(Mn1-O48) and Mn1-O27 are the two axially elongated bonds (2.236 (19) and 2.222 (21) Å, respectively). The Mn1-O48 distance (2.236 (19) Å) is similar to the lengths of other JT-elongated Mn-O bonds in **2** (2.126 (20)-2.237 (23) Å). A comparison of the core structures of **1** and **2** is provided in Figure 2. The top half shows the Mn_4O_2 "butterfly" structure in **1** and the disposition of its pic$^-$ ligands. The bottom half shows the $Mn_8O_4(pic)_4$ portion of **2**. Note that, in **1**, both of the μ_3-O atoms are trans to picolinate oxygens while, in **2**, some μ_3-O atoms are also trans to picolinate nitrogen atoms. This can be rationalized as a consequence of the need to accommodate the new interfragment Mn-O bonds. Also, the Mn_4 units in **2** are no longer in a "butterfly" arrangement. Apart from these small structural changes, we emphasize that the $[Mn_4O_2(OAc)_6(pic)_2]$ fragments of **2** are essentially identical with that in **1** vis-à-vis their formulation, gross structural arrangement, and metal oxidation level (all Mn^{III}). This is to be contrasted with the reductive dimerization of $Mn_3O(O_2CPh)_6(py)_2(H_2O)$ (Mn^{II}, $2Mn^{III}$) to $Mn_6O_2(O_2CPh)_{10}(py)_2(MeCN)_2$ ($4Mn^{II}$, $2Mn^{III}$) where the average Mn oxidation level decreases and the two $[Mn_3(\mu_3\text{-}O)]$ cores fuse to a $[Mn_6(\mu_4\text{-}O)_2]$ core.[3a] This is better described as a "cluster condensation" reaction[15] with the $[Mn_3O]$ cores no longer retaining their original identity. This is distinctly different from the conversion of **1** to **2** where no fusion of the two $[Mn_4O_2]$ cores has occurred and which we prefer to call a "building-block" aggregation.

The conversion of **1** to **2** (eq 1) can be rationalized as follows: removal of the carboxylate group bridging central Mn atoms Mn1 and Mn2 yields two five-coordinate centers, one of which is converted back to six-coordination via the new interfragment linkages (Mn1-O48 and its symmetry-related partner) (Figure 2) whereas Mn2 and Mn2′ remain five-coordinate. Note that

$$2Mn_4O_2(OAc)_7(pic)_2^- + 2Me_3SiCl \rightarrow [Mn_4O_2(OAc)_6(pic)_2]_2 + 2Me_3SiOAc + 2Cl^- \quad (1)$$

complex **2** still possesses two pic O atoms not bound to Mn (O39). In principle, carboxylate removal from **2** might yield further aggregation via conversion of O39 to a bridging mode (currently under investigation).

We recognize that formation of **2** from **1** relies on the picolinate and its flexibility in converting from η^2 to $\eta^2{:}\eta^1{:}\mu_2$. Since other $Mn/O/RCO_2^-$ complexes do not possess pic$^-$ ligands, similar transformations are ruled out. Nevertheless, the aggregation of fragments generated from carboxylate abstraction has the potential for general application either with deliberately added bridging ligands or with bound RCO_2^- groups themselves converting from μ_2 to μ_3 or μ_4 modes for interfragment linking.[16] With the feasibility of linking Mn_4O_2 units established, we are investigating application of this approach to the linking of ferromagnetically coupled species such as $Mn_4O_3Cl_4(OAc)_3(py)_3$[17] ($S = {}^9/_2$) and $Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4$ ($S = 14$) and determining the magnetic properties of higher nuclearity products.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, and bond distances and angles of **2** (8 pages). Ordering information is given on any current masthead page. A complete MSC structure report is available on request from the Indiana University Chemistry Library.

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Shape-Selective Olefin Epoxidation Catalyzed by Manganese Picnic Basket Porphyrins

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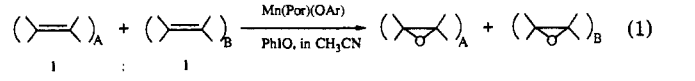
We have previously described the synthesis and characterization of the "picnic basket" porphyrins, which have a rigid cavity of variable dimensions on one face of the porphyrin ring.[1] Using ruthenium derivatives, we were able to control the regiochemistry of axial ligand coordination and to prepare stable dioxygen and dinitrogen complexes.[2] However, the picnic basket system was designed to effect catalytic, shape-selective oxygenations[3] and thus to mimic the enzyme family cytochrome P-450. Our early attempts to epoxidize olefins using manganese derivatives and iodosylbenzene failed to achieve shape selectivity. We were unable to seal the outside of the cavity by blocking the open face of the porphyrin with bulky *neutral* axial ligands such as 3,5-disubstituted imidazoles. Olefins were epoxidized on the open face of the porphyrin. Thus, these catalysts failed to show shape selectivity in the competitive epoxidation of olefin pairs.

We now describe conditions that result in catalytic olefin epoxidation within the cavities of a series of manganese picnic basket porphyrins. We have achieved substrate selectivities that reflect an interplay between the dimensions of the cavity vis-à-vis the shape of the olefin substrate. The solution to this problem involves the use of a bulky, *anionic* axial ligand and acetonitrile as a solvent with iodosylbenzene as the oxidant[4] (eq 1).



(1)

Our results are summarized in Table I. Very slow epoxidation is observed when the C_2 and C_4 baskets **1** and **2** are used (Figure 1). Apparently, a small amount of reaction occurs at the open face. In these cases the cavities are too restricted for reaction to occur inside. The C_6 basket, **3**, shows a dramatic selectivity as illustrated for *cis*-2-octene competing with *trans*-β-methylstyrene (70:1) and *cis*-2-octene with *cis*-cyclooctene (67:1). The flat, rigid xylyl basket, **6**, shows a slightly lower selectivity with *cis*-2-octene versus *trans*-β-methylstyrene (29:1) but dramatic shape selectivity for *cis*-2-octene versus tub-shaped *cis*-cyclooctene (>1000:1). The modest, inverted selectivities of the hindered open face tetramesitylporphyrin are provided for contrast. The selectivity within the C_8 basket, **4** falls sharply, giving ratios of 12.7:1

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(4) (a) To 4 μmol of Mn(Por)X (X = Br, Cl) in 2.5 mL of CH_3CN was added 20 equiv of $Et_2OLi(OAr)$. The solution was stirred at room temperature until the porphyrin Soret at 454 nm completely developed. $Olefin_A$ (125 equiv), $olefin_B$ (125 equiv), and PhIO (55 equiv) with a GC standard (nonane or dodecane) were then added. The epoxidation products were measured by GC as a function of time. With the catalysts Mn(C_6PBP)(OAr) and Mn(PXYLPBP)(OAr), the epoxidation yield of *cis*-2-octene based on PhIO is about 50–75% in 1 h. (b) The epoxidation rate with the catalysts Mn(C_2PBP)(OAr) and Mn(C_4PBP)(OAr) is at least 15 times slower than with Mn(C_6PBP)(OAr).

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Table I. Competitive Olefin Epoxidation[a]

catalyst[b]	epoxide ratio			
Mn(TPP)(OAr)	1.2	1.1	0.03	0.9
Mn(TMP)(OAr)	14.4	0.7	0.04	2.5
Mn(C_2PBP)(OAr)	0.4[c]	1.1[c]	0.05[c]	1.3[c]
Mn(C_4PBP)(OAr)	1.0[c]	2.1[c]	0.4[c]	1.8[c]
Mn(C_6PBP)(OAr)	70	67	1.7	>1000
Mn(PXYLPBP)(OAr)	29	>1000	7.0	>1000
Mn(C_8PBP)(OAr)	12.7	1.6	0.06	21.1
Mn(C_{10}PBP)(OAr)	8.8	0.2	0.04	17.9

[a] For experimental conditions, see ref 4. [b] OAr: 3,5-di-*tert*-butylphenoxide. TPP: tetraphenylporphyrin. TMP: tetramesitylporphyrin. [c] These reactions are very slow, implying that the reactions take place on the open face of the porphyrin.

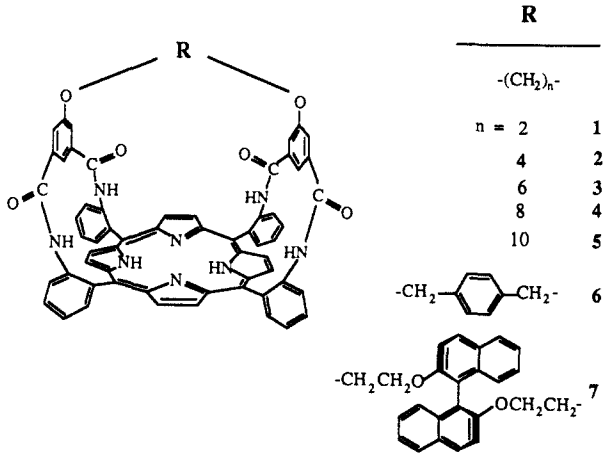

Figure 1. Picnic Basket Porphyrins.

and 1.6:1, respectively, for these two olefin pairs. The C_{10} basket, **5**, acts much more like the TMP case.

Terminal olefins are typically much less reactive in reactions with manganese porphyrin catalysts; entries showing the behavior of 1-octene versus cyclooctene for MnTPP and MnTMP illustrate this point. The C_6 basket shows a moderate reversal; 1-octene is 1.7 times more reactive. The *p*-xylyl case is more selective; the ratio is 7:1. Note, however, that in this case some reaction occurs with cyclooctene. We suppose that this slow oxidation occurs by "leaking" on the outer face during the long reaction times required by the terminal olefin.

The situation with trisubstituted olefins is very interesting; 2-methyl-2-pentene in competition with *cis*-2-octene reacts "normally" when MnTPP and MnTMP are used as the catalysts (ratios of 0.9 and 2.5, respectively). However, virtually no reaction of the trisubstituted olefin occurs within either the C_6 or *p*-xylyl baskets. The corresponding ratios are now >1000:1 for both basket catalysts. We speculate that this reactivity pattern reflects the required orientation of the Mn=O group and the olefin axis. Perhaps the alkene approaches the Mn–O bond from the side and is parallel to the porphyrin plane, as has been suggested by Groves[3a] for related iron catalysts and further discussed by Bruice.[5]

We also report a very modest case of catalytic asymmetric epoxidation when the chiral binaphthyl basket **7** is used. Styrene epoxide is formed in 13% ee as determined both by rotation ($[\alpha]_D^{20}$ = +2.8°, *c* = 1.7 in $CHCl_3$) and by NMR with a chiral shift reagent. Since the chiral site is far above the reaction locus, it is not surprising that the % ee is so small.[6] This does demonstrate that at least some (presumably all) reaction occurs within the cavity. This augurs well for the development of synthetically useful, efficient chiral catalysis.

Finally, we comment on catalyst stability. The shape-selective oxygenation can only be sustained under carefully controlled conditions. The acetonitrile solvent must be dry, and the anionic axial ligand must be present in excess. Otherwise, the blocking ligand is itself consumed by oxidation and the catalyst loses its shape selectivity as epoxidation occurs on the outer porphyrin face. In one case, we have studied the epoxidation of a 1:1 mixture of *cis*-2-octene and cyclooctene using the Mn *p*-xylyl complex, **6**; 600 turnovers/catalyst were achieved without measurable loss of shape selectivity.

We seem to be on the verge of predictable, shape-selective, catalytic oxygenation with a readily available, variable series of synthetic catalysts. For example, highly regioselective epoxidation of dienes should be possible.

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Hydrolysis of RNA by Transition-Metal Complexes

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Hydrolysis of phosphate esters has been studied extensively due to the relevance of this chemistry to biological systems. Consequently, transition-metal complexes have been examined as phosphate ester hydrolysis catalysts in an effort to model the reactions catalyzed by the ATPase and phosphatase class of enzymes. These studies have mostly employed activated *p*-nitrophenyl phosphate ester[1] or phosphate anhydrides (ATP) as substrates.[2] In addition, it is well-known that many divalent cations are capable of catalyzing the hydrolysis of RNA.[3] Examples of

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