# Synthesis, Catalytic Activity in Oxidation Reactions, and Recyclability of Stable Polyoxometalate-Centred Dendrimers

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**Abstract:** Nine- and 27-armed dendrimers with a peroxophosphotungstate core were synthesized by an ionic-bonding approach and used as air-stable, recoverable catalysts for oxidation reactions using hydrogen peroxide.

**Keywords:** catalyst stability; homogeneous catalysis; oxidation; polyoxometalate-centred dendrimers; recyclability; synthesis

Dendrimers and metallodendrimers are generating much attention for their potential applications in nanosciences.[1] The use of these macromolecules in catalysis is an emerging field[2] as they may allow the facilitated recovery of the catalysts. In this context, a variety of metal complexes have been placed at the core of dendritic catalysts. Convergent synthetic methods have been widely used;[3] their advantage being that they can lead to bifunctional pure dendrons. The use of polyoxometalates (POMs) as oxidation catalysts is a significant area, important also with regard to environmentally benign synthetic catalytic procedures.[4] There have been only two reports concerning the use of dendritic-polyoxometalate catalysts in oxidation reactions; both describe dendrimers with POMs at the peripheral positions. In the first report, the groups of Newkome and Hill have prepared two dendritic tetra-(POM) molecules with $[HP_2V_3W_{15}O_{59}]^{5-}$ units covalently bonded to a tetra-armed core and have used them as a recoverable catalyst in the oxidation of tetrahydrothiophene to tetrahydrothiophene oxide by *t*-BuOOH and $H_2O_2$.[5a] The second report describes our recent finding of the synthesis of recoverable ionic dendritic POM catalysts $[PO_4\{WO(O_2)_2\}_4]^{3-}$ based on the $CpFe^+$ activation of polymethylarenes, and their efficiency in the catalytic oxidation of cyclooctene and sulfides.[5b] POMs have not yet been used as catalysts in the core position of dendrimers. Thus, our interest in the field of recoverable dendritic catalysts prompted us to synthesize such dendritic compounds and to test their utility as air-stable and recoverable oxidation catalysts.

The synthetic approach that was used is summarized in Scheme 1.

Tri- and nona-allyl dendrons,[6] **1a** and **1b**, were reacted with tri-*n*-hexylamine to obtain the requisite cationic quaternary ammonium dendrons, **2a** and **2b**, (70 and 60% yield, respectively) that can be used as counter cations for a catalytically active anionic polyoxometalate. We have used the tri-anionic POM complex $[PO_4\{WO(O_2)_2\}_4]^{3-}$, known for its catalytic efficiency in alkene epoxidation[5b,7] and alcohol oxidation with hydrogen peroxide.[7] Thus, $[PO_4\{WO(O_2)_2\}_4]^{3-}$ can be attached to dendrons, **2a** and **2b**, by electrostatic bonding. The reaction of **2a** and **2b** with an aqueous solution of the commercially available heteropoly acid $H_3PW_{12}O_{40}$ and $H_2O_2$ yielded the epoxy-terminated 9- and 27-armed dendrimers, **3a** and **3b** that have a $[PO_4\{WO(O_2)_2\}_4]^{3-}$ species at the core in a one-pot reaction with 90 and 95% yields, respectively. A dinuclear peroxotungstate species $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ also formed, was removed with the aqueous phase[7f]. The heteropolyacid $H_3PW_{12}O_{40}$ decomposed to $[PO_4\{WO(O_2)_2\}_4]^{3-}$,[8] which both catalysed the epoxidation of the olefinic termini and became the anionic core of **3a** and **3b**. $^1H$ NMR spectra showed the complete disappearance of the signals at 5.54, 5.03 and 2.42 ppm attributed to $CH_2CH{=}CH_2$ and the appearance of a broad multiplet at 2.91–2.43 ppm assigned to the terminal epoxide groups. These two dendrimers were fully characterised by NMR ($^1H$, $^{13}C$ and $^{31}P$), elemental analysis and IR. The data are consistent with the proposed structures (see the Supplementary Material section). Compared to dendritic-polyoxometalate catalysts with POMs at the peripheral position recently reported in our group with the same POM unit that are air sensitive (over periods of several days),[5b] polyoxometalate-centred den-

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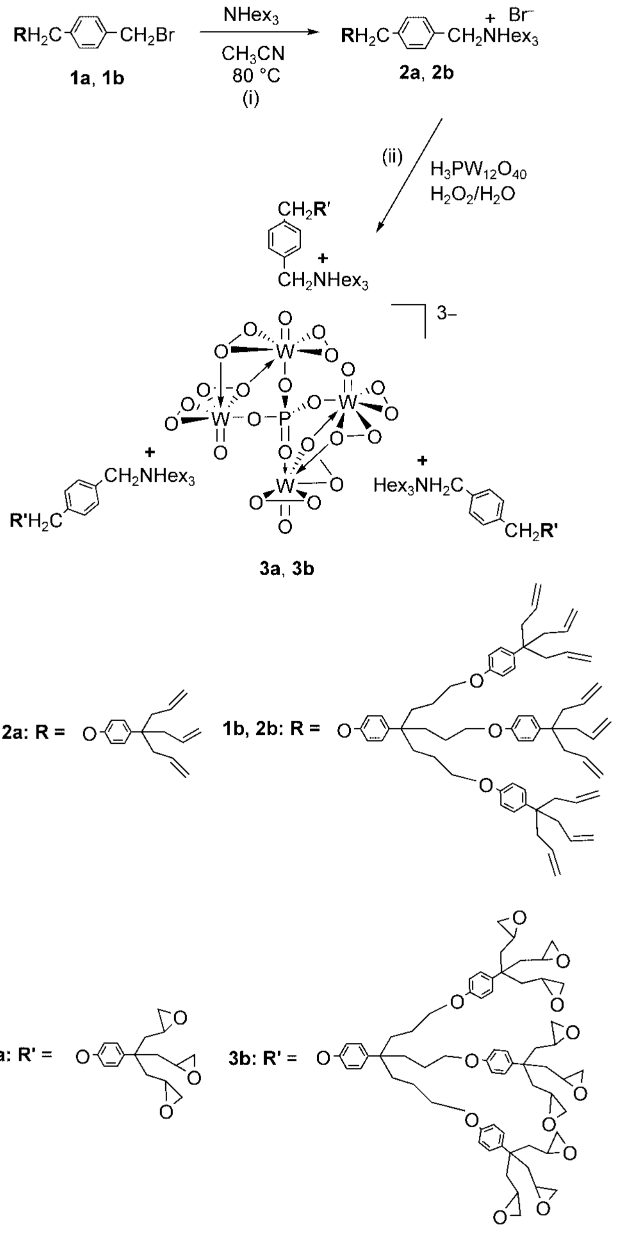
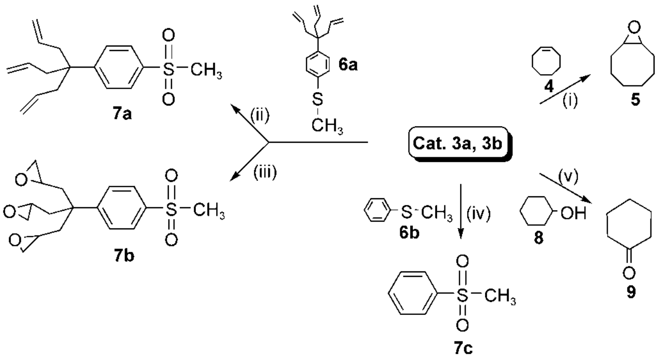


**Scheme 1.** Syntheses of polyoxometalate-centred poly-epoxides dendrimers **3a** and **3b** by ionic bonding. (i) **2a**: 16 h, 70%; **2b**: 16 h, 60%. (ii) **3a**: RT, 1.5 h, 90%; **3b**: RT, 2 h, 95%.

drimers **3a** and **3b** are air stable; they can be stored and handled without any special precautions.

Various catalytic oxidation reactions were performed using 0.4 mol % of **3a** or **3b** according to Scheme 2.

Epoxidation of cyclooctene **4** with 35% $H_2O_2$ at 30 °C in an aqueous $CDCl_3$ biphasic system was monitored over time by plotting the ratio between the intensity of the disappearing $^1$H NMR signal of cyclooctene at 5.6 ppm *vs.* TMS and the rising peak of the epoxide at 2.9 ppm. The reaction was quantitative after 2 hours for **3a** and 5 hours for **3b**. The comparison between the 9-armed dendritic catalyst **3a** and the 27-armed dendrimer **3b** indicates a negative dendritic effect on the reaction kinetics (Figure 1). We believe that this negative dendritic effect arises from the increased bulk around the catalytic centre, as it has been reported that the increased bulkiness of a cation reduces the electrophilicity of $[PO_4\{WO(O_2)_2\}_4]^{3-}$.[9]



**Scheme 2.** Catalytic oxidation reactions using **3a** and **3b** (0.4 mol%). (i) **3a**: 2 h, 30 °C, 100%; **3b**: 5 h, 30 °C, 100%. (ii) **3a**: 20 min, 30 °C, 100%; **3b**: 1 h, 30 °C, 100%. (iii) **3a**: 120 h, 35 °C, 40%; **3b**: 120 h, 35 °C, 20%. (iv) **3a**: 2 h, 30 °C, 100%. (v) **3a**: 23 h, 35 °C, 95%; **3b**: 23 h, 35 °C, 78%.

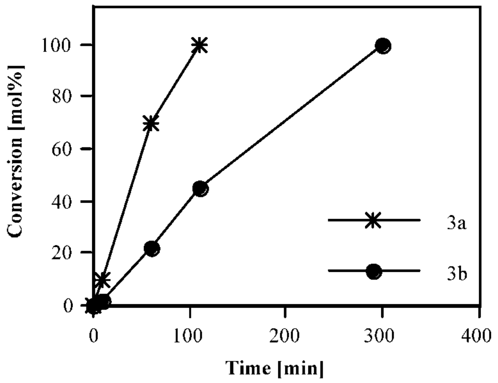


**Figure 1.** Kinetics of the epoxidation of cyclooctene catalyzed by **3a** and **3b**.

Table 1 lists the results of the oxidation of a variety of substrates with **3a** and **3b**. The negative dendrimer effect was also observed in the catalytic oxidation of triallylphenyl methyl sulfide (**6a**) to triallylphenyl methyl sulfone (**7a**) at 30 °C. While the formation of the corresponding sulfone was over in only 20 min with **3a**, the reaction was completed only after 1 h with **3b**. High selectivity to sulfone **7a** was obtained after a short time using **6a** as the substrate; neither sulfoxide nor the epoxidation of the double bonds was observed. However, for very long-time reactions, some compound **7b** could be obtained after epoxidation of allyl groups. Notably, the sulfonation of the larger **6a** with **3a** is over after 20 min, while the oxidation of phenyl methyl sulfide (**6b**) was complete only after 2 hours. Oxidation of cyclohexanol (**8**) to cyclohexanone (**9**) was also successful. After the

**Table 1.** Oxidation of representative alkenes, sulfides and alcohols using $H_2O_2$, catalysed by **3a** and **3b**.[a]

| Substrate | Catalyst | Temp. [°C] | Time [h][b] | Product | Conversion [%][c] |
|---|---|---|---|---|---|
| **4** | **3a** | 30 | 2 | **5** | 100 |
| **4** | **3b** | 30 | 5 | **5** | 100 |
| **6a** | **3a** | 30 | 0.33 | **7a** | 100 |
| **6a** | **3b** | 30 | 1 | **7a** | 100 |
| **6b** | **3a** | 30 | 2 | **7c** | 100 |
| **8** | **3a** | 35 | 23 | **9** | 95 |
| **8** | **3b** | 35 | 23 | **9** | 78 |
| **7a** | **3a** | 35 | 120 | **7b** | 40 |
| **7a** | **3b** | 35 | 120 | **7b** | 20 |

[a] Reaction conditions: catalyst (0.4 mol %), substrate (250 equivs.), $H_2O_2$ (800 equivs.), $CDCl_3$ (5 mL).
[b] Reactions were monitored by $^1H$ NMR.
[c] Conversion determined from the relative intensities of $^1H$ NMR signals of the substrate and the product.

first catalytic cycle, the catalysts were recovered without loss of activity for reaction times of up to 24 hours. The catalyst recycle experiment was carried out simply by precipitation of **3a** or **3b** from the organic layer with pentane (yields varied between 60 and 95%). The quality of the recovered catalyst was checked by $^1H$ and $^{31}P$ NMR before the second catalytic cycle, which showed no discernible loss in activity. The stability of these oxidation catalysts in solution for long periods of time was also verified.

In conclusion, we have described a one-pot synthesis of polyoxometalate-centred poly-epoxide dendrimers and their use as stable, recoverable catalysts for the epoxidation of an alkene, the selective oxidation of sulfide to sulfone and the oxidation of cyclohexanol to cyclohexanone. The bulk around the catalyst centre increased the stability of these new ionic dendritic polyoxometalate catalysts. The increased bulk is also compatible with a negative kinetic dendritic effect. These catalysts are air stable, easy to handle and were stored for several weeks in solution without degradation.

## Experimental Section

### General Procedure for the Synthesis of Dendritic Polyoxometalate Complexes 3a and 3b

To a water solution (0.160 mL) of commercial heteropolyacid $H_3PW_{12}O_{40}$ (0.096 mmol, 276 mg) was added $H_2O_2$ (4.8 mL, 35% in water). The mixture was stirred at room temperature for 30 minutes. Then, a $CH_2Cl_2$ solution (1.5 mL) of ammonium bromide salt (0.250 mmol, 170 mg of **2a** or 341 mg of **2b**) was added, and the mixture was stirred for an additional hour for **3a** and 2 hours for **3b**. The $CH_2Cl_2$ layer was dried over sodium sulfate and evaporated under reduced pressure, providing a white solid.

***9-Epoxide dendrimer* 3a:** Yield: 0.075 mmol, 233 mg (90%); $^1H$ NMR ($CDCl_3$, 200 MHz, broad signals): $\delta = 7.58$ (s, 12H, Ar), 7.30 (d, 6H, Ar), 7.00 (d, 6H, Ar), 5.07 (s, 6H, $CH_2O$), 4.75 (m, 6H, $NCH_2$), 3.13 (m, 18H, $NCH_2$), 2.91–2.00 (m, CH and $CH_2$); 1.80 (m, 18H, $CH_2$), 1.34 (m, 54H, $CH_2$), 0.90 (m, 18H, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 50.33 MHz): $\delta = 157.03$ ($C_q$, ArO), 138.95 ($C_q$, Ar), 137.15 ($C_q$, Ar), 132.97 ($C_q$, Ar), 127.85 (CH, Ar), 127.73 (CH, Ar), 126.46 (CH, Ar), 114.63 (CH, Ar), 69.34 ($CH_2O$), 58.46 ($CH_2N$), 48.89 (CH), 46.76 ($CH_2$), 42.70 ($C_q$-$CH_2$), 31.14 ($CH_2$), 25.85 ($CH_2$), 22.39 ($CH_2$), 22.11 ($CH_2$), 13.95 ($CH_3$); $^{31}P$ NMR (81 MHz, $CDCl_3$): $\delta = 2.96$ ($PO_4$); FTIR (KBr plates): $\nu = 1084-1052$ (P-O), 963 (W=O), 845 (O-O), 580 and 521 $cm^{-1}$ [$W(O_2)_{s,\,as}$]; anal.: calcd. (%) for $C_{126}H_{198}O_{36}NPW_4$: C 48.86, H 6.44; found: C, 47.93, H 6.30.

***27-Epoxide dendrimer* 3b:** Yield: 0.079 mmol, 432 mg (95%); $^1H$ NMR ($CDCl_3$, 200 MHz, broad signals): $\delta = 7.52$ (s, 12H, $CH_2$), 7.31 (d, 24H, Ar), 6.90 (d, 6H, Ar), 6.86 (d, 18H, Ar), 5.05 (s, 6H, $CH_2O$), 3.90 (broad, 18H, $CH_2O$), 3.20 (broad, 24H, $NCH_2$), 2.91–2.00 (br m, CH and $CH_2$), 1.80 (broad, $CH_2$), 1.37 (broad, $CH_2$), 0.88 (broad, $CH_3$); $^{13}C$ NMR ($CDCl_3$, 50.33 MHz): $\delta = 157.00$ ($C_q$, ArO), 156.14 ($C_q$, ArO), 139.07 ($C_q$, Ar), 138.53 ($C_q$, Ar), 136.10 ($C_q$, Ar), 132.48 ($C_q$, Ar), 127.76 (CH, Ar), 127.57 (CH, Ar), 127.47 (CH, Ar), 127.40 (CH, Ar), 127.31 (CH, Ar), 114.50 (CH, Ar), 114.25 (CH, Ar), 69.28 ($CH_2O$), 68.23 ($CH_2O$), 58.47 ($CH_2N$), 48.90 (CH), 46.62 ($CH_2$), 33.70 ($C_q$-$CH_2$), 31.14 ($CH_2$), 29.63 ($CH_2$), 25.89 ($CH_2$), 23.67 ($CH_2$), 22.41 ($CH_2$), 22.13 ($CH_2$), 13.91 ($CH_3$); $^{31}P$ NMR (81 MHz, $CDCl_3$): $\delta = 2.47$ ($PO_4$); FTIR (KBr plates): $\nu = 1080-1056$ (P-O), 959 (W=O), 830 (O-O), 580 and 521 $cm^{-1}$ [$W(O_2)_{s,\,as}$]; anal. calcd. (%) for $C_{270}H_{378}N_3O_{64}PW_4$: C 59.44, H 6.98; found: C 58.84, H 6.76.

### General Procedure for Catalytic Reactions using 3a and 3b and Catalyst Recovery Experiments

To a $CDCl_3$ solution (5 mL) of catalyst **3a** (0.005 mmol, 16 mg) or **3b** (0.005 mmol, 27 mg) were added 250 equivalents of substrate and 800 equivalents of 35% $H_2O_2$. The reaction mixture was stirred at 30 °C and the catalytic experiment was monitored by $^1H$ NMR. Upon completion, the $CDCl_3$ layer was separated and concentrated under vacuum to about 1 mL. The catalyst was precipitated by addition of 10 mL of pentane. The solid was filtered and washed with pentane (3 × 10 mL), giving **3a** between 64 and 77% yield (10–12 mg, 0.0032–0.0038 mmol) or **3b** between 62 and 95% yield (17–26 mg, 0.0031–0.0047 mmol) as a white solid. This white precipitate was analysed by $^1$H and $^{31}$P NMR before the second catalytic experiment.

The catalyst recycle experiment was carried out following the typical procedure and conditions described above for the first cycle, $CDCl_3$ and reactants were adjusted to the amount of catalyst used. The reaction was performed with cyclooctene **4**, aryl sulfide **6a** and thioanisole **6b** using the dried recovered catalysts **3a** and **3b**. The catalyst was totally dissolved in $CDCl_3$, and reactants were added to the solution. After completion of the reaction, the kinetics remained unchanged, as the data collected are comparable to those summarised in Table 1 for the first cycle. The catalyst was recovered and checked by $^1$H and $^{31}$P NMR, giving **3a** between 70 and 76% yield (7–9 mg) or **3b** between 77 and 86% yield (13–22 mg).

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## References

[1] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons, Concepts, Synthesis and Applications*, VCH-Wiley, Weinheim, **2001**; b) *Dendrimers and other Dendritic Polymers*, (Eds.: D. Tomalia, J. M. J. Fréchet), Wiley-VCH, New York, **2002**; c) *Dendrimers and Nanoscience*, (Ed.: D. Astruc), C. R. Chimie, Elsevier, Paris, Vol. 6, **2003**.

[2] a) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991; b) G. E. Oosterom, J. N. H. Reek, P. C. J. Kramer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* **2001**, *40*, 1828; c) R. Kreiter, A. Kleij, R. J. M. Klein Gebbink, G. van Koten, *Top. Curr. Chem.* **2001**, *217*, 163; d) R. van - Heerbeek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717.

[3] For a recent review on dendrons, see: S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3819.

[4] a) I. V. Kozhevnikov, *Catalysis by Polyoxometalates*, John Wiley & Sons, Chichester, **2002**; b) I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171; c) N. Mizuno, M. Misono, *Chem. Rev.* 1998, **98**, 199; d) R. Neumann, *Prog. Inorg. Chem*. **1998**, #37#47, 317.

[5] a) H. Zeng, G. R. Newkome, C. L. Hill, *Angew. Chem. Int. Ed*. **2000**, *39*, 1772; b) L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, *Angew. Chem. Int. Ed*. **2004**, *43*, 2924.

[6] S. Nlate, J.-C. Blais, D. Astruc, *Inorg. Chem. Acta* **2004**, *357*, 1670.

[7] a) C. Venturello, R. D'Aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Catal.* **1985**, *32*, 107; b) C. Venturello, R. D'Aloisio, *J. Org. Chem.* **1988**, *53*, 1553; c) Y. Ishii, Y. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587; d) Y. Ishii, M. Ogawa, *Reviews on Heteroatom Chemistry*, (Eds.: A. Ohno, N. Furukawa), MYU: Tokyo, **1990**, vol 3, p 121; e) R. Neumann, A. M. Khenkin, *J. Org. Chem.* **1994**, *59*, 7577; f) C. Aubry, G. Chottard, N. Platzer, J.-M. Brégault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, *Inorg. Chem.* **1994**, *33*, 871.

[8] a) L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Brégault, *Inorg. Chem.* **1994**, *33*, 871; b) A. J. Bailey, W. P. Griffith, B. C. Parkin, *J. Chem. Soc. Dalton Trans.* **1995**, 1833; c) D. C. Duncan, R. C. Chambers, E. Hecht, C. L. Hill, *J. Am. Chem. Soc.* **1995**, *117*, 681.

[9] F. P. Ballistreri, A. Bazzo, G. A. Tomaselli, R. M. Toscano, *J. Org. Chem.* **1992**, *57*, 7074.