deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-143946. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Cooperative Asymmetric Catalysis with Dendrimeric [Co(salen)] Complexes**

Rolf Breinbauer and Eric N. Jacobsen*

The synthesis of dendrimers with well-defined architectures has advanced at an accelerating pace since the first examples of cascade-like molecules were introduced in the late 1970s.[1] Indeed, highly pure polyamidoamine (PAMAM) and poly(propyleneimine) dendrimers are now commercially available at a moderate price, and good experimental procedures exist for the preparation of a variety of other dendrimeric compounds. Over the last several years, research in this area has extended from the synthesis and characterization of these compounds to the search for specific properties and functions that are a direct consequence of the dendritic architecture.[1e] One area that has attracted particular interest is in the development of so-called dendrimeric catalysts, and recently several groups have demonstrated that dendrimers bearing catalytic units covalently linked to the terminal sites can combine the best features of homogeneous and heterogeneous catalysts.[2, 3] Thus, a dendrimeric catalyst can present molecularly defined reactive sites in a macromolecule that can be reisolated easily by precipitation[3e,i] or filtration through a membrane.[3p–r]

The relative proximity of terminal sites may be controlled by the nature and generation number of the dendrimer. Therefore, at least in principle, a dendritic framework may be used to enforce and control cooperative interactions between catalyst units. However, while there have been a number of reports of cooperative binding effects with dendrimers incorporating recognition elements such as amino acids or carbohydrates,[4] no examples of enhanced catalytic activity due to cooperative effects have been reported in dendrimeric systems devised thus far.[5, 6]

In our ongoing studies of asymmetric ring opening (ARO) of epoxides by metal–salen complexes (H_2salen = bis(salicylidene)ethylenediamine),[7] substantial mechanistic evidence has been collected in support of a mechanism involving cooperative, bimetallic catalysis.[7, 8] This has led to a proposed mechanism for ARO reactions involving simultaneous activation of both epoxide and nucleophile by different metal–salen units (Figure 1a). Based on this hypothesis, we speculated whether dendrimeric analogues of these catalysts might reinforce cooperative catalytic activity in AROs (Figure 1b).

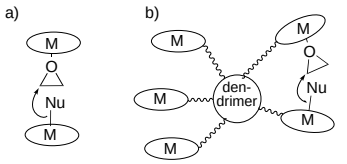
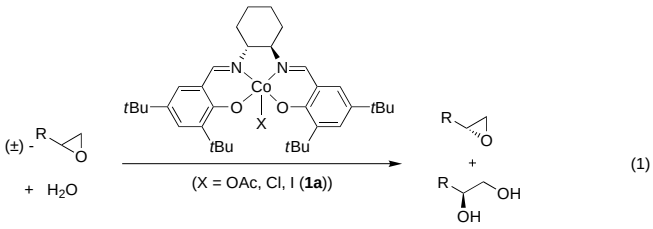


Figure 1. a) Proposed mechanism for cooperative catalysis in the asymmetric ring opening (ARO) of epoxides catalyzed by (salen)metal complexes. b) Cooperative catalytic ARO within a dendrimeric framework.

Herein we report the synthesis of dendrimer-bound [Co^{III}(salen)] complexes, and demonstrate that these catalysts indeed exhibit significantly enhanced catalytic activity in the hydrolytic kinetic resolution (HKR) of terminal epoxides [Eq. (1)].



We selected the commercially available NH_2-terminated PAMAM dendrimers for the syntheses of the dendrimeric [Co(salen)] catalysts. For example, 4-NH_2-PAMAM was derivatized by covalent attachment to chiral [Co^{II}(salen)] units through amide linkages by reaction with pentafluorophenyl ester derivative **1c** following standard peptide coupling methods (Scheme 1).[9] The resulting dendrimeric complex was purified by precipitation of concentrated THF solutions with hexanes followed by size-exclusion chromatography with Sephadex, and was characterized by FAB MS ($[M+Na]^+$: 2888, calcd for $C_{158}H_{224}Co_4N_{18}O_{16}$: 2865). Oxidation of the [Co^{II}(salen)] sites with elemental iodine in THF proceeded in quantitative yield and afforded the catalytically

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[**] Prof. M. T. Reetz (Max Planck-Institut für Kohlenforschung, Mülheim/Ruhr) and Mr. J. Hong (Harvard University) are gratefully acknowledged for stimulating discussions. This work was supported by the NIH (GM 43214). R.B. thanks Fonds zur Förderung der Wissenschaftlichen Forschung, Vienna (Erwin-Schrödinger-Fellowship) and Land Oberösterreich (Sonderförderung außerhalb des KIP-Programms) for postdoctoral fellowship support. H_2salen = bis(salicylidene)ethylenediamine.

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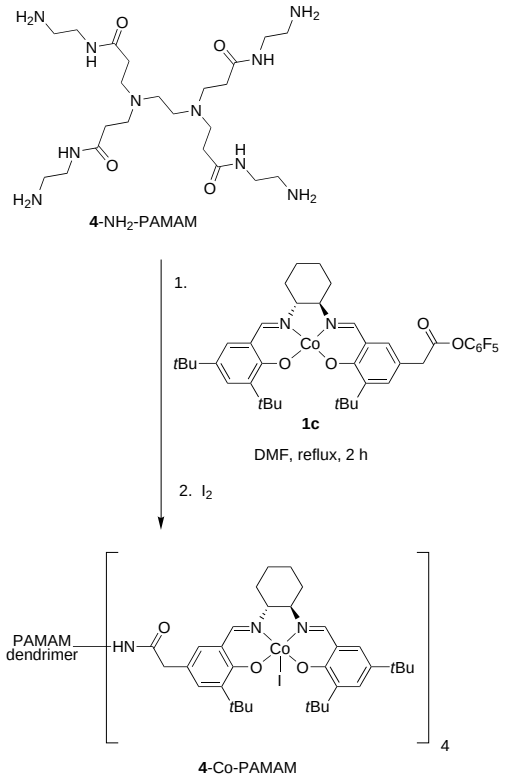


Scheme 1. Synthesis of dendrimer catalyst **4**-Co-PAMAM.

active Co^{III} dendrimer (**4**-Co-PAMAM) as a dark brown solid.[10, 11] In a similar manner, the higher generation **8**-Co-PAMAM and **16**-Co-PAMAM complexes were also prepared (Figure 2).

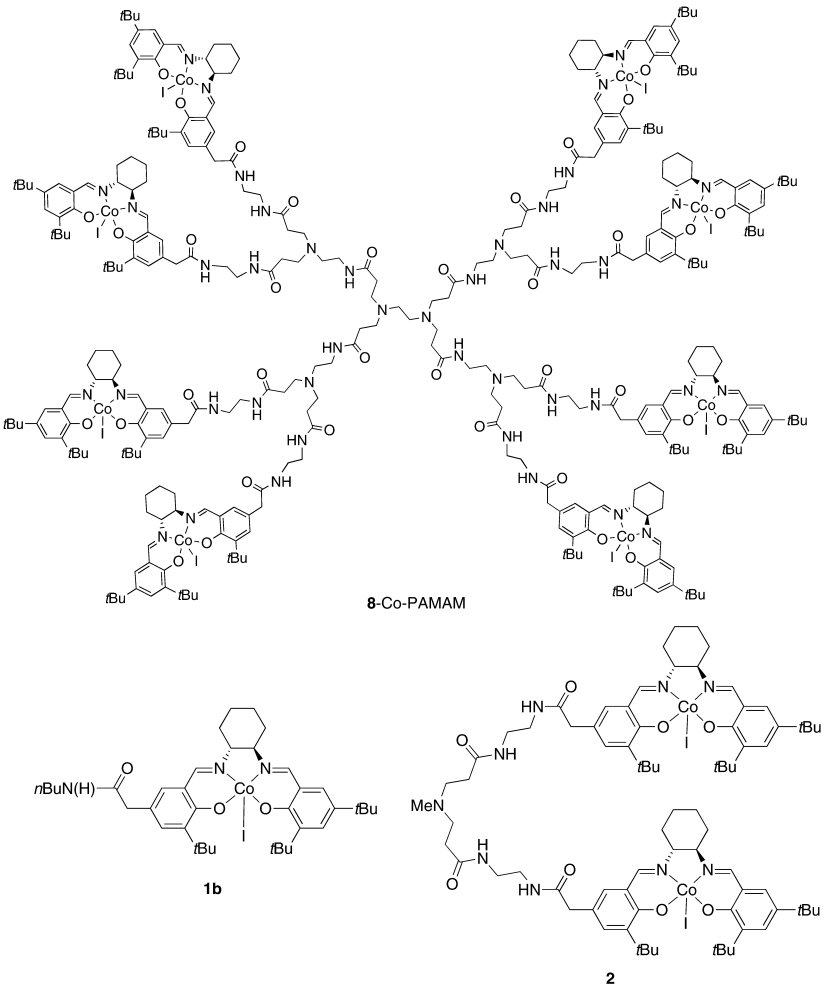
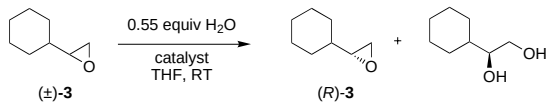


Figure 2. Structures of the dendrimeric catalyst **8**-Co-PAMAM and of model compounds **1b** and **2**. The dendrimeric catalyst **16**-Co-PAMAM (not shown) bears 16 [(salen)Co] units in a structure analogous to **8**-Co-PAMAM.

As a direct consequence of the second-order kinetic dependence of the HKR on the concentration of [Co(salen)] complex,[7d, 8c] reduction of catalyst loadings using the monomeric catalyst **1a** leads to sharp decreases in overall reaction rate; as a practical matter, attainment of useful rates ($t_{1/2} < 10$ h) in the HKR of a representative substrate such as vinylcyclohexane oxide (**3**) requires catalyst concentrations of about 2.5×10^{-2} M (0.5 mol % relative to racemic epoxide in solvent-free reactions). In order to assess whether intramolecular cooperativity could occur within the dendrimeric [Co(salen)] catalyst, we investigated the HKR of (±)-**3** using **8**-Co-PAMAM at a concentration of 2.0×10^{-4} M [Eq. (2), Table 1]. This corresponds to an overall loading of metal complex of 0.027 mol % relative to epoxide. As expected, reaction with the monomeric [Co^{III}(salen)] complex **1a** at the 0.025 mol % level led to no measurable conversion after 40 h. In contrast, the dendritic catalyst **8**-Co-PAMAM effected complete kinetic resolution of **3** under the same conditions, affording highly enantioenriched (> 98 % *ee*) epoxide at 50 % conversion.



(2)

Table 1. Hydrolytic kinetic resolution of (*rac*)-vinylcyclohexane epoxide ((±)-**3**) at low catalyst loading.

Catalyst	Catalyst loading [mol %][a]	Time [h]	Conversion [%][b]	*ee* of recovered epoxide [%][c]
(*R*,*R*)-**1a**	0.025	40	< 1	n.d.
8-Co-PAMAM (*R*,*R*)	0.027	20	50	98

[a] Catalyst loadings are on a per-cobalt basis relative to racemic epoxide. Catalyst concentrations are given in the text. [b] Determined by GC by integration against an internal standard (bromobenzene). [c] Determined by GC analysis using a commercial chiral column (γ-TA). n.d. = not determined.

Having demonstrated dramatically enhanced reactivity of the dendrimeric catalyst **8**-Co-PAMAM relative to monomer **1a**, we sought to establish the precise origins of the observed rate acceleration. In this vein we prepared monomer **1b**, which bears the same salen ligand substituents as that of the dendrimeric catalysts, and the dimeric model compound **2**, which mimics the tethered relationship of two catalyst units within a branch of the PAMAM dendrimers (Figure 2).[12] Kinetic studies of the HKR of (*rac*)-1,2-epoxyhexane ((±)-**4**) revealed that all of the dendrimeric catalysts were substan-

tially more reactive than the monomeric complex **1b**.[13] More significantly, the dendrimeric catalysts also displayed significantly higher catalytic activity than the dimeric model compound **2** (Figure 3). It is possible that this positive

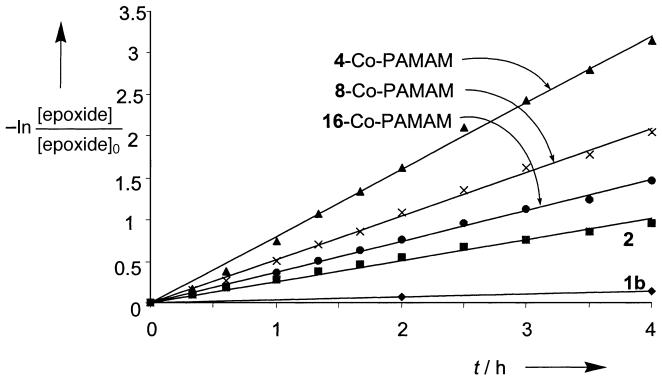


Figure 3. Rate plots for the HKR of (*rac*)-1,2-epoxyhexane ((±)-**4**) using 0.55 equivalents of H_2O in THF.

"dendrimer effect" arises from restricted conformations imposed by the dendrimer structure, thereby creating a greater effective molarity of [Co(salen)] units. Alternatively, the multimeric nature of the dendrimer may lead to higher order productive cooperative interactions between [Co(salen)] units.[8b] While the reactivity of the dendrimers increased on a per-molecule basis with increasing generations (Table 2), on a per-cobalt basis maximum reactivity was attained with **4**-Co-PAMAM.

Table 2. Kinetic data for the HKR of (*rac*)-1,2-epoxyhexane ((±)-**4**) catalyzed by the monomeric, dimeric, and dendrimeric [Co(salen)] catalysts.

Catalyst	k [$M^{-1}s^{-1}$][a]	No. of (salen)CoI units	Relative rate per [Co(salen)] unit	Diol *ee* [%] (conv, [%])[b]
1b	5.6×10^{-3}	1	1.0	98.2 (29.1)
2	7.9×10^{-2}	2	7.1	99.2 (37.0)
4-Co-PAMAM	5.4×10^{-1}	4	24	99.2 (42.8)
8-Co-PAMAM	6.7×10^{-1}	8	15	99.4 (40.1)
16-Co-PAMAM	9.4×10^{-1}	16	11	99.3 (39.8)

[a] Rate constants were obtained from plots of ln([epoxide]/[epoxide]$_0$) versus time (Figure 3) and calculated by dividing the slopes by the absolute concentration of catalyst. [b] *ee* values were determined at the indicated conversions of epoxide.

This work demonstrates for the first time enhanced reactivity in a dendrimeric catalyst resulting from cooperative reactivity between catalytic units. Further exploration and optimization of such multimeric catalysts in related asymmetric reactions appears warranted, and is the focus of our continuing efforts.

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[10] Although oxidation to the [(salen)Co^{III}(acetate)] complexes using $HOAc/O_2$ is the method of choice for the preparation of the monomeric catalysts (see ref. [7d]), this proved impractical with the PAMAM-Co complexes because of the basic amine sites in the dendrimer. The [(salen)Co^{III}(iodide)] complexes obtained by oxidation with I_2 have been found to display similar reactivity to the corresponding acetate complexes.[8c]

[11] **4**-Co-PAMAM: IR (KBr): $\tilde{\nu}_{max} = 3339, 2948, 2864, 1663$ (br.), 1609, 1526, 1435, 1253, 1170, 1031, 783; ^{1}H NMR (400 MHz, [D_6]DMSO): $\delta = 8.1$ (br., 8H), 7.83 (s, 4H), 7.79 (s, 4H), 7.47 (s, 4H), 7.43 (s, 4H), 7.33 (s, 4H), 7.29 (s, 4H), 3.62 (br.s, 16H), 3.38 (br.s, 12H), 3.10 (br.s, 16H), 2.6 – 2.2 (br., 16H), 1.98 (br., 4H), 1.89 (br., 4H), 1.76 (s, 36H), 1.72 (s, 36H), 1.60 (br.m, 8H), 1.28 (s, 36H); ^{13}C NMR (100 MHz, [D_6]DMSO): $\delta = 170.7, 164.4, 163.7, 162.5, 161.6, 141.9, 141.4, 135.6, 133.0, 132.2, 129.0, 128.5, 121.2, 118.4, 118.2, 69.2, 69.1, 41.2, 38.2, 35.7, 35.5, 33.5, 31.4, 30.3, 30.2, 29.5, 29.4, 24.2$.

[12] **1b**: IR (KBr): $\tilde{\nu}_{max} = 3365, 2950, 2864, 1630, 1611, 1526, 1436, 1254, 1170, 783$; ^{1}H NMR (400 MHz, [$D_6$]DMSO): $\delta = 8.00$ (t, $J = 5.6$ Hz, 1H), 7.85 (s, 1H), 7.80 (s, 1H), 7.50 (d, $J = 2.4$ Hz, 1H), 7.43 (d, $J = 2.4$ Hz, 1H), 7.33 (s, 1H), 7.30 (s, 1H), 3.62 (br.s, 2H), 3.35 (s, 2H), 3.10 (br.s, 2H), 3.05 (m, $J = 6.8$ Hz, 2H), 2.00 (br., 2H), 1.91 (br., 2H), 1.76 (s, 9H), 1.60 (br.m, 2H), 1.40 (m, $J = 7.2$ Hz, 2H), 1.32 (s, 9H), 1.28 (m, $J = 7.2$ Hz, 2H), 0.85 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, [D_6]DMSO): $\delta = 170.7, 164.6, 164.0, 162.8, 162.0, 142.2, 141.8, 135.9, 133.2, 132.3, 129.2, 128.7, 122.0, 118.8, 118.6, 69.3, 69.2, 41.4, 38.1, 35.7, 35.5, 33.5, 31.5, 31.2, 30.4, 30.3, 29.6, 29.4, 24.2, 19.5, 13.7$. **2**: IR (KBr): $\tilde{\nu}_{max} = 3307, 2949, 2862, 1658, 1620, 1526, 1435, 1253, 1170, 1030, 783$; ^{1}H NMR (400 MHz, [$D_6$]DMSO): $\delta = 8.1$ (br., 4H), 7.82 (s, 2H), 7.78 (s, 2H), 7.47 (s, 2H), 7.43 (s, 2H), 7.31 (s, 2H), 7.27 (s, 2H), 3.62 (br.s, 8H), 3.35 (br.s, 7H), 3.10 (br.s, 8H), 2.6 – 2.2 (br., 8H), 1.98 (br., 4H), 1.89 (br., 4H), 1.76 (s, 18H), 1.72 (s, 18H), 1.60 (br.m, 4H), 1.28 (s, 18H); ^{13}C NMR (100 MHz, [D_6]DMSO): $\delta = 171.7, 165.3, 164.7, 163.5, 162.6, 142.8, 142.4, 136.6, 133.9, 129.9, 129.5, 122.3, 119.4, 119.2, 70.1, 70.0, 42.0, 39.2, 36.6, 36.4, 34.3, 32.3, 31.2, 31.1, 30.4, 30.3, 25.1$; MS (FAB) of the corresponding Co^{II} complex: 1456 $[M+Na]^+$ (calcd exact mass: 1433.76).

[13] Experimental procedure for the kinetic experiments: 10 mL vials were charged with a stir bar and 12.5 μmol (referring to Co) catalyst **1b**, **2**, **4**-Co-PAMAM, **8**-Co-PAMAM, or **16**-Co-PAMAM. The catalysts were dissolved in THF (4.00 mL), then *(rac)*-1,2-epoxyhexane (3.00 mL, 25 mmol) and bromobenzene (200 μL; as an internal standard) were added to the dark brown solution. After the mixture had been stirred for 1 h at 4 °C, water (250 μL) was added. Reaction conversion was monitored by GC analysis (HP-5 column) of 20 μL aliquots withdrawn periodically from the reaction mixture.

Structural Characterization of a Cyclohexameric *meta*-Phenyleneethynylene Made by Alkyne Metathesis with In Situ Catalysts**

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Cyclophenyleneethynylenes (CPEs) have recently made a spectacular appearance as a novel class of carbon-rich supramolecular materials.[1, 2] Moore and co-workers have established *meta*-cyclophenyleneethynylenes (*m*-CPEs)[1–3] as tubular discotic liquid crystals[3d] and as porous, hydrogen-bonded, channel-forming organic solids.[4] Channels in *m*-CPEs are formed through a combination of hydrogen bonds and the internal cavities of the hexagonally packed *m*-CPE. However only a low-quality single-crystal X-ray structure of this exciting CPE was obtained[4] and to our surprise, no high-quality X-ray structures of *m*-CPE-derivatives are known.[2b, 5]

In the past CPEs have been made by the Pd/Cu-catalyzed coupling of the Heck – Sonogashira type. Substrates were either a preformed linear oligomer,[3] a half-cycle,[5] or 1-ethynyl-3-halo-substituted benzenes.[6] The latter compounds gave only very low yields of CPEs. Weiss et al.,[7] Fürstner et al.,[8] and our group[9] have reported that alkyne metathesis either with defined carbyne complexes[7, 8] or with in situ catalysts, which are obtained from $[Mo(CO)_6]$ and 4-chlorophenol in off-the-shelf 1,2-dichlorobenzene,[10, 11] is an excellent method for preparing saturated and unsaturated ring systems. Herein, we report the synthesis of the new hexameric *meta*-cyclophenyleneethynylenes **2a, b, d** from dipropynylated benzenes **1** by alkyne metathesis as well as the isolation of the corresponding polymers **3a – d** (Scheme 1).[12] The isolated *m*-CPE **2a** and its triosmiumdecacarbonyl complex **4a** have been characterized structurally by single-crystal X-ray diffraction analyses.

The monomers **1** were prepared from the corresponding diiodides[12] by Pd-catalyzed propynylations.[10] Heating **1a**, $[Mo(CO)_6]$, and either 4-chlorophenol or 4-trifluoromethylphenol in off-the-shelf 1,2-dichlorobenzene under a slow stream of nitrogen furnishes a mixture of oligomers and

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