

Rhodium phosphine complexes immobilized on silica as active catalysts for 1-hexene hydroformylation and arene hydrogenation

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Abstract

In immobilizing the rhodium complexes $[\text{Rh}(\text{acac})(\text{CO})(\text{P})]$ (**1**) and $[\text{Rh}(\text{acac})(\text{P})_2]$ (**2**) ($\text{P} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$) onto SiO_2 , acetylacetone is found to be released through protonation of the acac ligand by the acidic silica-OH groups. The resulting complexes $[\text{Rh}(\text{O}-\{\text{SiO}_2\})(\text{HO}-\{\text{SiO}_2\})(\text{CO})(\text{P}-\{\text{SiO}_2\})]$ (**1a**) and $[\text{Rh}(\text{O}-\{\text{SiO}_2\})(\text{HO}-\{\text{SiO}_2\})(\text{P}-\{\text{SiO}_2\})_2]$ (**2a**) were successfully tested with respect to their catalytic action on 1-hexene hydroformylation as well as benzene and toluene hydrogenation. The reaction outcome, viz. the formation of aldehydes versus isomerization, depends strongly on the presence and concentration of a phosphine co-catalyst. Thus, while **1a** gave only a 17% yield of aldehyde in the absence of phosphines, the yield is increased to 54% in the presence of phosphinated silica $\text{P}-\{\text{SiO}_2\}$ or even 94% if PPh_3 is added to the solution. Without extra added phosphine, both **1a** and **2a** effect mainly the isomerization of 1-hexene to 2-hexene. Pre-catalyst **1a** catalyzes also the hydrogenation of benzene at 10.5 atm H_2 and 90 °C to give cyclohexane with a TOF of 608 h^{-1} .

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1. Introduction

The separation of reaction products from the catalyst is an important drawback in homogeneous metal complex catalysis. Improvements may be sought in at least two directions. On the one hand, one can switch over to water-soluble catalysts as for instance accomplished in the Ruhr-Chemie/Rhone-Poulenc industrial hydroformylation process by rhodium [1]. However, this scheme is successful for the hydroformylation of propylene only, whereas the problem remains with the conversions of higher olefins. Another way to circumvent the separation problem can be the application of immobilized catalysts. An usually low-

ered catalyst activity [2] may partly be balanced with longer lifetimes and easier regeneration. Among the available supports for homogeneous catalysts, silica is most frequently selected as the carrier for rhodium catalysts used for the hydroformylation and/or hydrogenation of olefins. This choice is appealing in view of the low price of silica, its chemical neutrality, and a relatively easy immobilization procedure, often leading to a stable heterogenized catalyst.

Several catalysis experiments with immobilized rhodium complexes have been described in the literature. (i) Rhodium carbonyl thiolate complexes supported on silica exhibit high catalytic activity for the hydroformylation of 1-octene under mild conditions (60 °C, 1 atm CO/H_2) in the presence of an excess of a phosphorus ligand [3–5]. Both highest rate and regioselectivity have been reported in the case of taking $\text{P}(\text{OPh})_3$. It should be mentioned that the chemoselectivity for aldehydes is rather low because of competing isomerization of 1-octene [5]. (ii) Zwitterionic Rh(I) complexes have been heterogenized on partially dehydroxylated

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silica with the formation of hydrogen bonds between the sulfonate ligand coordinated to rhodium and the OH group of silica [6]. This arrangement has been shown to catalyze the hydrogenation of ethene and propene under solid–gas phase conditions, as well as the hydrogenation of styrene and hydroformylation of 1-hexene under solid–liquid phase conditions [6]. (iii) A rhodium complex containing xanthene-based diphosphine, immobilized on polysilicate, is capable of catalyzing the hydroformylation of 1-octene to nonanal and its subsequent hydrogenation to 1-nonanol under a pressure of 50 atm [7]. Variations observed in the selectivity with the method of catalyst preparation appears to be related to the variable acidic properties of the silica support [8]. (iv) Rhodium complexes incorporated into a polysiloxane matrix by the sol–gel method have been applied to the hydroformylation of 1-hexene at 20 atm of CO/H₂ with an average TOF of 164 mol_{sub} mol_{cat}⁻¹ h⁻¹. It is worthy noting that the *n/iso* ratio increases in the presence of PPh₃ taken in excess [9]. (v) Cationic Rh(I) complexes containing modified 1,3-bis(diphenylphosphinyl)propane attached to polysiloxane-based ligands with a spacer of six methylene units have been prepared as stationary phases for chemistry in interphases and applied for hydrogenation of 1-hexene at 10 atm of H₂ giving TOF in toluene of up to 1394 mol_{sub} mol_{cat}⁻¹ h⁻¹ [10]. (vi) The activity of Wilkinson-type catalysts immobilized on silica used for the hydrogenation of dodecene, cyclohexanone, and bromostyrene under H₂ (1.1 bar) has been found to be even comparable to homogeneous systems [11]. In addition, the catalysts can be easily recovered and recycled many times before gradual loss of activity. (vii) Rhodium complexes with diphenylphosphine-functionalized carbosilane dendrimers have been used as catalysts of 1-octene hydroformylation at 10 atm CO/H₂, noting that dendrimers with bidentate end groups gave less active catalysts relative to the monodentate cognates [12].

In the present paper, we describe our experiments of immobilizing two rhodium complexes, Rh(acac)(CO)(Ph₂PC-H₂CH₂Si(OMe)₃) and Rh(acac)(Ph₂PCH₂CH₂Si(OMe)₃)₂, which may be treated as analogs of industrially employed homogeneous catalysts. [Rh(acac)(CO)(PPh₃)] has been used by Union Carbide since nearly 30 years for propylene hy-

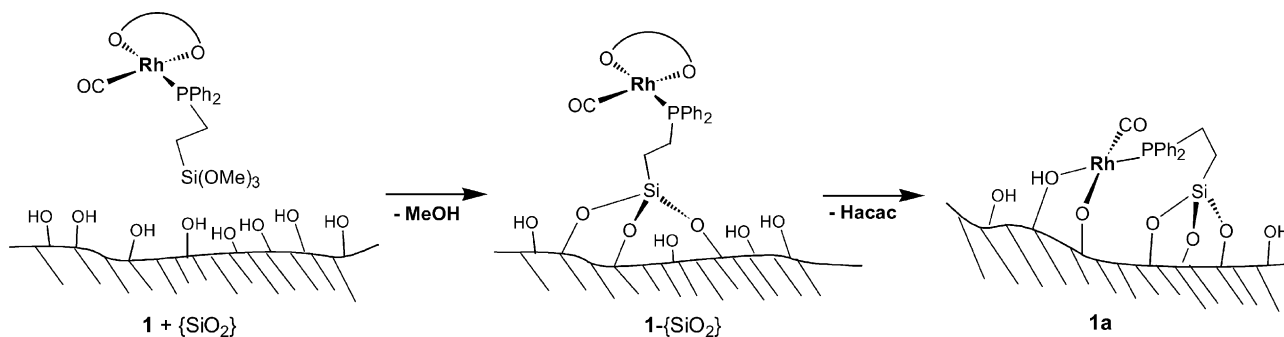
droformylation (Low Pressure Oxo (LPO) process), in the presence of an excess of free PPh₃. The bisphosphite complex Rh(acac)[P(OPh)₃]₂ has been used in the hydroformylation of unsaturated alcohols, dienes, and olefins as well as the hydrogenation of arenes [13–15].

2. Results and discussion

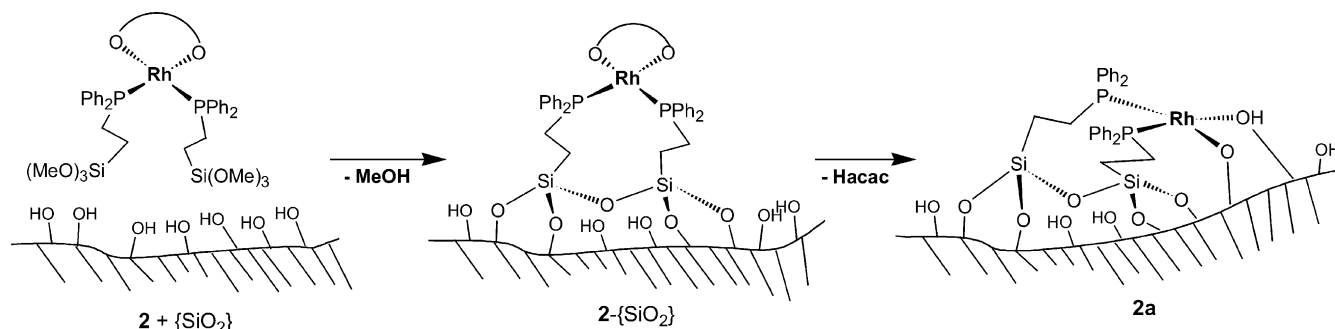
2.1. Preparation and characterization of immobilized rhodium complexes

The rhodium complexes were supported on silica in a two-step synthesis. In the first step, [Rh(acac)(CO)₂] and [Rh(acac)(C₂H₄)₂] were reacted with Ph₂PCH₂CH₂Si(OMe)₃ (henceforth abbreviated to P) giving **1** and **2**, respectively, in 83 and 83% isolated yield. It should be mentioned that it is not feasible to replace both carbonyls in [Rh(acac)(CO)₂] with phosphorus ligands owing to the high π-acceptor strength of CO [16,17]. Therefore, for **2** to be obtained, the more labile complex [Rh(acac)(C₂H₄)₂] was used as the starting material [18]. Both **1** and **2** were characterized by solution and solid state NMR spectroscopy, IR spectroscopy and elemental analysis. The ν(CO) position in the IR spectrum of **1** appears at 1975 cm⁻¹, while that in [Rh(acac)(CO)(PPh₃)] is found at 1982 cm⁻¹. This points to a slightly increased σ-donor property of P relative to PPh₃.

In the second step, **1** and **2** were grafted onto the silica surface by the method described in Section 4. In a similar way, P was tethered to silica (giving P- $\{SiO_2\}$) [19,20] for subsequent use as a modifying ligand in the hydroformylation reactions. However, things are not as simple as initially believed and presented by the complexes [Rh(acac)(CO)(P- $\{SiO_2\}$)] (**1**- $\{SiO_2\}$) and [Rh(acac)(P- $\{SiO_2\}$)₂] (**2**- $\{SiO_2\}$) shown by the first steps in Schemes 1 and 2. On the basis of the shift of the ³¹P-CP/MAS signal from 52.4 to 38.1 ppm for **1** before and after immobilization a change in the rhodium coordination sphere is implicated. In fact, the GC–MS analysis of the toluene supernatants after immobilization revealed the presence of free acetylacetonate (Hacac), obviously formed through protonation of the acac



Scheme 1.



Scheme 2.

ligand by the acidic silica OH groups. Quantitative analysis (GC–MS) shown that amount of Hacac evolved per one immobilized Rh varied from 0.97 to 1.05, confirming practically total removal of acac ligand during immobilization. Therefore, **1**- and **2**-{SiO₂} are better formulated as [Rh(O-{SiO₂})(HO-{SiO₂})(CO)(P-{SiO₂})] (**1a**) and [Rh(O-{SiO₂})(HO-{SiO₂})(P-{SiO₂})₂] (**2a**) (second steps in Schemes 1 and 2).

Hacac was also found in toluene solutions in which rhodium complexes were reacted with P-{SiO₂} and even with neat silica, i.e. in solutions containing [Rh(acac)(CO)₂] + P-{SiO₂}, [Rh(acac)(CO)₂] + SiO₂, and [Rh(acac)(CO)(PPh₃)] + SiO₂. Thus, the acac anion has been replaced with a Si-O⁻ anion and a Si-OH group. A similar Hacac elimination has been observed during the sol–gel impregnation of [Rh(acac)(CO)(siloxantphos)] on silica [8] and protonation of the allyl ligand in [Rh(η³-C₃H₅)₃] by silica [21]. Also, during the immobilization of [Rh(acac)(CO)₂] on ZnAl₂O₄ spinel Hacac displacement became evident [22]. The rhodium content of the heterogenized complexes as determined by inductively coupled plasma (ICP) (after treatment with HCl) was 1.65% for **1a** and 0.48% for **2a**. From single pulse, ³¹P solid state NMR spectroscopy 2.5% of Rh for **1a** was determined.

We employed also another method for tethering the rhodium complex onto the silica surface by reacting [Rh(acac)(CO)₂] with P-{SiO₂}. The product was isolated, washed with toluene, dried, and characterized by IR

spectroscopy. The two ν(CO) frequencies of similar intensities found at 2004 and 2078 cm⁻¹ may be assigned to a silica-attached dicarbonyl rhodium species best described by the formula [Rh(CO)₂(O-{SiO₂})(HO-{SiO₂})] (**3**). It structurally resembles the [Rh(CO)₂]⁺ cation immobilized on ZnAl₂O₄ spinel reported previously [22] with corresponding IR signals appearing at 2015 and 2088 cm⁻¹. The same complex (based on IR data) was formed on treatment of [Rh(acac)(CO)₂] with neat SiO₂. From this comparison it can be concluded that silica oxygens are more basic than the spinel oxygens. It is worth noting that the phosphine moiety in P-{SiO₂} does not displace CO in [Rh(acac)(CO)₂] in contrast to free P.

2.2. XPS studies 1 and 2 before and after immobilization

The X-ray photoelectron spectroscopy (XPS) method has been used for quantitative and qualitative characterizations of the obtained catalysts together with reference samples. The binding energies for Rh 3d_{5/2}, Rh 3d_{3/2}, Si 2p and P 2p as well as atomic ratios of Rh/P and Rh/Si on the surface of the samples are given in Table 1. The numerical binding energies confirm the presence of rhodium in the +1 oxidation state [3]. The slightly varying binding energies observed for Rh(+1) complexes under study may be used for their identification (Fig. 1). Rhodium/phosphorus atomic ratios calculated for **1a** and **2a** correspond very well to the stoichiometric ratios from

Table 1
XPS analysis of pre-catalysts **1a** and **2a** and the reference complexes Rh(acac)(CO)PPh₃ and Rh(acac)(PPh₃)₂

Sample	Binding energy (eV)				Atomic ratio	
	Rh		Si	P	Rh/P	Rh/Si
	3d _{5/2}	3d _{3/2}	2p	2p		
1a	309.38	314.12	103.4	132.55	1.04	2.78 × 10 ⁻²
2a	309.33	314.07	103.37	132.2	0.51	1.84 × 10 ⁻²
Rh(acac)(CO)PPh ₃	308.60	313.64		131.64	0.717	
3	309.8	314.48	103.4			0.89 × 10 ⁻²
Rh(acac)(PPh ₃) ₂	309.34	314.08		131.52	0.5	
2	309.33	314.07	102.2	131.75	0.41	9.12 × 10 ⁻²
P-{SiO ₂ }			103.5	132.2		

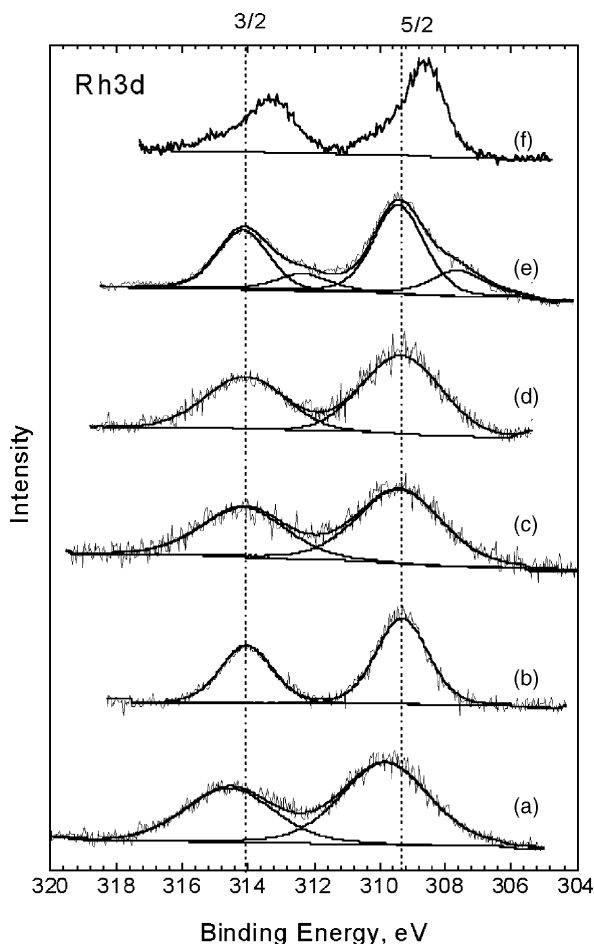


Fig. 1. XPS Rh 3d spectra of samples: (a) **3**, (b) **1**, (c) **1a**, (d) **2a**, (e) (acac)Rh(PPh₃)₂, (f) (acac)Rh(CO)(PPh₃).

the formulas [Rh(O-{SiO₂}){HO-{SiO₂}}(CO)(P-{SiO₂})] and [Rh(O-{SiO₂}){HO-{SiO₂}}(P-{SiO₂})₂].

Binding energies for Si 2p on the level 103.4–103.5 eV characterize the SiO₂ support. These figures were additionally used for the calibration. The binding energy of Si 2p of 102.2 eV for [Rh(acac)(Ph₂PCH₂CH₂Si(OMe)₃)₂] is in accordance with the silicones character of the Si(OMe)₃ group.

The symmetric shape of the P 2p spectra suggest only one form of phosphorus present in each system (PPh₂ or PPh₃). Fig. 2 shows the survey scan of modified silica and a narrow scan of P 2p peak. The determination of binding energies of P 2p were quite difficult due to the small concentration of P ([P]:[Si] = 2.2 × 10⁻²) and partial peak overlap with the satellites from Si 2p. Nevertheless, we were able to fit a value of ca. 132.2 eV.

2.3. Hydroformylation of 1-hexene in the presence of **1a**

Generally, the products obtained are aldehydes and the isomerization product 2-hexene according to Scheme 3 with the product ratio varying dramatically with the kind and amount of phosphine present as a co-catalyst. The results are shown in Table 2 valid for standard 1-hexene hydroformylation reaction conditions and toluene as the solvent. As is seen, in the absence of extra phosphine (entry 2) the conversion was almost quantitative alas with mainly isomerization having taken place. This should be compared with the results of the blank reaction with P-{SiO₂} in the absence of a rhodium complex at otherwise the same conditions in which case only 5% 2-hexene are obtained (entry 1). When the recycled catalyst (after removal of liquids by vacuum transfer) was employed (entries 3 and 4), the products yield remained

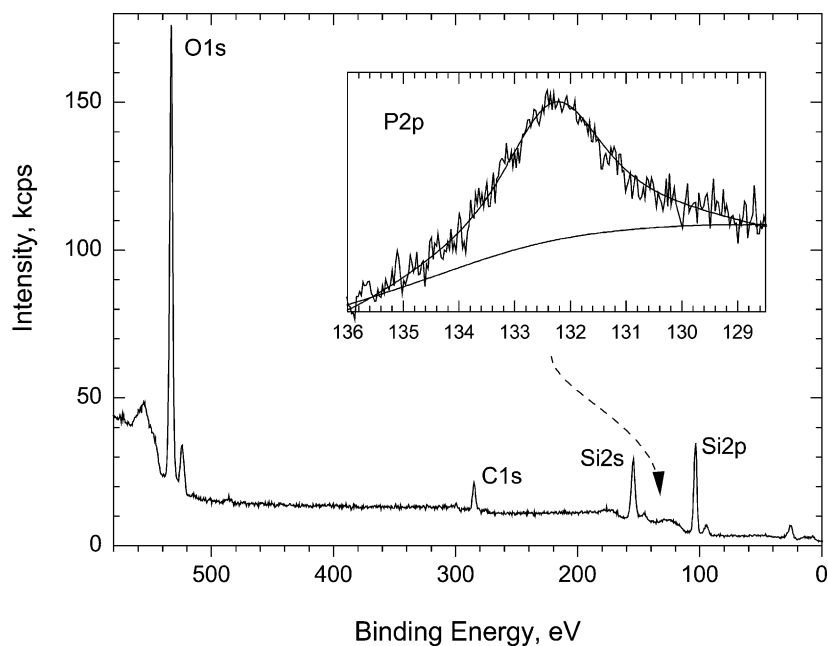
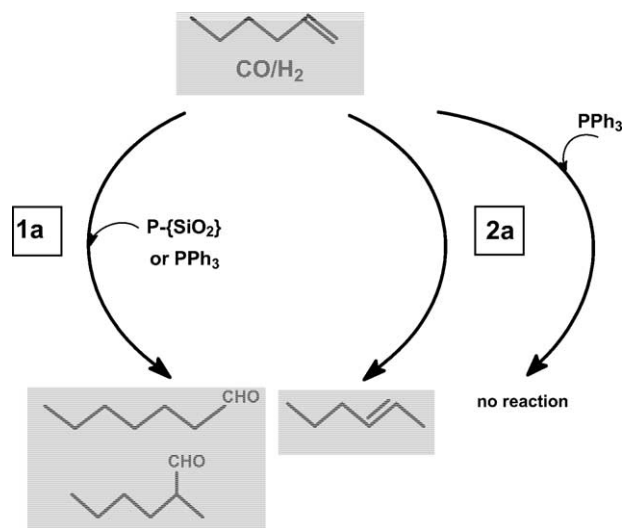


Fig. 2. XPS survey scan of phosphine supported on silica (P-{SiO₂}) and P 2p core-level spectra.



Scheme 3.

similar to this one in the first reaction (entry 2) (2-hexene: 82–84%, aldehydes: 13–15%). When switching over to neat 1-hexene, without toluene, the conversion decreased to 14% aldehydes and 71% 2-hexene (entry 6). Furthermore, lowering the temperature to 60 °C made the yield drop to the low value of 12% 2-hexene (entry 5).

In the presence of an excess of phosphinated silica P- $\{\text{SiO}_2\}$ (entries 7 and 9), the yield of aldehydes increased with concomitant suppression of the isomerization. The

best result (entry 8) was obtained after pre-treatment of **1a** with H_2/CO . Under this condition **1a** might have been transformed to a hydrido-carbonyl species, which is likely the active form of the catalyst. According to IR measurements, **1a** was transformed to a new species after only 1 h treatment under H_2/CO (10 atm, 80 °C).

It is not unexpected that compared to P- $\{\text{SiO}_2\}$ the presence of free PPh_3 is more effective with the results strongly varying with the phosphine concentration (entries 10–14). Thus the yield of aldehydes increased tremendously when the $[\text{PPh}_3]:[\text{Rh}]$ ratio changed from 5 to 19. Likewise, the n/i ratio increased in the same direction. Such a great effect of the phosphine concentration is worth emphasizing. At the lowest concentration used, $[\text{PPh}_3]:[\text{Rh}] = 5$, the product ratio was practically identical with that when no phosphine was present, with 2-hexene being the main product (82% yield). Doubling the concentration of phosphine increased the aldehyde yield from 14 to 86%. Further doubling resulted in a 94% yield.

An excellent result (95% aldehydes) was obtained for catalyst **3**, in the presence of an excess of free PPh_3 . Without adding extra PPh_3 , only 2-hexene was obtained in ca. 85% yield.

Since ICP analysis of rhodium in **1a** after hydroformylation showed a decrease from 1.65 to 1.44–1.45% (entries 11 and 12), or 1.1% (entry 13) depending on separation procedure, some leaching of rhodium during the reaction and participation of a soluble rhodium complex cannot be excluded in the system containing PPh_3 co-catalyst. In

Table 2
Hydroformylation of 1-hexene with **1a**^a

Entry	Additive	[P]:[Rh] ratio	Conversion (%)	Aldehydes yield (%)	2-Hexene ^b yield (%)	n/i	Rh (%)
1	P- $\{\text{SiO}_2\}$ ^c	0	5	–	5	–	–
2	– ^d	0	98	17	81	2.0	1.65
3	– ^d	0	95	13	82	2.1	
4	– ^d	0	97	15	82	2.0	
5	– ^e	0	12	–	12	2.1	
6	– ^f	0	85	14	71	2.2	
7	P- $\{\text{SiO}_2\}$	1.3	92	46	46	2.6	
8	P- $\{\text{SiO}_2\}$	1.3 ^g	70	54	16	2.6	
9	P- $\{\text{SiO}_2\}$	2.6	86	53	33	2.7	1.63 ^l
10	PPh_3	5 ^h	96	14	82	2.6	1.65 ^l
11	PPh_3	7.0 ^h	99	61	38	2.4	1.44 ^j
12	PPh_3	7.0 ^{h,i}	96	49	47	2.9	1.45 ^j
13	PPh_3	9.5 ^g	98	86	12	2.7	1.1 ^k
14	PPh_3	19.0 ^g	98	94	4	3.6	

^a Reaction conditions: 80 °C, 10 atm H_2/CO , 5 h, 1.5 cm³ of toluene, 1.5 cm³ of 1-hexene, [1-hexene]:[Rh] = 2400, P- $\{\text{SiO}_2\}$ = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si-}\{\text{SiO}_2\}$.

^b The mixture of *cis/trans* 2-hexenes/3-hexene was not found.

^c Blank experiment without **1a** pre-catalyst.

^d Catalyst recovered from the previous reaction and reused.

^e Reaction at 60 °C.

^f Reaction in neat 1-hexene.

^g Pre-catalyst **1a** activated for 3 h in toluene at 80 °C under 10 atm of H_2/CO before introduction of substrates.

^h Reaction time = 2.5 h.

ⁱ Catalyst recovered and reused with the new portion of PPh_3 .

^j Rhodium content (determined by ICP) in pre-catalyst separated after reaction by ultrafiltration.

^k Rhodium content (determined by ICP) in pre-catalyst separated after reaction by filtration.

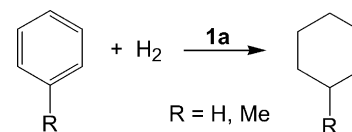
contrast, the rhodium content in **1a** recovered after reaction performed with P-{SiO₂} was practically unchanged (entry 9). We observed, that at higher excess of PPh₃ ([PPh₃]:[Rh] > 7) the density of solution increased and separation of catalyst by normal filtration was not complete. Some amounts of catalyst still remained in solution forming very fine suspension. This was confirmed by two experiments in which post-reaction solution was used for the next hydroformylation reaction. The solution obtained by normal filtration (from entry 13) gave 39% of aldehydes and only 13% of aldehydes were obtained with ultra-centrifugated solution from entry 11.

2.4. Hydroformylation of 1-hexene with **2a**

Catalytic tests with **2a** were performed under the same conditions as for **1a**. The reaction in neat 1-hexene produced only 29% of 2-hexene and traces of aldehydes. A better result (65% 2-hexene, 5% aldehydes) was obtained with toluene as the solvent (Table 3). The recycled catalyst was less active and produced mainly 2-hexene (90%) and only 7% of aldehydes. However, the product distribution remained unchanged upon using the recovered catalyst for the third time. The fact that 2-hexene was the main product instead of aldehydes appears to be related to the high ability of **2a** to catalyze the double bond shift noting the low *n/i* ratio (ca. 1.4) of the aldehydes formed. When the reaction was performed in the presence of PPh₃ very low conversion (4%) of 1-hexene to 2-hexene was observed.

2.5. Hydrogenation of benzene and toluene with pre-catalyst **1a**

Pre-catalyst **1a** used alone (i.e. without a phosphine co-catalyst) catalyzed also the hydrogenation of aromatic hydrocarbons such as benzene and toluene with 14–17% yields in 3 h (Scheme 4). The results are presented in Table 4. The yield increased to 31% when the catalyst was pretreated by heating at 90 °C under an atmosphere of H₂ (10.5 atm) for 3 h. The completely opposite effect, i.e. inhibition of hydrogenation, occurred upon treatment of **1a** with H₂/CO before adding benzene in which case no cyclohexane was formed.



Scheme 4.

A slightly better result (7% cyclohexane) was obtained with a catalyst that was recovered after 1-hexene hydroformylation. It can thus be concluded that CO acts as an inhibitor of the hydrogenation reaction, obviously due to strong bonding to rhodium. IR studies showed the presence of rhodium carbonyl clusters in a sample of **1a** reacted with CO.

2.6. IR studies of reactions of **1a** with H₂, CO, and H₂/CO

IR spectroscopy was used for the preliminary identification of the immobilized complexes formed upon treatment of **1a** with both H₂ and CO as well as with an H₂/CO mixture in the absence of 1-hexene. All experiments were performed in toluene (80 °C, 10 atm, 2 h). The IR spectra of the isolated complexes are shown in Fig. 3. Spectrum (A) belongs to **1a** heated under CO indicating the formation of a new species. The $\nu(\text{CO})$ at 1975 cm⁻¹ of the starting complex disappeared while three new bands at 1802 cm⁻¹ (bridging CO), 2009, and 2076 cm⁻¹ (both terminal CO) formed which may be attributed to a Rh(0) carbonyl species (Table 5). We suspect that the reduction of rhodium in the presence of CO is facilitated at the silica surface, since under the same conditions from soluble [Rh(acac)(CO)(PPh₃)] only small amounts of [Rh(acac)(CO)₂] are formed but no Rh(0) species. The participation of silica in the reduction process has been reported also for other supported rhodium complexes [23]. Likewise, the formation of rhodium carbonyls containing bridging CO groups was observed when **1a** reacted with CO in the presence of P-{SiO₂}. In contrast, no noticeable reaction with CO took place in the presence of PPh₃ as indicated by the $\nu(\text{CO})$ band at 1976 cm⁻¹ being essentially identical with that of **1a**.

The reaction of **1a** with H₂ leads to an unstable hydrido species characterized by a strong absorption at 2015 cm⁻¹ ($\nu(\text{Rh-H})$) together with lower intensity bands at 2040 and

Table 3
Hydroformylation of 1-hexene with **2a**^a

Entry	Catalyst (g)	Solvent	Conversion (%)	2-Hexene (%)	Aldehydes (<i>n + i</i>) (%)	<i>n/i</i>
15	0.08	–	30	29	1	1.3
16	0.08	Toluene	70	65	5	1.9
17	0.08 ^b	Toluene	97	90	7	1.4
18	0.07 ^c	Toluene	96	89	7	1.4

^a Reaction conditions: 80 °C, 10 atm H₂/CO, 5 h, 1.5 cm³ of toluene, 1.5 cm³ of 1-hexene or 3 cm³ of 1-hexene; [1-hexene]:[Rh] = 3200.

^b Second run with recycled catalyst.

^c Third run with recycled catalyst.

Table 4
Hydrogenation of benzene and toluene with **1a**^a

Entry	Substrate	Pre-treatment a catalyst in the absence of substrate	Product	Yield (%)	TOF (h ⁻¹)
19	Benzene		Cyclohexane	14	274
20	Benzene	Catalyst recovered after benzene hydrogenation ^b	Cyclohexane	17	494
21	Benzene	3 h, 10.5 atm of H ₂	Cyclohexane	31	608
22	Benzene	3 h, 10.5 atm of H ₂ /CO	–	–	–
23	Benzene	Catalyst recovered after hydroformylation (5 h)	Cyclohexane	7	137
24	Toluene		Methyl-cyclohexane	17	278

^a Reaction conditions: 10.5 atm of H₂, 90 °C, 4 cm³ of substrate (without solvent), *m*_{cat} 0.03 g (1.65% Rh), 5 h.

^b *m*_{cat} 0.02 g.

2080 cm⁻¹ (**B**). A very weak $\nu(\text{CO})$ band of a bridging CO ligand was observed at 1844 cm⁻¹. Similar spectra were obtained for the reaction products of **1a** heated with an H₂/CO mixture as well as for the catalyst isolated after the hydroformylation reaction test (**C**). The IR spectra of fresh samples taken out of the autoclave showed bands only in the 2000–2068 cm⁻¹ range, which can be assigned to terminal $\nu(\text{CO})$ frequencies and $\nu(\text{Rh-H})$. In the region of bridging CO groups (1800–1850 cm⁻¹) merely low intensity bands were observed. However, after a few minutes of evacuation an intensive absorption at 1800 cm⁻¹ appeared confirming

Table 5
IR data (in KBr) of **1a** exposed to CO, H₂ and CO/H₂ (80 °C, 10 atm, 2 h)

Reaction of 1a with	$\nu(\text{CO})$ and $\nu(\text{Rh-H})$
1a (neat)	1975
CO	1800 m, 2009 m, 2076 s
CO, P- $\{\text{SiO}_2\}$	1800 m, 2003 m, 2073 s
CO, PPh ₃	1976
H ₂	2015 s, 2040 m, 2074 s
H ₂ /CO	2022 s, 2048 s, 2075 s
H ₂ /CO, evacuation	1800 m, 2021 m, 2045 m, 2073 vs
H ₂ /CO, PPh ₃	1942 m, 1970 vs, 2005 s, 2050 w

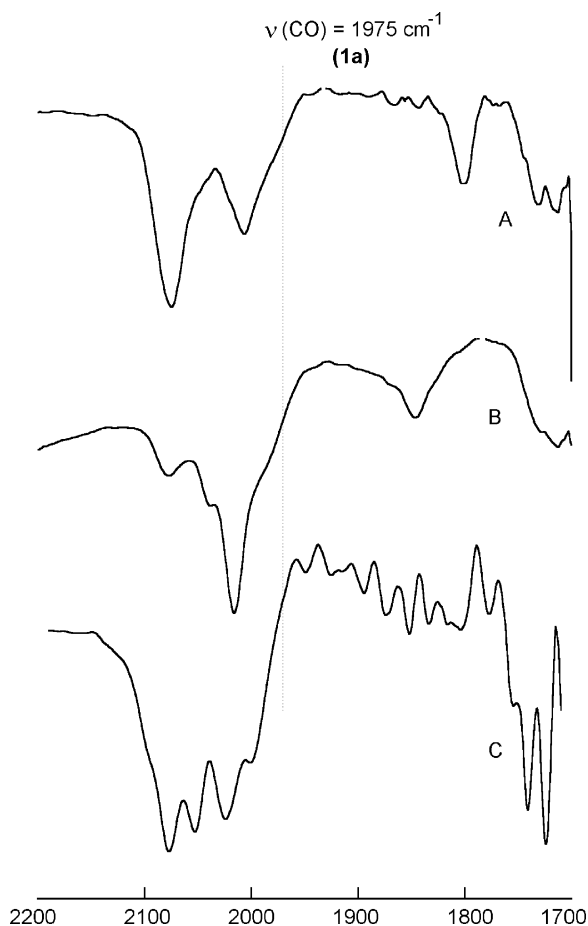


Fig. 3. IR spectra of complex **1a** after reaction with: (A) CO, (B) H₂, (C) H₂/CO (1:1) at 10 atm and 80 °C for 2 h.

the formation of a Rh(0) carbonyl complex with bridging CO. Also, in this case, the formation of an Rh–CO–Rh core is prevented by added PPh₃ and, therefore, only terminal carbonyls are detected in the IR spectrum (Table 5). The catalyst isolated after a reaction performed with the addition of PPh₃ shows an IR spectrum with three bands at 1946, 1974, and 2050 cm⁻¹ which may be assigned to $\nu(\text{CO})$ of terminal carbonyls and possibly to $\nu(\text{Rh-H})$.

3. Conclusions

1. Rhodium complexes [Rh(acac)(CO)(Ph₂PCH₂CH₂Si(OMe)₃)] (**1**) and [Rh(acac)(Ph₂PCH₂CH₂Si(OMe)₃)₂] (**2**) were found as convenient precursors for immobilization at silica and designing of new pre-catalysts.
2. It was proved, that during immobilization Hacac is completely removed after protonation by silica proton.
3. Immobilized complexes, [Rh(O- $\{\text{SiO}_2\}$)(HO- $\{\text{SiO}_2\}$)(CO)(P- $\{\text{SiO}_2\}$)] (**1a**) and [Rh(O- $\{\text{SiO}_2\}$)(HO- $\{\text{SiO}_2\}$)(P- $\{\text{SiO}_2\}$)₂] (**2a**), were characterized with ³¹P-CP/MAS, XPS and IR methods. The Rh/P ratios on the surface were determined as equal 1.04 for **1a** and 0.51 for **2a**, confirming complexes composition.
4. The pre-catalyst **1a** was found more active both in hydroformylation and in isomerization of 1-hexene compared with **2a**. Additionally **1a** catalyze hydrogenation of aromatic hydrocarbons (benzene and toluene).
5. P- $\{\text{SiO}_2\}$ as well as PPh₃ can be used as co-catalysts with **1a**, however, high concentration of PPh₃ may lead to

some rhodium leaching as well as creates some problems with separation of catalyst from the solution.

4. Experimental

4.1. General remarks

All manipulations were performed under an inert atmosphere of nitrogen or argon by using Schlenk techniques and a glove box. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures. The deuterated solvents were dried over 4 Å molecular sieves. All experiments were carried out with Merck silica (specific surface area $388 \pm 2 \text{ m}^2 \text{ g}^{-1}$). The silica has been treated in an UV-cleaning chamber prior to use to remove adsorbed organic impurities but has not been dried at elevated temperatures. $[\text{Rh}(\text{acac})(\text{CO})_2]$ and $[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$ were obtained according to literature methods [24,25].

Solution ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance-250 spectrometer operating at 250.13, 62.86, and 101.26 MHz, respectively, and were referenced to SiMe_4 and H_3PO_4 (85%). Infrared spectra were recorded on Mattson RS-10000, Nicolet Impact 400 and Perkin-Elmer 16PC FT-IR spectrometers. All solid-state ^{31}P -NMR spectra were recorded on a Bruker Avance 300 spectrometer (standard bore), equipped with a 4 mm broad-band MAS probe-head and ZrO_2 rotors. The rotational speed for all experiments was 12 kHz. Phosphorous spectra were referenced with respect to 85% $\text{H}_3\text{PO}_4(\text{aq})$ by setting the ^{31}P NMR peak of solid PPh_3 to -7.0 ppm. ^{31}P -CP/MAS spectra (cross polarization with magic angle spinning) were measured with a contact time of 3 ms and a relaxation delay of 6 s. Quantitative measurements were done by ^{31}P single pulse experiments with a relaxation delay time of 120 s. The reaction products obtained from hydroformylation and hydrogenation reactions were analyzed with GC-MS Hewlett-Packard 5890 II + Hewlett-Packard 5971 A instruments.

XPS spectra were recorded on SPECS UHV/XPS/AES system using Mg-K α source for excitation and equipped with a hemispherical analyzer operating in fixed analyzer transmission (FAT) mode with pass energy 10 or 20 eV. A power setting of 10 kV and 120 W was applied. The working pressure in an analyzing chamber was $<5 \times 10^{-10}$ mbar. The binding energy (BE) scale was calibrated by taking the Au 4f $_{7/2}$ peak at 84 eV. Correction of the energy shift due to the static charging of the samples was accomplished using as reference the C 1s peak at 284.8 eV and additionally where it was possible the Si 2p peak taken at 103.4 eV. The accuracy of the reported binding energies was ± 0.1 eV. For the XPS analysis, all sample specimens were obtained by pressing sample powders into thin disks which were mounted on sample holders and placed in a pre-chamber, outgassed to $<10^{-8}$ mbar at room temperature, and then transferred

to the analysis chamber. Stability of Rh spectra during the XPS measurements was proved by a series of successive measurements. The spectra were collected and processed by SpecsLab software. The data analysis procedure involved the following steps: data smoothing, background calculation.

4.2. Synthesis of complexes 1 and 2

4.2.1. $[\text{Rh}(\text{acac})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OMe})_3)] \mathbf{1}$

$[\text{Rh}(\text{acac})(\text{CO})_2]$ (100 mg, 0.387 mmol) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ (130 mg, 0.387 mmol) dissolved in 5 ml CH_2Cl_2 were stirred for 4 h at room temperature. The color changed from orange to dark green. After evaporation of the solvent the product was washed twice with Et_2O (10 ml) and separated as a dark green oil. Yield: 182 mg (83%). Analytically calculated for $\text{C}_{23}\text{H}_{30}\text{O}_6\text{PRhSi}$ (MG = $564.46 \text{ g mol}^{-1}$): C, 48.94; H, 5.34. Found: C, 49.09; H, 5.22. ^1H NMR (acetone- d_6 , 20 °C): $\delta = 7.61\text{--}7.47$ (m, 10H, PPh_2), 5.51 (s, 1H, MeCOCHCOMe), 3.49 (s, 9H, $\text{Si}(\text{OMe})_3$), 2.01 (s, 3H, MeCOCHCOMe), 1.81 (s, 3H, MeCOCHCOMe), 2.57–2.50 (m, 2H, PCH_2CH_2), 0.85–0.78 (m, 2H, PCH_2CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 20 °C): $\delta = 190.4$ (dd, $J_{\text{CRh}} = 76.1 \text{ Hz}$, $J_{\text{CP}} = 25.6 \text{ Hz}$, CO), 188.0 (s, MeCOCHCOMe), 185.4 (s, MeCOCHCOMe), 134.1 (d, $J_{\text{CP}} = 48.4 \text{ Hz}$, Ph^1), 133.5 (d, $J_{\text{CP}} = 10.4 \text{ Hz}$, $\text{Ph}^{2,6}$), 130.7 (d, $J_{\text{CP}} = 2.0 \text{ Hz}$, Ph^4), 128.7 (d, $J_{\text{CP}} = 9.7 \text{ Hz}$, $\text{Ph}^{3,5}$), 100.5 (s, MeCOCHCOMe), 50.2 (s, $\text{Si}(\text{OMe})_3$), 27.1 (s, MeCOCHCOMe), 26.4 (s, MeCOCHCOMe), 20.8 (d, $^1J_{\text{CP}} = 29.1 \text{ Hz}$, PCH_2CH_2), 4.3 (d, $^2J_{\text{CP}} = 2.8 \text{ Hz}$, PCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 20 °C): $\delta = 50.0$ (d, $^1J_{\text{PRh}} = 173.7 \text{ Hz}$, PPh_2). IR $\nu(\text{CO})$ 1975 cm^{-1} . ^{31}P -CP/MAS spectrum: $\delta = 52.4$ ppm.

4.2.2. $[\text{Rh}(\text{acac})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_2] \mathbf{2}$

$[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2]$ (100 mg, 0.387 mmol) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{Si}(\text{OMe})_3$ (258 mg, 0.772 mmol) dissolved in 5 ml CH_2Cl_2 were stirred for 4 h at room temperature. The color changed from orange to red. After evaporation of the solvent the product was washed twice with petroleum ether (10 ml) and separated as a yellow solid. Yield: 278 mg (83%). Analytically calculated for $\text{C}_{39}\text{H}_{53}\text{O}_8\text{P}_2\text{RhSi}_2$ (MG = $870.02 \text{ g mol}^{-1}$): C, 53.79; H, 6.13. Found: C, 53.97; H, 6.40. ^1H NMR (acetone- d_6 , 20 °C): $\delta = 8.11\text{--}7.93$ (m, 4H, PPh_2), 7.65–7.43 (m, 4H, PPh_2), 7.40–7.20 (m, 8H, PPh_2), 6.83–6.70 (m, 4H, PPh_2), 5.36 (s, 1H, MeCOCHCOMe), 3.43 (s, 18H, $\text{Si}(\text{OMe})_3$), 3.25–3.12 (m, 2H, PCH_2CH_2), 3.04–2.83 (m, 2H, PCH_2CH_2), 1.97 (s, 6H, MeCOCHCOMe), 0.29–0.14 (m, 2H, PCH_2CH_2), 0.12–0.05 (m, 2H, PCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6 , 20 °C): $\delta = 33.9$ (d, $^1J_{\text{PRh}} = 132.7 \text{ Hz}$, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 20 °C): $\delta = 184.4$ (s, MeCOCHCOMe), 135.0 (t, $J = 4.60 \text{ Hz}$, Ph), 133.4 (t, $J = 3.45 \text{ Hz}$, Ph), 131.1 (t, $J = 1.41 \text{ Hz}$, Ph), 131.1 (d, $J = 9.12 \text{ Hz}$, Ph), 130.5 (t, $J = 1.44 \text{ Hz}$, Ph), 128.9 (d, $J = 11.5 \text{ Hz}$, Ph), 128.5 (t, $J = 4.56 \text{ Hz}$, Ph), 128.3 (t, $J = 5.04 \text{ Hz}$, Ph), 98.6 (s, MeCOCHCOMe), 50.2 (s, $\text{Si}(\text{OMe})_3$), 27.5

(dt, $J_1 = 4.56$ Hz, $J_2 = 0.64$ Hz, PCH₂CH₂), 22.7 (s, MeCOCHCOMe), 3.3 (t, $J = 5.04$ Hz, PCH₂CH₂). ³¹P-CP/MAS spectrum: $\delta = 35.8$ ppm.

4.3. Immobilization of Ph₂PCH₂CH₂Si(OMe)₃, **1**, and **2**

The phosphine ligand Ph₂PCH₂CH₂Si(OMe)₃ as well as complexes **1** and **2** were immobilized by rigorously stirring a suspension of SiO₂ and an appropriate amount of ligand or complex (typically 0.280 mmol of substrate per 250 mg of SiO₂) in 18 ml of toluene under an atmosphere of dry nitrogen for 24 h at room temperature. The solid was separated by centrifuging. Upon removal of the supernatant, the silica was washed several times with dry toluene and CH₂Cl₂ and again centrifuged. The samples were dried under vacuum at room temperature for 24 h and characterized by means of ³¹P-CP/MAS NMR spectroscopy exhibiting signals at -14.7, 35.3, and 37.2 ppm, respectively, for immobilized Ph₂PCH₂CH₂Si(OMe)₃, **1**, and **2**.

The surface coverage was determined by means of ³¹P MAS NMR spectroscopy integrating the ³¹P signals of mixtures of the surface-immobilized compounds together with a weighted amount of [NBu₄]⁺PF₆⁻ as a standard utilizing single pulse experiments with a pulse delay of 120 s. The integral of the ³¹P signal of PF₆⁻ counterion in **1** has been set to unity. Values for the surface coverage for Ph₂PCH₂CH₂Si(OMe)₃ and **1** are 52 molecules/100 nm² ($8.63 \cdot 10^{-4}$ mmol m⁻²) and 44 molecules/100 nm² ($7.3 \cdot 10^{-4}$ mmol m⁻² = 2.5 mol% Rh).

4.4. Hydroformylation and hydrogenation reactions

Hydroformylation reactions have been performed in a steel autoclave (50 cm³) with magnetic stirring at 80 °C and 10 atm H₂/CO = 1. A suitable amount of catalyst in small Teflon vessel, 1.5 cm³ of toluene and 1.5 cm³ of 1-hexene were introduced to the autoclave in N₂ atmosphere. The autoclave was closed, filled with H₂ (5 atm) and with CO up to 10 atm. After the reaction the autoclave was cooled down and the liquid sample was analyzed by GC-MS. Hydrogenation reactions have been performed in a similar manner in 150 cm³ steel autoclave at 90 °C and 10.5 atm of H₂.

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