Communications

Asymmetric Catalysis

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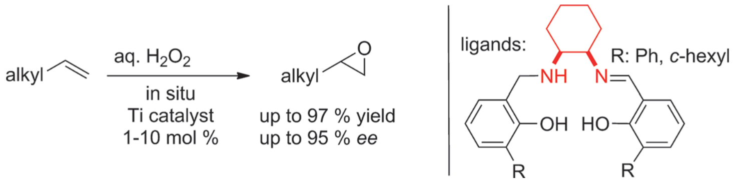
Titanium Salalen Catalysts Based on *cis*-1,2-Diaminocyclohexane: Enantioselective Epoxidation of Terminal Non-Conjugated Olefins with H_2O_2



Help for the neglected: Terminal, non-conjugated olefins, such as 1-octene, are difficult to epoxidize asymmetrically. Ti salalen complexes based on *cis*-1,2-diaminocyclohexane catalyze this demanding reaction giving high yields and enantioselectivities (up to 95% *ee*), with H_2O_2 as the oxidant. The X-ray structures of the μ-oxo and peroxo complexes shed light on the coordination behavior of this novel class of ligands.

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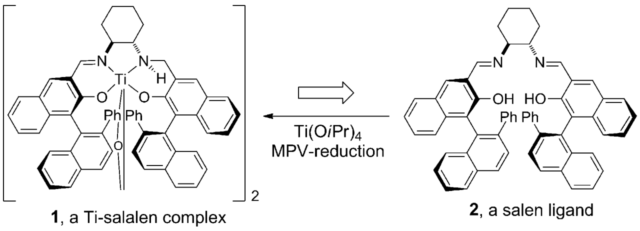
Titanium Salalen Catalysts Based on *cis*-1,2-Diaminocyclohexane: Enantioselective Epoxidation of Terminal Non-Conjugated Olefins with H_2O_2**

Albrecht Berkessel, Thomas Günther, Qifang Wang, and Jörg-M. Neudörfl*

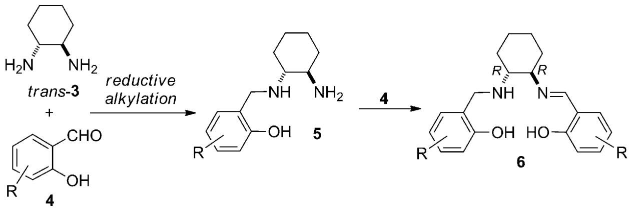
In 2005, Katsuki et al. introduced titanium salalen complexes, such as **1** (Scheme 1), as novel and highly enantioselective catalysts for the asymmetric epoxidation of a variety of non-functionalized olefins (both conjugated and non-conjugated) using hydrogen peroxide as the oxidant.[1] Salalen ligands are mono-reduced salens, carrying one imine and one amine functionality. For example, the catalyst **1** was reported to effect the epoxidation of 1,2-dihydronaphthalene with quantitative yield and over 99% *ee*. Even more remarkably, the epoxidations of 1-octene and vinyl cyclohexane were reported to proceed with 85% yield/82% *ee*, and 72% yield/95% *ee*, respectively. 1-Octene in particular is a terminal olefin notoriously difficult to epoxidize asymmetrically—the epoxide yields/enantioselectivities achieved by Katsuki et al. in 2005/2007 were the highest ever reported.[1]



Scheme 1. Titanium salalen catalyst **1**, and its salen precursor **2**.

Katsuki's seminal discovery was based on the "adventitious" Meerwein-Ponndorf-Verley-type mono-reduction of the corresponding salen ligand **2** (Scheme 1) when treated with Ti(O*i*Pr)$_4$, and sparked intensive further studies on related systems.[2] They furthermore disclosed that fully reduced and more readily available titanium salan complexes are similarly active and selective, albeit only for conjugated olefins.[3]

Our own work in this area aimed at simplifying the catalyst complexes such as **1**, while retaining its remarkable ability for the asymmetric epoxidation of non-conjugated olefins. In 2007, we disclosed a two-step approach to salalen ligands of type **6** (Scheme 2).[4] Our modular synthesis of salalen ligands begins with the reductive mono-alkylation of *trans*-DACH (*trans*-**3**; *trans*-1,2-diaminocyclohexane) with a salicylic aldehyde **4**. The resulting N-mono-alkylated *trans*-DACH **5** is then condensed with a second (or the same) salicylic aldehyde **4** affording the ligand **6**. In situ complexation of **6** with Ti(O*i*Pr)$_4$ affords the catalytically active complex.



Scheme 2. Modular synthesis of the *trans*-DACH-based ligands **6**.

The readily accessible ligands **6** (e.g. R = 6-Ph) turned out to be quite efficient for the epoxidation of conjugated olefins, and afforded for example, indene epoxide in 88% yield and 97% *ee*.[4] Unfortunately, less-reactive non-conjugated olefins, such as 1-octene, were epoxidized only with low efficiency, as a result of competing oxidative catalyst deactivation.

Our search for more endurable, yet readily available catalyst structures led us to exchange *trans*-DACH (*trans*-**3**) for *cis*-DACH (*cis*-**3**, Scheme 3). We have recently disclosed a practical one-step preparation of enantiopure mono-Alloc- (**7**) or mono-Boc-protected (**8**) *cis*-DACH.[5] These compounds were employed for the synthesis of the salalen ligands **12** and *ent*-**12** as outlined in Scheme 3. An initial survey of the catalytic performance of the titanium complexes derived from the *cis*-DACH ligand *ent*-**12**, relative to that of its *trans*-DACH counterpart **6** (R = 6-Ph), was performed using the substrate olefins **13**–**16** and a fixed reaction time of 18 h. The catalytically active Ti complexes were generated in situ by combining the respective ligands with one equivalent of Ti(O*i*Pr)$_4$ in methylene chloride at room temperature (see Experimental Section and Supporting Information for details). Olefin and internal standard were added, and the reaction was started by addition of 1.50 equivalents of

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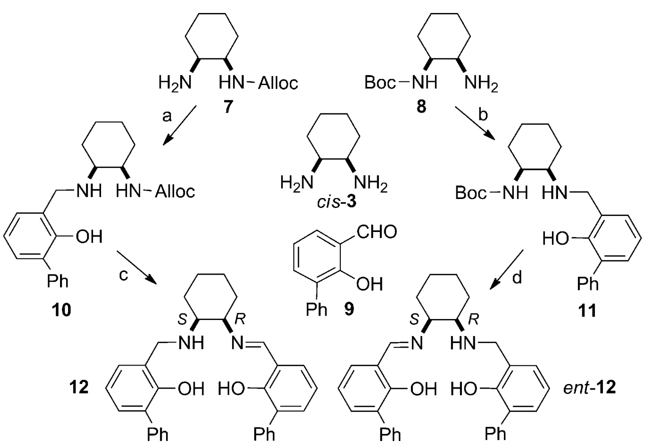
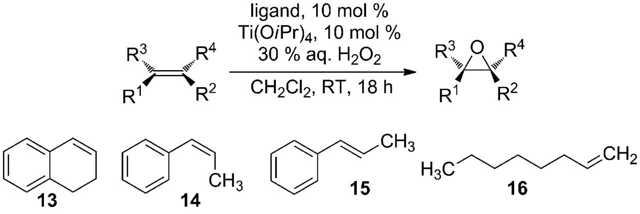


Scheme 3. Preparation of the *cis*-DACH derived salalen ligands **12** and *ent*-**12**. Reagents and conditions: a) **9**, EtOH; $NaBH_4$, MeOH; 93%; b) same as in (a), 87%; c) dimethylbarbituric acid, $Pd(OAc)_2$, PPh_3, CH_2Cl_2; **9**, EtOH, 38%; d) HCl, MeOH; **9**, EtOH, 59%.

aqueous hydrogen peroxide (30%). The results of the epoxidation experiments are summarized in Table 1.

We were delighted to see that the novel *cis*-DACH-derived Ti complexes are active epoxidation catalysts. Throughout, the epoxide yields achieved with the *cis*-ligand *ent*-**12** were higher than those of the *trans*-ligand **6** (R = 6-Ph). Note that the sense of induction was the same for *ent*-**12** and **6** (R = 6-Ph), emphasizing the importance of the sense of chirality at the Ti center (Λ in both cases). The chirality at the Ti center, in turn, is defined by the sense of chirality (here *R*) at DACH's "amine C-atom" (see Refs. [1,2,4] and X-ray crystal structures below). Table 1 additionally reflects the following features of our novel *cis*-DACH epoxidation catalyst: 1) both systems work particularly well for the cyclic *cis*-1,2-disubstituted conjugated olefin 1,2-dihydronaphthalene (**13**, entries 1, 2), with higher yield but somewhat lower *ee* value for the *cis*-DACH ligand *ent*-**12**, 2) stereospecificity: *cis*-β-methylstyrene (**14**, entries 3, 4) as an acyclic analogue of **13**, and *trans*-β-methylstyrene (**15**, entries 5, 6) are epoxidized stereospecifically, pointing to concerted rather than stepwise oxygen transfer, 3) for the non-conjugated terminal olefin **16** (1-octene), both epoxide yield and enantiopurity were higher for the ligand *ent*-**12** (entries 7, 8).

Table 1: Titanium-catalyzed asymmetric epoxidation: *trans*- and *cis*-DACH-salalen ligands **6** (R = 6-Ph) and *ent*-**12**.



Entry[a]	Substrate olefin	Ligand	Epoxide yield [%][b]	Epoxide *ee* [%][b]	Epoxide configuration[c]
1	**13**	**6**	87	95	1*S*,2*R*
2	**13**	*ent*-**12**	98	85	1*S*,2*R*
3	**14**	**6**	51	66	*cis*, 1*S*,2*R*
4	**14**	*ent*-**12**	70	59	*cis*, 1*S*,2*R*
5	**15**	**6**	17	31	*trans*, 1*S*,2*S*
6	**15**	*ent*-**12**	24	31	*trans*, 1*S*,2*S*
7	**16**	**6**	8	62	*R*
8	**16**	*ent*-**12**	20	79	*R*

[a] Reactions were performed with a molar ratio of substrate/ligand/$Ti(OiPr)_4$/aq.H_2O_2 of 1:0.1:0.1:1.5. [b] Determined by GC or HPLC analysis. [c] Major epoxide enantiomer, determined by comparison of the elution order with that of authentic samples in HPLC or GC analysis.

We furthermore observed that alcohols—including 2-propanol liberated during complex formation from $Ti(OiPr)_4$—and 1,2-diols (from hydrolytic oxirane opening) inhibit the catalytic epoxidation (quantitative data not shown). We therefore modified the in situ catalyst preparation so that, after ligand complexation by $Ti(OiPr)_4$ at room temperature, volatiles were removed in vacuo. The remaining solid Ti complex was then re-dissolved in methylene chloride, and the catalytic epoxidation was carried out as described before. The yield/*ee* time profile of 1-octene (**16**) epoxidation in the presence of the ligands **6** (R = 6-Ph) and **12** is shown in Figure 1, and reveals the following features: 1) the epoxide yield in the presence of ligand **6** (R = 6-Ph) is limited by catalyst deactivation, thus longer reaction time does not improve the yield (non-productive peroxide decomposition was excluded by control experiments); 2) for the more robust **12**, the epoxide yield increases continuously with time—after 4 days, 86% yield was achieved; 3) for both ligands, product *ee* value is not a function of time, thus excluding concomitant kinetic resolution.

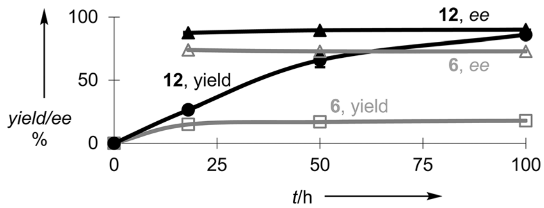
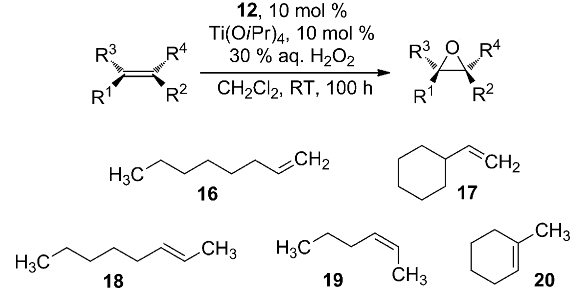


Figure 1. Reaction profiles of 1-octene epoxidation, carried out by the Ti complexes of ligands **6** (R = 6-Ph) and **12** ("in situ/vac" procedure).

Table 2 shows the results obtained for the non-conjugated olefins **16**–**20**, applying the improved "in situ/vac" procedure described above. With regard to 1-octene (**16**), we were delighted to see that the catalyst loading could be reduced to 2 mol% without appreciable loss of epoxide yield or enantioselectivity (Table 2, entries 1–3). Variation of the reaction temperature (0°C, entry 4; 40°C, entry 5) did not significantly affect enantioselectivity. However, at 40°C, competing catalyst deactivation severely limited the attainable epoxide yield (entry 5). Vinyl cyclohexane (**17**), also a terminal non-conjugated substrate, behaved analogously (entries 6–8). In line with the behavior of *trans*-β-methylstyrene (**15**, entries 5, 6, Table 1), enantioselectivity was poor for *trans*-2-octene (**18**, entry 9, Table 2), albeit at reasonably high olefin conversion and epoxide yield (ca. 80%). *cis*-2-Hexene (**19**), as a representative *cis*-internal olefin, was converted selectively into the *cis*-epoxide, with good conversion and yield, and intermediate *ee* value (62–63%, entries 10, 11). As exemplified by 1-

Table 2: Asymmetric epoxidation of non-conjugated olefins, using the *cis*-DACH ligand **12**, in situ/*vac* procedure.



Entry[a]	Substrate olefin	Olefin conversion [%][f]	Epoxide yield [%][f]	Epoxide *ee* [%][f]
1	**16**	90	86	89
2[b]	**16**	86	84	89
3[c]	**16**	83	83	89
4[d]	**16**	25	22	88
5[e]	**16**	68	51	87
6	**17**	87	87	81
7[d]	**17**	20	18	80
8[e]	**17**	56	50	80
9	**18**	82	78	16
10	**19**	n.d.[g]	74	63
11[d]	**19**	n.d.[g]	44	62
12	**20**	50	trace[h]	-

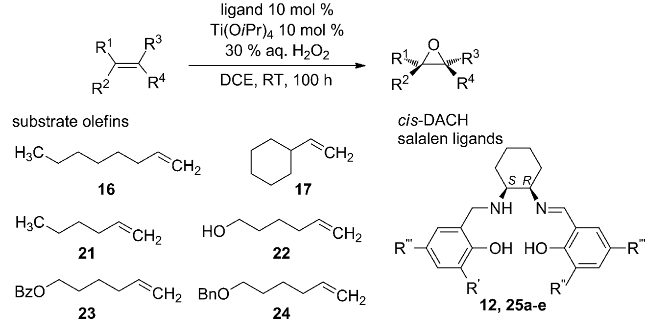
[a] In situ/vac procedure for catalyst preparation, reaction at room temperature with a molar ratio of substrate/ligand/Ti(O*i*Pr)$_4$/30% aq.H$_2$O$_2$ of 1:0.1:0.1:1.5. [b] 5 mol% of **12**/Ti(O*i*Pr)$_4$. [c] 2 mol% of **12**/Ti(O*i*Pr)$_4$. [d] 0°C, 50% aqueous H$_2$O$_2$. [e] 40°C. [f] Determined by chiral HPLC or GC. [g] As *cis*-2-hexene is highly volatile, olefin conversion could not be determined in a reliable fashion. [h] Epoxide is not stable under the reaction conditions.

methylcyclohexene (**20**, entry 12), trisubstituted olefins are not efficiently epoxidized by our catalytic system.

Our next optimization step concerned the reaction solvent. In brief (see Supporting Information for full data set), halogenated hydrocarbons are the solvents of choice, with 1,2-dichloroethane being optimal. In this solvent, vinyl cyclohexane (**17**) gave an almost quantitative (97%) epoxide yield, with 82% *ee* (Table 3, entry 2; compare to entry 6, Table 2). Finally, a further increase in enantioselectivity was achieved by variation of the 6-substituents (R′ and R″) of the ligand (Table 3). Methoxylation of the phenyl residues (ligands **25a–c**, entries 9–14) was inspired by Katsuki's observation that this modification was beneficial in the case of salan ligands.[3] Exchange of Ph for *c*-hexyl in R′ and R″ (ligands **25d** and **25e**, entries 15–24) was hoped to increase hydrophobic/dispersion interaction between the catalyst and the olefinic substrates in the presence of aqueous H$_2$O$_2$.[6] Table 3 reveals the following key features: 1) For the substrate 1-octene (**16**), methoxylation of the ligand does not alter the enantioselectivity (90% *ee*) but both olefin conversion and epoxide yield are adversely affected (entries 1, 9, 11, and 13). For vinyl cyclohexane (**17**), ligand methoxylation again did, at best, result in a slight improvement of enantioselectivity (84% versus 82% *ee*, entries 2, 10, 12, and 14). The doubly *c*-hexyl substituted ligand **25e** affords the highest enantioselectivity for 1-octene epoxide: 94% *ee* at a product yield of 88% (entry 17). In a preparative experiment (1 mol% catalyst; entry 18), even 95% *ee* resulted. To our knowledge, those are the best yields/selectivities achieved to date in the catalytic asymmetric epoxidation of 1-octene (**16**). Related 1-hexene (**21**) afforded the epoxide with somewhat lower enantioselectivity (89% *ee*, entry 21). For vinyl cyclohexane (**17**), the doubly *c*-hexyl substituted ligand **25e** again afforded the highest enantioselectivity (90% *ee*) at 89% isolated epoxide yield—and at a catalyst loading as low as only 2 mol% (entry 20). Most remarkably, switching from cyclohexyl (ligand **25e**) to 1-methylcyclohexyl substitution (ligand **25d**) completely shut down epoxidation activity for both olefin substrates (entries 15, 16). Furthermore, note that in the epoxidation of vinyl cyclohexane (**17**), the loading of the Ph-substituted catalyst **12** could be reduced to even 1 mol% at invariably high enantioselectivity, although some loss in epoxide yield occurred upon switching from 10 mol% (entry 2) to 2 mol% (entry 3) and finally 1 mol% of catalyst (entry 4). Of the functionalized substrates **22–24**, both the benzoate **23** (entry 23) and the benzyl ether **24** (entry 24) gave good product yields (91–94%) and 89–90% *ee* when epoxidized in the presence of ligand **25e**. For the alcohol 5-hexen-1-ol (**22**), good enantioselectivity (90% *ee*, entry 22) was observed, with the expected (see above) partial catalyst inhibition.

We were able to characterize the Ti complexes **26** and *ent*-**26**, derived from the *cis*-DACH salalen ligands **12** and *ent*-**12**, by X-ray crystallography.[7] Figure 2 (top) shows the X-ray crystal structure obtained from *ent*-**26**. As in the case of the

Table 3: Asymmetric epoxidation of the olefins **16**, **17**, **21–24** by the Ti complexes of ligands **12** and **25a–e**.



Entry[a]	L[b]	R′	R″	Olefin	Conversion [%][d]	Yield [%][d]	*ee* [%][d]
1	**12**	Ph	Ph	**16**	96	90	90
2	**12**	Ph	Ph	**17**	97	97	82
3	**12**	Ph	Ph	**17**	95	91[e]	82[e]
4	**12**	Ph	Ph	**17**	92	86[f]	82[f]
5	**12**	Ph	Ph	**21**	n.d.[g]	71	82
6	**12**	Ph	Ph	**22**	51[h]	44[h,i]	86[h]
7	**12**	Ph	Ph	**23**	94[j]	91[j]	87[j]
8	**12**	Ph	Ph	**24**	88[j]	70[j]	84[j]
9	**25a**	Ph	2-MeOPh	**16**	72	67	90
10	**25a**	Ph	2-MeOPh	**17**	51	48	84
11	**25b**	2-MeOPh	2-MeOPh	**16**	56	50	90
12	**25b**	2-MeOPh	2-MeOPh	**17**	54	51	83
13	**25c**	2-MeOPh	Ph	**16**	76	71	90
14	**25c**	2-MeOPh	Ph	**17**	74	73	82

Table 3: (Continued)

Entry[a]	L[b]	R′	R″	Olefin	Conversion [%][d]	Yield [%][d]	*ee* [%][d]
15	**25d**	Me-*c*-hexyl[c]	Me-*c*-hexyl[c]	**16**	n.d.	0	n.d.
16	**25d**	Me-*c*-hexyl[c]	Me-*c*-hexyl[c]	**17**	12	0	n.d.
17	**25e**	*c*-hexyl	*c*-hexyl	**16**	91	**88**	**94**
18	**25e**	*c*-hexyl	*c*-hexyl	**16**	90	**82**[f]	**95**[f]
19	**25e**	*c*-hexyl	*c*-hexyl	**17**	90	90	90
20	**25e**	*c*-hexyl	*c*-hexyl	**17**	90	**89**[e]	**90**[e]
21	**25e**	*c*-hexyl	*c*-hexyl	**21**	n.d.[g]	70	89
22	**25e**	*c*-hexyl	*c*-hexyl	**22**	38[h]	34[h,i]	90[h]
23	**25e**	*c*-hexyl	*c*-hexyl	**23**	94	94	90
24	**25e**	*c*-hexyl	*c*-hexyl	**24**	94	91	89

[a] Reactions were performed under the conditions summarized in Table 2, unless otherwise noted. [b] R‴ = H, except for ligand **25d**, where R‴ = Me. [c] 1-Methylcyclohexyl. [d] Determined by chiral GC or HPLC analysis. [e] 2 mol% of salalen ligand/Ti(O*i*Pr)$_4$; yield and *ee* value of isolated product (1 mmol scale in 1 mL of DCE) after Kugelrohr distillation. [f] 1 mol% of salalen ligand/Ti(O*i*Pr)$_4$; yield and *ee* value of isolated product (1 mmol scale in 0.5 mL of DCE) after Kugelrohr distillation. [g] As 1-hexene is highly volatile, olefin conversion could not be determined in a reliable fashion. [h] The reaction was monitored at 18 h. [i] Epoxide is not stable under the reaction conditions. [j] The reaction was monitored after 72 h.

related complexes derived from the *trans*-DACH ligands **6** (e.g. R = 6-Ph),[4] a doubly μ-oxo-bridged dimer is formed. The ligands *ent*-**12** are both coordinated to the Ti centers in a *cis*-β-mode, that is, with central chirality at the Ti atoms. The two "halves" of complex *ent*-**26** are homochiral (both 1*S*,2*R*,Λ),[8] and their relative orientation is *anti*. Note that the sense of chirality (Λ) is the same in the Ti complexes derived from both ligands **6**[4] and *ent*-**12**.

We were successful in isolating and characterizing (X-ray) the first three μ-oxo-μ-peroxo titanium salalen complexes **27**, *ent*-**27**, and **28**.[10] These complexes were obtained from the *cis*-DACH derived ligands **12**, *ent*-**12**, and **25e**, respectively, and Ti(O*i*Pr)$_4$ in the presence of aqueous H_2O_2. In both peroxo complexes *ent*-**27** and **28** (Figure 2, middle and bottom), the principal structure of the parent μ-oxo-bridged dimer *ent*-**26** (Figure 2, top) is maintained. One of the μ-oxo-bridges is exchanged for a doubly side-on coordinated peroxo ligand. The O–O distance in the peroxo ligand is 1.444(7) Å for *ent*-**27**, and 1.455 (5) Å for **28**, thus in the range typical for peroxide dianions side-on coordinated to Ti.[11]

The peroxo complex *ent*-**27** alone did not perform epoxidation, even of easy-to-epoxidize 1,2-dihydronaphthalene (**13**). Consequently, it does not represent the "loaded" oxygen-transferring state of the catalytic system. On the other hand, upon addition of aqueous H_2O_2, *ent*-**27** promoted the epoxidation of olefin **13** at a rate and enantioselectivity indistinguishable from the Ti complex *ent*-**26**.

In summary, we presented the first synthesis of chiral salalen ligands based on *cis*-DACH (*cis*-**3**), the structural characterization of their Ti complexes by X-ray crystallography, as well as their application in titanium-catalyzed asymmetric epoxidations with aqueous hydrogen peroxide. The readily accessible salalen ligand **25e**, carrying cyclohexyl substituents *ortho* to the phenolic hydroxy groups, proved particularly effective. As the most significant feature, *cis*-DACH derived Ti salalen catalysts provide high yields and enantioselectivities for non-conjugated terminal olefins—a notoriously difficult substrate class. The first titanium salalen peroxo complexes (**27**, *ent*-**27**, and **28**) were isolated and characterized by X-ray crystallography.

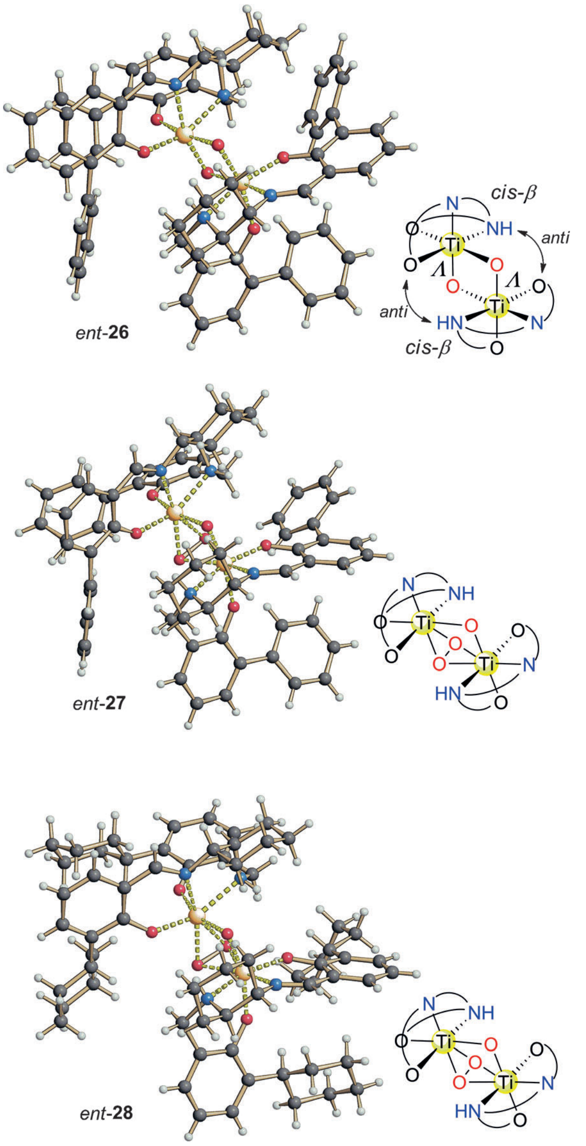


Figure 2. X-Ray crystal structures of Ti salalen complexes derived from *cis*-DACH (*cis*-**3**). Top: doubly μ-oxo-bridged dimer *ent*-**26** (from ligand *ent*-**12**). Middle: μ-oxo-μ-peroxo bridged dimer *ent*-**27** (from ligand *ent*-**12**). Bottom: μ-oxo-μ-peroxo bridged dimer *ent*-**28** [X-ray crystal structure determined for **28** (from ligand **25e**), enantiomer *ent*-**28** shown for ease of comparison].

Experimental Section

Asymmetric epoxidation of olefins using Ti salalen complexes from the "in situ/vac" procedure: The salalen ligand (10 μmol, 0.10 equiv) was added to a solution of Ti(O*i*Pr)$_4$ (2.8 mg, 3.0 μL, 10 μmol, 0.10 equiv) in water-free CH_2Cl_2 (500 μL). The mixture was stirred for 1 h at room temperature under argon. All volatiles were then evaporated at room temperature and 10^{-2} mbar. The olefin (0.10 mmol, 1.00 equiv), solvent (500 μL), 30% aqueous H_2O_2

(15.3 µL, 0.15 mmol, 1.50 equiv), and bromobenzene (22.4 mg, 15 µL, internal standard) were added. The reaction mixture was stirred at room temperature. For the epoxidation, no inert atmosphere was applied. If necessary, additional portions of H_2O_2 were added (peroxide test, KI/starch). An aliquot (50 µL) was withdrawn and diluted with *n*-hexane or CH_2Cl_2 (2 mL), and filtered through $MgSO_4$. The epoxide yield and the ratio of enantiomers were analyzed by HPLC or GC based on calibrations versus internal standard.

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[7] CCDC 915578 (**26**·DCM), 915579 (**27**·DCM), 915580 (*ent*-**26**·DCM), 915581 (*ent*-**27**·2DCM) and 915582 (**28**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] A literature survey revealed that the assignment of the Λ/Δ-descriptor for the chirality of octahedral coordination compounds is not uniform. The assignments made herein are based on the algorithm proposed by Herrero and Usón (Ref. [9]).

[9] S. Herrero, M. A. Usón, *Dalton Trans.* **2008**, 4993 – 4998.

[10] For a Ti salan peroxo complex by Katsuki et al., see: S. Kondo, K. Saruhashi, K. Seki, K. Matsubara, K. Miyaji, T. Kubo, K. Matsumoto, T. Katsuki, *Angew. Chem.* **2008**, *120*, 10349 – 10352; *Angew. Chem. Int. Ed.* **2008**, *47*, 10195 – 10198.

[11] A CSD search for Ti peroxo (side-on) complexes gave 40 hits, with O–O bond lengths ranging from 1.42–1.49 Å. Among those, the vast majority of O–O bond lengths fall in the range 1.44–1.48 Å.

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