Enantioselective Heterogeneous Epoxidation and Hetero-*Diels-Alder* Reaction with Mn- and Cr-salen Complexes Immobilized on Silica Gel by Radical Grafting

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Vinyl-substituted chiral salens (salen = bis(salicylidene)ethylidenediamine) are used for attachment to Me_3Si-hydrophobized silica gel (controlled-pore glass, CPG), carrying covalently bound mercaptopropyl 'substituents', by AIBN-mediated radical addition of SH groups to styryl C=C bonds (*Scheme 1*, *Table 1*, and *Figs. 1* and *2*). The immobilized Mn- and Cr-salen complexes, thus accessible, have been employed in enantioselective epoxidations (*Scheme 2*, *Tables 2* and *3*, and *Fig. 3*) and hetero-*Diels-Alder* additions of aldehydes to *Danishefsky*'s diene (*Scheme 3*, *Tables 4* and *5*, and *Figs. 4* and *5*), with an emphasis on multiple use of the immobilized catalysts. The enantioselectivities (es) of the two reactions were very similar to those reported for homogeneous conditions. After five to seven runs, all the CPG-bound Mn-salen complexes performed somewhat less well (70 instead of 75% es with styrene; *Fig. 3*). The Cr complex, which was shown to give rise to a linear relationship between the enantiomeric purities of ligand and product under homogeneous conditions (*Fig. 4*), exhibited the opposite behavior: after five runs, the enantioselecitivity of the hetero-*Diels-Alder* reaction had risen (from an average of 76 to *ca.* 83%) to remain constant for another five runs (*Fig. 5*). We have established for both catalysts that no reaction takes place in the supernatant solution (no leaching of catalytically active Mn or Cr species from the CPG into solution; heterogeneity test; *Tables 3* and *5*). The results described are yet another demonstration for the successful 'conversion' of homogeneous to heterogeneous catalysts by immobilization on hydrophobic CPG, with multiple application of the same catalyst batch.

1. Introduction. – salen (= bis(salicylidene)ethylidenediamine) is one of today's preferred ligands, and many interesting reactions have already been performed stereoselectively with the derived chiral metal complexes [1][2]. Several approaches have been applied to immobilize salens to profit from the advantages of heterogeneous catalysis: the potential of re-using the catalyst many times and the ease of its separation from the reaction mixture. In a recent literature survey, we found more than 100 papers dealing with this subject.

The two types supports that have been used mostly for immobilization are organic polymers and zeolites. Immobilization in organic polymers – at that time with achiral salen – has been achieved as early as 1980 [3]. Apart from work about salen-based conducting polymers [4], enantioselective epoxidation is by far the most common application in the field of salens on polymeric supports [5], but there are also examples of reductions [6] and hydrolytic kinetic resolutions of terminal epoxides [7]. When salens are immobilized in zeolites, the 'ship-in-the-bottle' and the complexation approach are those most commonly used [8]. When the former strategy is applied, the

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aldehyde and diamine components are small enough to get into the cavities of a zeolite, where they form the salen molecules, which are then too large to escape from the supercages. In the complexation approach, for example, aluminium-modified zeolites are ion-exchanged with Mn-salen complexes [9][2]).

Surprisingly, few groups have tried to use simple silica gel as a support. Apart from work on the adsorptive immobilization (of achiral salen, for analytical purposes) on hydrophobic silica membrane disks [11], the first ones to covalently immobilize salen on silica gel were *Salvadori* and co-workers [12]. They chose the radical addition of immobilized SH groups to a vinyl-substituted Mn-salen complex. The material obtained was used for catalytic enantioselective epoxidations, but re-use of the catalyst was not studied. Another example of a salen immobilized on silica gel comes from *Jacobsen* and co-workers [7b] [13]. Here, spherical silica was chosen as the support, and the resulting material was packed in a column and used in a continuous-flow apparatus for the hydrolytic kinetic resolution of terminal epoxides. Interestingly, the results were very good, even though it is known that this reaction shows a nonlinear effect [13][3]). In another study, which, up to now, has not yet been published in full detail [16], the immobilization was performed *via* a hydrosilylation reaction of a vinyl-substituted salen with a silica support carrying Si–H group. Alternatively, the same salen was hydrosilylated in solution with $ClMe_2SiH$ and then grafted on the surface of normal silica gel. Finally, an interesting study comes from *Baiker* and co-workers [17]: with salicylaldehyde, (aminopropyl)trimethoxysilane, and cobalt or copper acetates, a complex was formed that could be incorporated without destruction in silica aerogels and xerogels *via* a sol-gel process. The preformation of the complex was shown to be important to prevent hydrolysis of the imine group during the sol-gel process.

Some time ago, we reported on the immobilization of TADDOL on silica gel [18]. In that case, the material had to be hydrophobic, and the degree of hydrophobization turned out to be crucial for applications of the derived heterogeneous Ti-TADDOLates in organometallic reactions like, for example, the addition of Et_2Zn to PhCHO. After having gained some knowledge in the preparation of immobilized salens by dendritically cross-linking polymerization [19], the aforementioned results of *Salvadori* and co-workers [12] prompted us to further study the radical-grafting method with our hydrophobic mercaptopropyl silica gel.

2. Preparation and Characterization of Mn-salen Immobilized on Controlled-Pore Glass (CPG). – As salen derivatives to be immobilized, we chose compounds **1**–**3** (*Scheme 1*), which are readily available in few steps starting from simple chemicals and by literature procedures [5c] [19]. Compound **2** had been part of our previous studies: the derived polystyrene copolymer showed excellent performance in successive catalytic epoxidations [19], and compound **3** was the salen immobilized in the previously mentioned investigation by *Salvadori* and co-workers [12].

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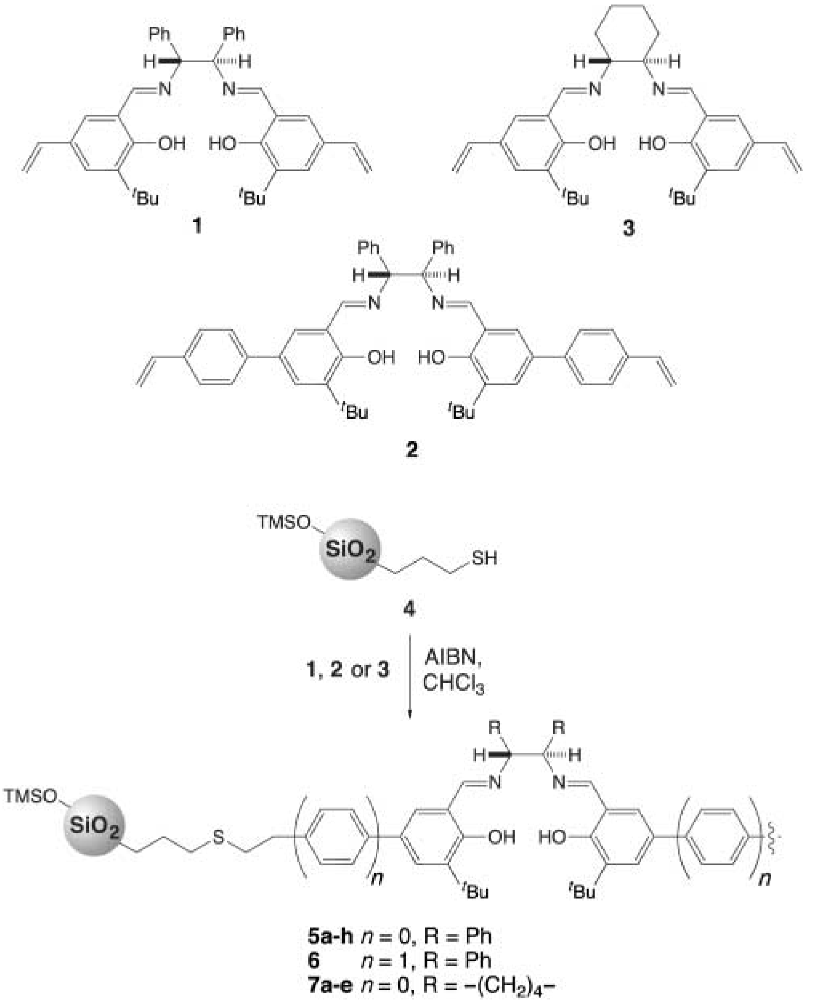
[2]) *Che* and co-workers published another example of a coordinative immobilization [10]: they used an aminopropyl-functionalized MCM-41 zeolite as a ligand for a soluble complex resembling a Cr-salen. However, in that case the bridging diamine is not a vicinal one but rather the diamino analog of BINOL.

[3]) For a review about nonlinear effects see [14] and for a discussion about site-interaction with supported molecules, see [15].

Scheme 1. *Preparation of the Heterogeneous Salens* **5**–**7** *from the Soluble Precursors* **1**–**3** *and CPG-Type Hydrophobic 3-Mercaptopropyl Silica Gel* **4**. For specifications of **5a**–**h** and **7a**–**e**, see *Table 1*.



The grafting reaction on the CPG silica gel **4** took place in $CHCl_3$ in the presence of AIBN. In the formula representation of the products **5**, **6**, and **7**, the second C=C bond on the right hand side in *Scheme 1* is omitted. Some of these C=C bonds will certainly have reacted, too, *e.g.* with another sulfanyl radical. However, the resulting structure is difficult to present in a drawing. In *Table 1*, we give an overview over the different conditions used for the immobilization reaction. Inspired by literature procedures [12][20], in a first experiment, 3 equiv. of the soluble precursor **1** and 1 equiv. of AIBN were used (→ **5a**). After washing and drying, a yellow powder was isolated (*Fig. 1*). To determine the degree of conversion, the content of SH groups was determined with *Ellman*'s SH test [21]. However, since the silica-gel samples were hydrophobic, and the test as described in the literature uses an aqueous medium, a modified procedure had to

Table 1. *Various Conditions Used for the Grafting Reaction to Give the Silica Gels* **5a**–**h**, **6**, *and* **7a**–**e.** c_0(SH): SH Content before the reaction. c_1(SH): SH Content after the reaction. Loading refers to salen content, determined gravimetrically

Product	Precursor	Equiv. of Precursor	Equiv. of AIBN	c_0(SH) [mmol g^{-1}]	c_1(SH) [mmol g^{-1}]	Loading [mmol g^{-1}]	
5a	**1**	3	1	0.40	0.04	0.19	
5b	**1**	2	1	0.40	0.04	0.17	
5c	**1**	2	0.5	0.40	0.06	0.21	
5d	**1**	2	0.5	0.40	0.03	0.26	evaporation[a])
5e	**1**	2	1	0.40	0.07	0.17	Ar stream[b])
5f	**1**	2	1	0.37	0.03	0.31	hydrophilic[c])
5g	**1**	2	0.5	0.40	0.03	0.18	styrene[d])
5h	**1**	2	0.5	0.40	0.05	0.28	more conc.[e])
6	**2**	2	1	0.40	0.01	0.92	evaporation[a])
7a	**3**	2	1	0.40	0.06	0.24	
7b	**3**	2	0.5	0.40	0.06	0.22	
7c	**3**	2	1	0.37	0.04	0.28	hydrophilic[c])
7d	**3**	2	0.5	0.40	0.05	0.17	styrene[d])
7e	**3**	2	0.5	0.40	0.05	0.32	more conc.[e])

[a]) Slow evaporation of reaction solvent over 24 h. [b]) Reaction was performed in a V-shaped two-necked flask with reflux condensor and an Ar stream to mix the suspension. [c]) Hydrophilic 3-mercaptopropyl-functionalized silica gel was used. [d]) 6 equiv. styrene were added to the reaction mixture. [e]) Only 1/3 of the amount of solvent was used, as compared to the other batches.

Fig. 1. *Samples of the silica gels* **5**, **8**, **15**, *and* **7** (from left to right)

be developed. With the addition of 20% EtOH to the test solution, the SH content could easily be analyzed with a slightly different extinction coefficient ($\varepsilon = 12915$ l mol^{-1} cm^{-1}) for the calculation. As can be seen from the results in *Table 1*, 90% of the SH groups had reacted. However, this figure cannot be used to determine the loading of the silica gel with salen because there is no strict 1 : 1 stoichiometry between SH groups and salen molecules: the formation of salen chains and the bridging connection between two SH groups cannot be excluded. Thus, the loading had to be determined gravimetrically, a crude method providing numerical values that have to be interpreted with due care. Here, only tendencies are discussed: for example, with only 2 equiv. of the salen precursor **1** (→ **5b**), a slightly lower loading was obtained. The loading can be increased with only 0.5 equiv. of AIBN (→ **5c**). Allowing slow evaporation of the solvent over a period of 24 h, an even higher loading could be obtained (→ **5d**). With precursor **2**, by this method, *all* salen was immobilized (→ **6**), leading to the highest loading in the whole series, and washing yielded colorless solutions (salen and its derivatives have an intensive yellow color). The highest loading with salen **1** and hydrophobic silica gel has so far been obtained by making the solution more concentrated (→ **5h**). This procedure is the preferred one, since the reaction conditions can be controlled somewhat better than with the slow-evaporation method. During the reaction, the suspension cannot be stirred because the silica gel would be ground to a fine powder, which would be difficult to handle. Thus, in the batches described so far, the reaction flask was rotated. To check whether the way of mixing has an effect on the catalytic performance, in another batch, a stream of Ar was used instead (→ **5e**), resulting in lower loading. Also, the influence of the polarity of the support on the catalytic performance has been studied. Thus, in one batch *hydrophilic* 3-mercaptopropyl silica gel was used (→ **5f**). Finally the addition of styrene (→ **5g**) could possibly have a positive effect both on loading and on catalytic performance *via* the formation of poly(salen-styrene) chains perpendicular to the surface. However, at least as far as the degree of loading is concerned, this approach did not turn out to be superior (for the catalytic performance, *vide infra*). The same strategies have been used for the immobilization of salen **3** (→ **7a** – **e**) with the same tendencies in the loadings being observed, except for **7b**.

To characterize the heterogeneous salens thus obtained, ^{13}C-MAS-NMR spectra were recorded (*Fig. 2*), which nicely corresponded to the spectra of the corresponding soluble precursors. Some peaks in the solid-phase spectra are rotational side bands. This could be verified by using a different rotational frequency for the sample during the data acquisition. As could be expected, the silica-gel samples gave only very weak signals from vinyl C-atoms. Comparing the two spectra, there are mainly two more prominent signals in the solid-phase spectra: at $\delta = 0$ ppm, from the TMS groups that make the silica gel hydrophobic, and at $\delta = 11$ ppm. This latter signal is due to one of the C-atoms of the 3-mercaptopropyl linker⁴). We have also measured DRIFT (diffuse reflectance infrared *Fourier* transform) spectra of some of the silica gels prepared. This is an easier but less informative method of characterization. For example, the signals of the aromatic C,H bonds in silica gel **5b** could clearly be seen at 3089, 3062, 3032, and 3000 cm^{-1}. The soluble analog **1** displays the corresponding signals at 3084, 3062, 3030, and 3001 cm^{-1}.

3. Epoxidations with CPG-Immobilized Mn-salens. – As in our previous investigations [19], the enantioselective epoxidation was chosen as the first test reaction. The heterogeneous Mn-salens **8** and **9** (*Scheme 2*; *cf.* also *Fig. 1*) were prepared, and the

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⁴) The signals of the other C-atoms of the linker are hidden under the intense peaks around 30 ppm.

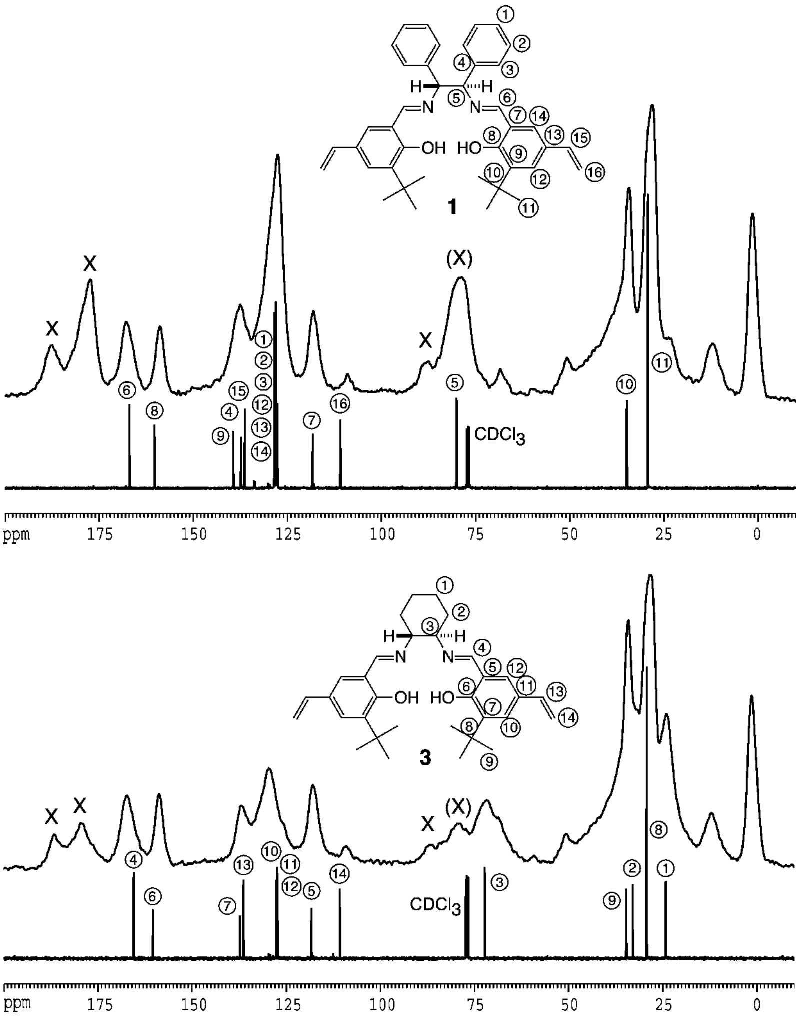

Fig. 2. *Characterization of the heterogeneous salens* **5** *and* **7** *by MAS-NMR.* The upper part shows a superposition of the ^{13}C-MAS-NMR spectrum (100 MHz, 5-kHz rotational frequency) of the heterogeneous salen **5h** with the ^{13}C-NMR spectrum (100 MHz) of the soluble precursor **1**. For convenience, the assignment of the peaks is included. Analogously, the lower part shows the corresponding spectra of silica gel **7e** and compound **3**. Peaks labeled with 'X' are rotational side bands. Sometimes these peaks coincide with other signals (label '(X)').

same protocols as for our salen-styrene copolymers were applied. The conversion and enantioselectivity obtained with silica gel **8d** and styrene (**10**) were virtually identical to those obtained with *Jacobsen*'s catalyst (*Table 2*). Lowering the temperature made the reaction slower but not more selective. Olefin **12** could also be oxidized with good enantioselectivity. Compared with our previously published salen polymers, the selectivities were in the same order or only slightly better [19].

Scheme 2. *Preparation of the Heterogeneous Mn-salens* **8a**–**h** *and* **9**, *and Enantioselective Epoxidation Reactions with the Silica-Gel-Bound Reagents*

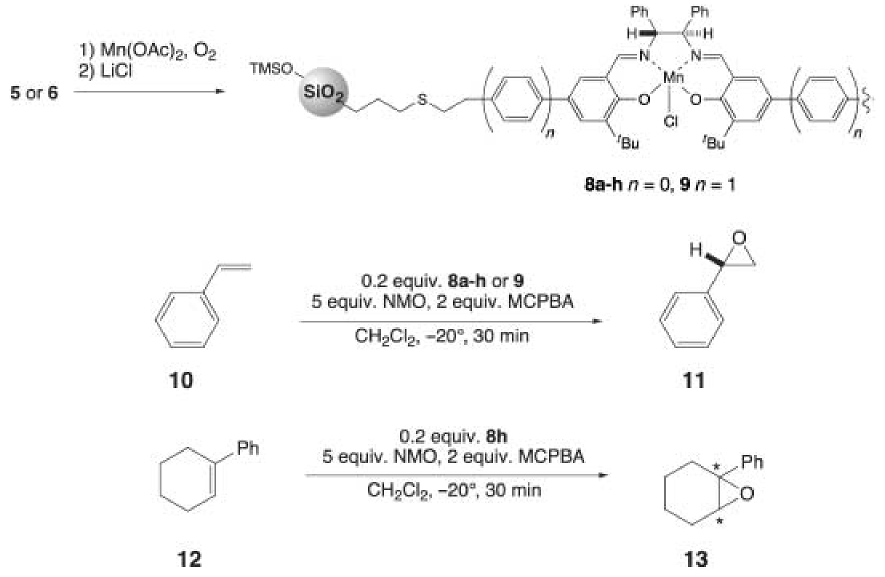

Table 2. *Conversions and Enantioselectivities in the Epoxidation of styrene* (**10**) *and 1-Phenylcyclohexene* (**12**) *with Different Mn-salen Materials*

Mn-salen	Alkene	Temp./°	Conversion/%	% es	
Jacobsen's catalyst	**10**	– 20	quant.	75.0	from [19]
8d	**10**	– 20	95	74.3	1st run
8h	**10**	– 72	67	75.7	after 30 min
			83	75.1	after 90 min
8h	**12**	– 20	77	80.8	1st run
		– 20	71	82.0	2nd run

In our opinion, the re-usability is of utmost importance for a heterogeneous catalyst of this type in order to justify the increased effort of its preparation. Re-use of the catalysts **8** and **9** turned out to be possible (*Fig. 3*). Over up to seven runs, both conversion and enantioselectivity slowly dropped. It is remarkable that loading, polarity of the support (hydrophilic/hydrophobic), and the addition of styrene during the grafting step do not have a big influence on the catalytic performance. Materials **8b** and **8e** (each with a loading of 0.17 mmol g^{-1}) provide the best conversions, whereas the enantioselectivities obtained with silica gel **8g** are slightly higher; the difference in performance is very small, however. Only material **9** gave rise to significantly lower conversions⁵).

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[5] With the corresponding polymeric material, a constant enantioselectivity of 81% es over ten runs had been achieved [19].

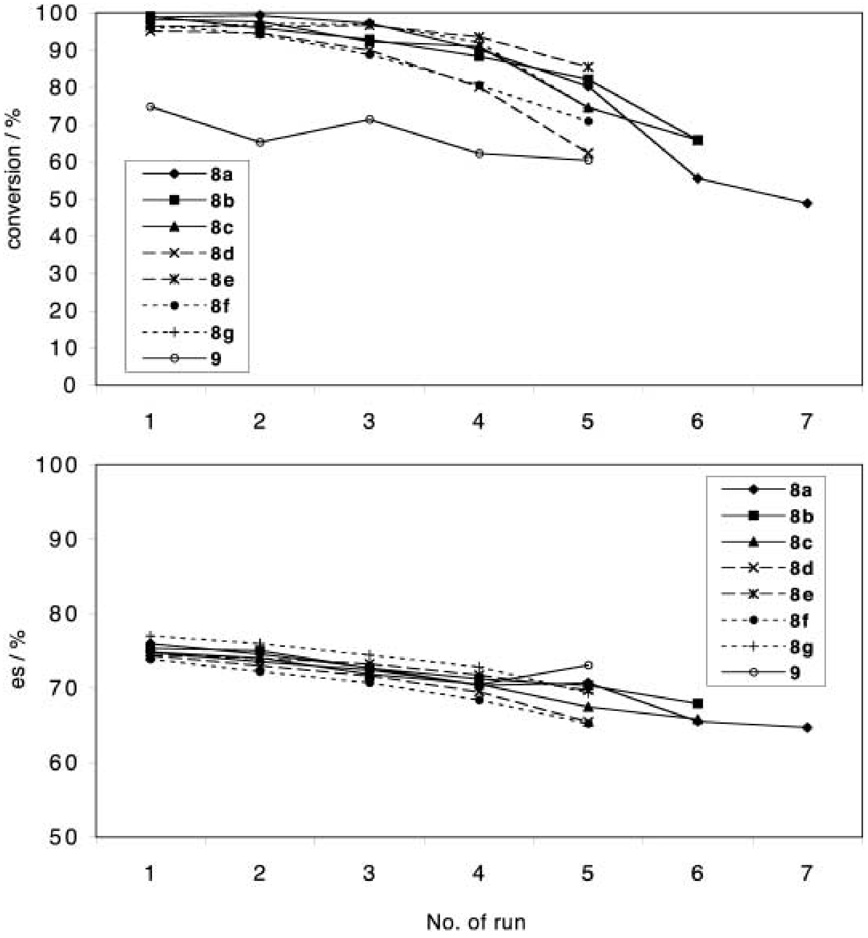

Fig. 3. *Multiple-use studies with the heterogeneous Mn-salens* **8a**–**g** *and* **9** *in the epoxidation of styrene*

Interestingly (and in contrast to the silica-bound TADDOLs [18]), all efforts to restore the enantioselectivity to the level of the respective first run failed. Both excessive washing with EtOH, acetone/H_2O, or acetone/H_2O/HCl, and reloading of the silica gel with Mn salts between some of the runs, shown in *Fig. 3*, did not have the desired effect. The reason is probably an accumulation of by-products that could not be washed away because the recovered silica gel was always heavier after the reaction than before – despite excessive washing with different solvents.

Leaching of salen units could be another reason for the decrease of performance. To check this hypothesis, we performed a heterogeneity test (*Table 3*) in the respective fourth runs with the materials **8f** and **8g**. After a reaction time of 2 min, a sample of the liquid phase – without any silica gel – was withdrawn and analyzed. After 30 min this sample was analyzed again, and the result was compared with that obtained from the 'main' reaction. As can be seen, in both cases, the reaction came to a standstill in the sample, which did not contain the catalyst, whereas the 'main' reaction proceeded as

Table 3. *Heterogeneity Test during the Respective Fourth Runs with Styrene* (**10**) *and the Heterogeneous Mn-salens* **8f** *and* **8g**

Mn-salen		Conversion/%	% es
8f	Sample of solution, taken after 2 min	55	65.9
8f	This sample after 30 min	55	65.2
8f	'Main' reaction after 30 min	81	68.4
8g	Sample of solution, taken after 2 min	57	69.9
8g	This sample after 30 min	60	68.7
8g	'Main' reaction after 30 min	92	72.8

expected. Thus, it can be concluded that no Mn-salen species were present in the supernatant solution.

4. CPG-Immobilized Cr-salens as Chiral *Lewis* Acids in a Hetero-*Diels-Alder* Reaction. – As the second reaction to be tested, we chose the hetero-*Diels-Alder* addition of *Danishefsky*'s diene to aldehydes [22], which had been performed with an immobilized salen for the first time in our group [19]. It was not known whether this reaction shows a nonlinear effect [14], an important issue in heterogeneous catalysis because, when a nonlinear effect is detected, it is likely that the outcome of the reaction with an immobilized catalyst will be different from that obtained with the soluble analogue: depending on the support, an interaction of several catalytic units is unlikely or even impossible [15]. As can be seen in *Fig. 4*, the reaction with caproaldehyde shows a perfectly linear correlation between the enantiomer purity of product and of catalyst. It is indicated but not proven by this result that there is no multiple participation of catalytic units.

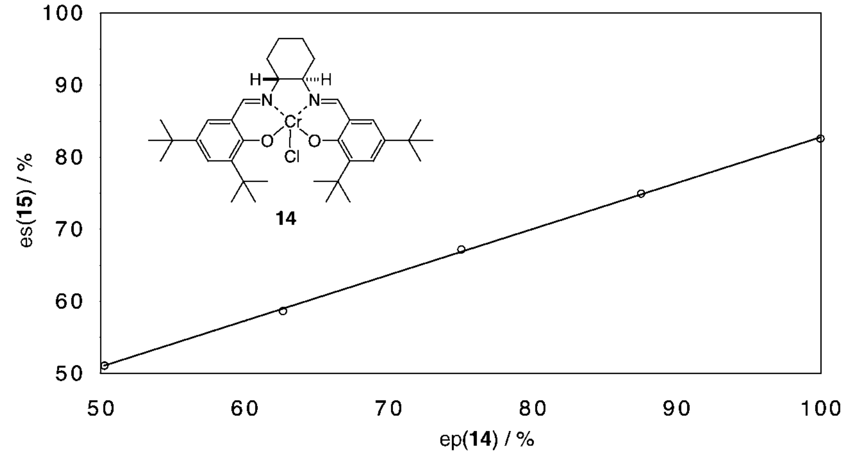

Fig. 4. *Result of the NLE investigations with the soluble Cr-salen* **14** *in the hetero-*Diels-Alder *reaction of* Danishefsky'*s diene with caproaldehyde*

To obtain the heterogeneous Cr-salens **15a** – **e**, the silica gels **7a** – **e** were treated with $CrCl_2$ in an open flask (*Scheme 3*; *cf.* also *Fig. 1*). In comparison with the soluble Cr-salen **14**, the heterogeneous Cr-salen **15b** afforded the cycloadduct **17** with almost the same conversion and enantioselectivity (*Table 4*). Performing the reaction at lower temperature led to a slight increase in enantioselectivity but rendered the reaction very slow. The addition of benzaldehyde to *Danishefsky*'s diene (**16**) could also be successfully catalyzed by **15b**, with a slightly lower performance in the first run compared to that of the soluble catalyst **14**; interestingly, the selectivity was better in the second run! This tendency was found several times when studying the re-usability of the heterogeneous Cr-salens **15a**–**d** in the cycloaddition (*Fig. 5*). Whereas the conversion showed some fluctuation, the enantioselectivity increased with the number of runs up to a certain level. Between two runs, the catalyst was washed with *t*-BuOMe and Et_2O. Similar behavior had been found in our group with the salen-styrene copolymers [19]. However, the cause for this pleasant feature could not be identified; the analytical access to these materials is difficult. Again, the studies showed that surface polarity, loading, and addition of styrene during the grafting did not have a big influence on the catalytic performance in this reaction.

Scheme 3. *Preparation of the Heterogeneous Cr-salens* **15a**–**e** *and Enantioselective hetero-*Diels-Alder *Reactions with these Silica Gels*

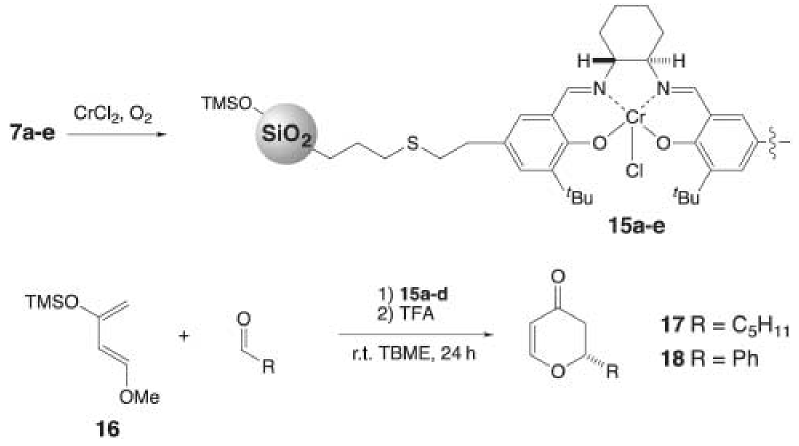

Table 4. *Results of the Hetero-*Diels-Alder *Reaction* (→ **17**, **18**) *with Different Aldehydes and Different Cr-salens*

Cr-salen	Aldehyde	Temp.	Conversion/%	% es	
14	Caproaldehyde	r.t.	97	82.6	
15b	Caproaldehyde	r.t.	91	79.8	1st run
15b	Caproaldehyde	0°	7	84.0	after 24 h[a])
			62	82.7	after another 24 h at r.t.[a])
14	Benzaldehyde	r.t.	n.d.	80.0	from [19]
15b	Benzaldehyde	r.t.	69	74.2	1st run
15b	Benzaldehyde	r.t.	72	77.6	2nd run

[a]) Results of the eleventh run with the immobilized Cr-salen **15a**.

After ten runs with caproaldehyde (→ **17**), two more runs were carried out with benzaldehyde (→ **18**), with the same material **15b**. The conversions were relatively low (*ca.* 30%) but the enantioselectivities obtained with this 'used' catalyst were pleasantly

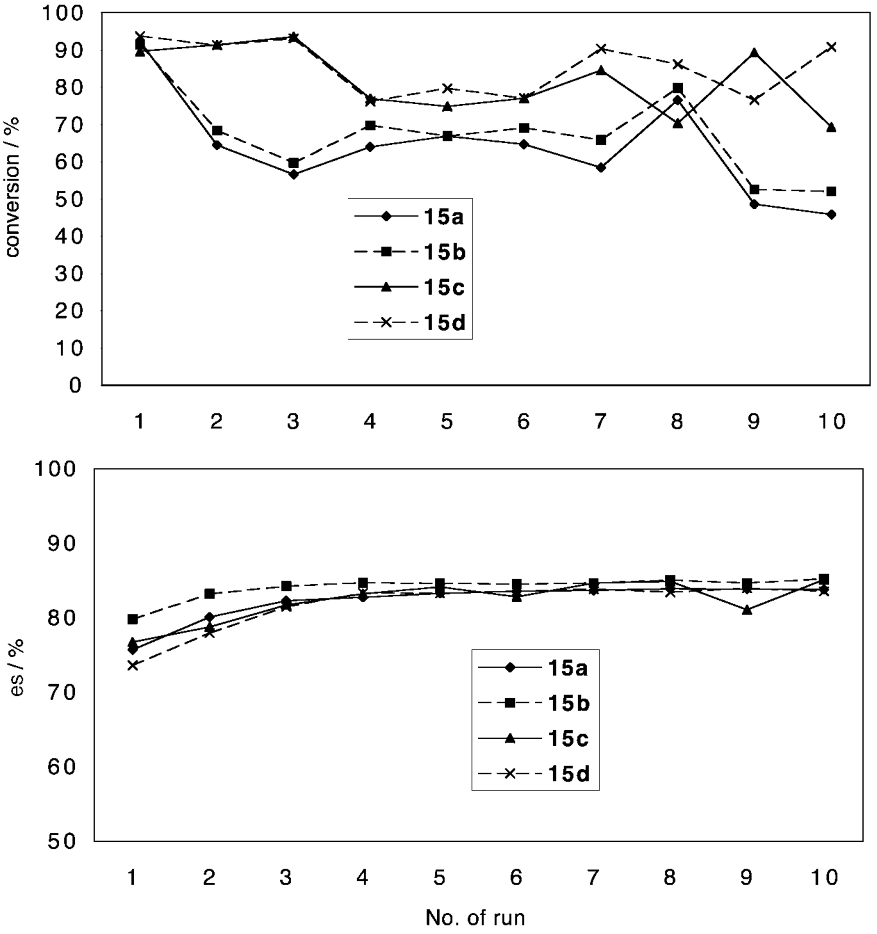

Fig. 5. *Multiple-use studies with the heterogeneous Cr-salens* **15a–d** *in the hetero-*Diels-Alder *reaction of* Danishefky*'s diene with caproaldehyde*

close (79.5 es and 78.9% es) to those observed with the soluble Cr-salen **14**. In addition, these experiments showed the efficiency of the washing protocol between two runs: after the eleventh run only 1% of product **17** (from the tenth run) could be detected in the solution containing the 'new' product **18**.

A heterogeneity test was also conducted for the hetero-*Diels-Alder* reaction (*Table 5*): the reaction came to a standstill in a sample of the reaction solution when

Table 5. *Heterogeneity Test during the First Run with the Heterogeneous Cr-salen* **15d** *in the Hetero-*Diels-Alder *Reaction* (→ **17**, **18**)

	Conversion/%	% es
Sample of solution, taken after 2 min	68	71.8
This sample after 30 min	62	71.5
'Main' reaction after 30 min	94	73.6

separated from the heterogeneous catalyst, whereas the 'main' reaction proceeded to completion within the usual period of time.

5. Conclusions. – We have further elaborated the concept of immobilization of salens on 3-mercaptopropyl silica gel in a radical-grafting step. With the derived Mn-salens, enantioselective epoxidation reactions could be successfully catalyzed. Re-use of the catalysts was possible, however, the performance decreased with every run. The Cr derivatives of the heterogeneous salens were active in the enantioselective hetero-*Diels-Alder* reaction of aldehydes with *Danishefsky*'s diene, and the enantioselectivities obtained were as good as with a soluble analogue. Re-using the catalyst was possible here, too, and the enantioselectivity even increased slightly in the first runs. We are confident that this level could have been kept for many more runs, and only shortage of time kept us from proving this.

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Experimental Part

General. Flash chromatography (FC): silica gel *60* (*Fluka*, 230–400 mesh ASTM), N_2 pressure 0.2 bar. Gas chromatography (GC): *Carlo-Erba GC 8000* top, column: *Supelco β-DEX* (30 m, 0.25 mm), injector temp. 200°, detector temp. 225°, carrier gas: H_2 (1 bar). DRIFT: *Perkin-Elmer 2000 FT-IR* (Prof. *Baiker*, Laboratorium für Technische Chemie, ETH-Zürich), Ar stream, 50°, background: KBr. NMR: *Varian Mercury-300*, solid phase spectra: *Bruker AMX-400* and *Avance 400*, rotor: 4 and 7 mm (NMR service of the Laboratorium für Anorganische Chemie, ETH-Zürich), Support: CPG (*Grace GmbH*, In der Hollerhecke, D-67547, Worms), type *332* (*SP 2-8319.01*), pore size 200 Å, spec. surface area 280–355 $m^2 g^{-1}$, pore volume 1.55 ml g^{-1}, particle size 35–70 μm; when silica gel was dried *in vacuo*, a sintered filter was used between the flask containing the silica gel and the vacuum pump. Silica-gel suspensions must not be stirred with a magnetic stirring bar. Instead, the reaction flask containing the silica-gel can, for example, be shaken with a *IKA Vibrax VXR* (with *VX-5* option) from *Jahnke & Kunkel* or rotated in a *Büchi Kugelrohr* oven. Silica gel **4** was obtained according to the route described in [18]⁶) and 4-methylmorpholine 4-oxide was dried *in vacuo* at 100° prior to use.

Radical Immobilization of salen on 3-Mercaptopropyl Silica Gel (*General Procedure*). *Detailed Example for the Synthesis of Silica Gel* **5h** (*c.f.* the remarks about the concentration in the text and the caption to *Table 1*). To a 25-ml V-shaped two-necked flask with septum were added silica gel **4** (998 mg, 0.4 mmol, c(SH) = 0.4 mmol g^{-1}), salen **1** (468 mg, 0.8 mmol, 2 equiv.) dissolved in $CHCl_3$ (4 ml), and AIBN (33 mg, 0.2 mmol, 0.5 equiv.) dissolved in $CHCl_3$ (1 ml). Then, a connecting tube with sinter filter and a *Vigreux* column were added as reflux condenser. Mixing was accomplished by turning this setup with the motor of a *Büchi Kugelrohr* oven with the reaction vessel being immersed in an oil bath (75°). During the reaction time (24 h), the solvent was refilled several times. Then, the silica gel was filtered off, washed with $CHCl_3$, THF, acetone, and CH_2Cl_2 (200 ml each), and dried *in vacuo* to give **5h** as a yellow powder (1.197 g, c(SH) = 0.05 mmol g^{-1}). The loading was determined by the weight difference to be 0.28 mmol g^{-1}.

Synthesis of **8a**–**h** *and* **9** *by Loading of the Heterogeneous salens* **5** *and* **6** *with Mn* (*General Procedure*). *Detailed Example for the Synthesis of Silica Gel* **8f**. In a 25-ml V-shaped two-necked flask with septum and reflux condenser, silica gel **5f** (346 mg, 0.107 mmol, loading 0.31 mmol g^{-1}) was suspended in EtOH (5 ml) and DMF (10 ml). Then, $Mn(OAc)_2 \cdot 4\,H_2O$ (263 mg, 1.07 mmol, 10 equiv.) was added, and the suspension was heated to 80° and mixed with a stream of air. No magnetic stirring bar was used! After the addition of the Mn salt, the silica gel turned black. After 3 h, LiCl (91 mg, 2.15 mmol, 20 equiv.) was added, and the suspension was heated for another 3 h under air stream. Then, the material was filtered off, washed with THF and CH_2Cl_2 (200 ml each), and dried *in vacuo* to afford **8f** as a brown powder (355 mg; *cf. Fig. 1*).

Enantioselective Epoxidation of Alkenes **10** *and* **12** (*General Procedure*). *Detailed Example for the Epoxidation of Styrene* (**10**) *with Silica Gel* **5c**. Silica gel **5c** (293 mg, 0.062 mmol, 0.2 equiv.; loading 0.21 mmol

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⁶) Details of the procedure have been described in a full paper [23].

g^{-1}) was suspended in a 25-ml V-shaped two-necked flask with CH_2Cl_2 (4 ml), and styrene (35 µl, 0.308 mmol, 1 equiv.) and 4-methylmorpholine 4-oxide (180 mg, 1.538 mmol, 5 equiv.) were added. After cooling the mixture to $-20°$, *m*-chloroperbenzoic acid (70%, 152 mg, 0.615 mmol, 2 equiv.) was added, and the flask was shaken in the cooling bath. To monitor the reaction, a sample of the solvent was taken with a syringe (*ca.* 10 µl) and shaken with Et_2O (0.5 ml) and KOH soln. (1M, 0.5 ml). Then, the org. layer was analyzed with GC (90°, t_R 3.2 min (styrene, **10**), 12.2 min (major enantiomer, (*R*)-**11**), 12.7 min (minor enantiomer); for the epoxidation of compound **12**: 120° for 10 min, 1.5°/min, 140° for 10 min, t_R 18.8 min (**12**), 23.5 min (major enantiomer of **13**), 23.8 min (minor enantiomer)). After 30 min of reaction time, the silica gel was allowed to sedimentate, and then as much as possible of the slightly brown reaction solvent was carefully removed with a syringe. Then, CH_2Cl_2 (25 ml) was added, and again the supernatant soln. was withdrawn. This washing procedure was repeated two more times. Subsequently, the silica gel was dried *in vacuo* (319 mg) and used for the next run. To isolate the product of the reaction, a KOH soln. (1M, 100 ml) was added to the combined washing solns., the phases were separated, and the aq. layer was washed two more times with CH_2Cl_2. Then, the combined org. phases were washed with H_2O and dried ($MgSO_4$). After evaporation of the solvent, the product **10** was isolated as slightly brownish oil (35 mg, 0.29 mmol, 95%). Remaining traces of Mn compounds were removed by prep. TLC (hexane/acetone 6:1) to afford **10** as a colorless oil (22 mg, 0.18 mmol, 60%). The spectroscopic data were in accordance with those of a commercially available sample.

Synthesis of **15a–e** *by Loading of the Heterogeneous salens* **7a–e** *with Cr* (*General Procedure*). *Detailed Example for the Reaction with Silica Gel* **7b**. The silica gel (316 mg, 0.07 mmol, loading 0.22 mmol g^{-1}) was suspended under Ar in THF (5 ml), and $CrCl_2$ (9.4 mg, 0.076 mmol, 1.1 equiv.) was added. After shaking under Ar for 4.5 h, the flask was opened, and shaking was continued overnight. Then, the material was filtered off, washed with THF (100 ml) and toluene (50 ml), and dried *in vacuo* to afford **15b** as an ochre powder (318 mg; *cf. Fig. 1*).

Enantioselective Hetero-Diels-Alder *Reaction with Silica Gels* **15a–e** (*General Procedure*). *Detailed Example for the Reaction with Caproaldehyde and Silica Gel* **15b**. Silica gel **15b** (92 mg, 0.02 mmol, 0.02 equiv.; loading 0.22 mmol g^{-1}) was suspended in a 25-ml V-shaped two-necked flask in *t*-BuOMe (1 ml). Then, *Danishefsky*'s diene (**16**, 190 µl, 1 mmol, 1 equiv.) and caproaldehyde (123 µl, 1 mmol, 1 equiv.) were added, and the mixture was shaken at *r.t.* To monitor the reaction, a sample of the reaction soln. was taken (*ca.* 10 µl), and Et_2O (0.5 ml) and a drop of CF_3COOH were added. After shaking, H_2O was added (0.5 ml), and the mixture was shaken again. Then, the org. layer was analyzed with GC (120°, t_R 2.8 min (caproaldehyde), 24.9 min (minor enantiomer), 25.7 min (major enantiomer, (*S*)-**17**); for the reaction with benzaldehyde: 155°, t_R 1.8 min (benzaldehyde), 21.5 min (minor enantiomer), 22.3 (major enantiomer, (*R*)-**18**)). After 1 d of reaction time, the silica gel was allowed to sediment, and the supernatant soln. was carefully removed with a syringe. Then, Et_2O (25 ml) was added, and the supernatant soln. was again removed. This procedure was repeated two more times. The washed silica gel was dried *in vacuo* (90 mg) and used for the next run. After twelve runs, 96 mg of silica gel could be recovered. To isolate the product, washing solns. were combined, and two drops of CF_3COOH were added. After evaporation of the solvent, the crude product was purified by FC (20 g, hexane/AcOEt 4:1) to afford **17** (71 mg, 0.42 mmol, 42%). The spectroscopic data were in accordance with literature data [22].

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