Synthesis and Catalytic Properties of Manganese Porphyrins Incorporated into Phosphonate Networks

David Deniaud,[†] Bernd Schöllorn,[§] Daniel Mansuy,[§] Jean Rouxel,[‡]
Pierrette Battioni,[§] and Bruno Bujoli*,[†]

*Laboratoire de Synthèse Organique, URA CNRS 475, 2 Rue de la Houssinière,
44072 Nantes Cedex 03, France, Institut des Matériaux de Nantes, UM CNRS 0110,
2 Rue de la Houssinière, 44072 Nantes Cedex 03, France, and Laboratoire de Chimie et
Biochimie Pharmacologiques et Toxicologiques, URA CNRS 400, Université René Descartes,
45 Rue des Saints-Pères, 75270 Paris Cedex 06, France*

Received January 3, 1995. Revised Manuscript Received March 1, 1995[⊗]

Two manganese porphyrins, tetrafunctionalized by phosphonic acid ends [R(*meso*) = C_6H_4-PO_3H_2 (**4b**), $C_6F_4NHC_3H_6PO_3H_2$ (**4d**)] have been prepared. These compounds reacted with Zn(II) salts in water or methanol to give insoluble zinc phosphonates, in which the corresponding porphyrin was part of the matrix. These hybrid materials behave as supported oxidation catalysts, in the epoxidation of cyclooctene with PhIO. Very similar catalytic yields were observed between the hybrid solid and its phosphonic acid precursor.

Introduction

In 1978, Alberti et al. reported the synthesis of a new class of hybrid organic–inorganic layered materials, based on the reaction of phosphonic acids RPO_3H_2 with zirconium precursors in aqueous medium, yielding compounds having the general formula $Zr(RPO_3)_2$ (eq 1).[1]

$$ZrOCl_2 + 2RPO_3H_2 \rightarrow Zr(RPO_3)_2 + H_2O + 2HCl \quad [R = CH_2OH, C_6H_5] \quad (1)$$

Then, Dines and co-workers prepared in the early 1980s a wide range of tetravalent metal phosphonates analogues by this method: $M^{IV}(RPO_3)_2$ [M^{IV} = Zr, Ti, Th, Ce, U].[2] The structure of these lamellar compounds is very close to that of α-zirconium hydrogen phosphate $Zr(HOPO_3)_2 \cdot H_2O$ (α-ZrP) and consists of slabs made of coplanar metal atoms linked together by phosphonate groups.[3] The organic radicals R are lying above and below the inorganic sheets, with an orientation roughly perpendicular to these layers. More recently, the use of phosphonic acids for the synthesis of metal phosphonates has been extended, leading to new structural models with vanadium(IV),[4,5] and divalent (Mg, Mn, Zn, Ca, Cd, Cu, Fe, Ni, Co)[6–8] and trivalent (La, Sm, Ce, Fe, Bi)[9,10] metals. All these materials are generally layered with various linkages within the inorganic network dependent upon the nature and the oxidation state of the metallic center.

Since 1988, we have intensively studied the chemistry of divalent (Fe, Cu, Mn, Ni, Co, Zn) metal phosphonates and reported the original magnetic behavior of some of these layered compounds.[11] At the same time, it seemed to us very attractive to use the reactivity of phosphonic acids to incorporate manganese porphyrins into phosphonate networks, in order to prepare supported homogeneous catalysts. In fact, simple Mn(porphyrin)Cl complexes were found to be active homogeneous catalysts for many oxidation reactions with H_2O_2 as oxidizing agent in the presence of nitrogen base cocatalysts.[12] By immobilization of these metallic complexes on a solid insoluble support, one could expect to combine the advantages of homogeneous and heterogeneous catalysts. The main goal is to maintain the favorable properties of the homogeneous catalyst while making it insoluble and thus easier to separate from the

---

[†] Laboratoire de Synthèse Organique.
[‡] Institut des Matériaux de Nantes.
[§] Université René Descartes.
[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1995.

(1) Alberti, G.; Costantino, U.; Alluli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.

(2) Dines, M. B.; DiGiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92. Dines, M. B.; Griffith, P. C. *Polyhedron* **1983**, *2*, 607. Dines, M. B.: Griffith, P. C. *Inorg. Chem.* **1983**, *22*, 567. Dines, M. B.; Cooksey, R. E.; Griffith, P. C.; Lane, R. H. *Inorg. Chem.* **1983**, *22*, 1004.

(3) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311. Poojary, M. D.; Hu, H. L.; Campbell, F. L.; Clearfield, A. *Acta. Crystallogr.* **1993**, *B49*, 996.

(4) Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3842. Huan, G.; Jacobson, A. J.; Johnson, J. W.; Corcoran, E. W. *Chem. Mater.* **1990**, *2*, 91. Huan, G.; Johnson, J. W.; Jacobson, A. J.; Merola, J. S. *J. Solid State. Chem.* **1990**, *89*, 220. Huan, G.; Jacobson, A. J.; Johnson, J. W.; Goshorn, D. P. *Chem. Mater.* **1992**, *4*, 661.

(5) Chen, Q.; Zubieta, J. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 261. Chen, Q.; Salta S.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 4485. Khan, M. I.; Lee, Y. S.; O' Connor, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1994**, *6*, 721 and references therein.

(6) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781. Cao, G.; Lynch, V. M.; Mallouk, T. E. *Solid State Ionics* **1988**, *26*, 63. Cao, G.; Lynch, V. M.; Yacullo, L. N. *Chem. Mater.* **1993**, *5*, 1000.

(7) Martin, K. J.; Squattrito, P. J.; Clearfield, A. *Inorg. Chim. Acta* **1989**, *155*, 7. Zhang, Y.; Clearfield, A. *Inorg. Chem.* **1992**, *31*, 2821. Bhardwaj, C.; Hu, H.; Clearfield, A. *Inorg. Chem.* **1993**, *32*, 4294.

(8) Bujoli, B.; Pena, O.; Palvadeau, P.; Le Bideau, J.; Payen, C.; Rouxel, J. *Chem. Mater.* **1993**, *5*, 583. Le Bideau, J.; Bujoli, B.; Jouanneaux, A.; Payen, C.; Palvadeau, P.; Rouxel, J. *Inorg. Chem.* **1993**, *32*, 4617. Le Bideau, J.; Payen, C.; Palvadeau, P.; Bujoli, B. *Inorg. Chem.* **1994**, *33*, 4885. Le Bideau, J.; Payen, C.; Jouanneaux, A.; Bujoli, B. *J. Mater. Chem.* **1994**, *4*, 1319. Drumel, S.; Janvier, P.; Barboux, P.; Bujoli-Doeuff, M.; Bujoli, B. *Inorg. Chem.* **1995**, *34*, 148. Drumel, S.; Bujoli-Doeuff, M.; Janvier, P.; Bujoli, B. *New J. Chem.*, in press.

(9) Palvadeau, P.; Queignec, M.; Venien, J. P.; Bujoli, B.; Villieras, J. *Mater. Res. Bull.* **1988**, *23*, 1561. Bujoli, B.; Palvadeau, P.; Rouxel, J. *Chem. Mater.* **1990**, *2*, 582. Janvier, P.; Drumel, S.; Piffard, Y.; Bujoli, B. *C. R. Acad. Sci. Paris, Ser. II* **1995**, *320*, 29.

(10) Cao, G.; Lynch, V. M.; Swinnea, J. S.; Mallouk, T. E. *Inorg. Chem.* **1990**, *29*, 2112. Wang, Y.; Zhang, Y.; Hu, H.; Frausto, R. R.; Clearfield, A. *Chem. Mater.* **1992**, *4*, 864.

(11) Le Bideau, J. Ph.D. Thesis, Nantes, 1994.

(12) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462 and references therein.

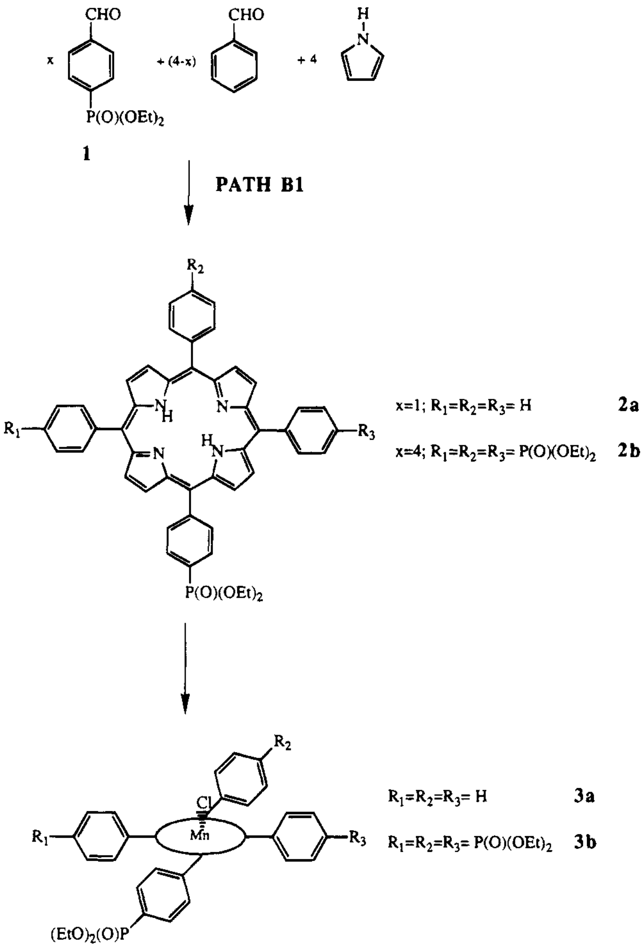
0897-4756/95/2807-0995$09.00/0

products, with also possible reactivity enhancement due to the participation of the inorganic part. For this purpose, many studies have previously reported the adsorption or intercalation of metalloporphyrins on various solids (montmorillonite, fluorohectorite, alumina, silica, LDH, α-ZrP, polymers, zeolites, etc.).[13] However, the covalent binding of porphyrins on solid supports has not received much attention until now. The anchoring of a complex on inorganic networks can be achieved by two different approaches: (path A) using derivatized solids (silica, montmorillonite, polystyrene) with surface organic binding groups able to provide stable links with the active catalytic center,[14,15] (path B) functionalization of the porphyrin complex with polymerizable moieties that will later allow the assembly of the final material.[16] Taking into account our experience in the field of the chemistry of divalent and trivalent metal phosphonates, we have decided to investigate the possibility of preparing manganese porphyrins supported on phosphonate host structures, according to path B. This paper describes the synthesis of some porphyrinic precursors followed by our first immobilization experiments, along with the catalytic properties of the resulting hybrid compounds.

Results and Discussion

Preparation of the Supported Porphyrins. The first step of this project was to prepare manganese porphyrins bearing phosphonate ester groups $P(O)(OR)_2$ that would be finally converted to phosphonic acid functions prior to the polymerization reaction. Two different strategies were developed, depending on whether the desired $P(O)(OR)_2$ groups were brought before the synthesis of the porphyrin (path B1) or after (path B2). The synthesis of porphyrins **2a** and **2b** (14 and 30% yield resp.) according to path B1 (Scheme 1) was performed in the conditions of Adler et al.[17] and required the use of the functionalized benzaldehyde **1**: 4-bromobenzaldehyde was acetalized with ethylene glycol and then reacted with diethylphosphite[18] in the presence of a catalytic amount of $Pd^0(P(C_6H_5)_3)_4$ and, after removal of the acetal in H_2SO_4/THF, **1** was obtained with an overall yield of 65% based on 4-bromobenzaldehyde. The introduction of the phosphonate group was also possible by lithiation and treatment with diethyl chlorophosphate as proposed by Ungashe et al.,[16] but the yield of this reaction did not exceed 50%. **2a** and **2b** were then metalated using manganese(II) acetate in refluxing DMF[19] to give **3a** and **3b** (60% yield).

Scheme 1



Porphyrin **3d** was obtained, according to path B2 (Scheme 2), by nucleophilic substitution[20] of the fluorine atoms in para position of the pentafluorophenyl groups of $Mn(TF_5PP)Cl$, **3c**,[19,21] with diethyl 3-aminopropyl phosphonate **5** (78% yield). **5** was easily prepared by an original method: reduction of diethyl 2-cyanoethyl phosphonate (using $NaBH_4/CoCl_2{\cdot}6H_2O$[22] (70% yield)), obtained by condensation of the sodium salt of diethyl phosphite with acrylonitrile[23] (65% yield). The phosphonate ester groups of **3a**, **3b**, and **3d** were converted into their acidic PO_3H_2 form, using bromotrimethylsilane with subsequent hydrolysis, to give **4a**, **4b**, and **4d** in quantitative yield. These compounds were then treated according to one of the two following procedures:

(1) The desired metalloporphyrin was refluxed with 100 equiv of zinc chloride in water for 5 days.

---

(13) Cady, S. S.; Pinnavaia, T. J. *Inorg. Chem.* **1978**, *17*, 1505. Kameyama, H.; Suzuki, H.; Amano, A. *Chem. Lett.* **1988**, 1117. Battioni, P.; Lallier, J. P.; Barloy, L.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1149. Carrado, K. A.; Winans, R. E. *Chem. Mater.* **1990**, *2*, 328. Giannelis, E. P. *Chem. Mater.* **1990**, *2*, 627. Barloy, L.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1990**, 1365. Traylor, T. G.; Byun, Y. S.; Traylor, P. S.; Battioni, P.; Mansuy, D. *J. Am. Chem. Soc.* **1991**, *113*, 7821. Barloy, L.; Lallier, J. P.; Battioni, P.; Mansuy, D.; Piffard, Y.; Tournoux, M.; Valim, J. B.; Jones, W. *New J. Chem.* **1992**, *16*, 71. Kim, R. M.; Pillion, J. E.; Burwell, D. A., Groves J. T., Thompson, M. E. *Inorg. Chem.* **1993**, *32*, 4509. Pattou, D.; Labat, G.; Defrance, S.; Séris, J. L.; Meunier, B. *Bull. Soc. Chim. Fr.* **1994**, *131*, 78. Gaillon, L.; Bedioui, F.; Devynck, J. *J. Mater. Chem.* **1994**, *4*, 1215 and references therein.

(14) Battioni, P.; Bartoli, J. F.; Mansuy, D.; Byun, Y. S.; Traylor, T. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1051.

(15) Li, D. Q.; Buscher, T.; Swanson, B. I. *Chem. Mater.* **1994**, *6*, 803. Salhi, S.; Vernières, M. C.; Bied-Charenton, C.; Faure, J.; Revillon, A. *New J. Chem.* **1994**, *18*, 783.

(16) Ungashe, S. B.; Wilson, W. L.; Katz, H. E., Scheller, G. R., Putvinski, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 8717.

(17) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(18) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Synthesis* **1981**, 56.

(19) Kobayashi, H.; Higuchi, T.; Kaizu, Y.; Osada, H.; Aoki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 4969. Jones, R. D.; Summerville, D. A.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 4416.

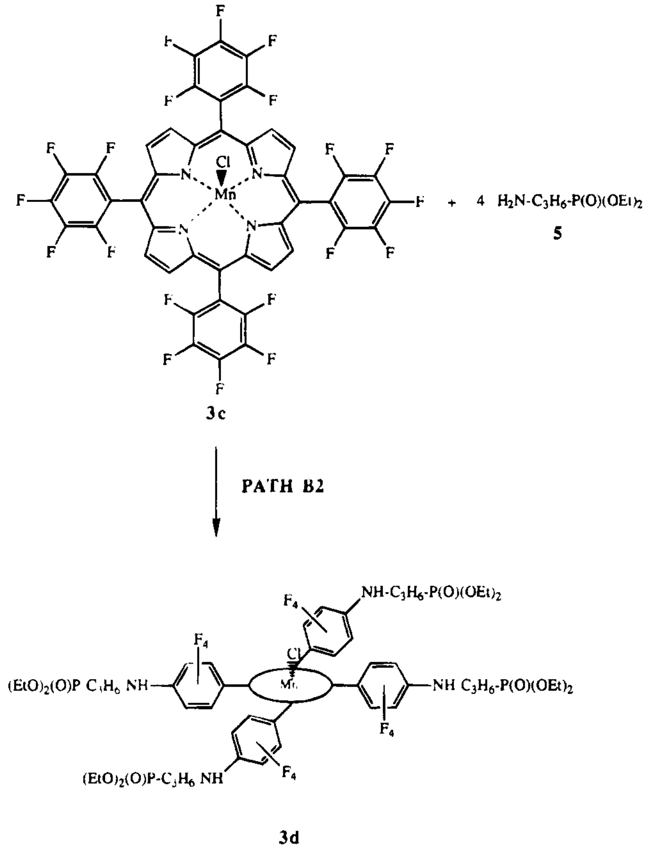
(20) Battioni, P.; Brigaud, O.; Desvaux, H.; Mansuy, D.; Traylor, T. G. *Tetrahedron Lett.* **1991**, *32*, 2893.

(21) La, T.; Richards, R.; Miskelly, G. M. *Inorg. Chem.* **1994**, *33*, 3159.

(22) Satoh, T.; Suzuki, S.; Suzuki, Y.; Miyaji, Y.; Imai, Z. *Tetrahedron Lett.* **1969**, *52*, 4555.

(23) Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis*; Academic Press: London, 1979.

Scheme 2

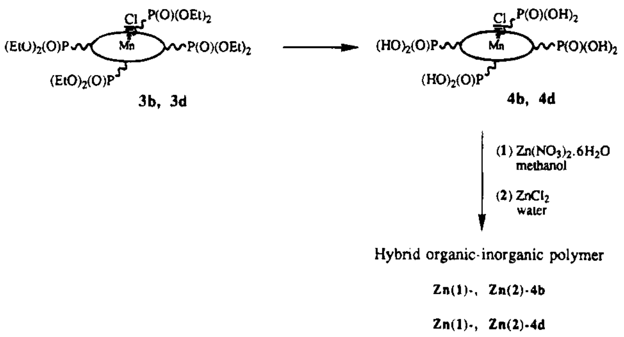


(2) The desired metalloporphyrin was refluxed with 100 equiv of zinc nitrate hexahydrate in methanol for 5 days.

In the case of the monofunctionalized metalloporphyrin **4a**, no precipitate formation was detected. Taking the literature into account, as compound **4a** bears only one phosphonic acid group, one would expect to get a two-dimensional solid. However, the bulkiness of the macrocycle probably does not allow such an arrangement, thus explaining that no organized structure was observed. Instead, a soluble complex is likely present in the solution.

For the tetrafunctionalized metalloporphyrins **4b** and **4d**, a reaction was observed both in water and methanol, to give insoluble zinc phosphonates (called respectively **Zn(1)-4b**, **Zn(2)-4b**, **Zn(1)-4d**, and **Zn(2)-4d** as a function of the nature of the starting metalloporphyrin and of the polymerization procedure used), in which the porphyrinic center was encapsulated (Scheme 3).[24]

Scheme 3



Characterization of the Supported Metalloporphyrins. The four solids (**Zn(1)-4b**, **Zn(2)-4b**, **Zn(1)-4d**, **Zn(2)-4d**) were characterized using various techniques, and the collected data are summarized in Table 1. From chemical analyses, we can see that the four compounds exhibit very similar formulations, with a zinc to porphyrin ratio of 3:1. However, the water content depends on the nature of the precursor. This was confirmed by TGA data which showed that for the most part, the dehydration occurs between 25 and 100 °C, giving evidence of weakly bound water molecules. The manganese to phosphorus ratio remained unchanged after immobilization of the macrocycle on the phosphonate network, suggesting that this metal was still present in the porphyrinic cage. This was also supported:

(i) By UV–visible data showing nearly identical absorptions (particularly for the Soret band) for the hybrid material and its phosphonic acid precursor. We have also checked that the main characteristic infrared bands of porphyrins **4b** and **4d** were present, at the same frequencies, in the corresponding zinc phosphonates. Logically, only modifications in the PO_3 region are observed.

(ii) By ^{31}P MAS NMR experiments giving well-defined signals for the phosphorus atoms. As manganese(III) is a paramagnetic nucleus, this observation means that the Mn atoms are not connected to the PO_3 units. No ^{31}P MAS NMR signal was detected for the manganese analogue of **Zn(2)-4d** (porphyrin **4d** reacted with manganese acetate instead of zinc nitrate). All the recorded ^{31}P MAS NMR spectra (Figure 1) exhibit a single signal, and it is reasonable to assume that only one environment is present for the phosphorus atoms and that the PO_3 groups are only connected to zinc atoms that are diamagnetic. Of course, we cannot exclude the possible migration of a portion of the manganese atoms toward the PO_3 groups, but this phenomenon can be considered as very limited.

(iii) By the catalytic activity observed for the four compounds (Table 2).[24]

As the four compounds were amorphous, no structural information could be obtained from X-ray diffraction studies. However, porphyrins **4b** and **4d** are tetrafunctionalized with PO_3H_2 moieties, and therefore the corresponding hybrid materials are likely three-dimensional.

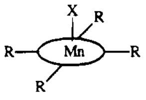
Finally, a dramatic difference was observed between **Zn(1)-**, **Zn(2)-4b** on one hand, and **Zn(1)-**, **Zn(2)-4d** on the other hand, with high surface areas (around 300 m^2 g^{-1}) for the former samples, and very low values (around 5 m^2 g^{-1}) for the latter. The main difference between precursors **4b** and **4d** is the nature of the linker between the porphyrin ring and the phosphonic acid moieties, with consequences on the porphyrin–PO_3H_2 distances, and on the rigidity of the precursor. A rigid configuration is present in the case of **4b** (phenyl spacer) and the resulting **Zn(1)-** and **Zn(2)-4b** hybrids seem to have a relatively open structure (average pore diameter of 17 Å). In **4d** (tetrafluorophenyl–NH–CH_2–CH_2–CH_2 spacer), a flexible character is given by the NH–C_3H_6 chain, and the surface area of the corresponding im-

---

[24] We have also checked that the nonmetalated form of porphyrins **4b** and **4d** reacted similarly with zinc salts, according to protocols (1) and (2). The resulting solids were used in the catalytic experiments as references, in order to confirm that the porphyrinic zinc phosphonates were inactive, unless manganese was present in the macrocycle (see Table 2).

Table 1. Experimental Data for the Supported Metalloporphyrins

	Zn(1)-4b	Zn(2)-4b	Zn(1)-4d	Zn(2)-4d
chemical analyses[a]	$H_2Zn_3(POR)\cdot 14H_2O$ $R = C_6H_5PO_3$ $X = Cl^-$	$H_2Zn_3(POR)\cdot 14H_2O$ $R = C_6H_5PO_3$ $X = NO_3^-$	$H_2Zn_3(POR)\cdot 8\ H_2O$ $R = C_6F_4NHC_3H_6PO_3$ $X = Cl^-$	$H_2Zn_3(POR)\cdot 8H_2O$ $R = C_6F_4NHC_3H_6PO_3$ $X = NO_3^-$
TGA % water loss	17.1 (17.2)[b]	16.3 (16.9)[b]	7.6 (7.7)[b]	7.8 (7.6)[b]
N_2 BET surface area ($m^2\ g^{-1}$)	300 APD:[c] 17 Å	260 APD:[c] 17 Å	6	3
^{31}P MAS NMR σ_{iso} (ppm)	16.2	17.5	28.3	28.9
UV−vis (nm)	465 (Soret) 522, 574, 612	468 (Soret) 522, 573, 610	458 (Soret) 505, 561, 600, 676	460 (Soret) 505, 561, 600, 677
	[466 (Soret), 518, 568, 606][d]		[462 (Soret), 557, 679][d]	

[a] POR = 

; [b] calculated value ; [c] APD = average pore diameter; [d] values for the corresponding molecular precursor **4b** or **4d**.

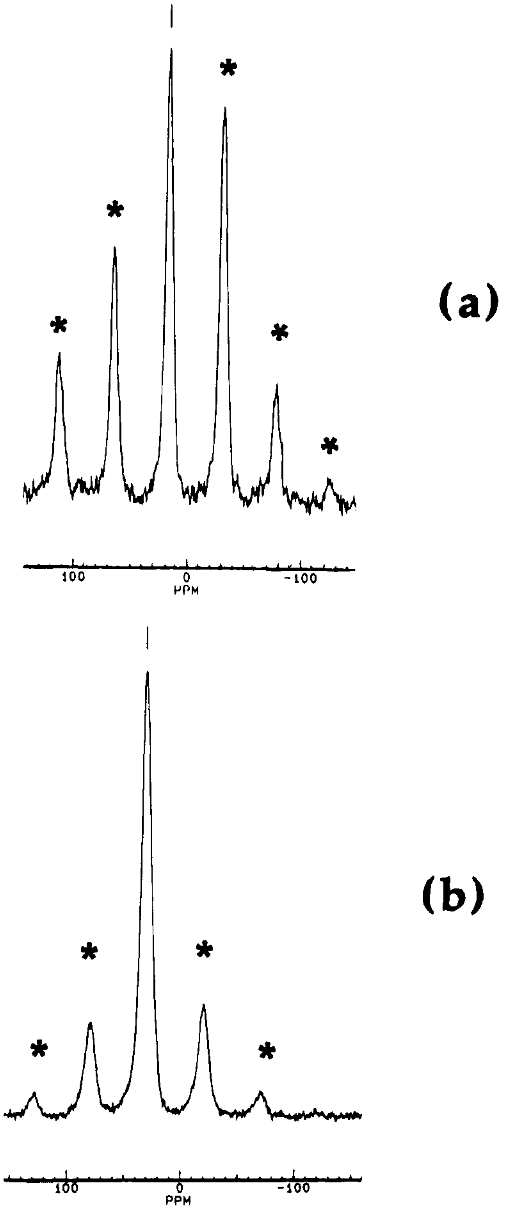


Figure 1. ^{31}P MAS NMR spectra of (a) **Zn(2)-4b** and (b) **Zn-(2)-4d**. The asterisks denote rotation bands.

Table 2. Catalytic Activity of the Supported Metalloporphyrins in the Epoxidation of Cyclooctene by PhIO[a]

catalyst	epoxide yield after 2 h (%)	epoxide yield after 24 h (%)
Zn(1)-4b	61	68
Zn(2)-4b	65	70
3b	71	96
blank1[b]	6 after 4 h	
Zn(1)-4d	58	91
Zn(2)-4d	64	86
3d	95	98
blank2[c]	11 after 4 h	

[a] Addition of PhIO (20 equiv relative to catalyst) to a cyclooctene/catalyst mixture (800:1) in CH_2Cl_2/CH_3CN (1:2); catalyst concentration 10^{-3} mol l^{-1}. [b] Free-base form of **4b** reacted with zinc nitrate, according to protocol (**2**). [c] Free-base form of **4d** reacted with zinc nitrate, according to protocol (**2**).

mobilized porphyrins, **Zn(1)-** and **Zn(2)-4d**, is very low (packing or aggregation of the porphyrin units? folding of the NH-C_3H_6 chains?). Complementary experiments are under way to study the influence of the rigidity and length of the spacer on the surface area and porosity of the resulting supported porphyrins, looking for an easier accessibility to the catalytic sites present in the internal volume of the solid for better catalytic performances.

Catalytic Tests. All the supported porphyrins were tested for their ability to catalyze the epoxidation of cyclooctene by PhIO. The results obtained are presented in Table 2 and lead to the following observations:

(i) As previously observed between Mn(TPP)Cl and Mn(TF$_5$PP)Cl, the epoxidation yield is higher for **3d**, compared to **3b**.

(ii) The catalytic activity of the two series of hybrid compounds is demonstrated, showing the interest of this strategy of immobilization.

(iii) For a given series, the catalytic performances do not seem to be influenced by the protocol (1 or 2) used for the preparation of the catalysts, that are probably nearly identical. This is confirmed by the data of Table 1 (similar chemical formulas, ^{31}P MAS NMR isotropic chemical shifts, surface areas, UV−vis spectra, etc.).

(iv) Finally, a very interesting information is given by the comparison of the catalytic properties of the hybrid materials with those of the corresponding precursors (in homogeneous medium). Porphyrin **3b** and **Zn(1)-** or **Zn(2)-4b** (high surface area; the main part of the catalytic sites are accessible) exhibit roughly similar reactivities. On the other hand, due to the low surface area of **Zn(1)-** and **Zn(2)-4d** (only one part of the catalytic sites are accessible), the epoxidation reaction proceeds more slowly for the supported compounds, than for **3d**. However, after 24 h, a yield close to the one observed for **3d** is finally obtained. The preparation of diethyl 4-formyl-2,3,5,6-tetrafluorophenylphosphonate and of the corresponding supported metalloporphyrin should be very instructive.

Conclusion

From the results mentioned above, the tetrafunctionalization of manganese porphyrins by phosphonic acid groups appears to be an efficient strategy for the immobilization of these macrocycles as insoluble solids, leading to a new class of hybrid organic–inorganic materials. Furthermore, their use as supported oxidation catalysts appears to be very promising: very similar yields are observed for the molecular porphyrinic precursors (homogeneous medium) and the corresponding zinc phosphonates (supported catalysis). However, the kinetics of the reaction is strongly affected by the decrease of the surface area and porosity of the supported metalloporphyrins, and a correlation seems to exist between these two parameters and the structure of the organic precursor (length and rigidity of the linker between the para position of the *meso* phenyl ring and the phosphonic acid group). Therefore, for the improvement of such systems, developments are actually in progress, trying to functionalize efficient porphyrins (i.e., Mn(TDCPP)Cl–imidazole system, etc.)[12,25] with phosphonic acid groups bound to the macrocycle via long and rigid spacers.

Finally, an accurate knowledge of the environment around the catalytic site would be helpful, and K-edge zinc and manganese EXAFS measurements will be performed to confirm the location of the Zn and Mn atoms and to get structural information about these solids.

Experimental Section

General Methods. The chemical analyses were performed by the C.N.R.S. Analysis Laboratory (Vernaison). ^1H, ^{19}F, and ^{31}P NMR spectra were recorded in $CDCl_3$ on an AC 200 Bruker spectrometer. Chemical shifts were referenced to TMS for ^1H, C_6F_6 for ^{19}F and 85 wt % H_3PO_4 for ^{31}P. ^{31}P solid-state MAS NMR spectra were recorded at room temperature on an MSL-400 NMR Bruker spectrometer at the frequency of 161.98 MHz. Samples were spun in an Andrew type rotor at a speed of ca. 8 kHz. Chemical shifts were externally referenced to 85 wt % H_3PO_4. FTIR spectra were obtained on a Nicolet 20SX FT-IR spectrometer with the usual KBr pellet technique. A Perkin-Elmer TGS2 thermogravimetric analyzer was used to obtain TGA thermograms, that were run in an air atmosphere from room temperature to 200 °C at a scan rate of 2 °C/min. The surface areas and average pore diameter were determined by analyzing the N_2 adsorption/desorption isotherms according to the BET method, using an Ankersmit Quantasorb Junior apparatus. UV–visible spectra were recorded in solution on a Secomam S1000 spectrophotometer and in the solid state (diffuse reflectance) on a Pye Unicam SP8-100 spectrophotometer. Energy-dispersive X-ray spectroscopy (EDAX) measurements were carried out using a Jeol JM-35C SEM with a Tracor TN5500 micro Z attachment. Standard mass spectra were recorded on a Hewlett-Packard HP5989 quadrupole mass spectrometer. CI mass spectra were recorded on a Ribermag R1010 mass spectrometer.

Bromo-4-(1,3-dioxolan-2-yl)benzene. The acetalization of 4-bromobenzaldehyde was performed according to a previously described procedure.[26] After distillation under vacuum (bp 90 °C, 0.5 mmHg), the product was obtained as a colorless liquid in 90% yield; ^1H NMR δ (ppm) 4.0 (4 H, s, CH_2), 5.75 (1 H, s, CH), 7.4 (4 H, m, C_6H_4).

Diethyl 4-(1,3-dioxolan-2-yl)phenylphosphonate. To a stirred mixture of toluene (30 mL), diethyl phosphite (12.2 mL, 95 mmol), triethylamine (13.2 mL, 95 mmol), and bromo-4-(1,3-dioxolan-2-yl)benzene (19.8 g, 86.5 mmol), a catalytic amount of tetrakis(triphenylphosphine)palladium(0) (5 g, 4.3 mmol) was added under a nitrogen atmosphere, and the resulting mixture was stirred at 90 °C for 24 h. After cooling, the reaction medium was filtered on Celite and the filtrate was evaporated under reduced pressure. After distillation of the residue under vacuum (bp 155 °C, 0.5 mmHg), the compound was isolated as a colorless liquid in 85% yield; ^1H NMR δ (ppm) 1.25 (6 H, t, Et), 4.1 (8 H, m, CH_2 and Et), 5.85 (1 H, s, CH), 7.7 (4 H, m, C_6H_4); MS *m/e* 286 (18), 285 (100).

Diethyl 4-Formylphenylphosphonate (1). A mixture of 25 mL of 1 N sulfuric acid, 25 mL of THF, and 7.15 g (25 mmol) of diethyl 4-(1,3-dioxolan-2-yl)phenylphosphonate was stirred at ambient temperature for 8 h. At the end of the period, CH_2Cl_2 (200 mL) was added and the organic layer was washed with saturated NH_4Cl solution, dried over $MgSO_4$, and evaporated. After distillation under vacuum (bp 135 °C, 0.5 mmHg), **1** was obtained as a colorless liquid in 85% yield; ^1H NMR δ (ppm) 1.35 (6 H, t, Et), 4.15 (4 H, d of q, Et), 7.7 and 8.4 (4 H, m, C_6H_4), 10.1 (1 H, s, CHO); MS *m/e* 242 (18), 169 (100).

P3p-P(O)(OEt)$_2$PPH$_2$ (2a). A solution of 2 g (8.3 mmol) of aldehyde **1**, 2.55 mL of benzaldehyde (24.9 mmol), and 2.3 mL (33.15 mmol) of pyrrole in 30 mL of propionic acid was refluxed in a flask protected from light, at 150 °C for 2 h. The mixture was evaporated to dryness, and after flash chromatography of the residue on a neutral alumina column (eluent: 25% ethyl acetate in dichloromethane), the resulting dark oil was crystallized in acetonitrile/ethyl acetate (4:1) to give **2a** in 14% yield as violet crystals: mp 269 °C; ^1H NMR δ (ppm) 1.35 (6 H, t, Et), 1.7 (2 H, s, NH), 4.4 (4 H, d of q, Et), 7.8 (9 H, m, 3,4,5H–C_6H_5), 8.4 (10 H, m, 2,3,5,6H–C_6H_4, and 2,6H–C_6H_5), 8.9 (8 H, s, CH–py); CI(C_2H_4) MS *m/e* 750 M$^+$; UV–vis (CH_2Cl_2) λ_{max} (ϵ) 417 nm (Soret, 4.3×10^5), 514 (1.8×10^4), 549 (7.8×10^3), 590 (5.5×10^3), 646 (4.7×10^3). Anal. Calcd for $C_{48}H_{39}N_4O_3P$: C, 76.78; H, 5.23; N, 7.46. Found: C, 76.28; H, 5.23; N, 7.49.

Tp-P(O)(OEt)$_2$PPH$_2$ (2b). A solution of 2 g (8.3 mmol) of aldehyde **1** and 0.55 mL (8 mmol) of pyrrole in 30 mL of propionic acid was refluxed in a flask protected from light, at 150 °C for 1.5 h. The mixture was evaporated to dryness, and after flash chromatography of the residue on a neutral alumina column (eluent: 1.5% methanol in dichloromethane), the resulting dark oil was crystallized in acetonitrile to give **2b** in 30% yield as violet crystals: mp 271 °C; ^1H NMR δ (ppm) 1.5 (24 H, t, Et), 2.25 (2 H, s, NH), 4.4 (16 H, d of q, Et), 8.3 (16 H, m, C_6H_4), 8.8 (8 H, s, CH–py); ^{31}P NMR δ (ppm) 17.9; CI-(NH_3) MS *m/e* 1159 $(M + 1)^+$; UV–vis (CH_2Cl_2) λ_{max} (ϵ) 418 nm (Soret, 4.9×10^5), 514 (2.0×10^4), 548 (8.6×10^3), 589 (6.3×10^3), 645 (4.0×10^3). Anal. Calcd for $C_{60}H_{66}N_4O_{12}P_4$: C, 62.17; H, 5.74; N, 4.83. Found: C, 61.66; H, 5.76; N, 4.81.

Mn(P3p-P(O)(OEt)$_2$PP)Cl (3a) and Mn(Tp-P(O)(OEt)$_2$-PP)Cl (3b). A solution of 0.5 mmol of porphyrin **2a** or **2b** and 1.22 g (5 mmol) of manganese(II) acetate tetrahydrate in 75 mL of DMF, was stirred and refluxed for 2 h. The mixture was filtered on celite and evaporated. The residue was purified on a neutral alumina column (eluent: 3% methanol in dichloromethane). The good fraction dissolved in dichloromethane was stirred over NaCl for 10 min, filtered, and evaporated to give **3a** or **3b** as a green solid in 70% yield. **3a** UV–vis (CH_2Cl_2) λ_{max} (ϵ) 375 nm (5.1×10^4), 400 (4.2×10^4), 477 (Soret, 1.0×10^5), 527 (5.6×10^3), 581 (9.1×10^3), 617 (1.0×10^4). Anal. Calcd for $C_{48}H_{37}N_4O_3PMnCl$: C, 68.70; H, 4.44; N, 6.68. Found: C, 68.48; H, 4.46; N, 6.59. **3b** UV–vis (CH_2Cl_2) λ_{max} (ϵ) 373 nm (5.3×10^4), 398 (4.7×10^4), 472 (Soret, 1.0×10^5), 523 (5.6×10^3), 576 (1.1×10^4), 612 (9.8×10^3); ^{31}P MAS NMR δ (ppm) 19.9. Anal. Calcd for $C_{60}H_{64}N_4O_{12}P_4MnCl$: C, 57.76; H, 5.17; N, 4.49. Found: C, 57.52; H, 5.07; N, 4.46. For the two compounds, the Mn/P and Mn/Cl ratios measured by EDAX were in good agreement with the expected values.

Mn(TF$_5$PP)Cl (3c). This compound was prepared from *meso*-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin, TF$_5$-PPH$_2$, as previously described.[19, 21]

---

(25) TDCPP = 5,10,15,20-tetrakis(2′-dichlorophenyl)porphyrin.

(26) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; John Wiley and Sons: New York, 1991.

Mn(TF$_4$p-NHC$_3$H$_6$P(O)(OEt)$_2$PP)Cl (3d). A solution of 0.42 g (0.4 mmol) of **3c** in 4 mL of dry THF with 5 drops of dry DMF was treated with 2.22 g (12 mmol) of aminophosphonate **5** and 0.52 mL (4 mmol) of triethylamine. The mixture was refluxed for 12 h. The THF was evaporated and the remaining crude product was taken up in dichloromethane and stirred with water for 1 h. The organic phase was washed 2 times with 0.5% hydrochloric acid and several times with water (until neutral pH). The product was purified by chromatography on a silica gel column (eluent: 40% ethanol in dichloromethane). To obtain the chloro complex, a solution of the product in dichloromethane was treated with HCl gas. After precipitation with cyclohexane, **3d** was obtained as a green solid in 78% yield. CI(NH$_3$) MS *m/e* 1733 $(M - C_2H_5)^+$; UV–vis (CH$_2$Cl$_2$) λ_{max} (ϵ) 360 nm (2.1×10^4), 458 (Soret, 5.1×10^4). 566 (7.8×10^3), 660 (2.0×10^3). Anal. Calcd for $C_{72}H_{76}ClF_{16}MnN_8O_{12}P_4$: C, 49.03; H, 4.34; N, 6.35. Found: C, 49.09; H, 4.03; N, 6.34. The Mn/P and Mn/Cl ratios measured by EDAX were in good agreement with the expected values. To confirm the substitution of the fluorine atom in the para position, the same experiment as above was performed, starting from the free base TF$_5$PPH$_2$, leading to the free base form of **3d,** TF$_4$*p*-NHC$_3$H$_6$P(O)(OEt)$_2$PPH$_2$. ^{1}H NMR δ (ppm) −2.9 (2 H, s, pyrrole NH), 1.4 (24 H, t, CH$_3$). 1.9−2.25 (16 H, m, CH$_2$CH$_2$P), 3.8 (8 H, m, NCH$_2$), 4.2 (16 H, d of q, OCH$_2$), 4.5 (4H, br s, NH), 8.9 (8 H, s. CH-py); ^{19}F NMR δ (ppm) 2.9 (8F, d), 23.5 (8F, d); ^{31}P NMR δ (ppm) 32.1; CI(NH$_3$) MS *m/e* 1675 M$^+$; UV−vis (CH$_2$Cl$_2$) λ_{max} (ϵ) 421 nm (Soret, 2.7×10^5), 512 (1.9×10^4), 546 (4.9×10^3), 587 (6.2×10^3), 645 (1.0×10^3). Anal. Calcd for $C_{72}H_{78}F_{16}N_8O_{12}P_4$: C, 51 62; H, 4.69; N, 6.69. Found: C, 51.61; H, 4.75; N, 6.69.

General Procedure for the Hydrolysis of the Phosphonate Ester Groups. Synthesis of Mn(P3p-P(O)(OH)$_2$PP)Cl (4a), Mn(Tp-P(O)(OH)$_2$PP)Cl (4b), and Mn(TF$_4$p-NHC$_3$H$_6$P(O)(OH)$_2$PP)OCH$_3$ (4d). A solution of 1 mmol of porphyrin in 16 mL of dry DMF was treated with 1.54 g (15 mmol) of NaBr, 2.8 mL (20 mmol) of triethylamine, and 2.6 mL (20 mmol) of chlorotrimethylsilane. The mixture was stirred under nitrogen for 24 h at 60 °C, then filtered, and evaporated. For **4a** and **4b**, the solid was suspended in 60 mL of water with 0.5 mL of concentrated HCl added and stirred for 3 h. After filtration, the solid was washed with water and ethyl acetate and dried at room temperature. Yield 95%. For **4d**, the residue was suspended in 60 mL of a mixture of acetic acid/THF/water (3/1/1) and stirred for 3 h at room temperature. After evaporation of the solvents, the solid was washed with acetone and dichloromethane, dissolved in methanol and purified on a Sephadex LH20 column, using methanol as eluent. Methanol was then evaporated to give the porphyrinic phosphonic acid in 95% yield. **4a** green solid; UV−vis (C$_2$H$_5$OH) λ_{max} 375 nm, 399, 471 (Soret), 519, 571, 608. **4b** green solid; UV−vis (C$_2$H$_5$OH) λ_{max} 380 nm, 400, 466 (Soret), 518, 568, 606. **4d** black solid; UV−vis (C$_2$H$_5$OH) λ_{max} (ϵ) 369 nm (2.8×10^4), 390 (2.2×10^4), 462 (Soret, 5.4×10^4), 557 (7.0×10^3), 679 (9.0×10^2); ^{31}P MAS NMR δ (ppm) 28.8. For the three compounds, the Mn/P and Mn/Cl ratios measured by EDAX were in good agreement with the expected values.

Diethyl 2-Cyanoethylphosphonate. In 100 mL of dry ethanol, 2.76 g (0.12 mol) of sodium was stirred under a nitrogen atmosphere. After complete dissolution of sodium, 15.5 mL (0.12 mol) of diethyl phosphite in 40 mL of toluene was added and the solution was stirred at room temperature for 1 h. Then, 7.9 mL (0.12 mol) of acrylonitrile in 40 mL of toluene was added dropwise over 45 min, and the reaction medium was allowed to stir overnight. Water was then added and the mixture was extracted with CH$_2$Cl$_2$. The organic layer was dried, evaporated and the resulting oil was distilled under vacuum (bp 108 °C, 0.5 mmHg) to yield a colorless liquid (65%); ^{1}H NMR δ (ppm) 1.3 (6 H, t, Et), 2.1 (2 H, m, CH$_2$P), 2.7 (2 H, m, CH$_2$CN), 4.15 (4 H, d of q, Et); MS *m/e* 191 (1), 136 (100).

Diethyl 3-Aminopropylphosphonate (5). A mixture of 15 g of the above nitrile (78.5 mmol) and 3.75 g of CoCl$_2$·6H$_2$O (15.8 mmol) was dissolved in 250 mL of dry methanol. The solution was stirred and kept at −20 °C while 29.7 g of sodium borohydride (785 mmol) was added in small portions. Evolution of hydrogen gas was observed, and then black precipitates appeared during the addition of sodium borohydride. When the addition was complete, the solution was allowed to warm slowly to room temperature and stirring was continued for 1 h at 20 °C. Concentrated hydrochloric acid was then poured into the reaction mixture till the black precipitate was dissolved, leading to a blue solution that was extracted with dichloromethane to remove the unreacted nitrile (1.2 g). The pH of the aqueous phase was then raised to 9 by addition of ammonium hydroxide, and the solution was evaporated to dryness. The resulting blue solid was dissolved in 150 mL of ammonium hydroxide, 300 mL of dichloromethane was added, and the mixture was stirred for 0.5 h, filtered on Celite and decanted. The organic layer was dried over magnesium sulfate and evaporated to yield pure **5** (70%) as a pale yellow liquid; ^{1}H NMR δ (ppm) 1.3 (6 H, t. Et), 1.6 (2 H, s. NH$_2$), 1.9 (4 H, m, CH$_2$CH$_2$P). 2.75 (2 H, t, CH$_2$NH$_2$). 4.1 (4 H, d of q, Et); MS *m/e* 195 (1), 125 (100).

General Procedure for the Preparation of the Supported Porphyrins. A mixture of 250 mg of porphyrin **4b** or **4d** and 100 equiv of ZnCl$_2$ (for compounds Zn(1)) or Zn(NO$_3$)$_2$·6 H$_2$O (for compounds Zn(2)) was stirred and refluxed in water (for compounds Zn(1)) or methanol (for compounds Zn(2)) for 5 days. The resulting zinc phosphonates were washed several times with water, then methanol and acetone, until the supernatant was colorless. After filtration, the solids were then dried at room temperature. Yield 95%. **Zn(1)-4b** green solid. Anal. Calcd for $C_{44}H_{54}N_4O_{26}P_4Zn_3MnCl$: C, 36.06; H, 3.71; N, 3.82; P, 8.45; Zn, 13.39; Mn, 3.75; Cl, 2.42. Found: C, 35.75; H, 3.59; N, 3.81; P, 8.17; Zn, 13.22; Mn, 3.40; Cl, 2.44. **Zn(2)-4b** green solid. Anal. Calcd for $C_{44}H_{54}N_5O_{29}P_4Zn_3Mn$: C, 35.42; H, 3.64; N, 4.69; P, 8.30; Zn, 13.15; Mn, 3.68. Found: C, 35.26: H, 3.55; N, 4.67; P, 8.21; Zn, 12.98; Mn, 3.31; IR (ν_a NO$_3$): 1384 cm^{-1}.[27] **Zn(1)-4d** black solid. Anal. Calcd for $C_{56}H_{54}N_8F_{16}O_{20}P_4Zn_3MnCl$: C, 35.90; H, 2.90; N, 5.98; P, 6.61; Zn, 10.47; Mn, 2.93; Cl, 1.89. Found: C, 35.57; H, 2.83; N, 6.00; P, 6.85; Zn, 10.30; Mn, 2.76; Cl, 2.12 **Zn(2)-4d** black solid. Anal. Calcd for $C_{56}H_{54}N_9F_{16}O_{23}P_4Zn_3Mn$ C, 35.40; H, 2.86; N, 6.63; P. 6.52; Zn, 10.32; Mn, 2.89. Found: C, 35.14; H, 2.77; N. 6.59; P, 6.39; Zn, 10.49; Mn, 2.81; IR (ν_a NO$_3$) 1384 cm^{-1}.[27] The TGA, UV−visible, ^{31}P MAS NMR data and N$_2$ BET surface areas for the four compounds are listed in Table 1.

All the starting materials were purchased from Aldrich and used as received. The catalytic experiments were performed as previously described.[14]

Acknowledgment. We acknowledge with grateful thanks Philippe Barboux (URA CNRS 1466) for the MAS NMR measurements.

CM950002W

---

(27) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy,* 2nd ed., Academic Press: New York, 1975; p 330.