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Journal of Organometallic Chemistry 627 (2001) 44–54

Journal of Organometallic Chemistry

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Immobilized rhodium hydrogenation catalysts

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Received 31 August 2000; received in revised form 16 January 2001

Abstract

The showcase catalyst for olefin hydrogenations is Wilkinson's complex $ClRh(PPh_3)_3$ (**1**). Here, the Wilkinson-type catalyst $ClRh[Ph_2P(CH_2)_3Si(OEt)_3]_3$ (**2**), *trans*-$ClRh(CO)[Ph_2P(CH_2)_3Si(OEt)_3]_2$ (**3**), and the chelate complex $ClRh(PPh_3)[Ph_2PCH_2CHOHCH_2PPh_2]$ (**4**) have been synthesized using the bifunctional ligands $Ph_2P(CH_2)_3Si(OEt)_3$ (**5**) and $Ph_2PCH_2CHOHCH_2PPh_2$ (**6**), and fully characterized. The dihydride complex **4(H)$_2$** has been generated in situ and characterized with NMR. Complexes **2**, **3**, and **4** have been immobilized on silica, giving **2i**, **3i**, and **4i**, respectively, which have been studied by solid-state NMR. The catalytic activities of **2i**–**4i** for the hydrogenation of 1-dodecene (**7**), 2-cyclohexen-1-one (**8**), and 4-bromostyrene (**9**) are compared with those of the homogeneous analogs **2** and **3**, as well as with **1**. While there are no substantial differences between **1** and **2** concerning TON and TOF, **2i** shows reversed activity for the three test samples: dodecene gives the lowest TOF, followed by bromostyrene and cyclohexenone. However, TON and maximal yield are the same for **1**, **2**, and **2i**. In contrast to **1** and **2**, the immobilized catalyst **2i** can be recycled seven times, **4i** three times. Catalysts **3** and **3i** give maximal TOF for the hydrogenation of **7**, followed by **8** and **9**. The yields are below 100% for the homogeneous catalyst **3**, but immobilization (**3i**) gives maximum yields for all substrates. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Immobilized catalysts; Olefin hydrogenation; Rhodium complexes; Bifunctional ligands; Silica support; Solid-state NMR

1. Introduction

In a world of rapidly shrinking resources the so-called "green" chemistry becomes more and more important. Homogeneous catalysts are the showcase materials being studied in this direction for many decades, and they are still improved following different strategies: they are tailored according to the needs of the catalytic reaction, and are made more and more efficient [1,2], also by combining two different catalysts [3,4]. Furthermore, several approaches have been developed to combine the advantages of homogeneous and heterogeneous catalysts like easy separation of reactants, products, and catalysts, as well as high activity and selectivity: For example, water soluble catalysts [5–7] for use in biphasic media have been applied in the Rhône–Poulenc process [5]. Biphasic fluorous catalysis makes progress [8–10], and also immobilizing catalysts via the sol–gel process [11], by anchoring them to a polymer matrix [12–16], or subjecting them to microencapsulation [10,17]. The key feature of all these different approaches is to improve the possibility of catalyst recovery and recycling.

For some time our group, like others, has pursued this idea [12,13] by immobilizing homogeneous catalysts on silica supports [18,19] via bifunctional linkers like $Ph_2P(CH_2)_3Si(OEt)_3$ (**5**). Silica is an inexpensive, reasonably well-defined material [20–22], and its reaction with ethoxysilane groups has been studied in detail [23,24], and applied in countless cases recently [25–29]. The real breakthrough for clean immobilization came when we learned how to avoid side-products stemming from the immobilization procedure [30,31]. Suspension NMR [32] and multinuclear solid-state NMR [18,22,31] have served as powerful tools for investigating the amorphous solid materials. At the present state we are able to immobilize any arbitrary phosphine complex on the silica surface via covalent bonding, cleanly and in a well-defined manner. As an example, here we present the immobilized catalysts of the Wilkinson type, which can easily be separated from the reaction mixture, and recycled many times. Their activity with respect to the

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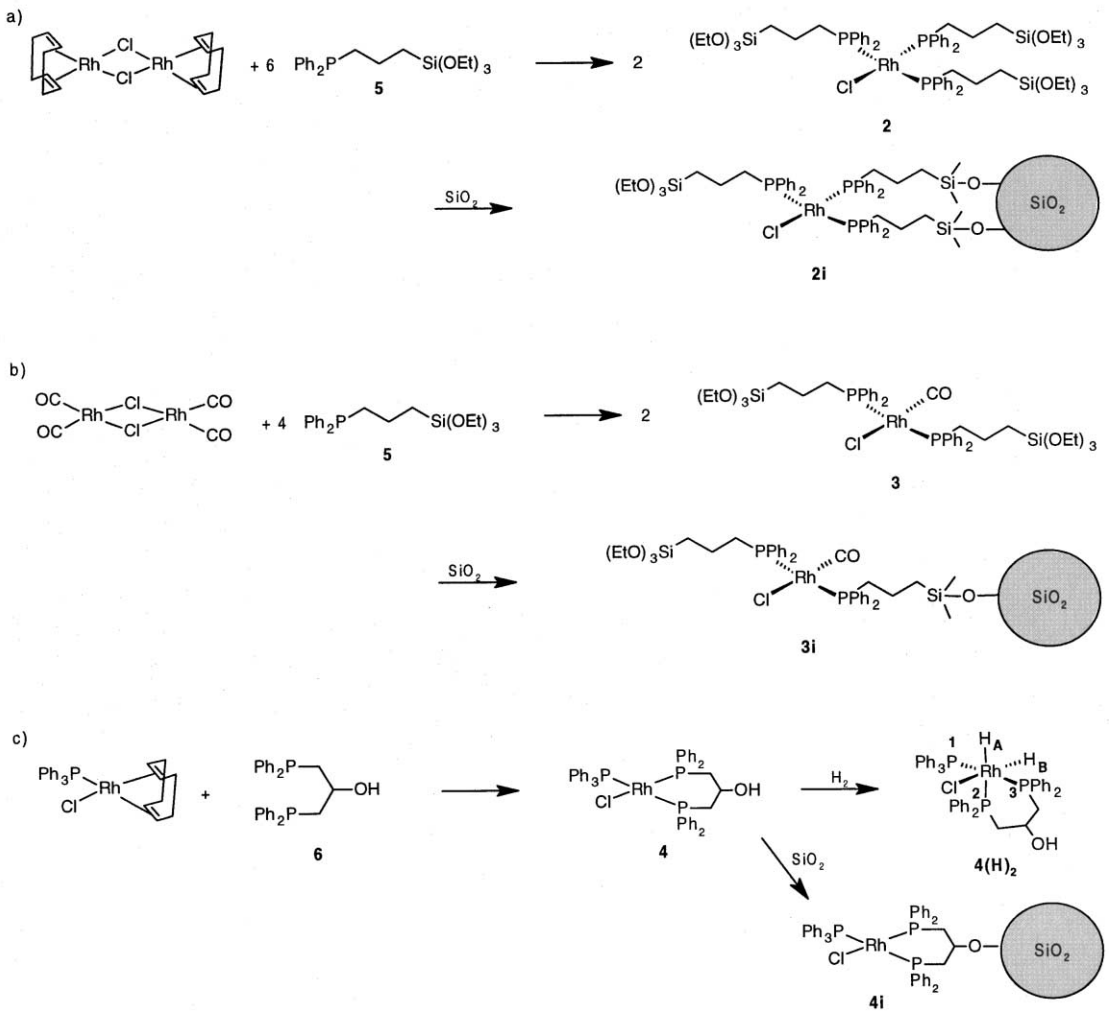
PII: S0022-328X(01)00696-9

hydrogenation of standard substrates is studied, because hydrogenation is one of the most important and best developed areas of catalysis [33]. We find that the hydrogenation activity of our immobilized species can favorably compete with the activity of corresponding homogeneous analogs. Furthermore, an immobilized rhodium carbonyl complex is studied, and in this case turn over numbers (TON) are even higher than for the analog in solution.

2. Results and discussion

2.1. Synthesis of molecular catalysts

As shown in Scheme 1a, the most efficient synthesis of the rhodium complex $ClRh[Ph_2P(CH_2)_3Si(OEt)_3]_3$ (**2**) uses $[(COD)RhCl]_2$ (COD = cyclooctadiene) as the starting material. Without further purification, which would be difficult due to the ethoxysilane groups, low volatility, and missing inclination of **2** to crystallize, it is obtained quantitatively, and in analytically pure form. Attempts to synthesize **2** by ligand exchange starting from $ClRh(PPh_3)_3$ (**1**) were not successful, because PPh_3 could not be removed from the reaction product, and furthermore dimers were formed. Using $RhCl_3 \cdot 3H_2O$ as a precursor [34] was unsuccessful, because of cross-linking of the ethoxysilane groups under the acidic reaction conditions. In principle, **2** can be synthesized in its immobilized form **2i** by treating silica modified with $Ph_2P(CH_2)_3Si(OEt)_3$ (**5**) with Wilkinson's catalyst [35], and removing PPh_3 by washing the solid. However, a threefold ligand exchange would not be guaranteed due to steric reasons, leading to a less well-defined catalyst. Furthermore, **2i** cannot be removed from the silica surface to give **2** without destruction, because of the harsh conditions needed to break the strong covalent siloxane bonds [24]. Similarly, a second catalyst, $ClRh(CO)[Ph_2P(CH_2)_3Si(OEt)_3]_2$ (**3**), could be synthesized starting from $[(CO)_2RhCl]_2$, as depicted in Scheme 1b. Another catalyst, $ClRh(PPh_3)[Ph_2PCH_2CHOHCH_2PPh_2]$ (**4**), was obtained by reacting



Scheme 1. Syntheses of the catalysts **2**–**4i**.

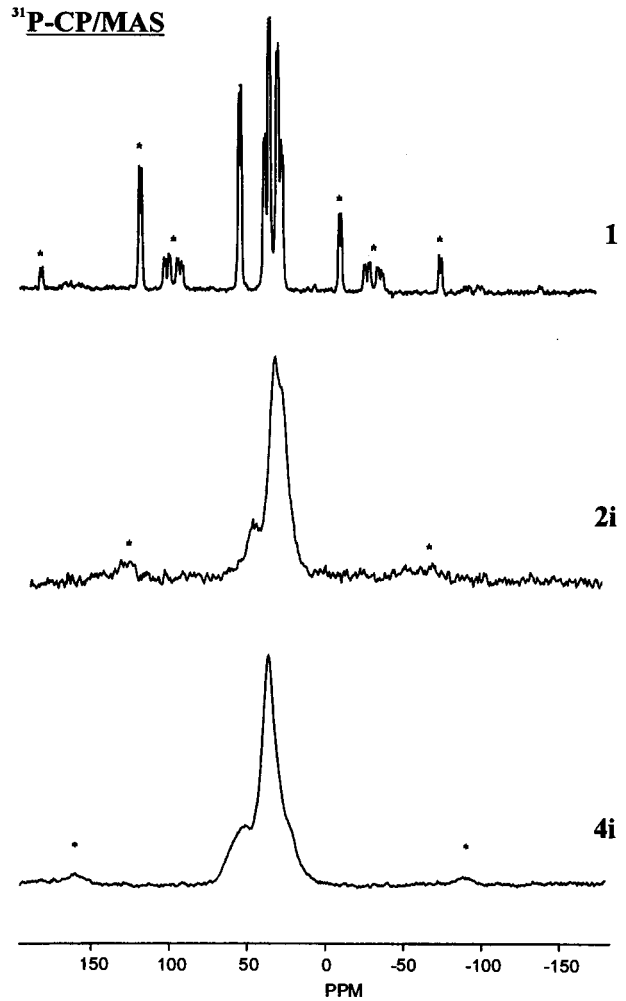


Fig. 1. 121.4 MHz ^{31}P CP/MAS NMR spectra of polycrystalline **1**, and the immobilized catalysts **2i** and **4i**, recorded with spinning speeds of 8 (**1**), 12 (**2i**), and 15 kHz (**4i**). Rotational sidebands are denoted by asterisks.

$Cl(PPh_3)Rh(COD)$ with the chelating phosphine **6** (Scheme 1c). The characterization and NMR signal assignments were straightforward, and the δ and J data are in the expected areas (see Section 4), and therefore do not need any detailed discussion.

Since it is known that in dihydride complexes chelating ligands can assume other than the expected coordination sites [36,37], we also investigated the reaction of **4** with molecular hydrogen in situ. When treating **4** within an NMR tube with 1 bar hydrogen pressure, a 1:1 mixture of **4** and $\mathbf{4(H)_2}$ (Scheme 1) is obtained, as determined by ^{31}P-NMR spectroscopy. The reaction is not fully reversible, even when $\mathbf{4(H)_2}$ is treated with fresh solvent and subjected to vacuum. The geometry shown in Scheme 1c can be deduced from the NMR data: the very large and characteristic ^2J(P,P) value of 376.2 Hz indicates the *trans* arrangement of two phosphine moieties, which typically display coupling constants in the range of 370–567 Hz [38]. Since the chelate ligand cannot assume two *trans* positions, one of the coupling partners must be PPh_3. The second phosphine moiety of coordinated **6** has to be in position 2 due to its characteristic small ^1J(Rh,P) value of 87.2 Hz. The latter comes very close to the corresponding value in $H_2ClRh(PPh_3)_3$ ($\mathbf{1(H)_2}$) [39], or the fluorinated phosphine complex [8], both with 90 Hz. The positions 1 and 3 for PPh_3 and P_3 are furthermore corroborated by the coupling constants $^1J(Rh,P_1) = 110.7$ Hz and $^1J(Rh,P_3) = 109.9$ Hz, which are comparable to the values in $\mathbf{1(H)_2}$ (114 Hz) [39] and the fluorinated version (108 Hz) [8]. Additionally, the *cis* coupling constants $^2J(P_1,P_2)$, and $^2J(P_2,P_3)$ with 24.2 Hz both lie well within the typical range of 9–35 Hz [38], and correspond, e.g. very well with the value of 17.5 Hz found for $\mathbf{1(H)_2}$ [39] or 24 Hz given for the fluorous analog [8]. In order to investigate the exact positions of hydride ligands, elegant methods can be applied nowadays, which make use of the parahydrogen [37,40]. In our case, however, the assignment is already unambiguous, due to the characteristic *trans* coupling $^2J(P_2,H_A) = 162.2$ Hz, which comes close to the value in $\mathbf{1(H)_2}$ (152 Hz) [39,41]. So, interestingly, the chelating ligand **6** does not assume the two positions *trans* to Cl and PPh_3, but rather one coordination site *trans* to PPh_3, and one *trans* to H; perhaps this accommodates its sterical demand better due to the four phenyl groups and the large bite angle of about 91° (value of the analog 1,3-bis(diphenyl-phosphino)propane [42]) as compared to, e.g. 85° in bis(diphenyl-phosphino)ethane [42].

2.2. Immobilization of catalysts

The molecular catalysts **2** and **3** have been immobilized on silica to give **2i** and **3i** by stirring the support material in toluene with the appropriate amount of **2** or **3** at 60°C for about 5 h. As shown previously, the bonding to the support via siloxane bonds is sufficiently strong to prevent leaching due to linker detachment from the surface [23,24,30], even if there is just one siloxane bond formed [31]. Less robust is the C–O–Si bond formed, when **4** is immobilized [20,30] to give **4i**. In toluene, however, even with prolonged washing, no leaching could be detected by NMR, or coloring of the supernatant solution, prior to catalysis. The ^{31}P suspension NMR spectra [32] of the materials **2i**–**4i** showed rather broad signals in toluene as the suspension medium, probably due to a larger chemical shift anisotropy (CSA) as compared to nickel carbonyl compounds [32], and further efforts will be needed to improve the spectrum quality for rhodium complexes. However, the classical solid-state ^{31}P CP/MAS NMR spectra were readily recorded, and they prove the high quality of the immobilized species. As shown in Fig. 1, the ^{31}P-NMR signals of **2i** and **4i** correspond very well

to the isotropic line of the signal of **1**, which was first described by Veeman's group [43]. Of course in the case of **2i** and **4i** the line splittings due to the P–P and Rh–P couplings are no longer visible. The silica surface is too inhomogeneous to allow as good a resolution as in the case of crystalline material. Interestingly, as in the case of immobilized nickel complexes [18], the rotational sidebands of the signals of **2i** and **4i** have lower intensity than the ones of crystalline **1**. So, the CSA seems to become smaller, while the residual linewidth increases due to the immobilization. The linewidth in the spectrum of **4i** excludes mere physisorption of **4** on the silica surface ([23] and references cited therein). Fig. 2 shows the ^{31}P CP/MAS NMR spectrum of **3i**, and of crystalline *trans*-Cl(CO)Rh(PPh_3)$_2$ (**13**) for comparison. In every respect, the situation is the same as with **2i** and **4i**.

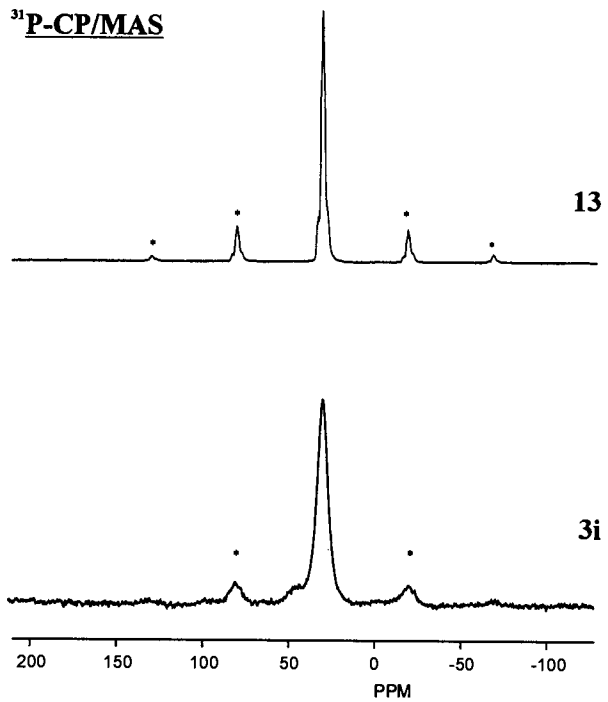
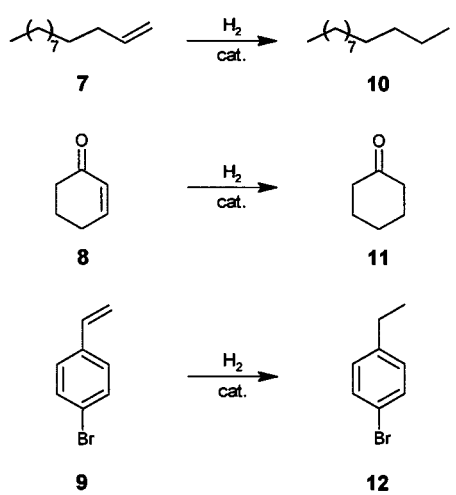


Fig. 2. 161.9 MHz ^{31}P CP/MAS NMR spectra of polycrystalline *trans*-(PPh_3)$_2$Rh(CO)Cl (**13**) and **3i**, both recorded with a spinning speed of 8 kHz. For further details see Section 4.



Scheme 2. The substrates dodecene, cyclohexenone, and bromostyrene, and their hydrogenation products dodecane, cyclohexanone, and ethylbromobenzene.

There is no ^{31}P-NMR signal of uncomplexed phosphine in the shift region of -12 to -25 ppm visible in any of the cases, **2i**–**4i**. Additionally, there is no oxidic species [30] present in any case. Therefore, we can be sure that the molecular catalysts **2**–**4** have been immobilized cleanly and in a well-defined manner. The chemical shifts of **2i**, **3i**, and **4i** are about the same as the ones for **2**, **3**, and **4** in solution; slight differences might be due to the different surroundings of the molecules, solvent molecules or silica surface.

2.3. Catalytic hydrogenation behavior of all catalysts

We sought to test all catalysts with a range of simple representative alkenes (Scheme 2). 1-Dodecene (**7**) was chosen as a monofunctional alkene, which could be a candidate for isomerization besides hydrogenation. 2-Cyclohexen-1-one (**8**) is a test reagent for chemoselectivity of the catalysts, because the C=O functionality could, in principle, be reduced as well. Furthermore, special behavior of this substrate might be detectable, because α,β-unsaturated ketones are more nucleophilic than monofunctional alkenes, and should bind to the Rh centers more readily. Finally, 4-bromostyrene (**9**) was chosen as a sterically, and from the standpoint of chemoselectivity, more demanding olefin with a bromo substituent as an additional functionality, as well as an aromatic ring system adjacent to the alkene double bond. One has to observe chemoselectivity especially carefully when studying supported catalysts, because due to our earlier [30] and ongoing experience, unexpected and quite weird transformations of substrates can happen on oxidic surfaces. Finally, this set of olefins guaranteed us easy comparison with other systems of immobilized catalysts, e.g. the fluorous catalysts [8].

The only hydrogenation products of these substrates with all the catalysts presented in this paper are dodecane (**10**), cyclohexanone (**11**), and 4-bromoethylbenzene (**12**), as proved by NMR and GC–MS (Scheme 2). Only in the case of **3** (but not with **3i**!), the hydrogenation of 1-dodecene gave $< 5\%$ 2- and 3-dodecene as by-products, as found in Ref. [8], too. However, no isomerization whatever could be detected with the Wilkinson-type catalysts.

First of all, Wilkinson's catalyst **1** served as a reference for the catalytic hydrogenation activity with **7**–**9**, using the conditions described in Section 4, and the

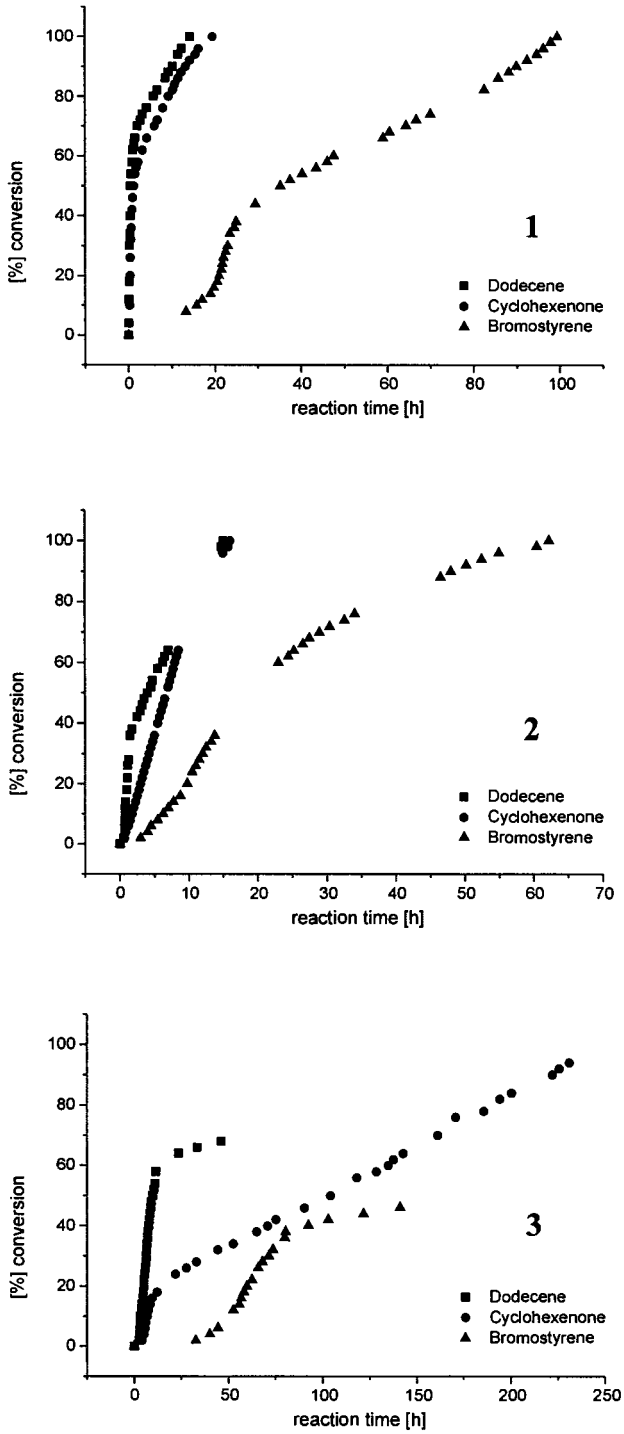


Fig. 3. Graphical representation of the substrate conversion (corresponding to hydrogen uptake) during the catalytic hydrogenation of dodecene, cyclohexenone, and bromostyrene with **1** (top), **2** (middle), and **3** (bottom). For details see Section 4 and supplementary material; yields, reaction temperatures and times see Table 1.

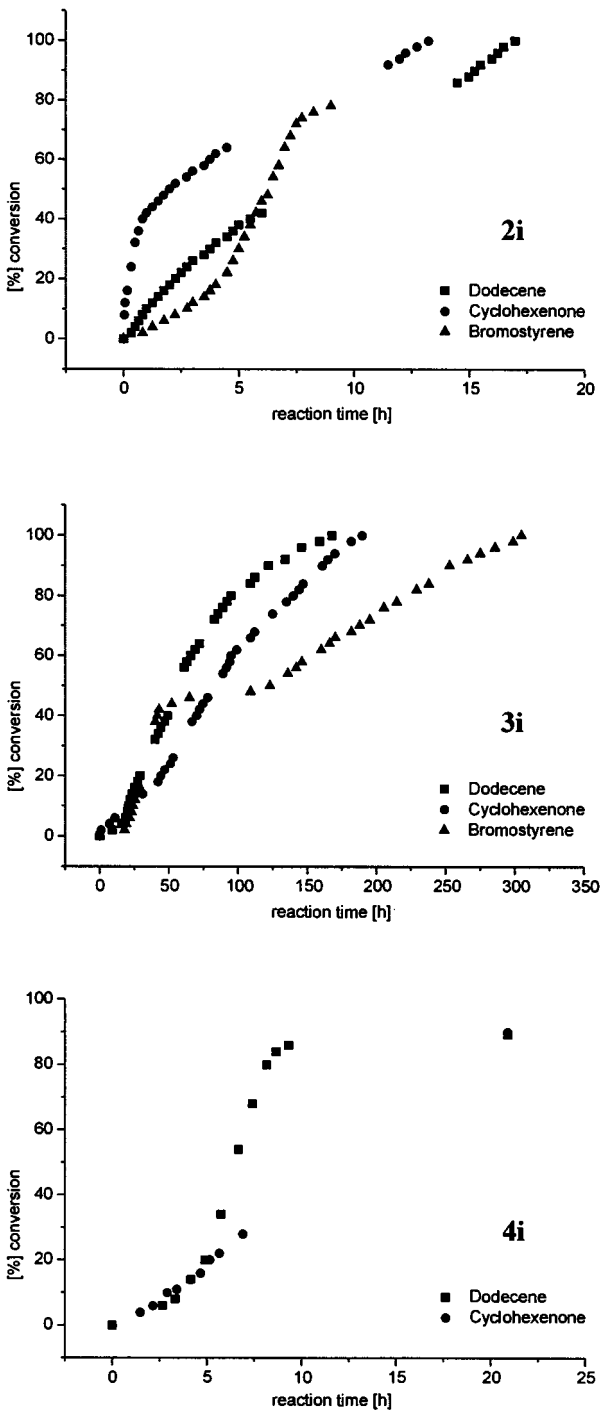


Fig. 4. Graphical representation of the substrate conversion (hydrogen uptake) during the catalytic hydrogenation of dodecene, cyclohexenone, and bromostyrene with **2i** (top), **3i** (middle), and **4i** (bottom). For details see Section 4 and supplementary material; yields, reaction temperatures and times see Table 1.

apparatus displayed in Fig. 7. The results are shown in Fig. 3.

While dodecene and cyclohexenone were both hydrogenated equally rapidly with 100% yield within 20 h, bromostyrene needed about 100 h for the completion of the reaction, and there is an induction period of about 20 h. Although it is well known that alkyl phosphines give much less effective Wilkinson-type catalysts than aryl phosphines [44], complex **2** performs nearly as well as **1** with all three substrates, and the same characteris-

Table 1
Product yields and reaction times for the hydrogenation of substrates dodecene, cyclohexenone, and bromostyrene. The reactions were run at ambient temperature, if not stated otherwise. In all experiments 0.01 mmol of free or immobilized catalyst in 5 ml THF (**1**) or toluene (**2**–**4i**) was stirred with 1 mmol of substrate, while hydrogen was admitted (Fig. 7, and Section 4)

Catalyst	Dodecene		Cyclohexenone		Bromostyrene	
	Reaction time (h)	Product yield (%)	Reaction time (h)	Product yield (%)	Reaction time (h)	Product yield (%)
1	14	100	20	100	100	100
					8 (45°C)	100
					30 (70°C)	100
2	15	100	16	100	62	100
					6 (45°C)	100
					18 (70°C)	100
2i	17	100	13	100	9	79
3	46	68	231 (70°C)	94	141 (45°C)	46
3i	168	100	190 (70°C)	100	305	100
4i	12 (60°C)	99	23 (60°C)	100	–	–

tics are seen in the curves (Fig. 3). Obviously it does not make too much of a difference, when just one of the substituents at the P ligand is an alkyl one, and two phenyl groups remain. Furthermore, the longer alkyl chains and bulky ethoxy groups do not seem to interfere with the catalytic activity of **2** by, e.g. decreasing mobility in solution. An interaction of the oxygen atoms with the rhodium centers via hemilabile coordination, as found with Ru complexes [11], also does not seem to take place. Interestingly, in the case of **3**, dodecene and bromostyrene are hydrogenated to give the same products as with **1** and **2**, but the reaction with cyclohexenone is substantially more sluggish now.

The immobilization of **2** and **3** changes the picture somewhat (Fig. 4): with **2i**, the reaction rates of cyclohexenone and bromostyrene are still comparable to the ones obtained with **2**. Only the hydrogenation of dodecene proceeds at a slower pace now. This is probably due to the fact that the long molecule dodecene has to diffuse with the right end into the pores of the support now, in order to find the catalytic center, an effect that is well known and exploited with polymer-supported catalysts [45]. The yields, however, are still very high in all cases (Table 1). Interestingly, immobilization of **3** increases the reaction times, but also the yields for all three substrates (Fig. 4, Table 1). Here, the catalyst **3i** might profit from the strict separation of the reaction centers on the silica surface, since it is well known that one mechanism of deactivation of hydroformylation catalysts is dimerization [46].

Catalyst **4i** performs in the same way as **2i** towards dodecene and cyclohexenone, concerning yield, and just needs a little higher temperature of 60°C for the reaction (Fig. 4, Table 1). The chelating ligand obviously does not impede the catalytic reaction. Using higher temperatures in the system **1**/bromostyrene and **2**/bromostyrene removes the induction periods, and substantially reduces the reaction times (Fig. 5). However, the catalytic activity

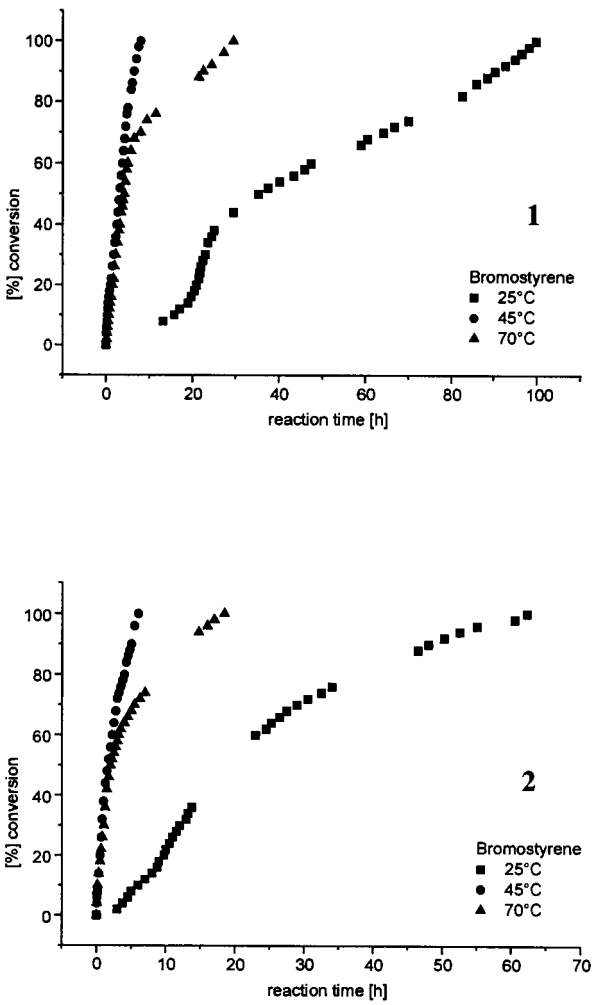


Fig. 5. Graphical representation of the substrate conversion (hydrogen uptake) during the catalytic hydrogenation of bromostyrene with **1** (top) and **2** (bottom), at 25, 45, and 70°C. For details see Section 4, supplementary material, and Table 1.

Table 2
Yields and reaction times, when the immobilized catalysts **2i** and **4i** are recycled. After each cycle the support is washed and fed with fresh solvent and dodecene as the substrate using the same conditions as described in Table 1

Number of cycles	**2i** (RT)		**4i** (60°C)	
	Reaction time (h)	Product yield (%)	Reaction time (h)	Product yield (%)
1	17	100	12	99
2	22.5	100	24	64
3	77.5	100	24	53
4	67	91		
5	248	77		
6	302	60		
7	480	49		

does not increase linearly when raising the temperature, but there is an optimum temperature range around 45°C.

As compared to Wilkinson's catalyst, and other immobilized catalyst systems, e.g. the fluorous one [8], the performance of **2i**, **3i**, and **4i** is very good, and the chemoselectivity is not changed by the anchoring to silica. Furthermore, in contrast to **1**, the catalyst can easily be removed from the reaction mixture by letting it settle down and decanting the supernatant solution. In this respect our immobilized catalysts are already superior to homogeneous catalysts, which cannot be recycled easily.

2.4. Recycling of immobilized catalysts

Next, the possibility of recycling of **2i** and **4i** was tested, using dodecene as the substrate. When catalyst **2i** is recycled batch-wise six times, the yields are high for the first four times, and even 100% for the first three times. Then, the reactions slow down gradually, and the yield drops to about 50% after the seventh run (for details see Table 2 and Fig. 6). In order to check, whether this drop in the yield was due to the repeated opening and closing of the hydrogenation apparatus (Fig. 7, Section 4), or whether the maximum possible TON (sometimes called "natural lifetime") of **2i** had already been reached, the sixfold amount of substrate was added at once. The yield was 100% in this case, and the reaction rate was high, which rules out the latter assumption. Future attempts indeed could improve the "recycling" characteristics of the hydrogenation reaction with a continuous catalysis setting in a closed system. Unfortunately, the type of deactivation could not readily be determined, because the solid-state NMR spectrum of used catalyst only shows the signals of intact catalyst. With **4i**, the recycling behavior is not quite as satisfactory as with **2i** (Table 2), in this case probably due to the weak bonding of the ligand to the support via a C–O–Si bond. Here, the situation could be improved by using chelating ligands containing an ethoxysilane group [11] for robust anchoring of the catalyst on the support. There is an ongoing effort in our labs to find easy syntheses for this type of ligand [50].

3. Conclusions

To sum it up, we demonstrate with Wilkinson-type complexes that, using the proper conditions and linkers, they can easily be immobilized on commercial silica. They are still very active with respect to the hydrogenation of different substrates, and the chemoselectivities are not changed by the immobilization. The catalysts can easily be removed from the reaction mixtures, and recycled many times before they gradually lose catalytic activity. Therefore, they can be compared favorably with other systems of immobilized catalysts. In addition to that, the immobilization procedure is quite simple, and the linkers needed for it are easy to synthesize. The simplification of syntheses also for chelating ligands containing ethoxysilane groups for still stronger bonding to the support and therefore longer lifetime of the immobilized catalysts is part of our ongoing research interests.

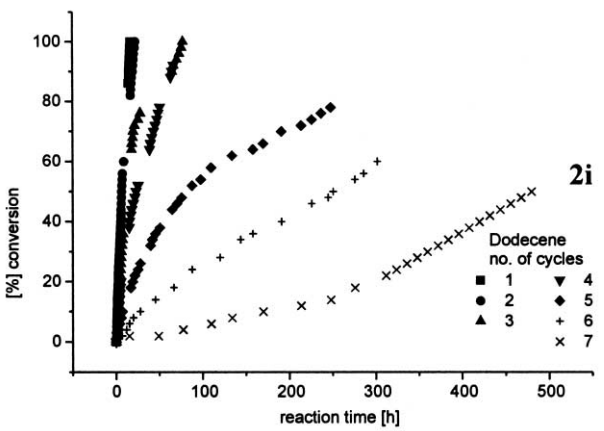


Fig. 6. Graphical representation of the recycling behavior of **2i** with respect to hydrogenation of dodecene (for details see Section 4, supplementary material, and Table 2).

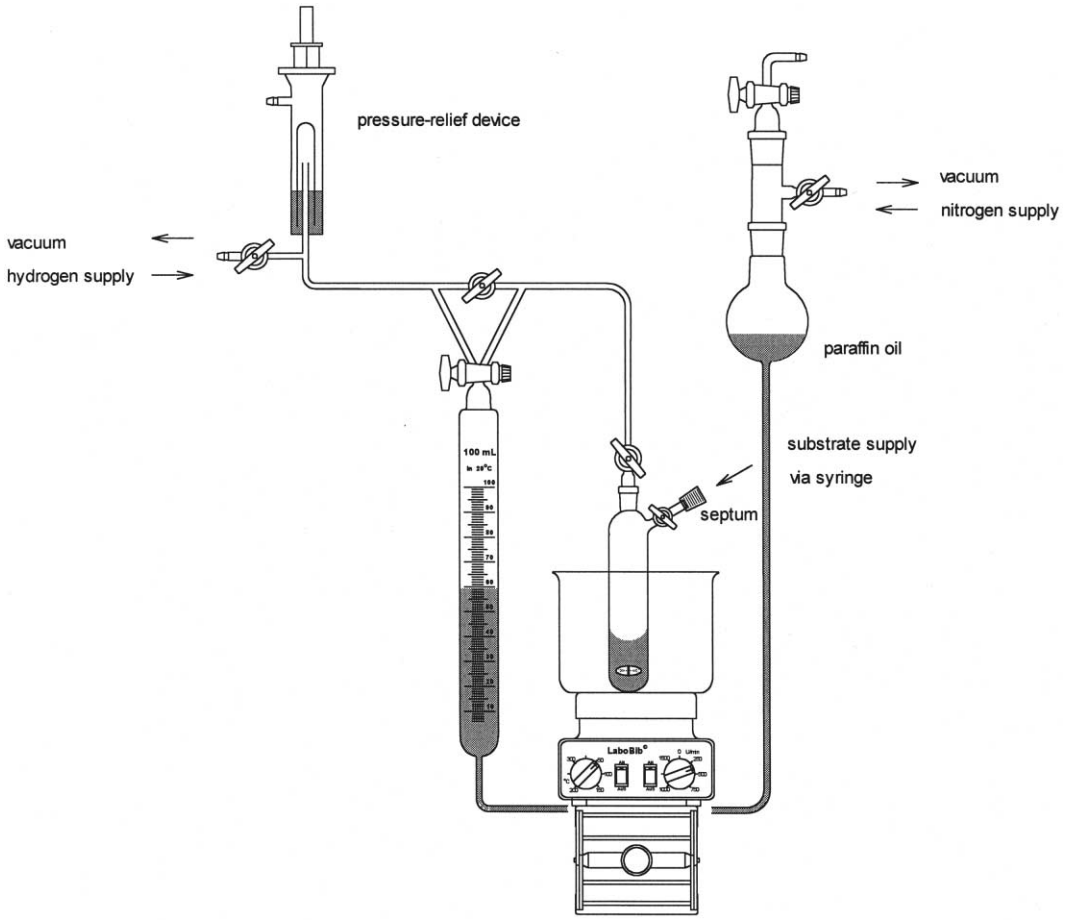


Fig. 7. Schematic presentation of the experimental setting used for the hydrogenation reactions (work principle see text and Section 4).

4. Experimental

4.1. General comments

All catalytic reactions were performed under inert gas using Schlenk techniques, prior to admitting hydrogen. They were proved to be fully reproducible by being repeated several times. Solvents were dried by standard methods, and oxygen was removed. The identity of molecular compounds was checked by elemental analysis, mass spectrometry, and their solution-state NMR spectra, and IR spectra where appropriate. Immobilized species were studied by solid-state NMR. For GC analyses of the hydrogenation products a Chrompack Model CP-9003 instrument was used. All starting materials were commercially available, if not described below. As a support Merck silica 40 (specific surface area 750 $m^2\,g^{-1}$; average pore size 40 Å; particle size 0.063–0.2 mm) that was dried at 600°C in vacuo (10^{-2} Pa for 12 h) in order to condense surface silanol groups [20], was used.

4.2. Liquid-state NMR spectroscopy

All the spectra were recorded on Bruker WH 200, Bruker AC 300, Bruker DRX 300, and Bruker DRX 500 NMR spectrometers. The deuterated solvents served as internal standards for ^{1}H- and ^{13}C-NMR spectra, and the chemical shifts were recalculated with respect to TMS. H_3PO_4 (85%) was the external chemical shift standard for ^{31}P-NMR measurements. When necessary, the shift assignments were corroborated by 2D COSY NMR spectra.

4.3. Solid-state NMR spectroscopy

All solid-state ^{31}P-NMR spectra were recorded on a Bruker MSL 300 or a digital Bruker Avance 400 NMR spectrometer equipped with an ultrashield widebore magnet, and a 4 mm multinuclear double-bearing MAS probehead. The modified silica was loosely filled into the ZrO_2 rotors in a glove box. Cross polarization (CP) and magic angle spinning (MAS) with rotational speeds up to 15 kHz were applied. The contact time was 1 ms, and the relaxation delay was 10 s for all surface-immobilized compounds. The ^{31}P CP/MAS NMR spectra were referenced with respect to 85% H_3PO_4(aq.) by setting the ^{31}P-NMR peak of solid $(NH_4)H_2PO_4$ to $+0.81$ ppm. The Hartmann–Hahn match was set by using solid $ClRh(PPh_3)_3$ (**1**). For the exponential multiplication line-broadening factors of up to 100 Hz was applied.

4.4. Synthesis of $ClRh[PPh_2(CH_2)_3Si(OEt)_3]_3$ (2)

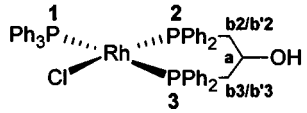
The ligand $PPh_2(CH_2)_3Si(OEt)_3$ (**5**) was synthesized as described in Ref. [30]. A solution of **5** (143 mg, 0.366 mmol) in 3 ml of toluene was added to a solution of $[Rh(COD)Cl]_2$ (30 mg, 0.061 mmol) in 5 ml of toluene. The color changed from yellow to dark orange. After all volatile substances were removed in vacuo an orange-brown viscous oil was obtained. Yield: 79 mg (0.060 mmol, 100% with respect to $[Rh(COD)Cl]_2$). HR-MS (FAB^+) 1273.4440 (Calc. for $C_{63}H_{93}O_9P_3RhSi_3$: 1273.4396). Anal. Found: C, 58.15; H, 7.49; P, 6.81. Calc. for $C_{63}H_{93}ClO_9P_3RhSi_3$ (1308.408 g mol^{-1}): C, 57.76; H, 7.16; P, 7.09%. $^{31}P\{^1H\}$-NMR (toluene-d_8, 121.49 MHz, 23°C, δ ppm): 39.85 (dt, $^2J(P, P_{trans}) = 39.6$ Hz, $^1J(Rh,P_{trans}) = 186.9$ Hz); 25.62 (dd, $^2J(P,P_{trans}) = 39.6$ Hz, $^1J(Rh,P_{cis}) = 138.9$ Hz). ^{1}H-NMR (toluene-d_8, 300.13 MHz, 23°C, nuclei of the ligand *trans* to Cl carry a prime, δ ppm): 7.74–6.57 (m, 20H, PPh_2); 7.04–6.92 (m, 10H, PPh_2); 3.76–3.65 (2 overlapping q, 18 H, $-CH'_2CH_3$, $-CH_2CH_3$, $^3J(H,H) = 6.8$ Hz); 2.50 (m, 4H, PCH_2–); 2.14 (m, 4H, $PCH_2CH_2CH_2$); 2.03 (t, 2H, PCH'_2, $^3J(H,H) = 6.8$ Hz); 1.98–1.85 (m, 2H, $CH_2CH'_2CH_2$); 1.12 (t, 27H, CH_3, CH'_3, $^3J(H,H) = 6.8$ Hz); 0.71 (t, 4H, CH_2Si, $^3J(H,H) = 7.9$ Hz); 0.46 (t, 2H, CH'_2Si, $^3J(H,H) = 7.9$ Hz). $^{13}C\{^1H\}$-NMR (toluene-d_8, 75.47 MHz, 23°C, nuclei of the ligand *trans* to Cl carry a prime, δ ppm): 135.60 (C_{ipso}); 135.31 (C'_{ipso}); 131.54 (C'_{ortho}, C'_{meta}); 131.42 (C_{ortho}, C_{meta}); 129.52 (C'_{para}); 129.21 (C_{para}); 58.80 (OCH_2, $OC'H_2$); 33.77 ($PC'H_2$); 32.83 (PCH_2); 19.06 (CH_3); 18.90 ($C'H_3$); 16.45 ($CH_2C'H_2CH_2$); 16.41 ($CH_2CH_2CH_2$); 12.85 ($C'H_2Si$); 12.69 (CH_2Si).

4.5. Synthesis of trans-$Cl(CO)Rh[PPh_2(CH_2)_3Si(OEt)_3]_2$ (3)

A solution of **5** (100 mg, 0.257 mmol) in 3.5 ml of toluene was added to a solution of $[Rh(CO)_2Cl]_2$ (25 mg, 0.064 mmol) in toluene. After the mixture was stirred for 25 min, during which time the color changed from yellow to dark brown, all volatile substances were removed in vacuo, and a dark brown viscous oil was obtained. Yield: 125 mg (0.128 mmol, 100% with respect to $[Rh(CO)_2Cl]_2$). HR-MS (FAB^+) 918.2360 $[M-CO]^+$ (Calc. for $C_{42}H_{62}ClO_6Si_2P_2Rh$: 918.2304). Anal. Found: C, 54.30; H, 6.74; P, 6.26. Calc. for $C_{43}H_{62}ClO_7P_2RhSi_2$ (947.440 g mol^{-1}): C, 54.51; H, 6.60; P, 6.54%. IR (neat, cm^{-1}): $\nu_{CO} = 1970$, $\nu_{RhCl} = 960$. $^{31}P\{^1H\}$-NMR (benzene-d_6, 121.49 MHz, 23°C, δ ppm): 24.11 (d, $^1J(Rh,P) = 123.6$ Hz). ^{1}H-NMR (benzene-d_6, 300.13 MHz, 23°C, δ ppm): 7.86 (d, 8H, H_{ortho}, $^3J(H,H) = 6.4$ Hz); 7.1–6.95 (m, 12H, H_{meta}, H_{para}); 3.77 (q, 12H, OCH_2, $^3J(H,H) = 7.1$ Hz); 2.90–2.75 (m, 4H, PCH_2); 2.11–1.95 (m, 4H, $CH_2CH_2CH_2$); 1.14 (t, 18H, CH_3, $^3J(H,H) = 7.1$ Hz); 0.86 (t, 4H, CH_2Si, $^3J(H,H) = 7.9$ Hz). $^{13}C\{^1H\}$-NMR (benzene-d_6, 75.47 MHz, 23°C, δ ppm): 188.39 (dt, CO, $^1J(Rh,C) = 73.5$ Hz, $^2J(P,C) = 15.8$ Hz); 134.85 (t, C_{ipso}, $^1J(P,C) = 21.0$ Hz); 133.95 (t, C_{meta}, $^3J(P,C) = 6.1$ Hz); 133.58 (t, C_{ortho}, $^2J(P,C) = 10.5$ Hz); 129.93 (C_{para}); 58.50 (OCH_2); 30.86 (t, PCH_2, $^1J(P,C) = 13.3$ Hz); 19.29 ($CH_2CH_2CH_2$); 18.66 (CH_3); 12.85 (t, CH_2Si, $^3J(P,C) = 7.2$ Hz).

4.6. Synthesis of $ClRh(PPh_3)[Ph_2PCH_2CHOHCH_2PPh_2]$ (4)

To a solution of $Cl(PPh_3)Rh(COD)$ (76 mg, 0.149 mmol) [47] in 20 ml of THF, a solution of ligand **6** (64 mg, 0.149 mmol) [48] in THF was added. The color changed from yellow to orange. After the mixture was stirred for 1 h the solvent and COD were removed in vacuo, and **4** was yielded quantitatively as an orange oil.



MS (FAB): 793.1 $[M-Cl]^+$. HR-MS (FAB^+) = 793.1448 $[M-Cl]^+$ (Calc. for $C_{45}H_{41}OP_3Rh$ 793.1426). Anal. Found: C, 64.09; H, 5.55. Calc. for $C_{45}H_{41}OP_3ClRh$ (829.099 g mol^{-1}): C, 65.19; H, 4.98%. $^{31}P\{^1H\}$-NMR (toluene-d_8, 121.49 MHz, δ ppm): 40.19 (ddd, P_2, $^2J(P_2,P_1) = 36.1$ Hz, $^2J(P_2,P_3) = 51.1$ Hz, $^1J(Rh,P_2) = 177.6$ Hz); 32.81 (ddd, P_1, $^2J(P_2,P_1) = 36.1$ Hz, $^2J(P_1,P_3) = 357.2$ Hz, $^1J(Rh,P_1) = 133.9$ Hz); 24.45 (ddd, P_3, $^2J(P_2,P_3) = 51,1$ Hz, $^2J(P_1,P_3) = 357.2$ Hz, $^1J(Rh,P_3) = 136.2$ Hz. The signal assignment is additionally corroborated by a $^{31}P,^{31}P$-COSY spectrum. ^{1}H-NMR (benzene-d_6, 500.13 MHz, δ ppm): 8.0–6.8 (m, 35H, aryl-H); 3.68 (broad, 1H, OH); 3.07 (m, 1H, H_a); 2.70* (m, 1H, H_{b2}, $^2J(H_{b2},H_{b'2}) = 14.6$ Hz); 2.60 (m, 1H, H_{b3}, $^2J(H_{b3},H_{b'3}) = 14.6$ Hz); 2.05* (m, 1H, $H_{b'3}$, $^2J(H_{b'3},H_{b3}) = 14.6$ Hz); 1.91 (m, 1H, $H_{b'2}$, $^2J(H_{b'2},H_{b2}) = 14.6$ Hz); *signal assignments of $H_{b'3}$, H_{b3} and $H_{b'2}$, H_{b2} pairwise interchangeable. $^{13}C\{^1H\}$-NMR (benzene-d_6, 125.77 MHz, δ ppm): 137.22 (d, C_{ipso}, $^1J(P,C) = 20.7$ Hz); 136.41 (d, C_{ipso}, $^1J(P,C) = 25.4$ Hz); 136.11 (d, C_{ipso}, $^1J(P,C) = 21.7$ Hz); 135.46 (d, C_{ipso} of PPh_3, $^1J(P,C) = 11$ Hz); 134.88 (d, C_{ortho}, $^2J(P,C) = 13.1$ Hz); 134.24 (d, C_{ortho}, $^2J(P,C) = 10.4$ Hz); 134.10 (d, C_{ortho}, $^2J(P,C) = 14.1$ Hz); 133.57 (d, C_{ortho}, $^2J(P,C) = 10.4$ Hz); 132.10 (d, C_{ortho} of PPh_3, $^2J(P,C) = 9.4$ Hz); 131.65 (d, C_{meta}, $^3J(P,C) = 11.3$ Hz); 131.33 (d, C_{meta}, $^3J(P,C) = 11.3$ Hz); 130.84 (d, C_{meta}, $^3J(P,C) = 9.4$ Hz); 130.60 (d, C_{meta}, $^3J(P,C) = 9.4$ Hz); 127.10 (d, C_{meta} of PPh_3, $^3J(P,C) = 9.4$ Hz; 129.49 (s, C_{para}); 128.82 (s, C_{para}); 128.72 (s, C_{para}); 128.38 (d, C_{para} of PPh_3,

$^4J(P,C) = 1.8$ Hz); 128.1 (signal overlapping with solvent peak); 65.61 (t, C_a, $^2J(P,C) = 7.5$ Hz); 33.09* (broad, s, P2-CH_2); 28.88* (broad, s, P3-CH_2); *signal assignments interchangeable.

4.7. In situ generation of the dihydrogen complex 4(H)$_2$

Fifty-seven milligrams (0.069 mmol) of **4** were placed into a 5 mm NMR tube and dissolved in about 2 ml of toluene-d_8. Then, oxygen free hydrogen was gently bubbled into the solution at room temperature via a capillary. The color changed from orange to yellow. After the NMR tube was sealed with a glass stopper, the ^{31}P-NMR spectrum was recorded, which showed that about 50% of the complex has been transformed into **4(H)$_2$** (see Scheme 1, also for numbering). Besides the residual signals of **4**, the following ones of **4(H)$_2$** show up in the spectra: $^{31}P\{^1H\}$-NMR (toluene-d_8, 121.49 MHz, δ ppm): 42.27 (ddd, P_1, $^2J(P_1,P_2) = 24.2$ Hz, $^2J(P_1,P_3) = 376.2$ Hz, $^1J(Rh,P_1) = 110.7$ Hz); 29.31 (ddd, P_3, $^2J(P_3,P_2) = 24.2$ Hz, $^2J(P_3,P_1) = 376.2$ Hz, $^1J(Rh,P_3) = 109.9$ Hz); 15.09 (dt, P_2, $^2J(P_2,P_1) = {}^2J(P_2,P_3) = 24.2$ Hz, $^1J(Rh,P_2) = 87.2$ Hz). ^{1}H-NMR (toluene-d_8, 300.13 MHz, δ ppm): -7.63 (d, broad, H_A, $^2J(H_A,P_2) = 162.2$ Hz); -17.02 (s, broad, H_B).

4.8. Immobilization procedure

The complexes **2**, **3**, and **4** were immobilized according to the standard procedure given in Ref. [18], taking care to use the right solvent [24], here toluene, and the surface coverage with the corresponding complexes **2i**, **3i**, and **4i** was determined by weighing back the residual complex from the supernatant solution. The surface coverage corresponds to 129 mg of **2i** per gram of silica (**3i**: 117 mg g^{-1}; **4i**: 73 mg g^{-1}), or eight molecules of catalyst **2i** per 100 nm^2 of silica surface (**3i**: 10 molecules per 100 nm^2; **4i**: 7 molecules per 100 nm^2). The supported catalysts were washed several times with toluene, and then with THF, and finally dried in vacuo for 4 h at room temperature.

4.9. Hydrogenation procedure

For all hydrogenation experiments the following standard conditions were applied, in order to get maximal comparability — ratio of olefin to Rh catalyst, 100:1; olefin concentration, 0.1 mol l^{-1}; solvents, THF for **1**, toluene for **2**, **2i**, **3**, **3i**, and **4i**. The hydrogenation pressure was always 1.1 bar, the temperatures were within a range from 25 to 70°C, as given in Tables 1 and 2. The reaction times varied between 6 and 21 h, as given in the corresponding figures. All the hydrogenations were done under practically constant hydrogen pressure of 1 bar using the apparatus developed by the Helmchen group [49], which is depicted schematically in Fig. 7. Hereby, the weighed homogeneous or immobilized catalyst is placed into a Schlenk flask, the atmosphere of which is changed from nitrogen to pure hydrogen. Then, the solvent is added, and the mixture is stirred vigorously. Hydrogen is held at a predetermined level in a calibrated storage area sealed with degassed paraffin oil. After adding the olefin through the septum of the Schlenk flask with a syringe, the reaction is started by opening the valve connecting the reaction vessel with the hydrogen reservoir. The hydrogen uptake could then be monitored at the scale of the hydrogen reservoir.

After the hydrogenation reactions, the immobilized catalysts were allowed to settle down for about 3 min. The results of the hydrogenation were checked by direct GC–MS of the supernatant solutions. Only in case of **1**, **2**, and **3**, the catalysts had to be removed by flash chromatography prior to the application of GC, and determination of the yield by the removal of the solvent in vacuo. In the cases of **2i**, **3i**, and **4i**, the product yields could be determined directly after removal of solvent from the supernatant solutions.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG) for support via the Landesforschungsschwerpunktprogramm, and the Fonds der Chemischen Industrie for financial support. Furthermore we thank the company Bruker for a very generous gift of an accessory for our new Avance 400 NMR instrument. Finally Dr G. Raudaschl-Sieber (TU Munich) has to be thanked for recording one of the ^{31}P-CP/MAS NMR spectra.

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