DOI: 10.1002/chem.200500556

Synthesis of 9- and 27-Armed Tetrakis(diperoxotungsto)phosphate-Cored Dendrimers and Their Use as Recoverable and Reusable Catalysts in the Oxidation of Alkenes, Sulfides, and Alcohols with Hydrogen Peroxide

Sylvain Nlate,* Lauriane Plault, and Didier Astruc[a]

Abstract: A series of 3- and 9-armed dendrons, functionalized at the focal position to quaternary ammonium salts, were synthesized and characterized. The reaction of these ammonium dendrons with the heteropolyacid $H_3PW_{12}O_{40}$ in the presence of hydrogen peroxide led to a family of 9- and 27-armed air-stable polyoxometalate (POM)-cored dendrimers containing a catalytically active trianionic POM species $[PO_4\{WO(O_2)_2\}_4]^{3-}$ in the core. These POM-cored dendrimers are air-stable, efficient, recoverable, and reusable catalysts for the selective oxidation of alkenes to epoxides, sulfides to sulfones, and alcohols to ketones, in an aqueous/$CDCl_3$ biphasic system with hydrogen peroxide as the primary oxidant. A study of the countercation effects showed that the dendritic structure increased the stability of the POM species and facilitated the recovery of the catalyst up to the eighth cycle, whereas the increased bulkiness around the POM center led to a negative kinetic dendritic effect. Within the 9-armed POM-cored dendrimer series, the reaction kinetics were susceptible to the nature of the peripheral endgroups. Indeed, the 9-armed *n*-propyl-terminated POM-cored dendrimer was identified as the most active catalyst. In addition, the results obtained with POM-cored dendrimers versus tetraalkylammonium POMs ($\{[n\text{-}(C_8H_{17})_3NCH_3]^+\}_3[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $[\{nC_{18}H_{37}(75\%) + nC_{16}H_{33}(25\%)]_2N(CH_3)_2\}^+]_3[PO_4\{WO(O_2)_2\}_4]^{3-})$ clearly reveal that the dendritic structures are more stable than their nondendritic counterparts. After the reactions were complete, the dendrimer catalysts were easily recovered and recycled without a discernable lost of activity, whereas attempts to recover tetraalkylammonium POMs gave unsatisfactory results. A significant advantage of the dendritic structures is that they enable the recovery and recyclability of the POM catalyst, in contrast to the other tetraalkylammonium POMs.

Keywords: catalysis · dendrimers · oxidation · polyoxometalate · tungsten

Introduction

Dendrimers and metallodendrimers are generating much attention for their potential applications in various areas.[1] The increasing use of these macromolecules in catalysis is an emerging field because they may allow the facile recovery of the catalysts after use, an essential feature for reaction efficiency, economy, and environmental concern.[2] In this context, a variety of dendrimers, cores, branches, and endgroups have been assembled and used in different domains, such as supramolecular chemistry,[3] nanosciences,[1c] drug delivery,[4] and catalysis.[2,5] However, dendritic catalysts for oxidation reactions are relatively under represented.[6] Of those reported thus far, only a few are based on polyoxometalates (POMs). POMs are distinctive inorganic transition metal–oxygen clusters that are the source of fascinating architectures[7] and very rich redox chemistry,[8] upon with their catalytic activity in oxidation reactions is based.[9] Recently, a few heterogeneous[10] and homogeneous[11] dendritic polyoxometalate catalysts were reported and shown to be effective in oxidation reactions. For example, Bruce's group prepared heterogeneous dendrimer-templated mesoporous titanosilicate and vanadosilicate oxidation catalysts by means of sol–gel techniques, and have used them in the epoxidation of cyclohexene with *tert*-butyl hydroperoxide.[10] In homogeneous catalysis, only four reports concerning the

---

[a] Dr. S. Nlate, L. Plault, Prof. Dr. D. Astruc
Nanosciences and Catalysis Group, LCOO
UMR CNRS No 5802, University Bordeaux I
351 Cours de la Libération, 33405 Talence Cedex (France)
Fax: (+33) 540006994
E-mail: s.nlate@lcoo.u-bordeaux1.fr

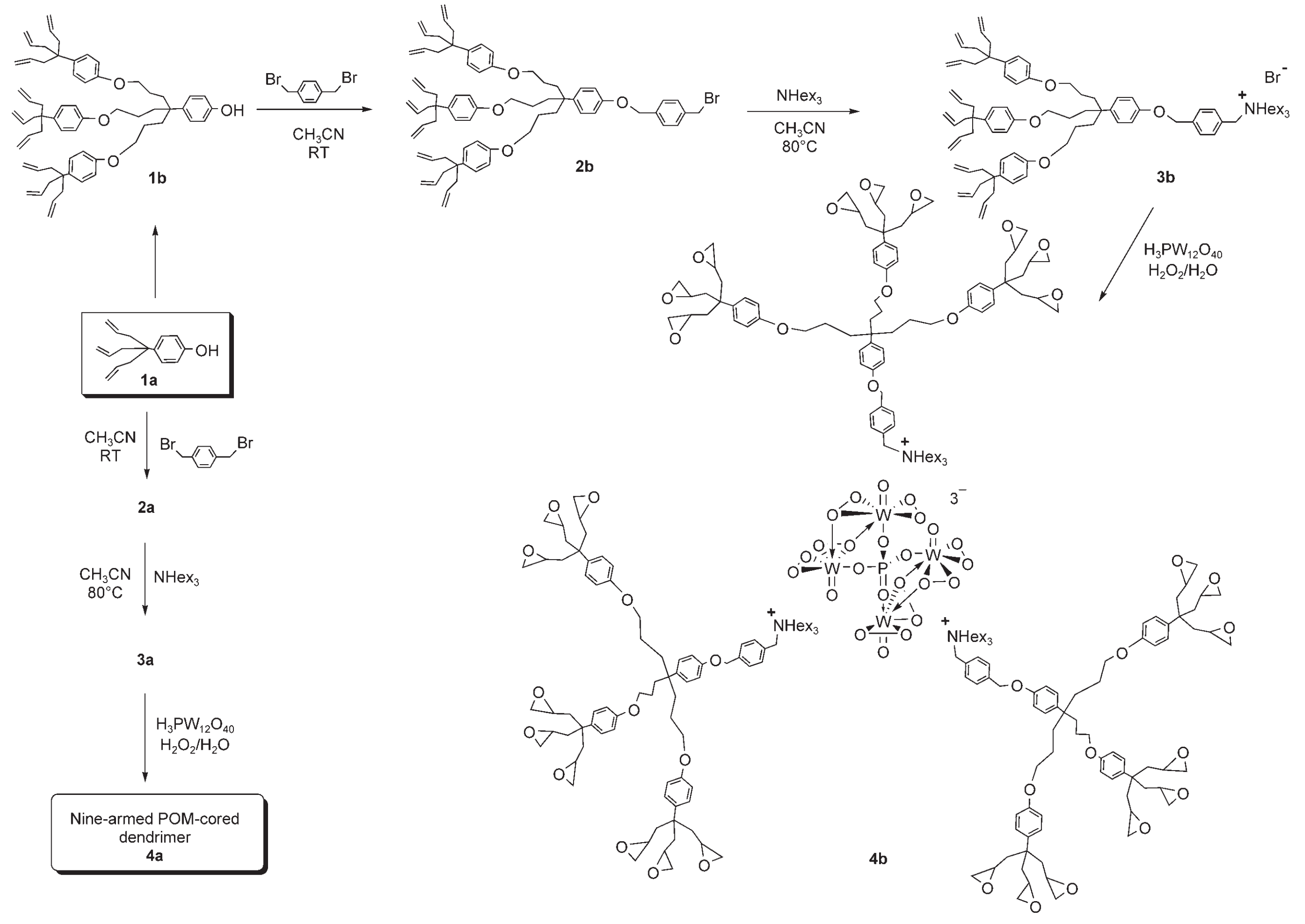
use of dendritic polyoxometalate catalysts in oxidation reactions are known. Three of them involve dendrimers with POM units at the peripheral positions. In the first, the groups of Newkome and Hill prepared two dendritic tetra-POM molecules with $[HP_2V_3W_{15}O_{59}]^{5-}$ units covalently bonded to a 4-armed core, and used them as a recoverable catalyst in the oxidation of tetrahydrothiophene to its sulfoxide by *t*BuOOH and H_2O_2.[11a] The second report describes the synthesis of recoverable dendritic POM catalysts based on electrostatic bonding[11b] by using the Venturello trianionic species $[PO_4\{WO(O_2)_2\}_4]^{3-}$,[12] and their application in the oxidation of cyclooctene and sulfides.[11b] Recently, Neumann and co-workers synthesized two generations of dendritic catalysts based on the in situ assembly of dendritic phosphonates with diperoxotungstates, yielding peroxophosphonatotungstate mixtures that are efficient in the epoxidation of alkenes with hydrogen peroxide.[11c] To the best of our knowledge, only one report involved the synthesis of POM-cored dendrimers and their application to catalytic oxidation reactions. In a preliminary communication, we recently reported a one-pot synthesis of epoxy-terminated 9- and 27-armed dendrimers that have a tetrakis(diperoxotungsto)phosphate species at the core. Their stability, solubility, catalytic efficiency in the oxidation reaction, and recyclability have been studied.[11d] We discovered that the stability of the anionic polyoxometalate unit in the oxidation reactions was dependent on the dendritic structure. Indeed, within the dendrimer series, the bulk increased the stability of the POM species, but decreased the reaction kinetics. The purpose of the current investigation is to point out the influence of dendritic countercations on the POM properties. It is well known from phase-transfer experiments that the organic structure of the cation not only influences its ability to transfer an anion from the aqueous to the organic phase, but it also strongly affects the rate of the reaction in the organic phase. Therefore, various tetraalkylammonium dendrons with various sizes and endgroups were used as countercations of the trianionic POM species. We investigated the dendritic effects on the solubility, stability, and catalytic properties. Herein, we describe the synthesis[13] (by ionic bonding between cationic ammonium dendrons and the trianionic POM species $[PO_4\{WO(O_2)_2\}_4]^{3-}$) and characterization of a family of 9- and 27-armed POM-cored dendrimers, respectively, terminated with epoxy, *n*-propyl, and aryl sulfide groups. We describe the synthesis, isolation, and characterization of POM-cored dendrimers as well as their use, recovery, and re-utilization in the catalytic oxidation of alkenes, sulfides, and alcohols with hydrogen peroxide. Indeed, it is essential to isolate and characterize the POM salts before their reactivity behavior is investigated. The effects of dendritic structure on the POM properties will be emphasized with respect to the tetraalkylammonium POM derivatives.

Results and Discussion

Synthesis and spectroscopic characterization of tetrakis(diperoxotungsto)phosphate-cored dendrimers

Formation of epoxy-terminated 9- and 27-armed POM-cored dendrimers: The synthetic strategy used to prepare these compounds is summarized in Scheme 1.

The selective reaction of *p*-dibromoxylene (in excess) with the phenol triallyl dendron **1a** and the phenol nonaallyl dendron **1b**[14] leads to the corresponding bromobenzyl dendrons **2a** and **2b**.[15] The triallyl and nonaallyl dendrons **2a** and **2b** were reacted with tri-*n*-hexylamine to give quaternary ammonium dendrons **3a** and **3b** in yields of 70 and 68 %, respectively. The ammonium cations **3a** and **3b** were then used as countercations for the trianionic POM complex $[PO_4\{WO(O_2)_2\}_4]^{3-}$ that is known for its catalytic efficiency in alkene epoxidation and alcohol oxidation with hydrogen peroxide.[11b,d,16,17] $[PO_4\{WO(O_2)_2\}_4]^{3-}$ was attached to the ammonium dendrons **3a** and **3b** by electrostatic bonding. We used the synthetic procedure involving peroxide-mediated decomposition of $H_3PW_{12}O_{40}$ that gives high yields and a good reproducibility.[11b,d,16,17] According to this procedure, the heteropolyacid $H_3PW_{12}O_{40}$ was decomposed in the presence of excess H_2O_2 to form the dinuclear peroxotungstate $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ and the trianionic peroxophosphotungstate $[PO_4\{WO(O_2)_2\}_4]^{3-}$. The latter reacts selectively with the ammonium dendrons **3a** and **3b** (phase-transfer agents) in a biphasic mixture of water and methylene chloride to give the epoxy-terminated 9- and 27-armed dendrimers **4a** and **4b**, which contain the $[PO_4\{WO(O_2)_2\}_4]^{3-}$ core, in yields of 90 and 95 %, respectively. The dinuclear peroxotungstate decomposition product $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ remained in the aqueous phase of the reaction mixture and was isolated as a potassium salt in the presence of potassium chloride. According to previous studies,[11b,d,16,17] it has clearly been established that $[PO_4\{WO(O_2)_2\}_4]^{3-}$ is selectively transferred into the organic phase with the phase-transfer agents, whereas $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$ remains in the aqueous phase. The appropriate choice of countercations allowed the selective isolation of the two peroxo salts. Interestingly, the trianionic species $[PO_4\{WO(O_2)_2\}_4]^{3-}$ catalyzed the epoxidation of the olefinic termini in a one-pot reaction and became the anionic core of **4a** and **4b**. ^1H NMR spectra showed the complete disappearance of the signals at $\delta = 5.54$, 5.03 and 2.42 attributed to $CH_2CH{=}CH_2$ and the appearance of a broad multiplet at $\delta = 2.91–2.43$ assigned to the terminal epoxide groups. These two POM-cored dendrimers were isolated from the organic layer and fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P), elemental analysis, and IR spectroscopy. The results summarized in Table 1 for significant data are consistent with the proposed structures. Only one signal was obtained in the ^{31}P NMR for **4a** ($\delta = 2.96$) and **4b** ($\delta = 2.74$). These values are comparable to those obtained for the Arquad salt of the $[PO_4\{WO(O_2)_2\}_4]^{3-}$ species ($\delta = 3.12$); (Arquad = $[nC_{18}H_{37}$-



Scheme 1. Syntheses of the epoxy-terminated 9- and 27-armed POM-cored dendrimers **4a** and **4b**.

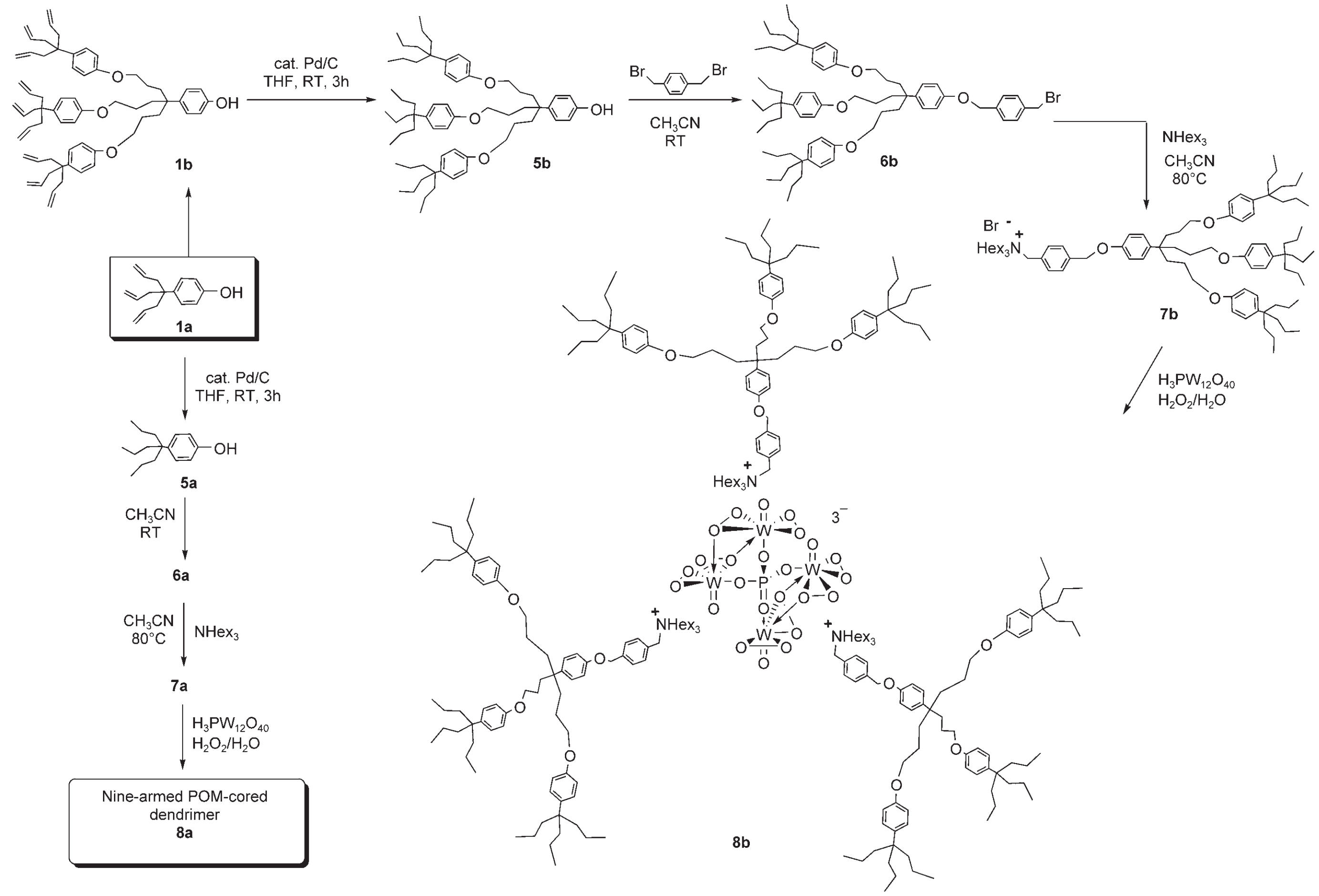
Table 1. Representative analytical data for 9- and 27-armed POM-cored dendrimers **4a**,**b**, **8a**,**b**, and **13a**,**b**.

POM-Cored dendrimers	^{31}P NMR [δ]	Elemental analysis [%]	C	H	IR $\tilde{\nu}$ [cm^{-1}]
4a	2.96	calcd	48.86	6.44	1084, 1052, 963, 845
		found	47.93	6.30	580, 521
4b	2.74	calcd	59.44	6.98	1080, 1056, 959, 830
		found	58.84	6.76	580, 521
8a	3.02	calcd	50.53	7.39	1083, 1052, 969, 840
		found	49.59	6.56	580, 522
8b	3.54	calcd	64.06	8.60	1083, 1057, 974, 845
		found	64.75	8.47	590, 517
13a	2.87	calcd	54.80	6.44	1076, 1052, 963, 830
		found	53.90	5.93	580, 521
13b	2.08	calcd	65.00	6.82	1083, 1052, 963, 830
		found	64.46	6.58	580, 521

(75%) + nC$_{16}$H$_{33}$(25%)]$_2$N(CH$_3$)$_2$]), and n-tetrahexylammonium salts (δ = 0.37).

Polyoxometalate-centered dendrimers **4a** and **4b** are air-stable compounds. They can be stored and handled without any special precautions, in contrast to dendritic compounds with POMs located at their periphery. The latter are air sensitive over periods of several days.[11b] In spite of the acidic conditions used to prepare **4a** and **4b**, no destruction of the oxirane ring was observed; this is attributed to the protective effect of the biphasic system.

Formation of the* n*-propyl-terminated 9- and 27-armed POM-cored dendrimers: Catalytic hydrogenation of triallyl and nonaallyl dendrons **1a** and **1b** in the presence of Pd/C catalyst (10% Pd) led to quantitative yields of tri-n-propyl and nona-n-propyl dendrons **5a** and **5b**, respectively. The reaction was easily monitored in the ^{1}H NMR spectrum by the disappearance of the allyl signals at δ = 5.54, 5.03, and 2.42, and the appearance of a multiplet at δ = 1.64–1.54 and 1.09, which is assigned to the terminal n-propyl groups. We were also able to prepare **5b** by a convergent route, starting from **5a** and protected p-EtO$_2$CC$_6$H$_4$(CH$_2$CH$_2$I)$_3$ **1c**.[13] The n-propyl-terminated 9- and 27-armed POM-cored dendrimers



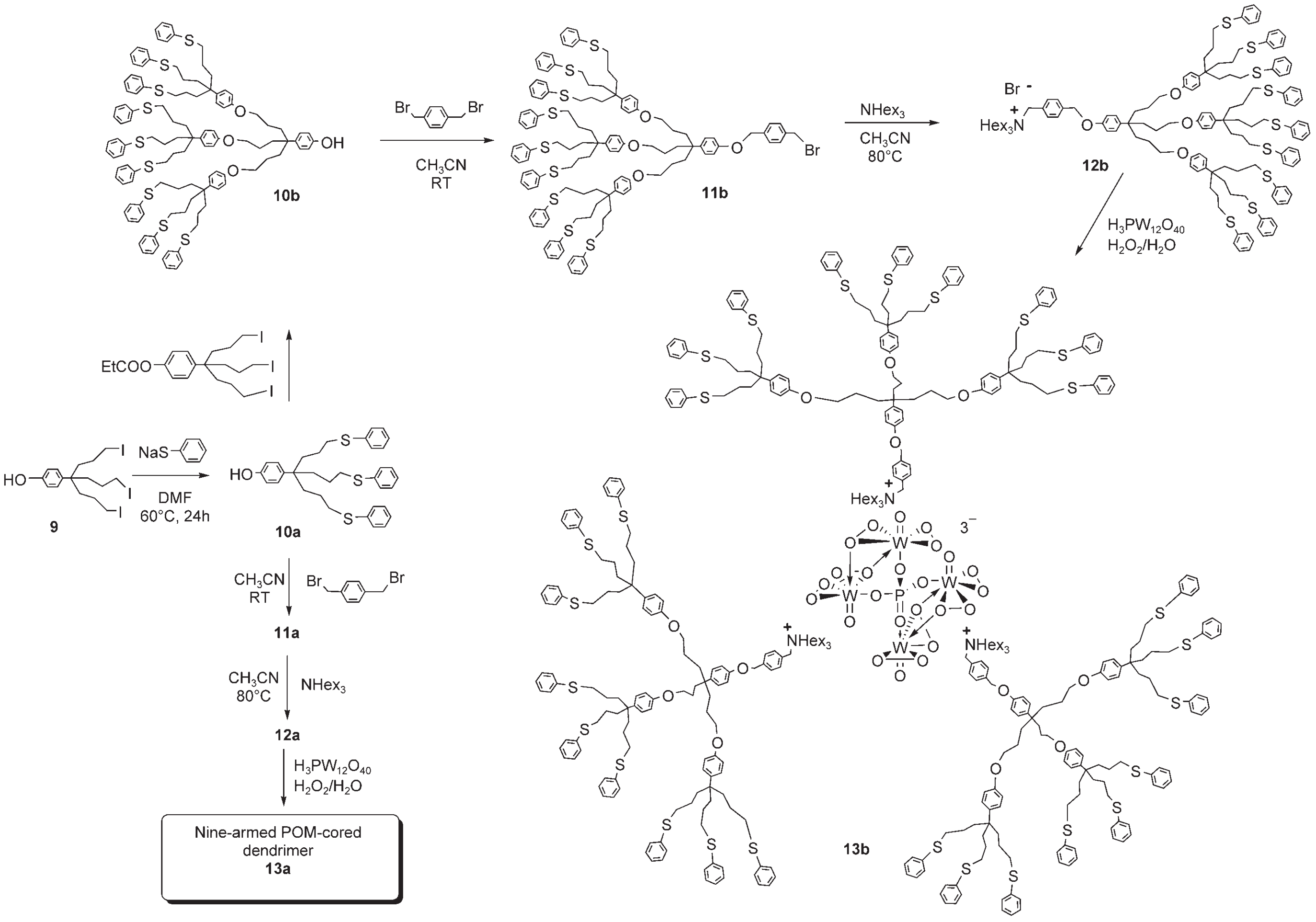
Scheme 2. Syntheses of the *n*-propyl-terminated 9- and 27-armed POM-cored dendrimers **8a** and **8b**.

8a and **8b** were easily prepared from **5a** and **5b** (Scheme 2), following the procedure already described for **4a** and **4b**.

The reaction of *p*-dibromoxylene with tri-*n*-propyl and nona-*n*-propyl phenol dendrons **5a** and **5b** gives the mono-substituted bromobenzyl derivatives **6a** and **6b** in very good yields (91 and 92%). The corresponding quaternary ammonium salts **7a** and **7b** were obtained by treatment of **6a** and **6b** with tri-*n*-hexylamine. The ammonium dendrons **7a** and **7b** react by electrostatic bonding with trianionic $[PO_4\{WO(O_2)_2\}_4]^{3-}$, to give 9- and 27-armed *n*-propyl POM-cored dendrimers **8a** and **8b**, as a light yellow solids, in 85 and 91% yields, respectively. Representative characterization data of **8a** and **8b** are summarized in Table 1. These data are consistent with the proposed structures. One ^{31}P NMR signal was observed for **8a** and **8b** ($\delta = 3.02$ and 3.54, respectively). These values are similar to those obtained for epoxy-terminated POM-cored dendrimers **4a** and **4b** (see Table 1).

Formation of aryl sulfide-terminated 9- and 27-armed POM-cored dendrimers: Aryl sulfide-terminated 9- and 27-armed POM-cored dendrimers **13a** and **13b** were prepared from triaryl and nonaaryl sulfide phenol dendrons **10a** and **10b**, respectively (Scheme 3).

The triaryl sulfide phenol dendron **10a** was synthesized in 85% yield by reaction of the known triiodo phenol dendron **9**[13] with the sodium thiophenolate salt without protection of the phenol function. The reaction was easily monitored in the ^{1}H NMR spectrum by the complete disappearance of the triplet at $\delta = 3.23$, assigned to the CH_2I groups, and the appearance of a new triplet at $\delta = 2.95$, attributed to the CH_2S groups. The convergent synthesis of the nonaaryl sulfide phenol dendrons **10b** was achieved by reacting the protected triiodo dendron p-$EtO_2CC_6H_4(CH_2CH_2I)_3$[13] **1c** and **10a** in DMF in the presence of K_2CO_3. Compound **10b** was obtained in 73% yield after chromatography. The coupling reaction of **10a** and **10b** with a large excess of *p*-dibromoxylene led to the monobrominated compounds **11a** and **11b** in 80 and 70% yields, respectively. The corresponding quaternary ammonium salts **12a** and **12b** were obtained in 89 and 82% yields from **11a** and **11b** with tri-*n*-hexylamine. The commercially available heteropolyacid $H_3PW_{12}O_{40}$ reacts with **12a** and **12b** in the presence of H_2O_2 to give the aryl sulfide-terminated 9- and 27-armed POM cored dendrimers **13a** and **13b** as light yellow solids, in 85 and 95% yields, respectively. Surprisingly, aryl sulfide termini are not sensitive to oxidation under these conditions. No trace of aryl sulfoxide or aryl sulfone was observed (see the Experimental Sec-



Scheme 3. Syntheses of the aryl sulfide-terminated 9- and 27-armed POM-cored dendrimers **13a** and **13b**.

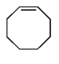
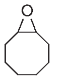
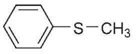
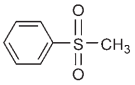
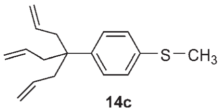
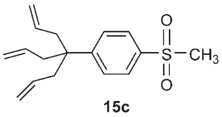
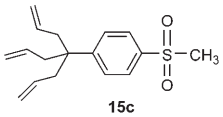
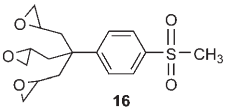
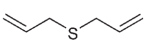
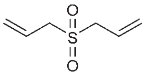
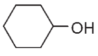
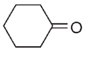
tion). An argument in support of this approach is that the signal attributed to the CH_2S group in the ^1H NMR spectrum was not shifted and remained similar to that obtained for the ammonium salts **12a** and **12b** ($\delta = 2.95$). In addition, correct (C,H) elemental analyses were obtained for **13a** and **13b**. As in the case of **4a**,**b** and **8a**,**b**, the ^{31}P NMR spectra of **13a** and **13b** show a signal at $\delta = 2.87$ and 2.08, respectively.

Catalytic oxidation reactions by using 9- and 27-armed POM-cored dendrimers 4a,b, 8a,b, and 13a,b: Among various substrates (alkenes,[16a,b,18] alkynes,[19] alcohols,[16a,b] diols,[16a,b] sulfides,[18] and amines[20]) already reported as good candidates in oxidation processes with heteropolyacids or their salts and hydrogen peroxide, we have selected some of them, included in Tables 2 and 3, as well as in Scheme 4, for catalytic oxidation tests. The reaction was accomplished by vigorous stirring at 35 °C of an aqueous/$CDCl_3$ biphasic mixture containing 250 equiv of the appropriate substrate, 800 equiv of hydrogen peroxide, and 0.4 mol % of the respective POM-cored dendrimers **4a**,**b**, **8a**,**b**, and **13a**,**b**. The reaction kinetics were monitored over time by plotting the ratio between the intensity of the disappearing ^1H NMR signals of the substrate versus TMS and the new peaks of the product.

The effects of the dendritic countercation on the POM stability, catalytic efficiency, and selectivity in the oxidation of various alkenes, sulfides, and alcohols were investigated. The results listed in Table 2 clearly show that the 9- and 27-armed POM-cored dendrimers **4a**,**b**, **8a**,**b**, and **13a**,**b** quantitatively oxidized alkenes to the corresponding epoxides, sulfides to sulfones, and secondary alcohol to ketones.

The oxidation of cyclooctene **14a** was monitored over time by plotting the ratio between the intensity of the disappearance of the ^1H NMR signal at $\delta = 5.6$ attributed to cyclooctene and the new peak of the epoxide **15a** at $\delta = 2.9$. As shown by entries 1–6, the POM-cored dendrimers **4a**,**b**, **8a**,**b**, and **13a**,**b** oxidized cyclooctene with 100 % conversion within the limits of ^1H NMR detection, with reaction times between 30 min and 5 h. The reaction complete after 30 min in the case of the 9-armed *n*-propyl terminated POM-cored dendrimer **8a**, 2 h for 9-armed epoxy dendrimer **4a**, and 5 h for 9-armed aryl sulfide **13a**. Five hours were generally required for the 27-armed catalysts **4b**, **8b**, and **13b** (entries 2, 4, and 6). The results included in Table 2 indicate that the 9-armed *n*-propyl-terminated POM-cored dendritic **8a** was the

Table 2. Oxidation of representative alkene, sulfide, and alcohols by H_2O_2, catalyzed by **4a**,**b**, **8a**,**b**, and **13a**,**b** at $T = 35\,°C$.[a]

Entry	Substrate	Catalyst	t[b]	Product	Conversion [%][c]
1	 **14a**	**4a**	2 h	 **15a**	100
2		**4b**	5 h		100
3		**8a**	30 min		100
4		**8b**	5 h		100
5		**13a**	5 h		100
6		**13b**	5 h		100
7	 **14b**	**4a**	10 min	 **15b**	100
8		**4b**	60 min		100
9		**8a**	5 min		100
10		**8b**	90 min		100
11		**13a**	20 min		100
12		**13b**	120 min		100
13	 **14c**	**4a**	10 min	 **15c**	100
14		**4b**	33 min		100
15		**8a**	5 min		100
16		**8b**	20 min		100
17		**13a**	15 min		100
18		**13b**	20 min		100
19	 **15c**	**4a**	22 h	 **16** + mono- and diepoxysulfones	11
20		**4b**	24 h		5
21		**8a**	23 h		95
22		**8b**	24 h		12
23		**13a**	20 h		11
24		**13b**	24 h		19
25	 **14d**	**4a**	10 min	 **15d**	100
26		**4b**	30 min		100
27		**8a**	5 min		100
28		**8b**	90 min		100
29		**13a**	90 min		100
30		**13b**	180 min		100
31	 **14e**	**4a**	22 h	 **15e**	91
32		**4b**	23 h		78
33		**8a**	20 h		95
34		**8b**	22 h		99
35		**13a**	21 h		85
36		**13b**	25 h		95

[a] Reaction conditions: catalyst (0.4 mol%), substrate (250 equiv), H_2O_2 (800 equiv), $CDCl_3$ (3 mL). [b] Reactions were monitored by ^1H NMR. [c] Conversion determined from the relative intensities of the ^1H NMR signals of the substrate and the product.

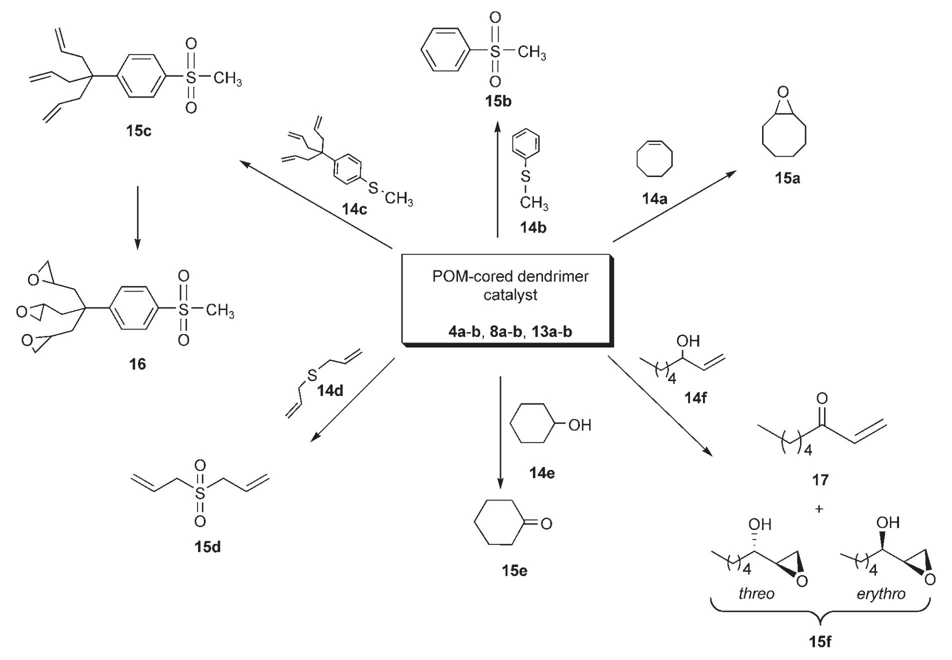
Table 3. Catalytic oxidation of 1-octen-3-ol (**14f**) with **4a**,**b**, **8a**,**b**, and **13a**,**b**, by H_2O_2.[a]

Catalyst	Reaction t [h][b]	Conversion [%][c]	Chemoselectivity Epoxide/Ketone		Diastereoselectivity (*threo*/*erythro*)	
			(**15f**)	(**17**)		
4a	24	85	75	10	70	30
4b	30	85	62	23	55	45
8a	3	93	85	8	44	56
8b	24	99	61	38	40	60
13a	55	84	52	32	53	47
13b	24	94	70	23	47	53

[a] Reaction conditions: catalyst (0.4 mol%), substrate (250 equiv), H_2O_2 (800 equiv), $CDCl_3$ (3 mL). [b] Reactions were monitored by ^1H NMR. [c] Conversion determined from the relative intensities of the ^1H NMR signals of the substrate and the product.

most reactive catalyst. The oxidation of cyclooctene with the 27-armed POM-cored dendrimers did not show any significant difference within this series (Figure 1b), in contrast to the 9-armed POM-cored dendrimer series (Figure 1a).

The oxidation of phenyl methyl sulfide **14b**, triallyl phenyl methyl sulfide **14c**, and diallyl sulfide **14d** with POM-cored dendrimers selectively gave the corresponding phenyl methyl sulfone **15b**, triallyl phenyl methyl sulfone **15c**, and diallyl sulfone **15d** with reaction times of up to 2 h (Table 2, entries 7–18 and 25–30). Neither the sulfoxide intermediate nor the epoxidation of allyl groups was observed in the cases of **14c** and **14d**. However, for reaction times of up to one day, the triallyl phenyl methyl sulfone **15c** provided the epoxy sulfone compound **16** (with probably the mono-and the diallyl phenyl methyl sulfone) in 5 to 95% conversion (Table 2, entries 19–24). Interestingly, the kinetics of sulfide oxidation decreased with 27-armed POM-cored dendrimers, and the sulfoxide intermediate could be observed. However, the reaction selectively led to the corresponding sulfone after total conversion of the sulfoxide. It was possible to observe the sulfoxide intermediate in reaction times up to



Scheme 4. Catalytic oxidation reactions with 0.4 mol% of 9- and 27-armed POM-cored dendrimers **4a**,**b**, **8a**,**b**, and **13a**,**b**, substrate (250 equiv), H_2O_2 (800 equiv), and $CDCl_3$ (3 mL).

3 min, even if 9-armed POM-cored catalysts were used. A comparison between the 9-armed dendritic catalysts and the 27-armed dendrimers shows a negative dendritic effect on the reaction kinetics. This negative dendritic effect is probably caused by the increased bulk around the catalytic center. It has been reported that the increased bulkiness of the cation reduces the electrophilicity of the peroxopolyoxo species.[18] When the ions are bulky, the interionic distance increases, thus decreasing the interionic interaction. In the case of the 27-armed POM-cored dendrimers, the bulkiness of the dendritic ammonium cation might be responsible for the large distance between the ammonium site of the dendron and the anionic POM.

In addition, within the 9-armed POM-cored dendrimer series, the lower electrophilicity of the aryl sulfide and epoxy endgroups in **4a** and **13a**, respectively, compared with the *n*-propyl groups of **8a**, might be responsible for the lower reactivity of **13a** and **4a** (Figure 1a).

The oxidation of cyclohexanol **14e** to cyclohexanone **15e** was also successful, with conversions between 75 and 100% and a reaction time of nearly one day (Table 2, entries 31–36). In the case of 1-octen-3-ol **14f**, the catalytic oxidation reaction gave a diastereoisomeric mixture of *threo*:*erythro*-1,2-epoxy-3-octanol **15f** as the major product, together with 1-octen-3-one **17** (Scheme 4 and Table 3) with excellent conversion rates. The reaction was easily monitored in the ^{1}H NMR spectrum by the disappearance of the three multiplets at $\delta = 5.84$, 5.15 and 4.10, attributed to the $CHOHCH{=}CH_2$ group, and the appearance of two multiplets at $\delta = 3.80$ and 3.40, respectively assigned to the CHOH group of (2*S*,3*R*)-1,2-epoxy-3-octanol (**15f**, *threo*) and (2*S*,3*S*)-1,2-epoxy-3-octanol (**15f**, *erythro*). The signals attributed to the epoxy group appear as a multiplet between $\delta = 3.01$ and 2.75. The α,β-unsaturated 1-octen-3-one **17** was identified by a new triplet at $\delta = 2.57$, assigned to the CH_2CO group. The chemoselectivity of olefin epoxidation predominates over alcohol ketonization. More interestingly, **8a** was the most efficient catalyst for the oxidation of 1-octen-3-ol **14f**, as obtained previously with cyclooctene and sulfide. The reaction time was only 3 h for **8a**, whereas 24 h were required in all the other cases. The *threo*:*erythro* diastereoselectivity given in Table 3 is comparable to that obtained with alkylammonium POM $[\{n\text{-}(C_8H_{17})_3NCH_3\}^+]_3[PO_4\{WO(O_2)_2\}_4]^{3-}$ (**18**, a ratio of 55:45 has already been reported),[22] and no significant diastereoselectivity difference was observed within the POM-cored dendrimer series. The increased bulk around the catalytic center does not appear to affect the stereocontrol of oxygen transfer to the allylic alcohols.

Recovery and reutilization of the POM-cored dendritic catalysts: Two reaction cycles were performed in order to test the stability of the POM-cored dendrimers **4a**,**b**, **8a**,**b**, and **13a**,**b** under catalytic reaction conditions. Cyclooctene **14a**, thioanisole **14b**, and cyclohexanol **14e** were used as model substrates (Table 4).

The catalyst was recovered by precipitation after each catalytic cycle and checked by ^{1}H and ^{31}P NMR before a new catalytic experiment was performed.

^{1}H and ^{31}P NMR characterization of the recovered catalyst showed the absence of any structural change. In addition, no discernable loss of activity was observed over the two catalytic cycles. Substrates **14a** and **14b** were quantitatively oxidized to the corresponding epoxide and sulfone, respectively, over the two cycles. An excellent conversion was also obtained in the oxidation of **14e**, despite longer reaction times (20–25 h) than those required for the alkene and the sulfide. The results obtained in these experiments reveal that all the POM-cored dendrimers studied are air-stable and easy to recover and handle. Interestingly, oxidation of **14a** and **14b** with the alkylammonium POMs $[\{n\text{-}(C_8H_{17})_3NCH_3\}^+]_3[PO_4\{WO(O_2)_2\}_4]^{3-}$ **18** and $[\{\text{Arquad}\}^+]_3[PO_4\{WO(O_2)_2\}_4]^{3-}$ **19** quantitatively led to epoxide **15a** in 150 and 120 min, respectively, and sulfone **15b** in 30 min under the same reaction conditions. These results are comparable with those obtained in the dendrimer series. However, an important difference was found in the recovery of the

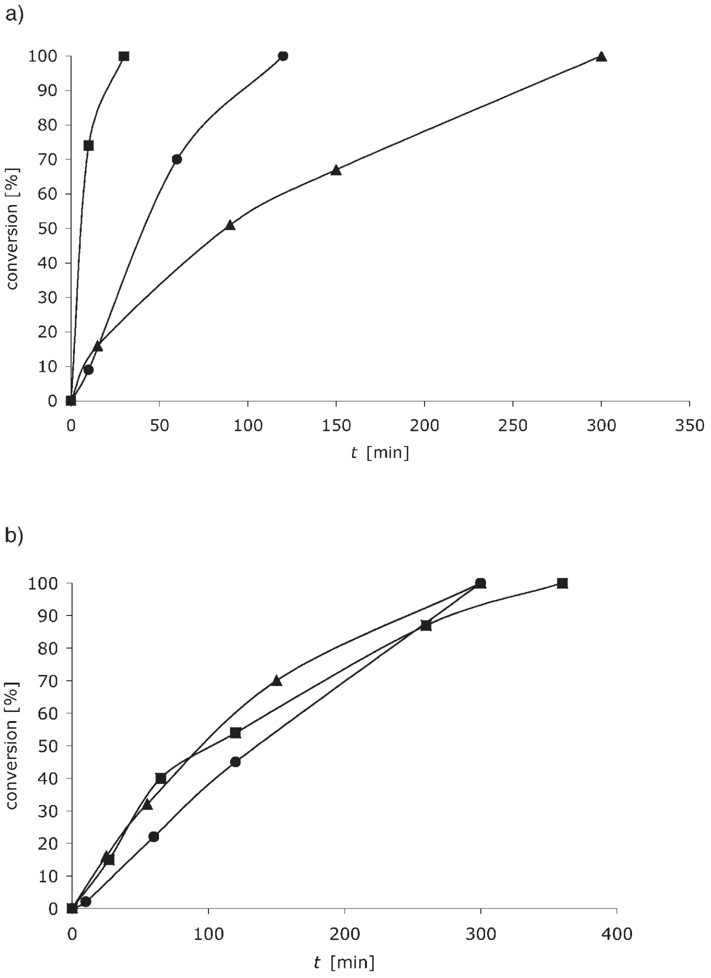


Figure 1. Kinetics of cyclooctene epoxidation. a) With 9-armed POM-cored dendrimers **4a** (●), **8a** (■), and **13a** (▲); b) with the 27-armed POM-cored dendrimers **4b** (●), **8b** (■), and **13b** (▲).

Table 4. Isolated yields of POM-cored dendrimers catalysts **4a**,**b**, **8a**,**b**, and **13a**,**b**, in the oxidation of cyclooctene (**14a**), thioanisole (**14b**), and cyclohexanol (**14e**) respectively, with H_2O_2, after the first and second runs.

Substrate	Catalyst	First cycle yield [%]	Second cycle yield [%]
cyclooctene (**14a**)	**4a**	75	67
	4b	96	85
	8a	80	50
	8b	70	60
	13a	75	70
	13b	80	70
thioanisole (**14b**)	**4a**	95	80
	4b	75	75
	8a	95	96
	8b	90	80
	13a	95	80
	13b	85	90
cyclohexanol (**14e**)	**4a**	95	75
	4b	85	75
	8a	90	70
	8b	80	76
	13a	91	85
	13b	95	85

catalyst. Indeed, the POM-cored dendrimers were easily recovered by precipitation without decomposition over two cycles, whereas precipitation of **19** after the first run was very difficult, and gave a small amount of a solid identified by two signals at $\delta = 0.5$ and -0.99 in the ^{31}P NMR spectrum. These ^{31}P NMR signals differed from those obtained for **19** at $\delta = 3.12$, indicating that the structure of these POM species had changed. Attempts to precipitate **18** after the first run were unsuccessful. These results indicate that the dendritic structures increase the stability of the anionic POM species, a key feature for the recovery and recycling of the POM catalysts in oxidation reactions. Interestingly, in the catalytic oxidation of thioanisole with the 9-epoxy-terminated POM-cored dendrimer **4a**, we were able to recover and reutilize the catalyst up to the eighth cycle without loss of activity. No decomposition of the catalyst was observed after the eighth cycle; the ^{31}P NMR signal remained similar to that obtained for **4a**.

Conclusion

A series of 9- and 27-armed polyoxometalate-centered dendrimers that bear epoxy, *n*-propyl, and aryl sulfide endgroups has been synthesized and characterized. These compounds are efficient catalysts in the epoxidation of cyclooctene, the selective oxidation of sulfides to sulfones, and the oxidation of cyclohexanol to cyclohexanone with hydrogen peroxide. Study of countercation effects reveals that the dendritic structures increase the stability of the POM unit, allowing the facile recovery and reutilization of the catalyst without loss of activity up to the eighth cycle, as for example, in the case of 9-epoxy-terminated POM-cored dendrimer **4a**. However, the dendritic structure of the cation decreases the reaction kinetics. It was observed that, within the 9-armed POM-cored dendrimer series, the reaction kinetics were sensitive to the nature of the peripheral endgroups. In contrast with aryl sulfide- and epoxy-terminated dendrimers, the *n*-propyl-terminated POM-cored dendrimer **8a** was the most active catalyst. In addition, it was also observed that increasing the dendritic structure of the cation decreased the reaction kinetics, probably on account of the lower electrophilic character of the POM unit. This series of 9- and 27-armed dendrimer catalysts are air-stable, easy to handle, and can be stored at room temperature without degradation.

Experimental Section

Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium/benzophenone under argon immediately prior to use. Acetonitrile (CH_3CN) was stirred overnight over phosphorus pentoxide and under argon, distilled from sodium carbonate, and stored under argon. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride just before use. All other chemicals were used as received. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25 °C with the following spectrometers: Bruker AC250FT (^{1}H: 250.13,

^{13}C: 62.91 MHz), Bruker AC200FT (^{1}H: 200.16, ^{13}C: 50.33, ^{31}P: 81.02 MHz). All chemical shifts are reported referenced to Me_4Si (TMS). Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne (France).

Synthesis of 3-armed ammonium dendrons

Bromobenzyl 3-allyl dendron (2a): A mixture of triallyl dendron **1a** (2.000 g, 8.77 mmol), K_2CO_3 (3.696 g, 26.40 mmol), and *p*-dibromoxylene (9.263 g, 35.09 mmol) in CH_3CN, was stirred for 4 d at room temperature. After removal of the solvent under vacuum, the product was extracted with pentane (3×30 mL), washed with water, and dried over sodium sulfate. The solvent was removed under vacuum and the product was purified by chromatography (silica gel, pentane/diethyl ether 9:1) to afford **2a** as a colorless oil (3.180 g, 91 %); ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.42 (s, 4H, Ar), 7.23 (d, 2H, Ar), 6.92 (d, 2H, Ar), 5.54 (m, 3H, CH=CH$_2$), 5.03 (m, 8H, CH=CH$_2$, CH$_2$O), 4.51 (s, 2H, BrCH$_2$), 2.43 (d, 6H, CH$_2$=CH-CH$_2$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.44 (C$_q$, ArO), 138.05 (C$_q$, Ar), 137.43 (C$_q$, Ar), 137.32 (C$_q$, Ar), 134.50 (CH=CH$_2$), 127.17 (CH, Ar), 127.79 (CH, Ar), 127.67 (CH, Ar), 117.54 (CH=CH$_2$), 114.06 (CH, Ar), 69.56 (CH$_2$O), 42.60 (C$_q$-CH$_2$), 41.82 (CH$_2$), 33.10 (BrCH$_2$); MALDI TOF MS: *m*/*z*: calcd for 434.37; found 433.42 $[M+Na]^+$; elemental analysis calcd (%) for $C_{24}H_{27}OBr$: C 70.07, H 6.62; found: C 70.58, H 6.80.

3-Allyl ammonium salt dendron (3a): A mixture of **2a** (0.390 g, 0.950 mmol) and tri-*n*-hexylamine (1.9 mL, 5.7 mmol) in CH_3CN was stirred for 16 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with pentane (3×50 mL) and dried under vacuum, to afford ammonium salt **3a** (0.424 g, 0.666 mmol, 70 %). ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.53 (s, 4H, Ar), 7.23 (d, 2H, Ar), 6.91 (d, 2H, Ar), 5.54 (m, 3H, CH=CH$_2$), 5.03 (m, 8H, CH=CH$_2$, CH$_2$O), 3.22 (m, 8H, NCH$_2$), 2.42 (d, 6H, CH$_2$CH=CH$_2$), 1.80 (m, 6H, CH$_2$), 1.34 (m, 18H, CH$_2$), 0.90 (m, 9H, CH$_3$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.20 (C$_q$, ArO), 140.29 (C$_q$, Ar), 138.50 (C$_q$, Ar), 134.49 (C$_q$, Ar), 132.70 (CH=CH$_2$), 128.19 (CH, Ar), 127.81 (CH, Ar), 126.71 (CH, Ar), 117.59 (CH=CH$_2$), 114.10 (CH, Ar), 69.02 (CH$_2$O), 62.80 (CH$_2$O), 58.79 (CH$_2$N), 42.72 (C$_q$-CH$_2$), 41.88 (CH$_2$), 31.17 (CH$_2$), 26.05 (CH$_2$), 23.61 (CH$_2$), 22.47 (CH$_2$), 22.43 (CH$_2$), 13.83 (CH$_3$) cm^{-1}; elemental analysis calcd (%) for $C_{42}H_{66}OBrN$: C 74.09, H 9.77; found: C 74.19, H 9.34.

3-n-Propyl phenol dendron (5a): 10 % Pd/C catalyst (5 mg, 0.046 mmol) was added to a THF solution (30 mL) of triallyl phenol dendron **1a** (0.500 g, 2.2 mmol) in a thick-walled tube capped with a Young's stopcock. The tube was flushed, pressurized with hydrogen, sealed, and stirred at room temperature for 3 h. The solvent was removed under vacuum, and the residue was extracted with pentane (3×20 mL) and filtered through celite. After evaporation of pentane, **5a** was obtained as a colorless oil (0.490 g, 2.090 mmol, 95 %). ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.21 (d, 2H, Ar), 6.80 (d, 2H, Ar), 4.75 (s, 1H, OH), 1.61 (m, 6H, CH$_2$), 1.06 (m, 6H, CH$_2$), 0.88 (t, 9H, CH$_3$); ^{13}C NMR ($CDCl_3$, 50.33 MHz): δ = 156.20 (C$_q$, ArO), 140.55 (C$_q$, Ar), 127.41 (CH, Ar), 114.06 (CH, Ar), 42.59 (C$_q$-CH$_2$), 41.21 (CH$_2$), 17.26 (CH$_2$), 14.80 (CH$_3$); elemental analysis calcd (%) for $C_{16}H_{26}O$: C 81.99, H 11.18; found: C 81.85, H 11.26.

Bromobenzyl 3-n-propyl dendron (6a): This compound was obtained as a colorless oil according to the procedure described above for **2a**, but from **5a** instead of **1a**. Yield: 90%; ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.43 (m, 4H, Ar), 7.23 (d, 2H, Ar), 6.93 (d, 2H, Ar), 5.05 (s, 2H, CH$_2$O), 4.62 (s, 2H, BrCH$_2$), 1.62 (m, 6H, CH$_2$), 1.08 (m, 6H, CH$_2$), 0.89 (t, 9H, CH$_3$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.19 (C$_q$, ArO), 140.50 (C$_q$, Ar), 138.21 (C$_q$, Ar), 136.71 (C$_q$, Ar), 128.54 (CH, Ar), 128.23 (CH, Ar), 113.87 (CH, Ar), 113.51 (CH, Ar), 42.66 (C$_q$-CH$_2$), 40.21 (CH$_2$), 16.70 (CH$_2$), 14.87 (CH$_3$); elemental analysis calcd (%) for $C_{24}H_{35}OBr$: C 68.73, H 8.41; found: C 68.32, H 8.64.

3-n-Propyl ammonium salt dendron (7a): This compound was obtained as a colorless solid according to the procedure described above for **3a**, but from **6a** instead of **2a**. Yield: 98 %; ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.38 (s, 4H, Ar), 7.18 (d, 2H, Ar), 6.93 (d, 2H, Ar), 5.01 (CH$_2$O), 3.42 (brs, 8H, NCH$_2$), 1.75 (brm, 12H, CH$_2$), 1.33 (brm, 30H, CH$_2$), 0.84 (brt, 18H, CH$_3$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 157.06 (C$_q$, ArO), 138.84 (C$_q$, Ar), 134.20 (C$_q$, Ar), 133.49 (C$_q$, Ar), 128.04 (CH, Ar), 127.81 (CH, Ar), 126.71 (CH, Ar), 114.10 (CH, Ar), 69.02 (CH$_2$O), 58.79 (CH$_2$N), 42.72 (C$_q$-CH$_2$), 41.88 (CH$_2$), 31.05 (CH$_2$), 25.80 (CH$_2$), 23.40 (CH$_2$), 22.70 (CH$_2$), 22.47 (CH$_2$), 13.90 (CH$_3$); elemental analysis calcd (%) for $C_{42}H_{72}OBrN$: C 73.44, H 10.56; found: C 72.75, H 11.05.

3-Aryl sulfide phenol dendron (10a): A mixture of triiodophenol dendron **9** (0.500 g, 0.820 mmol) and $NaSC_6H_5$ (0.647 g, 4.900 mmol) in DMF (20 mL) was stirred at 70 °C for 24 h. The mixture was then extracted with CH_2Cl_2 (3×20 mL), and the resulting solution washed with water and dried over sodium sulfate. After removal of the solvent under vacuum, the residue was washed with Et_2O (3×20 mL) and chromatographed (silica gel, diethyl ether/acetone 8:2) to afford **10a** as a beige solid (0.390 g, 0.694 mmol, 85 %). ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.82–7.53 (m, 15H, Ar), 6.95 (d, 2H, Ar), 6.71 (d, 2H, Ar), 2.95 (t, 6H, SCH$_2$), 1.64 (brm, 6H, CH$_2$), 1.44 (brm, 6H, CH$_2$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 154.50 (C$_q$, ArO), 139.22 (C$_q$, Ar), 135.95 (C$_q$, Ar), 134.20 (CH, Ar), 129.78 (CH, Ar), 128.22 (CH, Ar), 127.55 (CH, Ar), 115.83 (CH, Ar), 56.61 (SCH$_2$), 42.98 (C$_q$-CH$_2$), 35.76 (CH$_2$), 17.34 (CH$_2$); elemental analysis calcd (%) for $C_{34}H_{38}OS_3$: C 73.07, H 6.85; found: C 72. 75, H 6.30.

Bromobenzyl 3-aryl sulfide dendron (11a): This compound was obtained according to the procedure described above for **2a**, but from **10a** instead of **1a**. After removal of the solvent under vacuum, the product was extracted with CH_2Cl_2, (3×20 mL), and the solvent was evaporated under vacuum. The excess *p*-dibromoxylene was removed by washing the residue with Et_2O. Further purification by chromatography (silica gel, diethyl ether/acetone 8:2) afforded **11a** as a beige solid (0.531 g, 0.715 mmol, 80 %). ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.82–7.53 (m, 15H, Ar), 7.44 (s, 4H, Ar), 7.02 (d, 2H, Ar), 6.84 (d, 2H, Ar), 5.02 (s, 2H, CH$_2$O), 4.52 (s, 2H, CH$_2$Br), 2.95 (t, 6H, SCH$_2$), 1.68 (brm, 6H, CH$_2$); 1.43 (brm, 6H, CH$_2$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 157.38 (C$_q$, ArO), 139.47 (C$_q$, Ar), 137.67 (C$_q$, Ar), 136.97 (C$_q$, Ar), 134.11 (C$_q$, Ar), 132.59 (CH, Ar), 129.72 (CH, Ar), 128.27 (CH, Ar), 127.46 (CH, Ar), 125.61 (CH, Ar), 115.15 (CH, Ar), 115.03 (CH, Ar), 69.95 (CH$_2$O), 56.67 (SCH$_2$), 43.07 (C$_q$-CH$_2$), 35.88 (CH$_2$), 33.59 (CH$_2$Br), 17.31 (CH$_2$); elemental analysis calcd (%) for $C_{42}H_{45}OBrS_3$: C 67.99, H 6.11; found: C 67.30, H 6.50.

3-Aryl sulfide ammonium salt dendron (12a): This compound was obtained as a beige solid according to the procedure described above for **3a**, but from **11a** instead of **2a**. Yield: 0.573 g, 0.556 mmol, 84 %; ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.80–7.34 (brm, 19H, Ar), 7.01 (brd, 2H, Ar), 6.84 (brd,, 2H, Ar), 5.05 (brs, 2H, CH$_2$O), 3.26 (brs,, 8H, CH$_2$N), 2.94 (brt, 6H, SCH$_2$), 1.78 (br, CH$_2$), 1.64 (br, CH$_2$), 1.42 (br, 6H, CH$_2$), 0.86 (br, 9H, CH$_3$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.40 (C$_q$, ArO), 142.09 (C$_q$, Ar), 139.09 (C$_q$, Ar), 136.78 (C$_q$, Ar), 133.71 (C$_q$, Ar), 132.94 (CH, Ar), 129.32 (CH, Ar), 129.28 (CH, Ar), 127.81 (CH, Ar), 125.11 (CH, Ar), 114.72 (CH, Ar), 114.52 (CH, Ar), 69.40 (CH$_2$O), 58.85 (NCH$_2$), 56.24 (SCH$_2$), 42.69 (C$_q$-CH$_2$), 41.72 (CH$_2$), 35.46 (CH$_2$), 31.16 (CH$_2$), 26.08 (CH$_2$), 22.55 (CH$_2$), 22.40 (CH$_2$), 22.47 (CH$_2$), 16.77 (CH$_2$), 13.85 (CH$_3$); elemental analysis calcd (%) for $C_{60}H_{84}OBrNS_3$: C 71.25, H 8.37; found: C 70.58, H 7.68.

Synthesis of 9-armed ammonium dendrons

Bromobenzyl 9-allyl dendron (2b): A mixture of phenol-9-allyl dendron **1b** (0.500 g, 0.547 mmol), K_2CO_3 (0.230 g 1.645 mmol), and *p*-dibromoxylene (0.722 g, 2.735 mmol) in CH_3CN was stirred for 7 d at room temperature. After removal of the solvent under vacuum, the residue was extracted with pentane (3×30 mL). The solvent was removed under vacuum and the product was purified by chromatography (silica gel, pentane/diethyl ether 9:1) to provide **2b** as a colorless oil (0.570 g, 0.519 mmol, 95 %). ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.42 (s, 4H, Ar), 7.28 (d, 2H, Ar), 7.19 (d, 6H, Ar), 6.93 (d, 2H, Ar), 6.81 (d, 6H, Ar), 5.54 (m, 9H, CH=CH$_2$), 5.00 (m, 20H, CH=CH$_2$, CH$_2$O), 4.51 (s, 2H, BrCH$_2$), 3.88 (t, 6H, CH$_2$O), 2.41 (d, 18H, CH$_2$CH=CH$_2$), 1.86 (m, 6H, CH$_2$), 1.63 (m, 6H, CH$_2$); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.74 (C$_q$, ArO), 156.52 (C$_q$, ArO), 138.82 (C$_q$, Ar), 138.73 (C$_q$, Ar), 137. 45 (C$_q$, Ar), 136. 82 (C$_q$, Ar), 134.58 (CH=CH$_2$), 129.19 (CH, Ar), 127.78 (CH, Ar), 127.70 (CH, Ar), 127.50 (CH, Ar), 117.38 (CH=CH$_2$), 114.27 (CH, Ar), 113.72 (CH, Ar), 69.63 (CH$_2$O), 68.07 (CH$_2$O), 42.56 (C$_q$-CH$_2$), 41.99 (C$_q$-CH$_2$), 41.84 (CH$_2$), 33.68 (CH$_2$), 33.11 (BrCH$_2$), 23.66 (CH$_2$); MALDI TOF MS: *m*/*z*: calcd for 1119.45; found 1119.37

$[M+\mathrm{Na}]^+$; elemental analysis calcd (%) for $C_{72}H_{87}O_4Br$ (1096.38): C 78.88, H 8.00; found: C 78.80, H 8.06.

9-Allyl ammonium salt dendron (3b): This compound was obtained as a colorless solid according to the procedure described above for **3a**, but from **2b** instead of **2a**. Yield: 0.886 g, 0.648 mmol, 68 %; ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.56 (s, 4H, Ar), 7.28 (d, 2H, Ar), 7.19 (d, 6H; Ar), 6.97 (d, 2H, Ar), 6.82 (d, 6H, Ar), 5.53 (m, 9H, $CH{=}CH_2$), 5.00 (m, 20H $CH{=}CH_2$, and CH_2O), 3.88 (t, 6H, CH_2O), 3.30 (m, 8H, NCH_2), 2.42 (d, $CH_2CH{=}CH_2$), 1.83 (m, CH_2), 1.60 (m, CH_2), 1.40 (m, CH_2), 0.90 (m, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.76 (C_q, ArO), 156.52 (C_q, ArO), 140.18 (C_q, Ar), 137.53 (C_q, Ar), 134.58 ($CH{=}CH_2$), 132.75 (C_q, Ar), 128.15 (C_q, Ar), 127.56 (CH, Ar), 126.86 (CH, Ar), 124.06 (CH, Ar), 117.41 ($CH{=}CH_2$), 114.25 (CH, Ar), 113.74 (CH, Ar); 69.10 (CH_2O), 68.10 (CH_2O), 58.80 (CH_2N), 42.60 (C_q-CH_2), 42.09 (C_q-CH_2), 41.87 (CH_2), 33.70 (CH_2), 31.16 (CH_2), 26.53 (CH_2), 26.04 (CH_2), 23.70 (CH_2), 22.63 (CH_2), 22.40 (CH_2), 13.80 (CH_2); elemental analysis calcd (%) for $C_{90}H_{126}O_4BrN$: C 79.14, H 9.30; found: C, 78.80, H 8.64.

9-*n*-Propyl phenol dendron (5b): This compound was obtained as a colorless solid according to the procedure described above for **5a**, but from **1b** instead of **1a**. Yield: 0.489 g, 0.525 mmol, 96 %; ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.22 (d, 8H, Ar), 6.82 (d, 8H, Ar), 3.85 (t, 6H, CH_2O), 1.61 (m, 24H, CH_2), 1.05 (m, 24H, CH_2), 0.88 (t, 27H, CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.32 (C_q, ArO), 152.86 (C_q, ArO), 140. 51 (C_q, Ar), 140.31 (C_q, Ar), 127.56 (CH, Ar), 127.33 (CH, Ar), 114.56 (CH, Ar), 113.56 (CH, Ar), 68.18 (CH_2O), 42.80 (C_q-CH_2), 42.60 (C_q-CH_2), 40.22 (CH_2), 35.23 (CH_2), 29.56 (CH_2), 28.62 (CH_2), 16.70 (CH_2), 14.89 (CH_3); elemental analysis calcd (%) for $C_{64}H_{98}O_4$: C 82.53, H 10.60; found: C 81.79, H 10. 24.

Bromobenzyl 9-*n*-propyl dendron (6b): This compound was obtained as a colorless solid according to the procedure described above for **2a**, but from **5b** instead of **1a**. Yield: 0.440 g, 0.395 mmol, 92 %; ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.42 (s, 4H, Ar), 7.28 (d, 2H, Ar), 7.19 (d, 6H; Ar), 6.93 (d, 2H, Ar), 6.78 (d, 6H, Ar), 5.54 (m, 9H, $CH{=}CH_2$), 5.03 (s, 2H, CH_2O), 4.51 (s, 2H, $BrCH_2$), 3.88 (t, 6H, CH_2O), 1.89 (m, 6H, CH_2), 1.61 (m, 24H, CH_2), 1.05 (m, 24H, CH_2), 0.88 (t, 27H, CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.63 (C_q, ArO), 156.36 (C_q, ArO), 140.02 (C_q, Ar), 139.20 (C_q, Ar), 138.90 (C_q, Ar), 129.21 (CH, Ar), 128.12 (CH, Ar), 127.81 (CH, Ar), 127.54 (CH, Ar), 127.30 (CH, Ar), 114.32 (CH, Ar), 113.53 (CH, Ar), 69.49 (CH_2O), 68.15 (CH_2O), 42.60 (C_q-CH_2), 42.07 (C_q-CH_2), 40.64 (CH_2), 40.21 (CH_2), 33.70 (CH_2), 33.13 (CH_2Br), 23.75 (CH_2), 17.25 (CH_2), 14.84 (CH_3); elemental analysis calcd (%) for $C_{72}H_{105}O_4Br$: C 77.59, H 9.50; found: C 76.80, H 9.10.

9-*n*-Propyl ammonium salt dendron (7b): This compound was obtained as a colorless solid according to the procedure described above for **3a**, but from **6b** instead of **2a**. Yield: 0.886 g, 0.640 mmol, 80 %. After removal of the solvent under vacuum, the residue was washed with cooled pentane, and dried under vacuum. ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.53 (s, 4H, Ar), 7.16 (d, 2H, Ar), 6.92 (d, 2H, Ar), 6.77 (d, 6H, Ar), 5.05 (s, 2H, CH_2O), 3.86 (br, 6H, CH_2O), 3.22 (br, CH_2N), 1.89 (br, 6H, CH_2), 1.61 (m, CH_2), 1.32 (br, CH_2), 1.05 (br, CH_2), 0.88 (br, CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 157.19 (C_q, ArO), 156.36 (C_q, ArO), 140. 02 (C_q, Ar), 139. 24 (C_q, Ar), 138.90 (C_q, Ar), 129.21 (CH, Ar), 128.12 (CH, Ar), 127.75 (CH, Ar), 127.54 (CH, Ar), 127.30 (CH, Ar), 114.32 (CH, Ar), 113.53 (CH, Ar), 69.49 (CH_2O), 68.15 (CH_2O), 42.72 (C_q-CH_2), 42.07 (C_q-CH_2), 40.88 (CH_2), 31.05 (CH_2), 25.81 (CH_2), 22.75 (CH_2), 22.47 (CH_2), 16.28 (CH_2), 14.84 (CH_3), 13.92 (CH_3); elemental analysis calcd (%) for $C_{90}H_{144}O_4BrN$: C 78.10, H 10.49; found: C 77.06, H 9.98.

9-Aryl sulfide phenol dendron (10b): A mixture of 3-aryl sulfide phenol dendron **10a** (0.914 g, 1.340 mmol) and K_2CO_3 (0.348 g, 2.480 mmol) in DMF (20 mL) was stirred at room temperature for 30 min. To this mixture was added the protected triiodophenol dendron **10c** (0.200 g, 0.299 mmol) dissolved in DMF (10 mL). The reaction mixture was stirred for 2 d at room temperature. K_2CO_3 (0.188 g, 1.340 mmol) and water (0.350 mL) were added, and the reaction mixture was stirred at 40 °C for 48 h. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the resulting solution washed with water and dried over sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography (silica gel, diethyl ether/acetone 8:2) to afford **10b** as a beige solid (0.415 g, 0.218 mmol, 73 %). ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ = 7.82–7.52 (m, 45H, Ar), 7.00 (br, 8H, Ar), 6.72 (br, 8H, Ar), 3.86 (br, 6H, CH_2O), 2.95 (brt, 18H, SCH_2), 1.63 (br, 24H, CH_2), 1.48 (br, 24H, CH_2); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 157.26 (C_q, ArO), 157.13 (C_q, ArO), 139.00 (C_q, Ar), 135.84 (C_q, Ar), 133.66 (CH, Ar), 129.07 (CH, Ar), 127.81 (CH, Ar), 127.05 (CH, Ar), 125.17 (CH, Ar), 114.36 (CH, Ar), 68.19 (CH_2O), 56.25 (SCH_2), 42.58 (C_q-CH_2), 42.26 (C_q-CH_2), 41.96 (CH_2), 35.68 (CH_2), 23.78 (CH_2), 16.87 (CH_2); elemental analysis calcd (%) for $C_{118}H_{134}O_4S_9$: C 74.40, H 7.09; found: C 73.12, H 6.98.

Bromobenzyl 9-aryl sulfide dendron (11b): This compound was obtained as a beige solid according to the procedure described above for **2a**, but from **10b** instead of **1a**. Yield: 0.310 g, 0.146 mmol, 70 %; ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.80–7.36 (br, Ar), 6.97 (br, Ar), 6.75 (br, Ar), 5.15 (br, 2H, CH_2O), 4.49 (br, 2H, $BrCH_2$), 3.88 (br, 6H, CH_2O), 2.93 (br, 18H, SCH_2), 1.80 (br, CH_2), 1.46 (br, CH_2); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 139.15 (C_q, Ar), 134.10 (C_q, Ar), 129. 72 (C_q, Ar), 129.09 (CH, Ar), 128.90 (CH, Ar), 128.25 (CH, Ar), 127.62 (CH, Ar), 127.42 (CH, Ar), 114.79(CH, Ar), 69.71 (CH_2O), 69.59 (CH_2O), 56.68 (SCH_2), 43.02 (C_q-CH_2), 35.88 (CH_2), 33.32 (CH_2Br), 23.98 (CH_2), 17.32 (CH_2); elemental analysis calcd (%) for $C_{126}H_{141}O_4S_9Br$: C 72.79, H 6.73; found: C 72.29, H 6.66.

9-Aryl sulfide ammonium salts dendron (12b): This compound was obtained as a beige solid according to the procedure described above for **3a**, but from **11b** instead of **2a**. Yield: 0.298 g, 0.126 mmol, 89 %; ^{1}H NMR ($CDCl_3$, 200.16 MHz): δ = 7.80–7.35 (brm, Ar), 6.98 (br, Ar), 6.71 (br, Ar), 5.16 (br, 2H, CH_2O), 3.88 (br, 6H, CH_2O), 3.26 (br, CH_2N), 2.93 (br, 18H, SCH_2), 1.77 (br, CH_2), 1.65 (br, CH_2), 1.42 (br, CH_2), 0.87 (br, CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 156.57 (C_q, ArO), 139.07 (C_q, Ar), 133.72 (C_q, Ar), 132.84 (CH, Ar), 129.33 (CH, Ar), 128.61 (CH, Ar), 127.80 (CH, Ar), 127.11 (CH, Ar), 114.30 (CH, Ar), 68.18 (CH_2O), 58.90 (CH_2N), 56.29 (CH_2S), 42.37 (C_q-CH_2), 35.48 (CH_2), 31.16 (CH_2), 26.55 (CH_2), 26.08 (CH_2), 22.61 (CH_2), 22.40 (CH_2), 16.88 (CH_2), 13.86 (CH_3); elemental analysis calcd (%) for $C_{144}H_{180}O_4S_9BrN$: C 73.36, H 7.70; found: C 72.89, H 7.39.

General procedure for the synthesis of POM-cored dendrimers: H_2O_2 (4.8 mL, 35 % in water) was added to a solution of commercial heteropolyacid $H_3PW_{12}O_{40}$ (0.096 mmol) in water (0.160 mL). The mixture was stirred at room temperature for 30 min. A solution of ammonium bromide salt (0.250 mmol) in CH_2CH_2 (1.5 mL) was added, and the mixture was stirred for an additional hour for the 9-armed dendrimer and 2 h for the 27-armed dendrimer. The CH_2Cl_2 layer was washed with water (0.5 mL) and dried over sodium sulfate. The product was obtained by removing the solvent under vacuum.

9-Armed tetrakis(diperoxotungsto)phosphate-cored dendrimers

9-Epoxide tetrakis(diperoxotungsto)phosphate-cored dendrimer (4a): Light yellow solid (0.075 mmol, 233 mg, 90 %); ^{1}H NMR ($CDCl_3$, 200.16 MHz, broad signals): δ = 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, CH_2), 1.80 (m, 18H, CH_2), 1.34 (m, 54H, CH_2), 0.90 (m, 18H, CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 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 ($CDCl_3$, 81.02 MHz): δ = 2.96 (PO_4); FT-IR (KBr plates): $\tilde{\nu}$ = 1084–1052 (P–O), 963 (W=O), 845 (O–O), 580 and 521 cm^{-1} ($W(O_2)_{s,as}$); elemental analysis calcd (%) for $C_{126}H_{198}O_{36}N_3PW_4$: C 48.86, H 6.44; found: C 47.93, H 6.30.

9-*n*-Propyl tetrakis(diperoxotungsto)phosphate-cored dendrimer (8a): Light yellow solid (0.071 mmol, 210 mg, 85 %); ^{1}H NMR ($CDCl_3$, 200.16 MHz, broad signals): δ = 7.41 (m, 12H, Ar), 7.19 (d, 6H, Ar), 6.89 (d, 6H, Ar), 5.33 (s, 6H, CH_2O), 3.30 (NCH_2), 1.72 (CH_2), 1.33 (CH_2), 0.87 (CH_3); ^{13}C NMR ($CDCl_3$, 62.91 MHz): δ = 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), 58.06 (CH_2N), 42.70 (C_q-CH_2), 31.04 (CH_2), 25.87 (CH_2), 22.40 (CH_2), 21.75 (CH_2), 21.72 (CH_2), 16.71 (CH_3), 13.94 (CH_3); ^{31}P NMR ($CDCl_3$, 81.02 MHz): δ = 3.02 (PO_4), FT-IR (KBr plates): $\tilde{\nu}$ = 1083–1052 (P–O), 969 (W=O), 840 (O–O), 580 and 522 cm^{-1} ($W(O_2)_{s,as}$); elemental analysis calcd (%) for $C_{124}H_{216}O_{27}N_3PW_4$: C 50.53, H 7.39; found: C 49.59, H 6.56.

9-Aryl sulfide tetrakis(diperoxotungsto)phosphate-cored dendrimer (13a): Light yellow solid (0.070 mmol, 278 mg, 85 %); ^{1}H NMR (CDCl$_3$, 200.16 MHz, broad signals): δ = 7.82–7.36 (m, Ar), 6.99 (d, Ar), 6.86 (d, Ar), 5.03 (s, 6H, CH$_2$O), 2.95 (CH$_2$N and SCH$_2$), 1.77 (CH$_2$), 1.64 (CH$_2$), 1.41 (CH$_2$), 1.30 (CH$_2$), 0.86 (CH$_3$); ^{13}C NMR (CDCl$_3$, 62.91 MHz): δ = 156.79 (C$_q$, ArO), 139.07 (C$_q$, Ar), 133.74 (C$_q$, Ar), 133.66 (C$_q$, Ar), 129.32 (CH, Ar), 127.81 (CH, Ar), 127.79 (CH, Ar), 114.80 (CH, Ar), 69.34 (CH$_2$O), 58.38 (CH$_2$N), 56.24 (SCH$_2$), 42.84 (C$_q$-CH$_2$), 35.36 (CH$_2$), 31.08 (CH$_2$), 25.74 (CH$_2$), 22.35 (CH$_2$), 16.84 (CH$_3$), 13.92 (CH$_3$); ^{31}P NMR (81 MHz, CDCl$_3$): δ = 2.87 (PO$_4$); FT-IR (KBr plates): $\tilde{\nu}$ = 1076–1052 (P–O), 963 (W=O), 830 (O–O), 580 and 521 cm^{-1} ($W(O_2)_{s,as}$); elemental analysis calcd (%) for $C_{180}H_{252}O_{27}N_3PS_9W_4$: C 54.80, H 6.44; found: C 53.90, H 5.93.

27-Armed tetrakis(diperoxotungsto)phosphate-cored dendrimers

27-Epoxide tetrakis(diperoxotungsto)phosphate-cored dendrimer (4b): Light yellow solid (0.079 mmol, 432 mg, 95 %); ^{1}H NMR (CDCl$_3$, 200.16 MHz, broad signals): δ = 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$_2$O), 3.90 (br, 18H, CH$_2$O), 3.20 (br, 24H, NCH$_2$), 2.91–2.00 (brm, CH and CH$_2$), 1.80 (br, CH$_2$), 1.37 (br, CH$_2$), 0.88 (br, CH$_3$); ^{13}C NMR (CDCl$_3$, 62.91 MHz): δ = 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$_2$O), 68.23 (CH$_2$O), 58.47 (CH$_2$N), 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 (CDCl$_3$, 81.02 MHz): δ = 2.47 (PO$_4$); FT-IR (KBr plates): $\tilde{\nu}$ = 1080–1056 (P–O), 959 (W=O), 830 (O-O), 580 and 521 cm^{-1} ($W(O_2)_{s,as}$); elemental analysis calcd (%) for $C_{270}H_{378}N_3O_{64}PW_4$: C 59.44, H 6.98; found: C 58.84, H 6.76.

27-n-Propyl tetrakis(diperoxotungsto)phosphate-cored dendrimer (8b): Light yellow oily solid (0.076 mmol, 384 mg, 91 %); ^{1}H NMR (CDCl$_3$, 200.16 MHz, broad signals): δ = 7.54 (s, 4H, Ar), 7.16 (d, 6H, Ar), 6.92 (d, 2H, Ar), 6.77 (d, 6H, Ar), 5.02 (s, 2H, CH$_2$O), 3.86 (br, 6H, CH$_2$O), 3.23 (br, CH$_2$N), 1.75 (br, 6H, CH$_2$), 1.54 (br, CH$_2$), 1.32 (br, CH$_2$) 1.03 (br, CH$_2$) 0.88 (br, CH$_3$); ^{13}C NMR (CDCl$_3$, 62.91 MHz): δ = 157.19 (C$_q$, ArO), 140.53 (C$_q$, Ar), 128.50 (CH, Ar), 127.75 (CH, Ar), 113.53 (CH, Ar); 64.42 (CH$_2$O), 57.75 (CH$_2$N), 42.20 (C$_q$-CH$_2$), 39.97 (CH$_2$), 36.08 (CH$_2$), 31.40 (CH$_2$), 31.05 (CH$_2$), 26.05 (CH$_2$), 25.81 (CH$_2$), 22.75 (CH$_2$), 22.40 (CH$_2$), 21.84 (CH$_2$), 16.28 (CH$_2$), 14.62 (CH$_3$), 13.92 (CH$_3$); ^{31}P NMR (CDCl$_3$, 81.02 MHz): δ = 3.54 (PO$_4$); FT-IR (KBr plates): $\tilde{\nu}$ = 1083 and 1057 (P–O), 974 (W=O), 845 (O–O), 590 and 517 cm^{-1} ($W(O_2)_{s,as}$); elemental analysis calcd (%) for $C_{270}H_{432}N_3O_{36}PW_4$: C 64.06, H 8.60; found: C 64.75, H 8.47.

27-Aryl sulfide tetrakis(diperoxotungsto)phosphate-cored dendrimer (13b): Light yellow solid (0.079 mmol, 632 mg, 95 %); ^{1}H NMR (CDCl$_3$, 200.16 MHz, broad signals): δ = 7.86–7.39 (m, Ar), 7.01 (br, Ar), 6.80 (br, Ar) 5.16 (br, CH$_2$O), 3.89 (br, CH$_2$O), 3.08 (br, CH$_2$N), 2.95 (SCH$_2$), 1.71 (CH$_2$), 1.36 (CH$_2$), 1.30 (CH$_2$), 0.86 (CH$_3$); ^{13}C NMR (CDCl$_3$, 62.91 MHz): δ = 139.07 (C$_q$, Ar), 139.04 (C$_q$, Ar), 133.66 (C$_q$, Ar), 133.62 (C$_q$, Ar), 129.29 (CH, Ar), 128.45 (CH, Ar), 127.80 (CH, Ar), 127.79 (CH, Ar), 114.35 (CH, Ar), 68.31 (CH$_2$O), 58.80 (CH$_2$N), 56.23 (SCH$_2$), 42.58 (C$_q$-CH$_2$), 35.47 (CH$_2$), 31.18 (CH$_2$), 25.90 (CH$_2$), 22.39 (CH$_2$), 16.88 (CH$_3$), 13.81 (CH$_3$); ^{31}P NMR (CDCl$_3$, 81.02 MHz): δ = 2.74 (PO$_4$); FT-IR (KBr plates): $\tilde{\nu}$ = 1086 and 1057 (P–O), 974 (W=O), 845 (O–O), 590 and 522 cm^{-1} ($W(O_2)_{s,as}$); elemental analysis calcd (%) for $C_{432}H_{540}O_{36}N_3PS_{27}W_4$: C 65.00, H 6.82; found: C 64.46, H 6.58.

General procedure for the catalytic oxidation reactions with the 9-and 27-armed POM-cored dendritic catalysts and for the catalyst recovery experiments: The substrate (250 equiv) and 35 % H$_2$O$_2$ (800 equiv) was added to a CDCl$_3$ solution (3 mL) of catalyst (0.004 mmol). The reaction mixture was stirred at 35 °C and monitored by ^{1}H NMR. Upon completion, the CDCl$_3$ layer was separated and concentrated under a vacuum to ≈1 mL. The catalyst was precipitated by addition of Et$_2$O (10 mL). The solid was filtered and washed with Et$_2$O (3×10 mL) to afford the POM catalyst in a good-to-excellent yield (70–96 %, see Table 4, main text). The catalyst was recovered following the typical procedure and conditions described above for the first cycle, CDCl$_3$ and reactants being adjusted to the amount of catalyst used. The reaction was performed with cyclooctene **14a**, thioanisole **14b**, and cyclohexanol **14e** using dried, recovered compound **4a**,**b**, **8a**,**b**, and **13a**,**b**. The catalyst was completely dissolved in CDCl$_3$, and the reactants were added to the solution. After completion, the kinetics remained unchanged because the data collected were comparable to those summarized in Table 2 for the first cycle. The catalyst was recovered and checked by ^{1}H and ^{31}P NMR, with a yield between 50 and 96 % (Table 4).

Acknowledgements

Financial support from the University Bordeaux I, the CNRS, the IUF (DA) and the MRT (LP) is gratefully acknowledged.

---

[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, Vol. 6* (Ed.: D. Astruc), C. R. Chimie, Elsevier, Paris, **2003**; d) F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681.

[2] a) D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991; b) R. Kreiter, A. Kleij, R. J. M. Klein Gebbink, G. van Koten, *Top. Curr. Chem.* **2001**, *217*, 163; c) R. van Heerbeek, P. C. J. Kamer, P. W. N. M. van-Leeuwen, J. N. H. Reek, *Chem. Rev.* **2002**, *102*, 3717; d) L. J. Twyman, A. S. H. King, I. K. Martin, *Chem. Soc. Rev.* **2002**, *31*, 69.

[3] J.-M. Lehn, *Supramolecular Chemistry: Concepts and perspectives*, VCH, Weinheim, **1995**.

[4] a) G. R. Newkome, E. He, C. N. Moorefield, *Chem. Rev.* **1999**, *99*, 1689; b) A. W. Bosman, H. M. Janssen, E. W. Meijer, *Chem. Rev.* **1997**, *97*, 1665; c) I. Cuadrado, M. Moran, C. M. Casado, B. Alonzo, J. Losada, *Coord. Chem. Rev.* **1999**, *193–195*, 395; d) M. A. Hearshaw, J. R. Moss, *Chem. Commun.* **1999**, 1.

[5] G. E. Oosterom, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem.* **2001**, *113*, 1878; *Angew. Chem. Int. Ed.* **2001**, *40*, 1828.

[6] a) P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Am. Chem. Soc.* **1996**, *118*, 5708; b) P. Bhyrappa, J. K. Young, J. S. Moore, K. S. Suslick, *J. Mol. Catal. A Chem.* **1996**, *113*, 109; c) P. Weyermann, J.-P. Gisselbrecht, C. Boudon, F. Diederich, M. Gross, *Angew. Chem.* **1999**, *111*, 3400; *Angew. Chem. Int. Ed.* **1999**, *38*, 3215; d) P. Weyermann, F. Diederich, *J. Chem. Soc. Perkin Trans. 1* **2000**, 4231; e) F. Diederich, P. Weyermann, *Polym. Mater. Sci. Eng.* **2001**, *84*, 168; f) P. Weyermann, F. Diederich, *Helv. Chim. Acta* **2002**, *85*, 599; g) P. Weyermann, F. Diederich, J.-P. Gisselbrecht, C. Boudon, M. Gross, *Helv. Chim. Acta* **2002**, *85*, 571; h) C. Francavilla, M. D. Drake, F. V. Bright, M. R. Detty, *J. Am. Chem. Soc.* **2001**, *123*, 57; i) K. Ahsan, M. D. Drake, D. E. Higgs, A. L. Wojciechowski, B. N. Tse, M. A. Bateman, Y. You, M. R. Detty, *Organometallics* **2003**, *22*, 2883.

[7] a) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34; b) J. T. Rhule, C. L. Hill, D. A. Rud, R. F. Schinazi, *Chem. Rev.* **1998**, *98*, 327; c) D. E. Katsoulis, *Chem. Rev.* **1998**, *98*, 359; d) M. T. Pope, A. Müller, *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*, Kluwer Academic, Dordrecht, **2001**.

[8] For the multiple facets of POM chemistry, see refs. [7], [9]–[12] and the special issue dedicated to POMs: *Chem. Rev.* **1998**, *98*, whole Issue.

[9] a) I. V. Kozhevnikov, *Catalysis by Polyoxometalates*, Wiley, 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**, *47*, 317.

[10] M. C. Rogers, B. Adisa, D. Bruce, *Catal. Lett.* **2004**, *98*, 29–36.

[11] a) H. Zeng, G. R. Newkome, C. L. Hill, *Angew. Chem.* **2000**, *112*, 1841; *Angew. Chem. Int. Ed.* **2000**, *39*, 1772; b) L. Plault, A. Hauseler, S. Nlate, D. Astruc, J. Ruiz, S. Gatard, R. Neumann, *Angew. Chem.* **2004**, *116*, 2984; *Angew. Chem. Int. Ed.* **2004**, *43*, 2924; c) M. V. Vasylyev, D. Astruc, R. Neumann, *Adv. Synth. Catal.* **2005**, *347*, 39; d) S. Nlate, D. Astruc, R. Neumann, *Adv. Synth. Catal.* **2004**, *346*, 5517.

[12] C. Venturello, R. D'Aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Catal.* **1985**, *32*, 107.

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

[14] a) V. Sartor, L. Djakovitch, J.-L. Fillaut, F. Moulines, F. Neveu, V. Marvaud, J. Guittard, J.-C. Blais, D. Astruc, *J. Am. Chem. Soc.* **1999**, *121*, 2929; b) V. Sartor, S. Nlate, J.-L. Fillaut, L. Djakovitch, F. Moulines, V. Marvaud, F. Neveu, J.-C. Blais, *New J. Chem.* **2000**, *24*, 351.

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

[16] a) C. Venturello, R. D'Aloisio, *J. Org. Chem.* **1988**, *53*, 1553; b) Y. Ishii, Y. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* **1988**, *53*, 3587; c) Y. Ishii, M. Ogawa, *Reviews on Heteroatom Chemistry, Vol. 3* (Eds.: A. Ohno, N. Furukawa), MYU, Tokyo, **1990**, p. 121; d) R. Neumann, A. M. Khenkin, *J. Org. Chem.* **1994**, *59*, 7577; e) C. Aubry, G. Chottard, N. Platzer, J.-M. Brégault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, *Inorg. Chem.* **1991**, *30*, 4409.

[17] 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.

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

[19] a) F. P. Ballistreri, S. Failla, G. A. Tomaselli, *J. Org. Chem.* **1988**, *53*, 830; b) Y. Ishii, Y. Sakata, *J. Org. Chem.* **1990**, *55*, 5545; c) F. P. Ballistreri, S. Failla, E. Spina, G. A. Tomaselli, *J. Org. Chem.* **1989**, *54*, 947.

[20] F. P. Ballistreri, U. Chiacchio, A. Rescifina, G. A. Tomaselli, *Tetrahedron* **1992**, *48*, 8677.

[21] a) K. Mori, T. Otsuka, *Tetrahedron* **1985**, *41*, 553; b) K. Mori, T. Otsuka, *Tetrahedron* **1985**, *41*, 3253.

[22] C. Venturello, M. Gambaro, *J. Org. Chem.* **1991**, *56*, 5924.

Received: May 19, 2005