Dendrimers

Synthesis of Dendritic Polyoxometalate Complexes Assembled by Ionic Bonding and Their Function as Recoverable and Reusable Oxidation Catalysts**

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Dedicated to Professor David Carrillo
on the occasion of his 65th birthday

Dendrimers[1] are known for a number of potential applications in supramolecular chemistry,[2] nanosciences,[3] biology, and medicine,[4] and many of their transition- metal complexes[5] are especially promising in catalysis.[6] Whereas covalent-based metallodendrimers have been shown to act as catalysts in numerous cases, the ionic-bonding approach has only recently been mentioned.[7] We now wish to report a

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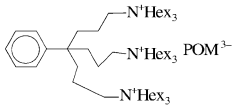
new series of five metallodendrimers based on ionic bonding between dendritic polyammonium polycations and trianionic polyoxometalates (POMs) and their use as recoverable and reusable catalysts in oxidation reactions. POMs are the source of fascinating architectures[8] and very rich redox chemistry[9] that provides the basis for their catalytic activity in oxidation reactions.[10] There is only one report of catalysis by using a dendritic-type framework that contains POMs: the oxidation of tetrahydrothiophene to its sulfoxide by *t*BuOOH and H_2O_2 was catalyzed by a compound consisting of four POM units covalently bonded to a tetradirectional core.[11]

Among the POM oxidation catalysts, we have selected the peroxophosphotunsgtate $[PO_4\{WO(O_2)_2\}_4]^{3-}$, which is known for its catalytic properties in olefin epoxidation and alcohol oxidation.[11,12] To build the supramolecular assembly of the dendritic oxidation catalysts in which each POM trianion is connected to a trication, we have designed tricationic tripods that consist of triammonium groups. For this purpose, our synthetic strategy involves polymethyl arenes in which each methyl group can be functionalized by three allyl groups by using the temporary complexation/activation by the 12-electron fragment $[CpFe]^+$ (see Scheme 1, the example is mesitylene).[13] Regioselective hydroboration of the nona-alcene **2**, which was produced from **1**, and oxidation of the nona-borane to give the primary nona-ol **3** followed by treatment with $SiMe_3Cl/NaI$ provided the nona-iodo compound **4**.[14] Alkylation of tri-hexylamine by using **4** gave the nona-ammonium salt **5** as an iodide that cannot be used as such for oxidation chemistry, because of facile oxidation of the iodide anion.[15] Treatment of **5** with $AgBF_4$ in ethanol gave the BF_4^- ammonium salt. The latter was transformed into the desired nona-ammonium salt **6** of $[PO_4[WO(O_2)_2]_4]^{3-}$ in dichloromethane by treatment with an aqueous solution of the commercial heteropolyacid $H_3PW_{12}O_{40}$ and H_2O_2. A peroxotungstate product, $[\{WO(O_2)_2(H_2O)\}_2O]^{2-}$, was easily removed, as it remained in the aqueous phase.[12d] This procedure was also applied to toluene and *p*-xylene providing the mono and bis(POM)-triammonium salts **7** and **8**. Standard characterization techniques, such as ^1H and ^{31}P NMR spectroscopies and elemental analysis, were applied to the dendrimers, the results of which are reported in the Supporting Information. AFM characterization of the tris(POM) dendrimer is shown in Figure 1, and the height of the complex recorded by this technique, 2.9 nm, indicates the presence of



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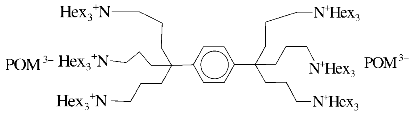

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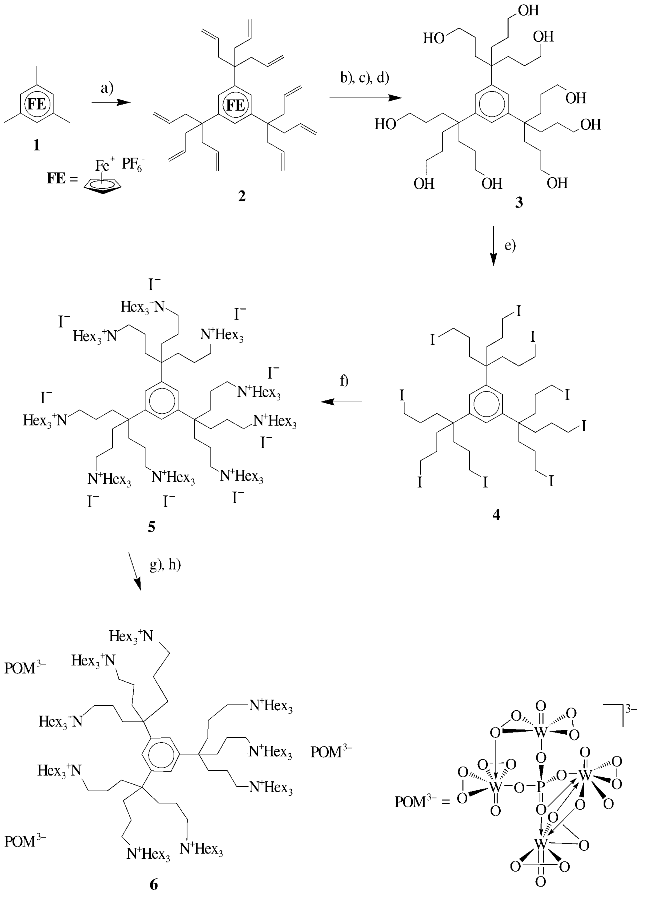


Scheme 1. Synthesis of the tris(POM) complex **6**. a) KOH, $CH_2{=}CH{-}CH_2Br$, DME, −50°C to RT. b) PPh_3, CH_3CN, RT, 12 h *hν* (Hg lamp). c) BH_3, isobutene, THF, RT, 12 h. d) aq NaOH, 3 M, H_2O, 30% H_2O_2, 50°C, 12 h. e) NaI, CH_3CN, Me_3SiCl, 50°C, 12 h. f) $NHex_3$, CH_3CN, 80°C, 12 h. g) $AgBF_4$, EtOH, RT. h) $H_3PW_{12}O_{24}$, H_2O_2, H_2O, CH_3Cl.

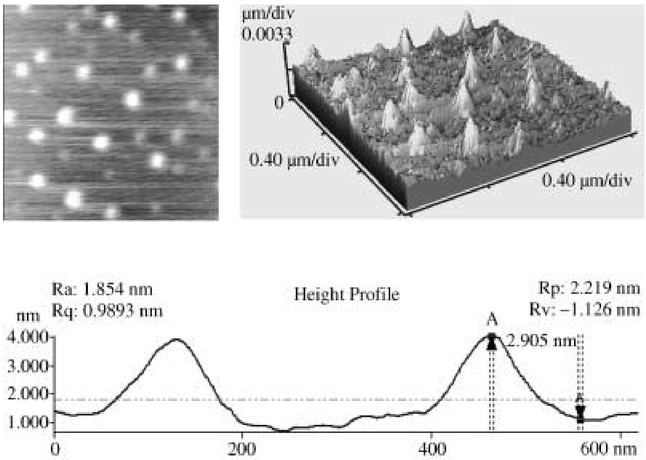
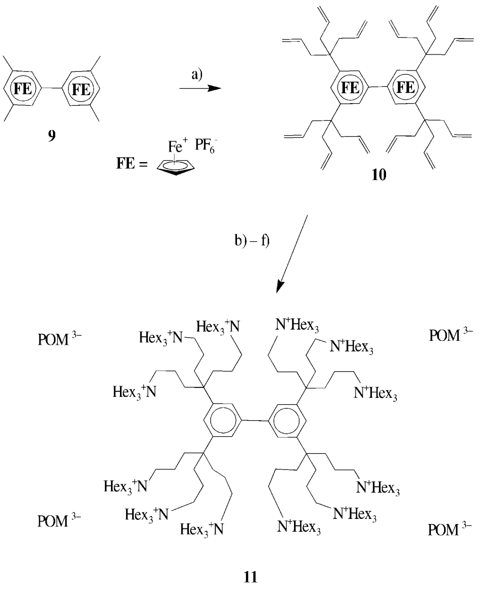


Figure 1. AFM images of the tris(POM) dendrimer **6** on graphite HOPG support shown in two dimensions (left) and three dimensions (right). The height is reproducibly 2.9 nm (bottom) indicating a monolayer of monomeric tris(POM) dendrimer **6**. AFM was operated in the tapping-mode with a resonance frequency of around 200 MHz. The tip has a radius of 10 nm.

monomeric species, a feature that is evidenced by the good solubility properties.

Since the trifunctionalization of polymethyl arenes used here requires that each methyl group be free of its methyl neighbor in the arene structure, thus it cannot be extended to more than three methyl groups on a single arene ring. To extend the arene system to four methyl groups, we used the dinuclear tetramethylbiphenyl complex **9**, which was recently shown to provide the dodeca-allyl derivative **10** by treatment with KOH/DME (DME = 1,2-dimethoxy ethane) and allyl bromide at room temperature.[16] This synthetic strategy was successfully employed and also provides the tetra(POM) polyammonium compound **11** according to Scheme 2.



Scheme 2. Synthesis of the tetra(POM) complex **11**. a) *t*BuOK, $CH_2{=}CHCH_2Br$, THF, 3 d, b) PPh_3, CH_3CN, RT, 12 h *hν* (Hg lamp). c) BH_3, isobutene, THF, RT, 12 h. d) aq. NaOH, 3 M, H_2O, 30% H_2O_2, 50°C, 12 h. e) NaI, CH_3CN, Me_3SiCl, 50°C, 12 h. f) $NHex_3$, CH_3CN, 80°C, 12 h. g) $AgBF_4$, EtOH, RT, h) $H_3PW_{12}O_{24}$, H_2O_2, H_2O, CH_3Cl.

We also wished to compare the stability, solubility, recovery, and reuse properties within a series of ionic dendrimers that contain between 1 and 6 POM units. Thus, we designed a new pathway to synthesize a hexa(POM) ammonium compound. Therefore, we used the new $[CpFe]^+$-induced hexa-alkenylation of the C_6Me_6 ligand of **12** to obtain **13** (Scheme 3),[17] followed by the analogous synthesis of the hexa-ol **14** and hexamesylate **15**. Then, the latter was allowed to react with the phenolate dendron *p*-O^--$C_6H_4C(allyl)_3$.[14,18] to give the 18-allyl dendrimer **16**, which was further converted to the octadecyl ammonium iodide, BF_4^-, and hexa(POM) salt **17** in a way similar to that described above for the mono-, bis-, and tris(POM). An important difference between this hexa(POM) salt **17** and the other salts (**6**, **8**, and **11**) however, is that it is insoluble in all common solvents, which indicates a polymeric form. Nevertheless, **17** has been characterized by its correct elemental analysis.

Epoxidation of cyclooctene by 35 % aq H_2O_2 in a biphasic water/$CDCl_3$ system was carried out at room temperature, and was catalyzed by 0.3 % equivalents of POM embedded in the ionic dendrimer. Under these conditions, monitoring of the kinetics by plotting the ratio between the intensity of the disappearing ^1H NMR signal of cyclooctene at $\delta = 5.6$ ppm versus TMS and that of the rising peak of the epoxide at $\delta = 2.9$ ppm versus TMS showed that the reaction was quantitative after 5 h. A comparison of the homogeneous mono-, bis-, tris-, and tetra(POM) catalysts indicated that there was no measurable dendritic effect on the reaction kinetics within this series.

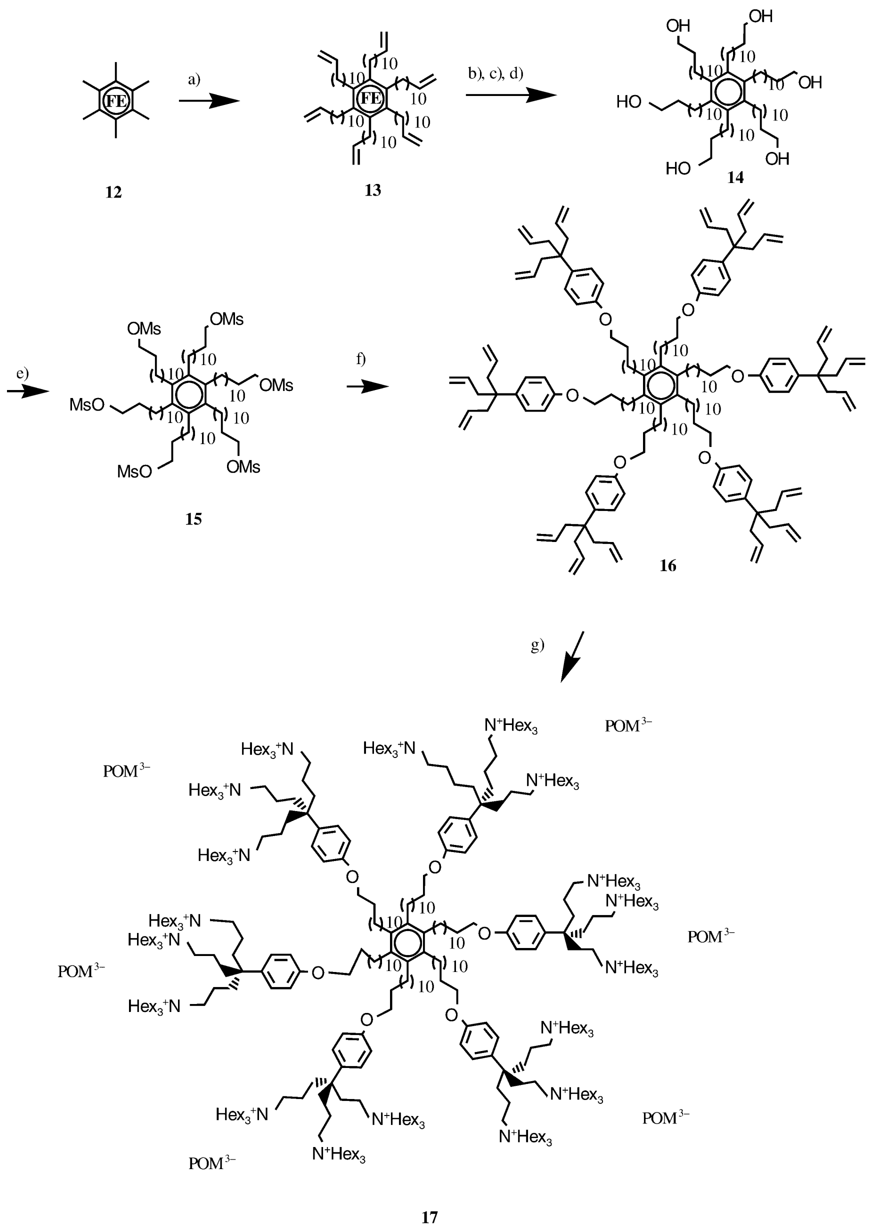
A dendritic effect, however, was noted in the recovery of the catalysts. The catalysts are precipitated from the organic phase by the addition of pentane leaving a clear solution in the case of the tris and tetra(POM) catalysts **6** and **11**, whereas precipitation of the mono(POM) catalyst **7** is tedious and leaves a white colloidal solution. Therefore, the recovery of the tri and tetra(POM) catalysts is easier than that of the mono(POM) catalyst. Out of a catalytic amount as low as 20 mg, the recovery of **6** by precipitation and filtration was between 80 and 85 % after each catalytic cycle, and the efficiency of this catalyst was reproducible. With **11**, the catalyst recovery reached 96 %. After catalysis, the ^{31}P NMR spectra of **6** and **11** were unchanged.

It was noticed however that, if the dendritic POM catalysts were left for several days in air, they became less soluble in $CDCl_3$, and their ^{31}P NMR spectrum changed (peak shift from $\delta = 3.45$ to 1.11 ppm). Then, their catalytic activity was suppressed. Preliminary experiments indicate that the mono(POM) catalyst is more sensitive to this deactivation than the tris and tetra(POM) catalysts. If the POM catalysts are kept under an inert atmosphere, they are not the subjects of deactivation. Although this deactivation procedure was very slow with **6**, since two catalytic cycles with recovery in air could be performed without storing this catalyst under an inert atmosphere, it is best to store the POM catalyst under argon for prolonged periods of time. Indeed, storage of **6** for several months under an inert atmosphere allows further catalytic use without problem.

A successful catalysis experiment was also carried out by using the heterogeneous hexa(POM) catalyst **17**, which led quantitatively to epoxycyclooctane and to direct recovery of the catalyst by filtration.

The oxidation of thioanisole to the corresponding sulfone by H_2O_2 in the biphasic water/$CDCl_3$ system could also be catalyzed by 0.1 % of the tris(POM) complex **6** and was selective and quantitative at room temperature after two hours. This reaction does not work in the absence of catalyst. The catalyst **6** was recovered analogously, as in the epoxidation experiments, and it was checked by ^{31}P NMR spectroscopy that it was unchanged after recovery.

In conclusion, we have designed and assembled nanosized ionic dendritic polyammonium POM oxidation catalysts **6**, **7**, **8**, **11**, and **17**, in which a peroxophosphotungstate trianion is bound to a tripod terminated by three trihexylammonium groups. A comparison of the homogeneous POM dendritic epoxidation catalysts showed that their efficiency (kinetics) were the same, but recovery of the soluble tris and tetra-



Scheme 3. Synthesis of the hexa(POM) complex **17**. a) KOH, 1-iodo-11-undecene, DME, 60 °C, 3 d. b) PPh_3, CH_3CN, $h\nu$,16 h (Hg lamp), RT. c) BH_3, isobutene, THF, 1 d, RT. d) NaOH, 30% H_2O_2, H_2O. e) CH_3SO_3Cl, C_5H_5N, HCl, 4 h, −5 °C-0 °C. f) p-O^--$C_6H_4C(allyl)_3$, KCO_3, Me_2CO, reflux 2.5 days.[14] g) BH_3, isobutene, THF, RT, 12 h, then aq NaOH, 3 M, H_2O, 30% H_2O_2, 50 °C, 12 h, then NaI, CH_3CN, Me_3SiCl, 50 °C, 12 h, then $NHex_3$, CH_3CN, 80 °C, 12 h, then $AgBF_4$, EtOH, RT, then $H_3PW_{12}O_{24}$, H_2O_2, H_2O, CH_3Cl. The locations of the counteranions are arbitrary.

(POM) catalysts **6** and **11** was complete, which was in contrast to that of the mono(POM) **7**, whereas the insoluble hexa-(POM) **17** worked heterogeneously. Characterization of **6** by AFM confirms its monomeric structure, and it can be stored under an inert atmosphere for months without change for efficient reuse as a catalyst. Finally, this synthetic and catalytic study shows the usefulness of the ionic-dendrimer approach for the design and efficient use of fully recyclable oxidation catalysts. The large dendritic POM catalysts may also prove interesting in the near future for continuous epoxidation by using a membrane reactor.[19]

Experimental Section

General procedure for the synthesis of dendritic POM complexes: The dendritic polyallyl, polyol, and polyiodo derivatives were synthesized according to procedures analogous to those described in references [14] and [16]. For the synthesis of the dendritic polyammonium polyiodide salts, a mixture of iodo compound and trihexylamine in CH_3CN was stirred for 12 h at 80 °C. After removal of the solvent under vacuum, the residue was washed with pentane and dissolved in about 2 mL of CH_3CN. Then, 30 mL pentane was added to precipitate the polyammonium polyiodide salt. The polyammonium BF_4^- salt was prepared by adding $AgBF_4$ to an ethanol solution of ammonium iodide salt. AgI precipitated immediately and was removed by filtration, the ethanol was removed by evaporation, and the residue was extracted with CH_2Cl_2. The solvent was then removed under vacuum, yielding the ammonium BF_4^- salt. The dendritic polyammonium POM salts were synthesized by adding H_2O_2 (35% in water) to a water solution of commercial heteropolyacid $H_3PW_{12}O_{40}$. The mixture was stirred at room temperature for 30 min. Then, a CH_2CH_2 solution of ammonium BF_4^- salt was added, and the mixture was stirred for an additional hour. The CH_2Cl_2 layer was dried over sodium sulphate and evaporated under vacuum, thus providing the desired dendritic POM complex as a white solid.

General procedure for catalytic reactions and catalyst recycling: The POM catalyst **6**, **7**, **8** or **11** (4.68 mmol) and cyclooctene (284 equiv per POM unit) were dissolved in 3 mL $CDCl_3$, then H_2O_2 (35% in water, 773 equiv per POM unit) was added. The mixture was stirred at room temperature, and the reaction was followed by ^{1}H NMR spectroscopy. After completion of the reaction, the $CDCl_3$ layer was concentrated under reduced pressure to about 1 mL, and 5 mL of pentane was added producing a white precipitate. The solid was filtered over celite then redissolved with CH_2Cl_2, and the solution was dried over sodium sulfate. The solvent was then removed under vacuum, yielding the POM complex as a white solid that was analyzed by ^{1}H and ^{31}P NMR spectroscopies, stored under nitrogen, and reused for a subsequent catalytic experiment.

Supporting Information available: Complete synthetic procedures and standard characterizations for all the dendrimers.

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