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[8] $[Fe(CO)(PMe_3)_2(`S_3')]$ (**4**): A THF suspension (30 mL) of $[\{Fe(CO)_2(`S_3')\}_2]$ (240 mg, 0.33 mmol) and PMe_3 (0.25 mL, 2.4 mmol) was stirred for one day. Undissolved material was removed by filtration and the red filtrate was evaporated to dryness. Purification of the residue by dissolution in MeOH (20 mL), filtration, evaporation to dryness, re-dissolution of the remaining residue in toluene (3 mL), and precipitation by adding *n*-pentane (15 mL) yielded pure **4** as red-brown powder. Yield 200 mg (62 %) .Elemental analysis calcd (%) for $C_{19}H_{26}FeOP_2S_3$ (483.39): C 47.11, H 5.41, S 19.86; found: C 47.19, H 5.59, S 20.06; IR (KBr): $\tilde{\nu} = 1932\ cm^{-1}$ (CO); MS (FD, CH_3CN); *m*/*z*: 484 $[Fe(CO)(PMe_3)_2(`S_3')]^+$; ^1H NMR (399.7 MHz, CD_2Cl_2): $\delta = 7.68$ (m, 1H; C_6H_4), 7.54 (m, 1H; C_6H_4), 7.42 (m, 2H; C_6H_4), 6.97 (m, 2H; C_6H_4), 6.83 (m, 2H; C_6H_4), 1.61 (d, 9H, $^2J_{P,H} = 9.4$ Hz; PC_3H_9), 1.36 (d, 9H, $^2J_{P,H} = 8.9$ Hz; PC_3H_9); $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): $\delta =$ 214.9 (dd, $^2J_{P,C} = 20.1$ Hz, $^2J_{P,C} = 21.1$ Hz, CO), 156.9 (d, $J_{P,C} = 9.1$ Hz), 154.7 (d, $J_{P,C} = 12.9$ Hz), 139.5 (d, $J_{P,C} = 17.4$ Hz), 138.5, 130.9, 130.5, 130.1, 129.0, 128.9, 128.1, 121.7, 121.3, (C_6H_4), 18.6 (d, $^1J_{P,C} = 29.2$ Hz), 18.0 (d, $^1J_{P,C} = 26.6$ Hz) (PCH_3); $^{31}P\{^1H\}$ NMR (161.7 MHz, CD_2Cl_2): $\delta = 21.05$, 14.23 (d, $^2J_{P,P} = 50.4$ Hz PC_3H_9).

[9] X-ray structure analysis of **1**: Dark red to black blocks of **1** were obtained directly from a saturated THF/MeOH reaction solution. Suitable single crystals were embedded in protecting perfluoropolyether oil. Data were collected on a Siemens P4 diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm), a graphite monochromator, and ω-scan technique. Absorption correction was applied on the basis of ψ scans ($T_{min} = 0.123$, $T_{max} = 0.149$). $C_{25}H_{30}FeNiOP_2S_5$, crystal size $0.09 \times 0.56 \times 0.52$ mm, monoclinic, space group $P2_1/n$, $a = 1032.4(2)$, $b = 1702.2(2)$, $c = 1712.6(3)$ pm, $\beta = 104.72(1)$, $V = 2.9109(7)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.559$ g cm^{-3}, $T = 220(2)$ K, $\mu = 1.632$ mm^{-1}, 8715 measured reflections ($4.2 < 2\theta < 56^\circ$), 7035 unique reflections, 5476 observed reflections, 438 parameters, $wR2 = 0.0832$, $R1 = 0.0379$ ($I > 2\sigma(I)$). The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2. The structure of **1** contains both enantiomers of **1**. A disorder is observed in which the two enantiomers share a single site. The site occupation factors have been refined giving 93.4(2) % for the major and 6.6(2) % for the minor component. The non-hydrogen atoms of the major component have been refined with anisotropic displacement parameters while the corresponding atoms of the minor component have been refined isotropically with group-wise refined isotropic diplacement parameters for the carbon atoms. The hydrogen atoms of the major component of **1** were taken from a difference Fourier map and were kept fixed with a common isotropic displacement parameter. No hydrogen atoms were taken into account for the minor component. CCDC 172509 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Highly Enantioselective Preparation of Multifunctionalized Propargylic Building Blocks**

Thomas Schubert, Werner Hummel, and Michael Müller*

Optically active propargylic alcohols are versatile building blocks in the synthesis of a broad variety of natural compounds and drugs.[1] Therefore, numerous synthetic approaches have been developed to obtain propargylic alcohols with high enantiomeric excesses. Chemical methods offer straightforward access to these compounds, for example, enantioselective reductions[2] or asymmetric zinc-mediated additions to aldehydes,[3] as well as enzymatic methods with oxidoreductases[4] or lipases[5]. Nevertheless, most published procedures do not give enantiomerically pure α,β-alkynyl-substituted methanols. Moreover, there has been only one report of a chiral α,β-alkynyl α-chloro- or α-bromohydrin. Corey and co-workers obtained (*R*)-4-triisopropylsilyl-1-chloro-3-butyn-2-ol by oxazaborolidine reduction of the corresponding ketone. However, the authors indicated that the bulky triisopropylsilyl group was essential for an *ee* of 95 %.[2c] In general, reduction methods applied to α-chloro- or α-bromo ketones need to be mild as a result of possible side reactions at the activated α position. Furthermore, zinc-mediated additions to aldehydes cannot be used for the preparation of α,β-alkynyl α-chloro- or α-bromohydrins.[6] Nevertheless, propargylic α-chlorohydrins could be easily transformed, for example, into epoxides, thus offering novel comprehensive applications in organic syntheses.

In preceding studies, we synthesized a broad variety of enantiopure propargylic alcohols by the enzymatic reduction of alkynones.[7] Thus, both enantiomers of α,β-alkynyl-substituted methanols are accessible. Our interest in a general approach to obtain optically pure building blocks as intermediates in organic syntheses encouraged us to continue our

[*] Dr. M. Müller, Dipl.-Chem. T. Schubert
Institut für Biotechnologie 2, Forschungszentrum Jülich GmbH
52425 Jülich (Germany)
Fax: (+49) 2461-613870
E-mail: mi.mueller@fz-juelich.de
Dr. W. Hummel
Institut für Enzymtechnologie
Heinrich-Heine-Universität Düsseldorf (Germany)

[**] We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (SFB 380). We thank Prof. Christian Wandrey for his continuous and generous support.

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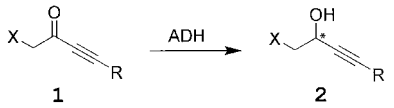
studies towards the reduction of α-halo propargylic ketones. We report herein a straightforward approach to both enantiomers of α,β-alkynyl α-chloro- or α-bromohydrins through the enzymatic reduction of the corresponding ketones. By subsequent treatment with a mild base, the alcohols were converted into propargylic epoxides to give other highly functionalized building blocks.

Our previous results provided evidence that in the reduction of propargylic ketones by oxidoreductases, one substituent of the substrate must not exceed a certain size.[7] Most likely, this substituent has to be small enough to fit into a cavity of the active site of the enzyme. Therefore, we synthesized a number of alkynones with diverse steric demands, and determined the ability of various alcohol dehydrogenases to reduce these compounds. In a UV assay, we identified three alcohol dehydrogenases (ADHs) that accept propargylic substrates with substituents of the size of chloro- and bromomethyl groups (data not shown). α-Halogenated propargylic ketones **1**, which were easily synthesized in one step,[8] were reduced by horse liver alcohol dehydrogenase (HLADH), *Thermoanaerobium brockii* ADH (TBADH), and *Lactobacillus brevis* ADH (LBADH) (Table 1). All these enzymes are commercially available.[9] Additionally, two are efficiently overproduced in a recombinant *Escheria coli* strain (TEADH and recLBADH).[10, 11] All these oxidoreductases reduce aromatic and aliphatic α-chloropropargylic ketones with high activity. α-Bromopropargylic ketones are also suitable substrates; however, the enzymatic activity of TBADH and recLBADH decreases, probably as a result of steric interactions. Interestingly, this characteristic differs for HLADH. This enzyme generally prefers cyclic ketones, whereas aliphatic compounds are known to be poor substrates.[12] Applying propargylic ketones, the α-halogenation increases the activity notably from nonhalogenated through chlorinated to brominated derivatives, thus making these compounds exceptional in the substrate range of HLADH.

Table 1. Relative enzymatic activities of HLADH, TBADH and recLBADH.



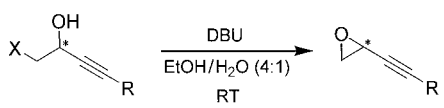
1 2

Alcohol		HLADH[a]	TBADH[a]	recLBADH[a]
		activity [%][b] (configuration)		
2a	X = Cl R = Ph	32 (*R*)	53 (*R*)	70 (*S*)
2b	X = Cl R = TBS	24 (*R*)	51 (*R*)	37 (*S*)
2c	X = Cl R = TMS	15 (*R*)	74 (*R*)	28 (*S*)
2d	X = Br R = TMS	35 (*R*)	4 (*R*)	18 (*S*)[c]
2e[d]	X = H R = Ph	6 (*S*)	47 (*S*)	142 (*R*)

Assay conditions: substrate (2 mM), NAD(P)H (0.25 mM), $MgCl_2$ (1 mM), TEA/NaOH buffer (100 mM), pH = 7.0. [a] All alcohols have an enantiomeric excess of > 99% as determined by HPLC (**2a**, **e**) or GC (Moshers ester of **2b**–**d**) on chiral stationary phase. The configuration of **2a** and **b** was determined by comparison of the optical rotation of the corresponding epoxide with literature data. The configuration of **2c**, **d** was determined with respect to mechanistic aspects of enzyme catalysis and by comparison of the NMR data of the corresponding *R* and *S* Mosher's ester. The configuration of **2e** was determined by comparison of the optical rotation with literature data. [b] The enzyme activity was determined by the decrease of the NAD(P)H extinction at 340 nm relative to the 100% standard (HLADH: cyclohexanone; TBADH: 2-butanone; recLBADH: ethyl 5-oxohexanoate). [c] *ee* 98.5%. [d] The change in configuration is because of the different CIP priorities. TMS = trimethylsilyl, TBS = *tert*-butyldimethylsilyl.

As a result of the low solubility of **1**, about 25% of a short-chain alcohol was added, surprisingly without any significant loss of enzymatic activity of HLADH and recLBADH.[13] Conveniently, as all the investigated ADHs recycle the cofactor $NAD(P)^+$ by oxidation of the auxiliary alcohol, the addition of a second $NAD(P)^+$-reducing enzyme was not necessary. The large excess of short-chain alcohol shifted the substrate/product equilibrium towards the desired propargylic alcohol **2**, thus resulting in almost quantitative conversions with high total turnover numbers (TTN) of the cofactor.[14] Enzymatic reductions could be carried out on a preparative scale by using deionized water instead of buffer[15] and were easily scaled up by using fed-batch technique. Thus, mmol quantities of substrate **1a** were converted by using as little as 0.005 mol% of cofactor, which corresponds to a TTN of 20000, and small amounts of recLBADH ($\sim$100 units enzyme g^{-1} substrate).[16] After a reaction time of 24–36 h, the pure product (NMR and GC analysis) was easily isolated by extraction without further purification in > 95% yield. HPLC analysis revealed > 99% conversion and, additionally, only one single enantiomer could be detected (*ee* > 99%).[17] Currently, investigations into the reduction of 1-(chloro or bromo)-3-butyn-2-one are in progress. recLBADH converts these substrates into enantiopure *R* alcohols **2** (X = Cl, Br; R = H), thus resulting in an interesting switch of the enantioselectivity of the enzymatic reduction. As the enantiomers (*S*)-**2** (X = Cl, Br; R = H) can be obtained by recLBADH reduction of **1b**–**d** and subsequent removal of the silyl protecting group, this enzyme offers unique access to a pair of enantiomers.

Propargylic alcohols **2** can easily be converted in good yield into the corresponding epoxides **3** without racemization. Treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in $EtOH/H_2O$ (4:1) at ambient temperature led to ring closure (Scheme 1). After workup by extraction, no further purification was necessary since by-products could not be detected. This general approach to enantiomerically pure terminal propargylic epoxides[18] offers multifaceted applications in organic chemistry as has been shown, for instance, by Hiyama and co-workers in the synthesis of HMG-CoA reductase inhibitor NK-104.[19] For this purpose, epoxide (*R*)-**3b** was obtained by ex-chiral pool synthesis in six steps and with an overall yield of 20%.[18a,b] Since terminal propargylic epoxides



2 3

Scheme 1. Conversion of chlorohydrins **2** into epoxides **3**.

and chlorohydrins can be selectively modified at C1 or C2 at their particular functionalities as well as at C3 or C4 at the triple bond,[20] these compounds are of great use in synthetic chemistry.

In conclusion, we have developed an efficient method to obtain halogenated propargylic alcohols **2** as well as terminal propargylic epoxides **3** with excellent enantiomeric excesses. The commercial availability and the easy handling of all components offers ready access to building blocks that were hardly known previously. The multifunctionality of these enantiopure C_4 units allows highly flexible synthetic transformations, thus making them interesting intermediates in the synthesis of natural compounds and drugs.

Experimental Section

(*S*)-**2a**: A solution of **1a** (1.56 g, 8.76 mmol) in 2-propanol (30 mL) was added over 20 h (25 μL min^{-1}) to a stirred solution of $NADP^+$ (3.6 mg, 4.2 μmol; 0.05 mol %), 2-propanol (30 mL) and recLBADH (150 U) in triethanolamine–HCl buffer (150 mL; 100 mM; 1 mM $MgCl_2$; pH 6.5) at room temperature. After stirring for an additional 28 h, deionized water (600 mL) was added, and the reaction mixture was extracted with CH_2Cl_2 (3×200 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give analytically pure (NMR, GC-MS) alcohol (*S*)-**2a** as a yellow oil (1.55 g, 8.60 mmol, 98 % yield). >99 % *ee*;[17] $[\alpha]_D^{20} = +25.4$ ($c = 1.4$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.56$ (d, $J = 6.1$ Hz, 1H; OH), 3.76 (dd, $J = 11.1$, 6.5 Hz, 1H; CHCl), 3.83 (dd, $J = 11.1$, 4.1 Hz, 1H; CHCl), 4.84 (m, 1H; CH), 7.36 (m, 3H; ArH), 7.47 (m, 2H; ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 49.3$ (C1), 63.2 (C2), 86.1, 86.6 (C3, C4), 122.0, 128.6, 129.1, 132.0 (ArC); HR-MS (EI): calcd for $C_{10}H_9ClO$: 180.0342, found: 180.0344.

(*R*)-**2a**: A solution of **1a** (1.56 g, 8.76 mmol) in ethanol (45 mL) was added over 2 h (15 mL h^{-1}) to a stirred solution of NAD^+ (6.0 mg, 8.42 μmol; 0.10 mol-%), ethanol (75 mL), and HLADH (250 U) in triethanolamine–HCl buffer (500 mL, 100 mM; pH 7.0) at room temperature. After stirring for an additional 34 h, deionized water (1000 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (3×300 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to yield analytically pure (NMR, GC-MS) alcohol (*R*)-**2a** as a yellow oil (1.53 g, 8.50 mmol, 97 %). >99 % *ee*);[17] $[\alpha]_D^{20} = -25.2$ ($c = 1.3$, $CHCl_3$);[17] ^1H NMR and ^{13}C NMR: as for (*S*)-**2a**.

(*R*)-**3a**: Alcohol (*R*)-**2a** (588 mg, 3.3 mmol) was added to a solution of DBU (1.5 mL, 10.0 mmol) in EtOH/H_2O (20 mL, 4:1). The mixture was stirred for 90 min at room temperature, followed by addition of H_2O (100 mL) and extraction with ethyl acetate (3×30 mL). The organic layers were dried over Na_2SO_4 and concentrated in vacuo to yield analytically pure (NMR, GC-MS) epoxide (*R*)-**3a** as an orange oil (441 mg, 3.1 mmol, 93 %). Purification by flash chromatography ('Iso-hexane'/ethyl acetate 30:1; 'Iso-hexane': Fluka 34969, mixture of isomers) yielded (*R*)-**3a** as a colorless oil (376 mg, 2.6 mmol, 80 %) >99 % *ee*;[21] $[\alpha]_D^{20} = -47.0$ ($c = 1.3$, acetone);[18c] $[\alpha]_D^{20} = -42$ ($c = 2.0$, acetone 78 % *ee*). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.02$ (d, $J = 3.3$, 2H; CH_2), 3.60 (t, $J = 3.3$, 1H; CH), 7.34 (m, 3H; ArH), 7.47 (m, 2H; ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 40.4$ (C2), 49.3 (C1), 83.6, 85.9 (C3, C4), 122.1, 128.5, 129.0, 132.1 (ArC).

Received: July 24, 2001 [Z17588]

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[10] S-ADH from *Thermoanaerobacter ethanolicus* (TEADH) has been proven to be extremely similar to TBADH (99.1 % sequence identity) and was cloned, sequenced, and expressed in *E. coli*: D. S. Burdette, C. Vieille, J. G. Zeikus, *Biochem. J.* **1996**, *316*, 115. Wet *E. coli* cells (150 g) that express TEADH yield approximately 60000 units of TEADH: see ref. [4f]. TEADH and TBADH showed identical relative enzymatic activities on ketones **1a–e** (for TBADH, see Table 1). In analytical batches, both enzymes converted substrate **1a** into enantiomerically pure (*R*)-**2a** (> 99 % *ee*). We thank Prof. Phillips for a kind donation of TEADH.

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[12] J. Peters in *Biotechnology*, *2nd ed.*, *Vol. 8a* (Eds.: H.-J. Rehm, G. Reed), Wiley-VCH, Weinheim, **1998**, pp. 437–439.

[13] An aqueous HLADH solution that contained 25 % ethanol and an aqueous recLBADH solution that contained 25 % 2-propanol showed >80 % remaining activity after 15 h. In contrast, TBADH displayed <40 % remaining activity under these conditions (25 % 2-propanol).

[14] In the case of the enzymatic reduction of **1b**, only moderate conversions were found. However, preliminary results suggest that the use of enzyme-coupled cofactor regeneration could result in quantitative conversion.

[15] The use of deionized water requires pH monitoring and adjustment with aqueous NaOH. In contrast to HLADH and recLBADH, a decrease in enzymatic activity of TBADH in deionized water was observed. For simplification of the g-scale conversions with recLBADH and HLADH, these reactions were performed in aqueous buffer.

[16] In a fed-batch optimized with respect to low amounts of cofactor, ketone **1a** (1.1 mmol) in deionized water (20 mL) and 2-propanol (8 mL) was quantitatively reduced as described in the experimental section by using $NADP^+$ (0.055 μmol) and recLBADH (20 U).

[17] Enantiomers of **2a** were separated by means of HPLC on a Chiralcel OB column (250×4 mm, equipped with a precolumn, 80×4 mm, Daicel Chem. Ind., 20 °C, 0.5 mL min^{-1}, 'Iso-hexane'/2-propanol 95:5), $R_t = 39.0$ min ((*S*)-**2a**), 44.7 min ((*R*)-**2a**).

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[18] Chiral nonracemic terminal propargylic epoxides have been described in: a) M. Lopp, T. Kanger, A. Müraus, T. Pehk, Ü. Lille, *Tetrahedron: Asymmetry* **1991**, *2*, 943; b) T. Kanger, P. Niidas, A.-M. Müürisepp, T. Pehk, M. Lopp, *Tetrahedron: Asymmetry* **1998**, *9*, 2499 (one example derived from tartaric acid derivative is given); c) R. Sánchez-Obregón, B. Ortiz, F. Walls, F. Yuste, J. L. García Ruano, *Tetrahedron: Asymmetry* **1999**, *10*, 947 (3 examples with *ee*'s up to 88% are given); synthetically useful enantioselectivities with terminal olefins are yet to be achieved with chiral (salen)Mn^{III} systems: E. N. Jacobsen in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), Wiley-VCH, New York, **1993**, p. 178.

[19] K. Takahashi, T. Minami, Y. Ohara, T. Hiyama, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2649.

[20] Alcohols (*R*)- and (*S*)-**2a** were converted into the corresponding *E*- and *Z* allylic alcohols by using Red-Al or Lindlar catalyst, respectively. The olefinic products were obtained in high yield, without racemization (*ee* >99%) and excellent *E*/*Z* ratios (Red-Al: *E*/*Z* 100:0; Lindlar catalyst: *E*/*Z* 5:95). Thus, another class of hardly known highly functionalized synthetic intermediates is easily accessible; T. Schubert, M. Müller, unpublished results.

[21] The *ee* values were determined by conversion of epoxide (*S*)-**3a** and rac-**3a** into the terminal nitrile, by treatment with a threefold excess of KCN in ethanol/water (4:1) at 50 °C for 4 h. The nitrile obtained was separated by means of HPLC on a Chiralcel OB column (20 °C, 0.5 mL min^{-1}, 'Iso-hexane'/2-propanol 95:5), R_t = 68.6 min ((*R*)-**3a**), 79.3 min ((*S*)-**3a**).

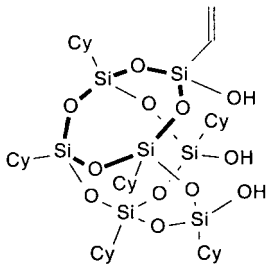
Titanium Silsesquioxanes Grafted on Three-Dimensionally Netted Polysiloxanes: Catalytic Ensembles for Epoxidation of Alkenes with Aqueous Hydrogen Peroxide**

Maria D. Skowronska-Ptasinska, Martinus L. W. Vorstenbosch, Rutger A. van Santen, and Hendrikus C. L. Abbenhuis*

Few catalysts have been truly efficient in alkene epoxidation with aqueous hydrogen peroxide. Development of such catalysts is an important goal since with regard to desirability, this oxidant comes only second to oxygen itself.[1] Currently, the best catalyst in this field is the synthetic titanium-containing zeolite, titanium silicalite-1 (TS-1),[2] which is active for a wide range of oxidation reactions, including epoxidation.[3] For TS-1, activity seems to originate from a *combination* of a robust active Ti(OSi≡)$_n$ site (n = 3, 4),[4] and its location in a hydrophobic channel or cavity in the MFI (ZSM-5) structure.[5] The resulting catalytic ensemble prevents poisoning of the active site by water as well as unproductive decomposition of the oxidant. A series of titanium silsesquioxane complexes with structural elements that are very similar to the active TS-1 site have been reported to function as homogeneous catalysts.[6] Although some of these complexes are stable in aqueous media,[7] none could perform alkene epoxidation with hydrogen peroxide. It is tempting to ascribe this to the lack of a combination of the active titanium site with a suitable hydrophobic environment. The same phenomenon can acount for the lack of catalytic activity in a study by Sherrington and Alder on Ti^{IV}-grafted polysiloxane networks prepared from silanol-rich supports. These materials, showed no activity in alkene epoxidation with 30% aqueous H_2O_2.[8] This can be ascribed to either the presence of residual silanol groups that make the materials more hydrophilic thus rendering unsuitable catalytic ensembles or to the presence of Ti centers with inappropriate structures.

Herein, epoxidation catalysts are reported that, like TS-1, epoxidize 1-octene but also substrates that are too large for TS-1 such as cyclooctene and cyclododecene. In this approach, ensembles are made from robust titanium silsesquioxane complexes. These are grafted on commercially available linear methylhydrosiloxane–dimethylsiloxane copolymers and then cross-linked by reaction with vinyl-terminated polydimethylsiloxanes. The resulting titanium polysiloxane materials are hydrophobic, three-dimensionally netted polymers that enclose the titanium sites in cavities that can, in principle, be varied according to the choice of the starting materials. Since titanium polysiloxanes are found to epoxidize alkenes with *aqueous* hydrogen peroxide, while titanium silsesquioxane complexes alone do not have this ability, we demonstrate the need for catalytic ensembles in this area of science.

Vinyl silsesquioxane trisilanol [$(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_9(OH)_3$] (**1**)[9] can be easily converted to new titanium silsesquioxane complexes [$(H_2C{=}CH)(c\text{-}C_6H_{11})_6Si_7O_{12}TiX$] (**2a**, X = η^5-C_5H_5 (Cp), **2b**, X = O*i*Pr) by reaction with [Cl_3TiCp] or [$Ti(O{i}Pr)_4$], respectively. These reactions are



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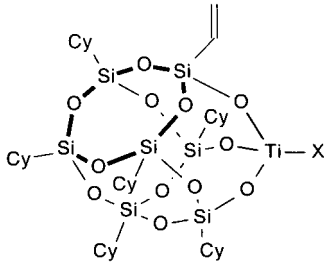

2a, X = η^5-C_5H_5
2b, X = O*i*Pr

similar to those previously described for the related, unfunctionalized silsesquioxane trisilanol [$(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$].[6b, 10] For both new complexes, the ^{13}C NMR spectra (400 MHz, $CDCl_3$) are particularly informative, showing four peaks for the cyclohexyl methine carbon atoms (ratio 2:1:1:2 for **2a** and 1:1:2:2 for **2b**) characteristic for C_2-symmetric, monomeric silsesquioxane titanium species. Attempts to obtain crystals of **2** suitable for X-ray analysis were unsuccessful thus far.

Vinyl-bearing metallosilsesquioxanes readily undergo platinum-catalyzed hydrosilylation,[11] thus for the immobilization

[*] Dr. H. C. L. Abbenhuis, Dr. M. D. Skowronska-Ptasinska, M. L. W. Vorstenbosch, Prof. Dr. R. A. van Santen
Schuit Institute of Catalysis
Eindhoven University of Technology
P. O. Box 513, 5600 MB Eindhoven (The Netherlands)
Fax: (+31) 40-24-55-05-4
E-mail: H.C.L.Abbenhuis@chem.tue.nl

[**] We thank Degussa/Creavis GmbH for financial support.

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