coverage ( $m/2$ ), then to  $m/4$ , and finally to  $m/10$ , TOF in a single run increases substantially. The improvement is greatest on going from  $m$  to  $m/2$  and  $m/4$ , when the time requirement for 100% conversion decreases from 15 h to about 10, and finally 9 h. Diluting **18i** further to  $m/10$ , however, only saves roughly another half hour. Therefore, we conclude that as soon as the active metal centers are far enough apart from each other, a condition reached here at  $m/4$ , no dimerization or agglomeration is possible any more and

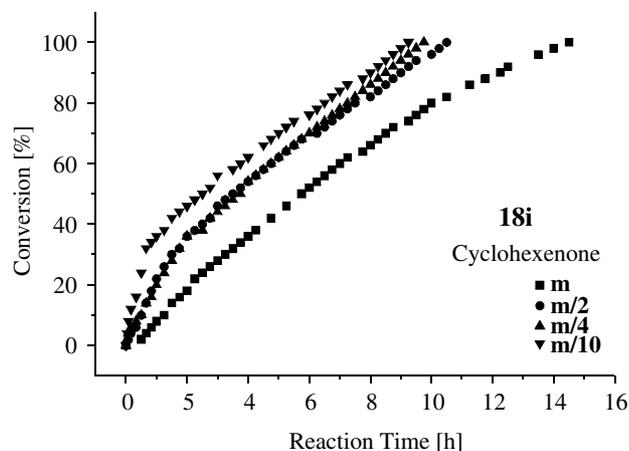


Figure 11. Hydrogenation of cyclohexenone (**13**) in toluene with catalyst **18i** immobilized with the indicated surface coverages ( $m$  denotes maximal surface coverage of 0.05 mmol of **18** on 1 g of  $\text{SiO}_2$ ) on silica with an average pore diameter of 60 Å.

the maximal lifetime of the catalyst with respect to this deactivation mechanism is reached. Further dilution to  $m/10$  is unnecessary and only increases the bulk material of the support, leading to “dead reactor volume” in potential industrial applications. The same observation is made for immobilized nickel catalysts [4b], and all our catalysts with chelating ligands [5–7].

The fact that the change of the surface coverage of the complexes also affects the catalytic activity further corroborates the assumption that during the immobilization step the metal centers are distributed evenly on the surface, and do not settle down in patches. This is also further evidence that with rigorously dried silica, which contains no more adsorbed water and only few isolated Si–OH groups [12d], no crosslinking of the ethoxysilane groups can take place [14,15], and therefore no “clustering” of the metal centers. Cross-checking this result with silica, which was only dried at 25 °C and should therefore be wet enough to allow crosslinking, leads to a loss of catalytic activity [7].

### 3.5. Influence of the average pore size of the support

The advantageous effect of diminished surface coverage is independent of the average pore diameter of the support [7], as can also be seen in figure 12 for the hydrogenation of cyclohexenone (**13**) with **18i** immobilized on silica with an average pore diameter of 100 Å. Again, the positive effect of dilution of **18i** on the surface is most pronounced when going from maximal surface coverage  $m$  to  $m/2$  and to  $m/4$ , while further dilution to  $m/10$  only has a minor effect. But larger pores should allow for better diffusion of bulky substrates to the innermost catalytic centers. Although for the compact cyclohexenone as the substrate the effect is not quite as pronounced than for **12** [7], for example it can be hydrogenated with **18i** ( $m/10$ ) on  $\text{SiO}_2$  (100 Å) in only 7.3 h, while 9.5 h is required for **18i** ( $m/10$ ) on  $\text{SiO}_2$

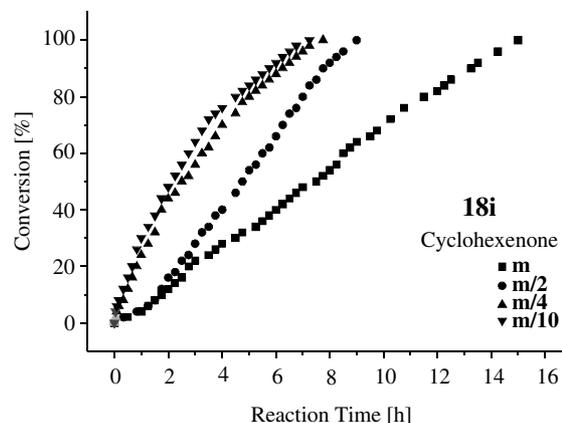


Figure 12. Hydrogenation of cyclohexenone (**13**) in toluene with catalyst **18i** immobilized with the indicated surface coverages ( $m$  denotes maximal surface coverage of 0.05 mmol of **18** on 1 g of  $\text{SiO}_2$ ) on silica with an average pore diameter of 100 Å.

(60 Å) as the support. So, especially for bulky substrates an average pore size of 100 Å is a good compromise between largest possible pores and mechanical stability of the silica. Using material without pores, such as glass beads, has the disadvantage that the specific surface area is very small, and therewith the bulk material as compared to surface-bound catalyst is too much. This is a disadvantage for possible industrial applications (see above), and also out of analytical reasons; the  $^{31}\text{P}$  content is then so low, that no signals can be obtained any more with solid-state NMR. Attempts to solve this problem by using very small particles only leads to the problems described above for aerosol.

### 3.6. Recycling and lifetime of the immobilized catalysts

Although there are noteworthy exceptions (see above), on going from homogeneous to immobilized catalysts, often the times required for quantitative conversion of the substrates increase, because now the substrates have to diffuse into the pores of the solid support. However, this disadvantage is made up for by the possibility of recycling the immobilized catalysts [4b–7].

All the chelating ligands improve the lifetimes of the immobilized catalysts substantially, which was to be expected regarding the results of a parallel project with nickel catalysts [4b,5]. While monodentate phosphine ligands with maximal surface coverage in the case of dodecene as the substrate only allowed the batch-wise recycling of the rhodium hydrogenation catalysts for seven times [6], with the catalysts **8i–11i** even with maximal surface coverage 100% conversion is reached for all substrates in every one of the 13 cycles. Additionally, the dilution on the surface has a beneficial effect also in the case of chelate complexes. This is for example shown with **9i** ( $m/2$ , 4 molecules per 100  $\text{nm}^2$ ) on silica and **12** as the substrate in figure 13 (the gaps correspond to the sleeping phases of C.M.). Therefore, we conclude that our chelating ligands generally, even for very

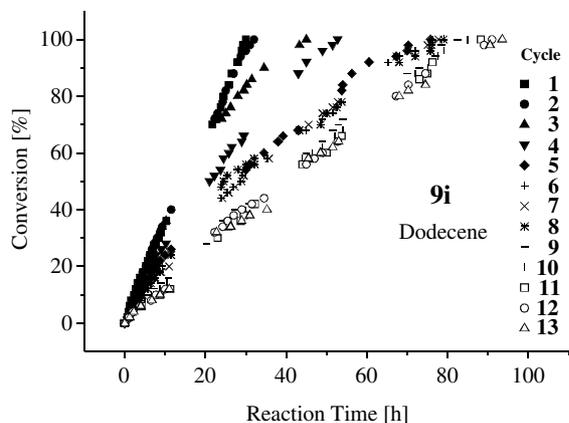


Figure 13. Batch-wise recycling of the catalyst: Hydrogenation of dodecene (**12**) in toluene with catalyst **9i** on silica (4 molecules of **9** per 100 nm<sup>2</sup> of surface) with a catalyst to substrate ratio of 1:100.

different metal moieties [4b,5,7], lead to diminished leaching and thus to improved stabilities and lifetimes of immobilized catalysts.

The next question arising concerns the deactivation mechanism of the Wilkinson-type catalysts. In a parallel project on carbonylnickel catalysts, it could be demonstrated with <sup>31</sup>P solid-state NMR that one main mechanism for loss of activity is the detachment of the metal center from the surface-bound phosphine linkers [5]. This, however, was never observed in the case of the Rh catalysts presented here, which have been studied before and after catalysis with <sup>31</sup>P CP/MAS NMR. Another obvious decomposition mechanism would be the oxidation of the phosphine ligands by traces of air entering the system during the refilling steps. This was found to happen in the case of the nickel system, and the lifetimes of the catalysts could be improved substantially by designing an arrangement for pseudo-continuous catalysis [5].

In the case of the rhodium catalysts **1i**, **8i–11i**, and **18i**, there are signs, which indicate that oxidation, or in general disturbing the system with refilling, might be the problem here, too. For example, in the case of **9i** with **12** as the substrate, which usually loses activity gradually from cycle to cycle (figure 13), there was an experiment, when the activity dropped substantially between the fifth and sixth cycle. Then it stayed on this level for the cycles 7–13. This is especially obvious when looking at the yields of the reaction (figure 14). Obviously, during the recharging of the Schlenk flask for the next run, about one third of the catalyst has been destroyed, but the remaining two thirds continued with hydrogenation. Two lessons can be learned from this: First, catalysis must be done by a measurable amount of metal centers. If only the often proclaimed “magic few atoms of rhodium metal” were responsible for the catalytic activity, traces of oxygen would lead to zero activity after one run. This point has to be clarified in future research with precisely executed poisoning experiments.

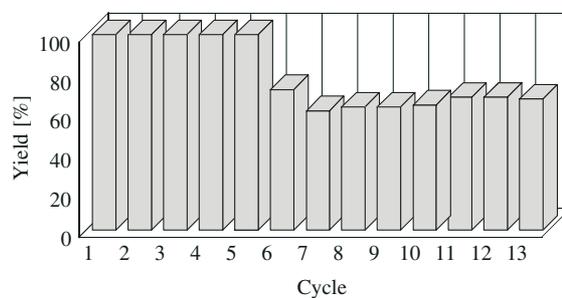


Figure 14. Yields of the batch-wise hydrogenation of dodecene (**12**) with catalyst **9i** in toluene at 25 °C with a catalyst to substrate ratio of 1:100. For details see text.

Nevertheless, this sub-optimal experiment also shows the value of immobilization: In solution organometallic compounds have the tendency to decompose “autocatalytically”, as soon as the process has started. One well-known example for this would be Ni(COD)<sub>2</sub>. Since the linkers are bound covalently to the support, and unlike merely physically adsorbed species [13,15] they cannot migrate on the surface, the dilution of the complexes is persistent. Thus, due to their fixed distance on the surface, the decomposition is not “contagious”, but only affects one metal center at a time.

Another indication that oxidation might be responsible for the stepwise loss of activity comes from solid-state NMR measurements. Figure 15 shows the <sup>31</sup>P solid-state NMR spectra of catalyst **18i** before and after 13 runs of catalytic hydrogenation of **12**. Since the spectra were recorded with CP [16,18] the signals cannot be integrated. So, it is not unusual that the resonance for the one phosphine *trans* to the Cl substituent at

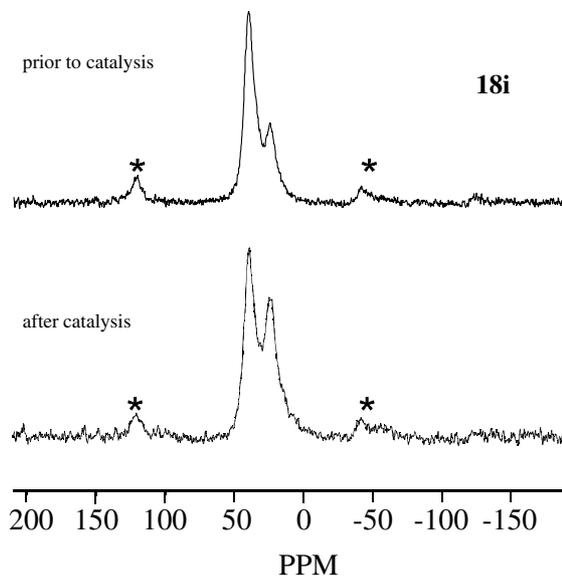


Figure 15. 161.9 MHz <sup>31</sup>P CP/MAS spectrum of **18i** on SiO<sub>2</sub> (40 Å) before (upper trace) and after (bottom spectrum) catalytic hydrogenation of **12**. Asterisks denote spinning sidebands. Signal assignments and discussion see text, for details of the measurement see ref. 18.

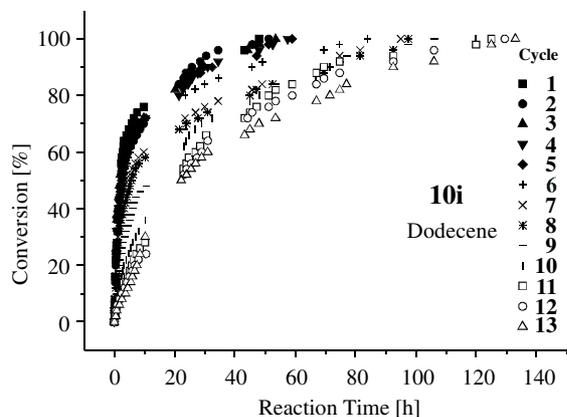


Figure 16. Batch-wise recycling of catalyst **10i**: Hydrogenation of dodecene (**12**) in toluene at 25 °C with a catalyst to substrate ratio of 1:100.

39.3 ppm is more intense than the signal for the two *cis* phosphines at 24.1 ppm (39.9 and 25.6 ppm for **18** in toluene- $d_6$ ). However, using the same measurement parameters, changes of signal intensities are qualitatively significant. While no signal for any dimeric species can be found, the signal at 24.1 ppm has gained intensity after catalysis. Since 25 ppm is the typical chemical shift range for oxidic and phosphonium-type species [9], we assume that some of the phosphine ligands have been oxidized, and show up in the spectrum as an additional signal overlapping with the one of the *cis* phosphines in **18i**. As in the case of nickel catalysts with phosphine linkers, this problem will best be solved by implementing a system for continuous catalysis in a closed apparatus in the future. The first preliminary experiments show that TONs of at least 8000 can be reached, if a catalyst to substrate ratio of 1:8000 is applied in one single run.

The spacer length of the phosphine ligands does not have a striking influence on the catalytic activity in homogeneous phase, or in one single run with immobilized catalysts, as the above results show. Nevertheless, the spacer length, and therewith the distance of the metal center from the potentially reactive and harmful silica surface, could play a role in repeated runs. The first results indicate that indeed the linkers with a propyl spacer seem to protect the metal center somewhat better than those with an ethyl bridge. As shown in figures 16 and 17, while **11i** has achieved quantitative hydrogenation of **12** within 86 h in the 13th run, **10i** needs 133 h for this task.

In conclusion, we could demonstrate that even simple measures can improve the efficiency, stability, and lifetime of immobilized catalysts. These results are of a general nature with respect to different catalytic reactions, metal centers, substrates, linkers, supports, surface coverages and pore diameters. They clearly further extend the utility of immobilized catalysts derived from the covalent linkage of homogeneous metal complexes to oxidic supports.

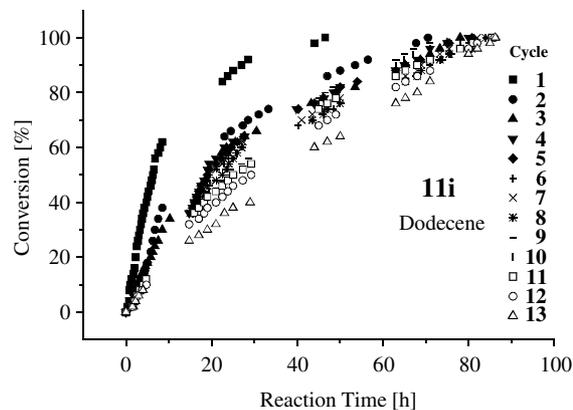


Figure 17. Batch-wise recycling of catalyst **11i**: Hydrogenation of dodecene (**12**) in toluene at 25 °C with a catalyst to substrate ratio of 1:100.

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