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Synthesis and Characterization of Poly(alumosiloxane)-Bound (Ether−phosphine)ruthenium(II) Complexes[1,2]

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The trimethoxysilyl-(T)-functionalized ruthenium(II) complex *cis*-$\mathrm{Cl(H)Ru(CO)(P{\sim}O)_3}$ [$\mathbf{2(T^0)_3}$] (P$\sim$O: P-coordinated ether−phosphine) is sol−gel processed with tetraethoxysilane (TEOS, $\mathbf{Q^0}$) and aluminum 2-propanolate [Al(O*i*Pr)$_3$]. All components are simultaneously polycondensed to result in the poly(alumosiloxane)-bound ruthenium complexes **A** and **B** with various amounts of aluminum. From ^{31}P and ^{13}C CP MAS NMR as well as IR spectroscopy it can be concluded that the complex fragment *cis*-$\mathrm{Cl(H)Ru(CO)(P{\sim}O)_3}$ is preserved during the immobilization. Polymers **A** and **B** show a remarkable number of Si−O−Al bonds in the ^{29}Si solid state NMR spectra. The aluminum is incorporated as tetrahedrally coordinated AlO$_4$ units with a formal negative charge. The 6-fold coordinated AlO$_6$ groups containing water and hydroxide groups as ligands are sited as interstitials and act as their counterions. Stoichiometric formulas of **A** and **B** derived by ^{27}Al and ^{29}Si solid state NMR spectroscopy and energy dispersive X-ray spectroscopy (EDX) suggest that the amount of aluminum can be adjusted by the applied stoichiometry. The two materials **A** and **B** act as hydrogenation catalysts of *trans*-crotylaldehyde and are easy to separate from the reaction mixture by simple centrifugation.

Introduction

Chemical systems in which the reactive centers are bound to polymeric matrices are gaining increasing significance.[2−17] The immobilization of transition metal complexes leads to systems which are able to combine the advantages of homogeneous and heterogeneous catalysis. In particular the presence of an adequate solvent or substrate (mobile phase) gives rise to a swelling of the polymers (stationary phase). The resulting mixture of a mobile and a stationary phase on a molecular scale is called “interphase”. Interphases are able to combine the adjustable activities and selectivities of homogeneous reaction types with a repeated use of the catalyst.[18−20]

Various strategies to build up stationary phases, consisting of the matrix, the spacer, and the reactive center, have been developed. Surface modified silica gel is widely used as a carrier matrix, since it is chemically resistant and its surface properties are well-defined. However, there are some problems with these systems: (i) the loading of the catalysts is low and limited by the external surface of the silica gel; (ii) catalysts leach from the support during catalysis due to low degrees of condensation of the ligands to the silica gel surface; (iii) poor swelling abilities of the silica gel reduce the formation of interphases.

One approach to overcome these problems is the simultaneous cocondensation of organo-(T)-silyl-functionalized transition metal complexes with D, T, or Q alkoxysilanes [$\mathrm{D = R_2Si(OR')_2}$, $\mathrm{T = RSi(OR')_3}$, $\mathrm{Q = Si(OR')_4}$; R, R′ = Me, Et] (sol-gel process).[21] The obtained two- and three-dimensional networks are stationary phases, in which the amount of the catalyst, the polarity of the matrix , and the mobility of the reactive centers can be varied in a wide range.[13,16] Furthermore, the detachment of the reactive centers is strongly reduced by the high degrees of condensation of these materials.

Lately it was demonstrated that Mg^{2+} doped samples of the T-functionalized (ether−phosphine)ruthenium(II) complex *cis*-$\mathrm{Cl(H)Ru(CO)(P{\sim}O)_3}$ (P$\sim$O: η^1-P-coordinated ether−phosphine ligand) show a remarkable catalytic activity in the hydrogenation of *n*-butyraldehyde.[13] The much higher turnover frequencies compared to samples without Mg^{2+} have been traced back to a

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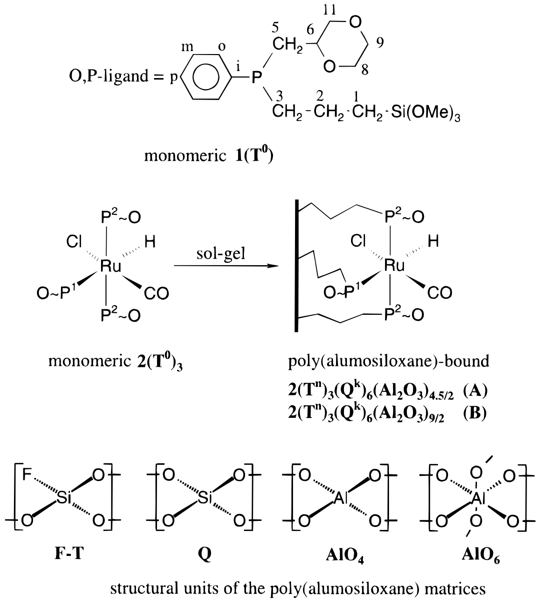
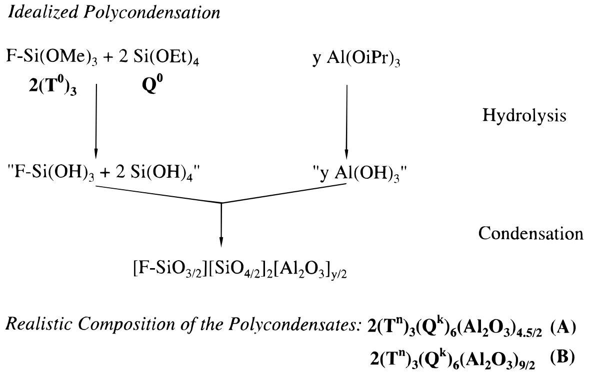
Scheme 1



Scheme 2



$F = [HRuCl(CO)]_{1/3}P(Ph)(CH_2CH_2OCH_2CH_2OCH_2)CH_2CH_2CH_2$-

T^n: T type silicon atom (three oxygen neighbors)

Q^k: Q type silicon atom (four oxygen neighbors)

k, n = number of Si-O-Si bonds

(Al_2O_3): formal description for all aluminum species (AlO_4 and AlO_6)

y = 4.5 (**A**) or 9.0 (**B**)

smaller particle size and a lower degree of condensation. In addition the partially ionic character of the Mg^{2+} doped polysiloxanes is responsible for a better separability of the stationary phase from the reaction mixture of *n*-butyraldehyde and *n*-butyl alcohol. However, the incorporation of Mg^{2+} lowers the degree of cross-linkages, which is not desirable for the long-time stability of the catalysts. It is thus of interest to find other sol−gel routes, which introduce ionic charges and do not decrease the cross-linkage of the matrices. Polyalumosiloxanes are promising candidates for such matrices, because aluminum is incorporated into the network via covalent bonds and accounts for ionic charges.

In all experiments we employed "hemilabile" ligands like ether−phosphines, which are strongly coordinated to the metal center via the phosphorus atom, while the weaker donor in the form of an ether moiety takes over the function of an intramolecular solvent in a catalytic cycle (see Scheme 1).[22]

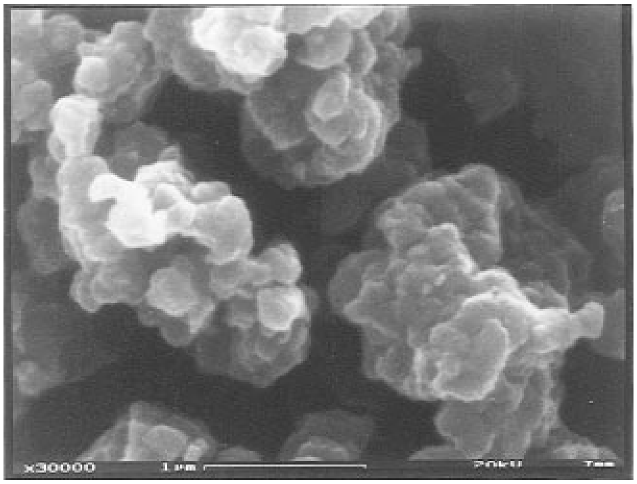


Figure 1. Scanning electron micrograph of the poly(alumosiloxane)-bound ruthenium complex **A**.

The new materials were characterized by multinuclear solid-state NMR spectroscopy.[23,24] The stereochemistry of the metal complexes, the integrity of the spacers, and the ligand backbone were established by ^{31}P and ^{13}C CP MAS NMR spectroscopy. ^{29}Si CP MAS and ^{27}Al MAS NMR spectroscopy were applied to characterize the poly(alumosiloxane) support. Furthermore energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM) were used to describe the materials. The catalytic properties were investigated in the case of the hydrogenation of *trans*-crotylaldehyde.

Results and Discussion

Sol−Gel Processing. The synthesis of the poly(alumosiloxane)-bound (ether−phosphine)ruthenium(II) complexes **A** and **B** was performed in a simultaneous sol−gel process (Scheme 2). In the first step two different amounts of $Al(OiPr)_3$ acting as aluminum-containing precursors were suspended in MeOH and hydrolyzed with an excess of water. Subsequently the resulting sols were added to mixtures of the monomeric complex *cis*-$Cl(H)Ru(CO)(P{\sim}O)_3$ [$\mathbf{2(T^0)_3}$] (Scheme 1) and $Si(OEt)_4$ ($\mathbf{Q^0}$) [Si(T):Si(Q):Al = 3:6:4.5 (**A**), 3:6:9 (**B**)]. To start the hydrolysis $Sn(OAc)_2(n\text{-}Bu)_2$ is necessary as a catalyst. The polycondensations are initiated with 1 M NaOH. In the course of the addition of aqueous NH_4HCO_3 voluminous gels precipitated. After washing and drying, gels **A** and **B** were obtained as ultrafine powders. The polymers consist of relatively small particles in the range of 0.1−0.5 μm [e.g., **A** in Figure 1]. Their BET surface areas are 60 and 70 m^2/g for **A** and **B**, respectively.

^{31}P, ^{13}C CP MAS NMR and IR Spectroscopic Characterization of Polymers A and B. The ^{31}P CP MAS NMR spectra of the cocondensed ruthenium complexes **A** and **B** display two isotropic signals caused by the different environments of the phosphorus nuclei P^2 and P^1 (Figure 2, Scheme 1). The chemical shifts of $\delta = +20$ (P^2) and -3 (P^1) correspond to those of the monomeric precursor complex $\mathbf{2(T^0)_3}$.[13] The line widths and the spinning side bands of the two compounds are basically identical. The IR spectra show only one absorption in the carbonyl region. Its frequency is in agreement with that of the monomeric complex $\mathbf{2(T^0)_3}$ in solution.[13] In addition to the ^{13}C resonances, which are attributed to the phenyl and ether carbon atoms (see Experimental Section), the ^{13}C CP MAS NMR spectra of these complexes reveal a complex pattern in the region between 28 and 13 ppm. This indicates the integrity of the ether−phosphine ligand, in particular the existence of

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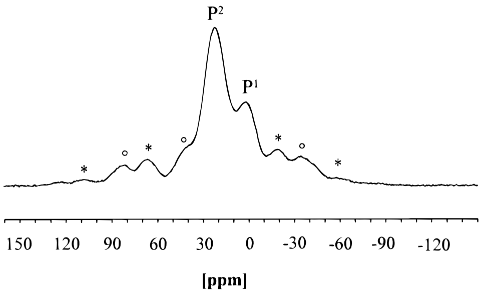

Figure 2. ^{31}P CP MAS NMR spectrum of material **A**. The spinning side bands of P^1 and P^2 are labeled with ○ and *, respectively.

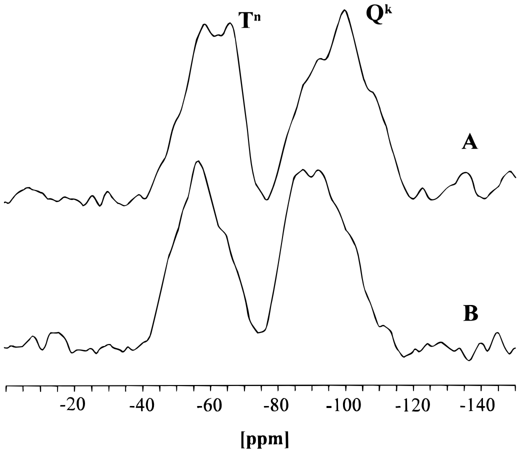

Figure 3. ^{29}Si CP MAS NMR spectra of **A** (top) and **B** (bottom).

the intact carbon−phosphorus and carbon−silicon bonds.[25] From this result we conclude that the supported ruthenium complexes in **A** and **B** are well-preserved throughout the sol−gel process and that the local vicinity of the phosphorus atoms, e.g., the geometry and flexibility of **A**, **B**, is comparable.

Characterization of the Poly(alumosiloxane) Matrices by ^{29}Si, ^{27}Al Solid State NMR Spectroscopy and Energy Dispersive X-ray Spectroscopy (EDX). In Figure 3 the ^{29}Si CP MAS NMR spectra of polymers **A** and **B** are displayed. They show two sets of resonances corresponding to the T^n type ($\delta = -47$ to -67) and Q^k type of silyl species ($\delta = -82$ to -110). The signals of the silyl groups are broad and structureless compard to the pure polysiloxane matrices. This is due to the formation of Si−O−Al bonds so that a total number of 15 Q^k and 9 T^n species may result. Both, Si−OH and Si−O−Al linkages lead to a downfield shift in the ^{29}Si solid state NMR spectra compared to Q^4 and T^3 units.[23,24] The increasing incorporation of aluminum into the matrix is thus reflected in a downfield shift of the centers of gravity of the Q^k and T^n groups in the ^{29}Si CP MAS NMR spectra of **A** and **B**. From the peak deconvolution three different T^n types ($n = 1-3$) and up to five different Q^k species ($k = 0-4$) are identified (see Table 1). On the basis of ^{29}Si CP MAS NMR spectroscopy a distinction between Si−O−Al and Si−OH is not possible. Because the silyl species show different cross-polarization dynamics, e.g., T_{SiH} and $T_{1\rho H}$, the intensities I_0 of the deconvoluted CP MAS spectra have to be corrected.[26−28] The experimentally determined T:Q ratios of 3:4.1 and 3:3.8 for **A** and **B**, respectively, are less than expected from the stoichiometric amounts applied. This suggests that some of the Q groups are incorporated into the matrix as bulk siloxane groups, e.g., $Si(O-Si)_4$ or $Si(O-Al)_4$, which cannot be detected by CP MAS NMR spectroscopy.[29,30] Therefore it was necessary to run ^{29}Si MAS single pulse excitation (SPE) NMR spectra to obtain the real T:Q ratio (Table 1). The deconvolution of the ^{29}Si SPE NMR spectra results in T:Q ratios of 3:6.1 (**A**) and 3:5.9 (**B**), which reflect the employed stoichiometry of T:Q, equals 3:6 quite well.

In the ^{27}Al MAS NMR spectra of compounds **A** and **B** two resonances are observed at $\delta = 56.5$ and 2.5 (see Figure 4 for polymer **B**). The chemical shifts are typical for tetrahedrally and octahedrally coordinated AlO_6 and AlO_4 units.[23,24] Although the quadrupolar coupling constants (QCC) of both alumina coordinations are in the same order of magnitude and no 5-fold coordinated AlO_5 species are detected in the 2D ^{27}Al Nutation NMR spectrum (see Figure 5), the ^{27}Al MAS NMR spectra of compounds **A** and **B** cannot be quantified just by simple integration of the peak areas.[31] The tetrahedrally coordinated AlO_4 species are incorporated into the polysiloxane framework and replace SiO_4 sites. This substitution leads to a formal negative charge per AlO_4 unit in the matrix. The 6-fold coordinated AlO_6 species can act as their counterions. It is expected that they are located between the Si(T)−Si(Q)−AlO_4 layers as interstitials and that their coordination sphere is a mixture of Al−O−Si, Al−OH, and Al−OH_2 species (see Scheme 2).

To determine the elemental composition and hence the Si:Al ratio of the sol−gel processed materials **A** and **B**, the energy dispersive X-ray spectroscopy (EDX) was applied (see Table 2).[32] The Ru:P ratio of 1:3 is within the limits of error and confirms the ^{13}C and ^{31}P CP MAS NMR results, that the ruthenium complex fragment *cis*-Cl(H)Ru(CO)$(P{\sim}O)_3$ exists in the matrix. The P:Si ratio measured using the EDX method is also in good agreement with the applied stoichiometry of three T^n and six Q^k groups. Therefore all employed Q^k groups are incorporated into the material, confirming the ^{29}Si MAS (SPE) NMR spectroscopic results that some of them cannot be detected by the cross-polarization NMR method due to the lack of protons in their vicinity. The two selected ratios of Si:Al = 2:1 and 1:1 for compounds **A** and **B**, respectively, are also reflected in the EDX data (Table 2).

Catalytic Activity of the Materials. α,β-unsaturated aldehydes are easily accessible through aldol condensation of aldehydes. The selective hydrogenation of the C=O double bond to the corresponding alcohol is thus a way to obtain particular substituted alcohols. Various ruthenium complexes have been proved to show high activities toward the selective hydrogenation of C=O vs C=C double bonds in model reactions with homogeneous as well as heterogeneous catalysts.[34−37]

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(26) The corrected intensities I_o were obtained by applying the following equation:[27]

$$I_{(Tc)} = \frac{I_0}{(1 - T_{SiH}/T_{1\rho H})}\left(e^{-T_c/T_{1\rho H}} - e^{-T_c/T_{SiH}}\right) \qquad (1)$$

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Table 1. Silyl Species, δ ^{29}Si, Relative I_0, T_{SiH}, and $T_{1\rho\mathrm{H}}$[a] Values of Catalysts **A** and **B**

		A				**B**			
notation	structural type	δ ^{29}Si (ppm)	T_{SiH} (ms)	I_0[b]	I_0[c]	δ ^{29}Si (ppm)	T_{SiH} (ms)	I_0[b]	I_0[c]
T^1	$F-SiO_{1/2}(OH/OAl)_2$	−47	0.76	0.5	1.1	−47		0.5	0.6
T^2	$F-SiO_{2/2}(OH/OAl)$	−58	0.96	6.5	5.8	−56	0.78	8.2	6.2
T^3	$F-SiO_{3/2}$	−67	1.03	3.0	2.9	−67	0.85	1.3	3.2
Q^0	$Si(OH/OAl)_4$	−83	1.01	0.9	1.1				3.8
Q^1	$SiO_{1/2}(OH/OAl)_3$	−88	0.88	1.2	4.0	−86	0.84	6.0	6.6
Q^2	$SiO_{2/2}(OH/OAl)_2$	−92		1.5	4.2				
Q^3	$SiO_{3/2}(OH/OAl)$	−99	0.96	8.9	5.9	−96/−101	0.93	6.8	6.0
Q^4	$SiO_{4/2}$	−110	1.92	1.0	3.0				1.4

[a] $T_{1\rho\mathrm{H}}$ is 5.8 ms (±0.1 ms) for all silyl moieties in **A** and **B**. [b] Calculated from ^{29}Si CP MAS NMR spectra in consideration of eq 1.[26] [c] Intensities from ^{29}Si MAS (SPE) NMR spectra.

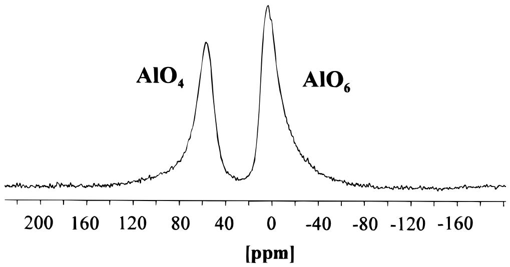

Figure 4. ^{27}Al MAS NMR spectrum of **B** (Rf = 13 kHz).

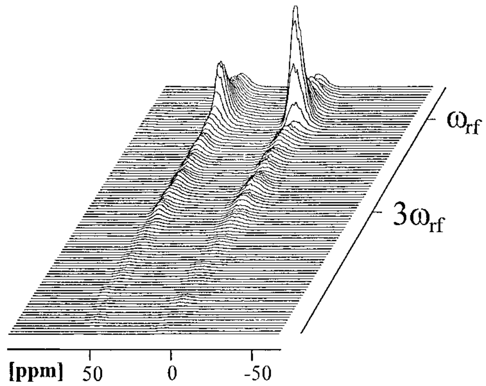

Figure 5. 2D ^{27}Al Nutation spectrum of **B** (Rf = 2.5 kHz, ω_{rf} = 120 kHz).

Table 2. Composition of the Polymer Matrices According to EDX Spectroscopy[a]

	for given elements[b]				
material	Ru	P	Si	Al	
A	1.0	3.0	9.0	4.5	ideal
	0.86 ± 0.06	2.90 ± 0.17	9.0	5.00 ± 0.77	found
B	1.0	3.0	9.0	9.0	ideal
	0.95 ± 0.15	2.53 ± 0.21	9.0	9.84 ± 0.86	found

[a] Additionally C, O, Cl, and minor amounts of Sn were found in the EDX spectrum. [b] The numbers of the individual elements represent the amount of atoms per monomeric unit. The values of Si were set to be 9.

In this work we employed *trans*-crotylaldehyde as a model substrate. The expected hydrogenation products are *n*-butyraldehyde, *cis*- and *trans*-crotyl alcohol and *n*-butyl alcohol. In the course of the catalytic reaction an increasing formation of side products (10%) is caused by condensation reactions of the crotylaldehyde.

The results of the catalytic experiments of the two ruthenium complexes **A** and **B** are displayed in Table 3. Below 80 °C no significant catalytic activity is found for the immobilized catalysts **A** and **B**. At 80 °C conversions of 20% are observed with chemoselectivities being higher than 3:1 with regard to the formation of the unsaturated alcohol. Increasing the temperature to 120 and 150 °C results in enhanced conversions up to 81% (**B**). Thereby the chemoselectivities decrease and considerable amounts of the dihydrogenation product *n*-butyl alcohol are formed. The better activities of catalyst **B** compared to catalyst **A** at elevated temperatures correlate with the higher aluminum content of **B** and thus with a stronger polarity of **B**. The two materials **A** and **B** were recovered from the reaction mixture by simple centrifugation, and after being washed with acetone and *n*-hexane they show the same catalytic activities (see Table 3).

Conclusion

Catalytically active ruthenium(II) complexes have been immobilized on poly(alumosiloxane) matrices by the sol−gel method. The amount of aluminum in the matrix can be adjusted by the applied stoichiometry and is reflected in the elemental analysis by EDX spectroscopy. The ^{29}Si solid state NMR spectra indicate numerous Si−O−Al linkages. Thus, the aluminum is homogeneously distributed within the polymer, and no domains are formed. A comparison between ^{29}Si CP MAS and ^{29}Si MAS (SPE) NMR spectra suggests that a considerable amount of Q^k groups is incorporated as bulk siloxane groups. In the ^{27}Al MAS NMR spectra tetrahedrally and octahedrally coordinated AlO_4 and AlO_6 species are detectable. These species carry ionic charges and are responsible for the high polarity of these matrices. Preliminary experiments in the hydrogenation of *trans*-crotylaldehyde show the catalytic potential of these catalysts toward the selective formation of the α,β-unsaturated alcohol. Catalyst **B** with more aluminum groups thereby shows the higher activity at enhanced temperatures. It is not necessary to precipitate the catalysts by addition of any solvent. They are easily recyclable by centrifugation and are thus good candidates for catalysis in a continuous flow type reactor.

Experimental Section

The elemental analyses were carried out on a Carlo Erba analayzer, Model 1106. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. Scanning electron micrograph was recorded on a Zeiss DSM 962 instrument with a tungsten cathode. The samples were sputtered with platinum to form layers of 15−20 nm thickness. The EDX data were measured with a Philips scanning electron microscope XL 30-FEG equipped with an EDAX DX-4 spectrometer system with ultrathin window ($Z > 5$ detectable). Beam voltages between 10 and 30 kV were used. The surface areas were determined by nitrogen sorption and calculated with the BET equation on a Micromeritics Gemini 2375. The hydrogenation experiments were carried out in 100 mL autoclaves under exclusion of oxygen [argon, 150 μmol catalyst with respect to ruthenium, 150 mmol of *trans*-crotylaldehyde]. The analyses were performed quantitatively on a GC 6000 Vega Series 2

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Table 3. Hydrogenation of *trans*-Crotylaldehyde[a]

						selectivity (%)			
catalyst	surface area (m^2/g)	particle size (μm)	temp (°C)	reaction time (h)	conversion (%)	*n*-butyraldehyde	*trans*-crotyl alcohol	*cis*-crotyl alcohol	*n*-butyl alcohol
A	60	0.1−0.5	80	4	20	19	73	4	4
			120	4	45	18	59	4	19
			150	1	65	23	51	5	21
			150[b]	1	63	22	55	5	18
B	70	0.1−0.5	80	4	20	19	72	4	5
			120	4	71	13	69	4	14
			150	1	81	18	46	4	32

[a] H_2 pressure = 50 bar, Ru:*trans*-crotylaldehyde = 1:1000. [b] Second run with recycled catalyst.

(Carlo Erba Instruments) with a FID and a capillary column SP 1000 [60 m; carrier gas, He (50 kPa); integrator, 3393 A (Hewlett Packard)].

The MAS solid state NMR spectra were recorded on Bruker multinuclear spectrometers with wide bore magnets (MSL 200, 4.7 T, ^{29}Si, ^{13}C; ASX 300, 7.05 T, ^{27}Al, ^{31}P) using samples of 100−400 mg in double-bearing rotors of ZrO_2. Magic-angle spinning was performed at 13 kHz (^{27}Al), 3.3 kHz (^{29}Si, ^{13}C), and 5 kHz (^{31}P) at room temperature. The spectra were taken using either cross-polarization (^{29}Si, ^{31}P, ^{13}C) or single-pulse excitation (^{27}Al) with high-power decoupling in all cases. All measurements were carried out under the exclusion of molecular oxygen. Frequencies, standards, and parameters: ^{29}Si, 39.75 MHz (Q_8M_8), contact time = 5 ms, recycle delay = 2 s (CP MAS) and 100 s (MAS), T_{SiH} by variations of the contact time (15−20 suitable experiments), $T_{1\rho H}$ by a spin lock−τ−CP experiment as described by Schaefer and Stejskal.[38] $T_{1\rho H}$ relaxation data were obtained using Bruker software SIMFIT. Peak deconvolution of the ^{29}Si CP MAS spectra was performed with the Bruker software GLINFIT: ^{13}C, 50.325 MHz [TMS, carbonyl resonance of glycine (δ = 170.09) as the second standard], contact time = 2 ms, recycle delay = 4 s using TOSS pulse sequence); ^{31}P, 121.49 MHz [85% H_3PO_4, $NH_4H_2PO_4$ (δ = 0.8) as the second standard], contact time = 1 ms, recycle delay = 2 s; ^{27}Al, 78.20 MHz, [0.1 M aqueous solution of $Al(NO_3)_3$], pulse length = 0.6 μs ($\leq\pi/12$ pulse), recycle delay = 500 ms. ^{27}Al chemical shifts are (as the data published in the literature) not corrected for second-order quadrupolar shifts. The 2D Nutation spectra were recorded at 78.20 MHz under MAS conditions (2.5 kHz), using a π pulse length of 4 μs corresponding to $\omega_{rf}/2\pi$ = 125 kHz. The pulse length was varied in 64 steps from 0.6 to 32.6 μs, with a 0.5 μs increment and zero filled to 128 points. The spectra were transformed into the phase-sensitive mode. To reduce the in-phase signal, the last recorded FID (t_1 = 32.6 μs) was subtracted from all other FIDs.

All manipulations were performed under argon by employing the usual Schlenk techniques. Methanol was dried with magnesium and distilled from $Mg(OMe)_2$. Acetone was distilled from P_4O_{10}. *n*-Hexane and toluene were distilled from sodium benzophenone ketyl. H_2O and $Si(OEt)_4$ (**Q^0**) (Aldrich) were distilled under argon prior to use. All solvents were stored under argon. The monomeric complex **2(T^0)$_3$** was synthesized as previously described.[13]

Sol−Gel Processing. Fine grinded Al(O*i*Pr)$_3$ was dipersed in 10 mL of methanol and 3 mL of water. The resulting sol was added to a mixture of **2(T^0)$_3$**, $Si(OEt)_4$ (**Q^0**), water, and (*n*-Bu)$_2$Sn(OAc)$_2$. This mixture was stirred in a sealed Schlenk tube for 2 h at room temperature. After specific amounts of aqueous 2 M NaOH were added the mixture was stirred for 16 h. Then methanol was removed in vacuo. Subsequently a saturated solution of NH_4HCO_3 (10 mL) was added dropwise under stirring. After 2 h the resulting precipitates were isolated by centrifugation and washed with an 1 M aqueous solution of NH_4HCO_3 and water (5 times each with 10 mL), then dried with acetone (10 times each with 10 mL), and stirred in *n*-hexane (50 mL, 4 h). Final aging of the materials was carried out by drying at 60 °C under vacuum for 8 h (densities 0.2−0.3 g/mL).

Carbonylchlorotris[(1,4-dioxanyl-2-methyl)phenyl(poly(alumosiloxanyl)propyl)phosphine-*P*,*P*′,*P*′′]hydridoruthenium(II)(Q^k)$_6$(Al$_2$O$_3$)$_{4.5/2}$ (A). A mixture of *cis*-Cl(H)Ru(CO)(P∼O)$_3$ [**2(T^0)$_3$**] (510 mg, 0.397 mmol), 4.5 equiv of Al(O*i*Pr)$_3$ (366 mg, 1.788 mmol), 6 equiv of $Si(OEt)_4$ [**Q^0**, 524 mg, 2.384 mmol], *n*-Bu$_2$Sn(OAc)$_2$ (10 mg, 0.03 mmol), and 2 M aqueous NaOH (9 mL, 1.788 mmol) was sol−gel processed to give a gray gel (yield of **A**, 714 mg). ^{31}P CP/MAS NMR: δ 20.4 (P^2), −3.4 (P^1). ^{13}C CP/MAS NMR (TOSS, 3.3 kHz): δ 128.8 (C-i,o,m,p), 72.0 (C-6,11), 66.5 (C-8,9), 50.3 ($SiOCH_3$), 27.3 (C-3,5), 18.0 (C-2), 13.7 (C-1). ^{29}Si CP/MAS NMR (silicon substructure): δ −47 (T^1), −58 (T^2), −67 (T^3), −83 (Q^0), −88 (Q^1), −99 (Q^3), −110 (Q^4). ^{27}Al MAS NMR: δ 55.2 (AlO_4), 3.0 (AlO_6). IR (KBr): ν(CO) 1924 cm^{-1}. Anal. Calcd for $C_{43}H_{61}Al_{4.5}ClO_{30.25}P_3RuSi_{6.9}$:[39] C, 31.01; H, 3.69; Cl, 2.13; Ru, 6.07. Found: C, 27.64; H, 4.70; Cl, 2.01; Ru, 5.75.

Carbonylchlorotris[(1,4-dioxanyl-2-methyl)phenyl(poly(alumosiloxanyl)propyl)phosphine-*P*,*P*′,*P*′′]hydridoruthenium(II) (Q^k)$_6$(Al$_2$O$_3$)$_{9/2}$ (B). A mixture of *cis*-Cl(H)Ru(CO)(P∼O)$_3$ [**2(T^0)$_3$**] (510 mg, 0.397 mmol), 9 equiv of Al(O*i*Pr)$_3$ (730 mg, 3.576 mmol), 6 equiv of $Si(OEt)_4$ [**Q^0**, 524 mg, 2.384 mmol], *n*-Bu$_2$Sn(OAc)$_2$ (10 mg, 0.03 mmol), and 2 M aqueous NaOH (18 mL, 3.576 mmol) was sol−gel processed to give a gray gel (yield of **B**, 740 mg). ^{31}P CP/MAS NMR: δ 19.1 (P^2), −2.9 (P^1). ^{13}C CP/MAS NMR (TOSS, 3.3 kHz): δ 129.2 (C-i,o,m,p), 72.4 (C-6,11), 66.2 (C-8,9), 50.3 ($SiOCH_3$), 27.6 (C-3,5), 18.0 (C-2), 14.0 (C-1). ^{29}Si CP/MAS NMR (silicon substructure): δ −47 (T^1), −56 (T^2), −67 (T^3), −86 (Q^1), −101 (Q^3). ^{27}Al MAS NMR: δ 56.5 (AlO_4), 2.5 (AlO_6). IR (KBr): ν(CO) 1936 cm^{-1}. Anal. Calcd for $C_{43}H_{61}Al_9ClO_{37}P_3RuSi_{7.2}$:[39] C, 27.25; H, 3.24; Cl, 1.87; Ru, 5.33. Found: C, 22.48; H, 4.64; Cl, 1.52; Ru, 5.10.

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(39) The given formula is the repeating unit of a polymer.