

**Catalytic Replacement of Unactivated Alkane Carbon-Hydrogen Bonds  
with Carbon-X Bonds (X = Nitrogen, Oxygen, Chlorine, Bromine, or  
Iodine). Coupling of Intermolecular Hydrocarbon Activation by  
Mn<sup>III</sup>TPPX Complexes with Phase-Transfer Catalysis**

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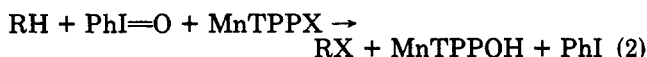
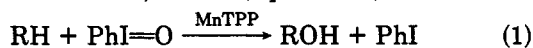
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A simple system has been devised to facilitate the first processes for the catalytic replacement of unactivated alkane C-H bonds with C-X bonds, X = nitrogen and iodine. The system also enables alkane C-H bonds to be replaced by C-X bonds, X = chlorine, bromine, and oxygen. The system is composed of two liquid phases and the oxidant iodosylbenzene (iodosobenzene). The alkane substrate, the Mn<sup>III</sup>TPPX catalyst, and the organic solvent (dichloromethane, chlorobenzene, or other aromatic hydrocarbon) constitute one phase, a saturated aqueous solution of the sodium salt of the anion to be incorporated into the alkane, NaX, X = N<sub>3</sub><sup>-</sup>, NCO<sup>-</sup>, I<sup>-</sup>, Br<sup>-</sup>, or Cl<sup>-</sup>, constitutes the second phase, and the sparingly soluble oxidant iodosylbenzene constitutes a third phase. When the two liquid phases and the oxidant iodosylbenzene are stirred under an inert atmosphere, both RX and ROH products are produced catalytically based on MnTPP and in reasonable yield based on iodosylbenzene. The MnTPP moiety functions as a catalyst for C-H bond cleavage and for phase transfer of X<sup>-</sup> from the aqueous phase to the organic phase where the functionalization chemistry takes place. The oxidant hypochlorite can be used in place of, but is less effective than, iodosylbenzene, and the oxidants hydrogen peroxide, periodate, and persulfate are ineffective. Product distributions obtained from the oxidation of cyclohexane, isobutane, 2,3-dimethylbutane, and *tert*-butylbenzene are most consistent with a product-determining step that involves transfer of X from manganese to a free alkyl radical intermediate.

The activation of hydrocarbon C-H bonds has been an explosively expanding field in the last few years. There are two general types of complexes that facilitate the stoichiometric activation of hydrocarbon C-H bonds under mild conditions in the liquid phase.<sup>1</sup> The first type are low-valent, highly polarizable, electron-rich species such as Ir(I) complexes<sup>2,3</sup> and the second type are high-valent electron-poor species such as Co(III) carboxylates.<sup>4</sup> The latter complexes also function as catalysts for the oxidation of organic substrates by dioxygen. However, the main role of the cobalt ions in these processes is to catalyze the decomposition of peroxide intermediates.<sup>5</sup> The specific involvement of the cobalt ion in C-H activation in these systems remains to be established.

Recently, metalloporphyrin complexes of Fe<sup>6</sup>, Cr<sup>7</sup>, and Mn<sup>8-10</sup> have been shown to catalyze the transfer of reduced oxygen to hydrocarbon substrates, with the Mn<sup>III</sup>TPPX-iodosylbenzene system<sup>9-11</sup> (TPP = tetraphenylporphyrin) being the most effective at catalyzing the functionalization of alkanes. The Mn<sup>III</sup>TPPX-iodosylbenzene system, X = Cl, Br, I, N<sub>3</sub>, results in the catalytic production of alcohol products, ROH, and the stoichiometric production of RX products from alkane, RH<sup>9,10</sup> (eq 1 and 2). The stoi-



chiometric oxidant iodosylbenzene is converted in high yield to the deoxygenated product iodobenzene in nearly all cases. In these systems, several high-valent Mn complexes derived from the oxidation of the Mn(III) reactant complex by iodosylbenzene, as well as long-lived freely diffusing alkyl radicals, have been shown to be intermediates.<sup>9,10</sup> The yield of RX products is limited in this system by the amount of X available—the 1 equiv present as the axial ligand on the starting Mn<sup>III</sup>TPPX catalyst. We previously demonstrated that if a second liquid phase of

aqueous NaN<sub>3</sub> is introduced, the RX product, alkyl azide, can be produced catalytically based on the Mn complex.<sup>12</sup> We report here that alkanes can be catalytically functionalized to produce alkyl azides, chlorides, bromides, iodides, or alcohols using systems with two liquid phases where the organic phase contains the alkane substrate and the Mn<sup>III</sup>TPPX catalyst and the aqueous phase contains the sodium salt of the function to be incorporated, X. In these systems the MnTPP moiety functions in a threefold capacity: it facilitates the cleavage of the C-H bonds, it activates X<sup>-</sup> for transfer to alkyl radical intermediates, and

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(10) Smegal, J. A.; Hill, C. L. *J. Am. Chem. Soc.* 1983, 105, 3515-3521. (11) Abbreviation: TPP is the 5,10,15,20-tetraphenylporphyrinato dianion ligand.

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Table I. Catalytic Functionalization of Cyclohexane Using Iodosylbenzene as the Oxidant<sup>a</sup>

no.	catalyst (Mn <sup>III</sup> TPPX')	X <sup>-</sup> in H <sub>2</sub> O <sup>b</sup>	product yields <sup>c</sup>				
			RX	RX'	c-C <sub>6</sub> H <sub>10</sub> O	ROH	PhI
1	MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	55		0.4	21	97
2	MnTPP(OAc)	N <sub>3</sub> <sup>-</sup>	53	<i>h</i>	<i>d</i>	20	95
3	MnTPPCL	N <sub>3</sub> <sup>-</sup>	54	<2	<i>d</i>	20	97
4	MnTPPCL	Cl <sup>-e</sup>	18		1	30	89
5	MnTPPCL	Cl <sup>-f</sup>	5		1	28	85
6	MnTPPCL	Cl <sup>-g</sup>	9		<i>h</i>	4	96
7	MnTPP(OAc)	Cl <sup>-</sup>	17	<i>h</i>	2	29	97
8	MnTPPN <sub>3</sub>	Cl <sup>-</sup>	13	10	1	27	95
9	MnTPP(OAc)	F <sup>-</sup>	<i>h</i>	<i>h</i>	2	47	73
10	MnTPP(OAc)	OAc <sup>-</sup>	<i>h</i>		1	46	63
11	MnTPP(OAc)	CN <sup>-</sup>	<i>h</i>	<i>h</i>	1	9	78
12	MnTPP(OAc)	NO <sub>2</sub> <sup>-</sup>	4	<i>h</i>	2	11	82
13	MnTPPBr	Br <sup>-</sup>	57		1	22	87
14	MnTPPI	I <sup>-</sup>	25		10	<i>h</i>	85
15	MnTPP(NCO)	NCO <sup>-</sup>	7		1	51	96
16	FeTPPCL	N <sub>3</sub> <sup>-</sup>	6	<i>d</i>	<1	9	99
17	FeTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	7		<1	10	103
18	CrTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	<1		1	4	98
19	VOTPP	N <sub>3</sub> <sup>-</sup>	<i>h</i>		<i>h</i>	<i>h</i>	100

<sup>a</sup> All reactions were run using CH<sub>2</sub>Cl<sub>2</sub> as solvent. Reaction conditions given in the Experimental Section. <sup>b</sup> Aqueous phase unbuffered unless designated otherwise. <sup>c</sup> Yields based on iodosylbenzene. <sup>d</sup> Value not determined. <sup>e</sup> Aqueous phase buffered at pH 7.4. <sup>f</sup> Aqueous phase buffered at pH 10.4. <sup>g</sup> Aqueous phase buffered at pH 2.1. <sup>h</sup> Below detectable limit (<<1%).

Table II. Functionalization of Cyclohexane Supported by Oxidants Other Than Iodosylbenzene<sup>a</sup>

catalyst	X <sup>-</sup> in H <sub>2</sub> O <sup>b</sup>	oxidant	product yields <sup>c</sup>			
			RX	RCl	c-C <sub>6</sub> H <sub>10</sub> O	ROH
MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	OCl <sup>-</sup>	1	1	<i>d</i>	<1
MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-e</sup>	OCl <sup>-</sup>	1	6	<i>d</i>	1
MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-f</sup>	OCl <sup>-</sup>	1	5	<i>d</i>	<1
MnTPPCL	N <sub>3</sub> <sup>-</sup>	OCl <sup>-</sup>	3	2	1	1
MnTPP(OAc)	N <sub>3</sub> <sup>-</sup>	OCl <sup>-</sup>	3	1	<1	<1
MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	IO <sub>4</sub> <sup>-</sup>		no products observed		
MnTPPBr	Br <sup>-</sup>	IO <sub>4</sub> <sup>-</sup>		no products observed		
MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	ROOH <sup>g</sup>	5	<i>d</i>	14	17
MnTPP(OAc)	NO <sub>2</sub> <sup>-</sup>	RCO <sub>3</sub> H <sup>h</sup>	<i>d</i>	<i>d</i>	<1	4
MnTPPN <sub>3</sub>	N <sub>3</sub> <sup>-</sup>	H <sub>2</sub> O <sub>2</sub> <sup>2-</sup>		no products observed		
MnTPPCL	Cl <sup>-</sup>	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>		no products observed		

<sup>a</sup> All reactions were run using CH<sub>2</sub>Cl<sub>2</sub> as solvent. Reaction conditions given in the Experimental Section. <sup>b</sup> Aqueous phase unbuffered unless designated otherwise. <sup>c</sup> Yields based on oxidant. <sup>d</sup> Below detectable limit (<<1%). <sup>e</sup> Aqueous phase buffered at pH 11.6. <sup>f</sup> Aqueous phase buffered at pH 2.3. <sup>g</sup> *tert*-Butyl hydroperoxide. <sup>h</sup> *m*-Chloroperoxybenzoic acid.

it replenishes X<sup>-</sup> by phase transfer from the aqueous phase. In all three processes the MnTPP moiety functions catalytically.

### Results and Discussion

The catalytic functionalization of alkanes by Mn<sup>III</sup>TPPX-oxidant/NaX<sub>aq</sub> systems is summarized in Tables I-III. Table I gives the product distributions resulting from the functionalization of an exemplary alkane substrate, cyclohexane, using the most successful oxidant, iodosylbenzene. Table II shows the product distributions resulting from cyclohexane functionalization using several other oxidants and Table III gives product yields for functionalization of three other alkane substrates. All these reactions, like the one-phase reactions delineated previously,<sup>9,10</sup> are run anaerobically to eliminate products resulting from MnTPP-catalyzed autoxidation.

The data in Table I show that with iodosylbenzene as the stoichiometric oxidant, the MnTPP moiety can catalytically produce both alkyl azides or bromides in yields >50% and alcohols in yields around 20% based on iodosylbenzene (reactions 1-3 and 13, Table I, respectively). The chlorination and iodination reactions are less successful, with the yields of chloride products averaging around 15% (reactions 4-7, Table I) and the yields of

iodide products averaging around 25% (reaction 14, Table I) based on iodosylbenzene. Alkane C-H bonds can be replaced by the nitro function in low yield (reaction 12, Table I) but not by the fluoride, acetate, or cyanide functions (reactions 9-11, Table I, respectively). The yields of RX products, X = N<sub>3</sub>, NCO, I, Br, Cl, OAc, CN, and F, parallel the expected abilities of intermediate radicals to attack X when ligated to a transition metal. These abilities in turn parallel the tendency of these ligands to bridge in inner sphere processes (N<sub>3</sub> (high reactivity) and Br (high reactivity) > Cl > F (low reactivity), OAc, and CN (low reactivity))<sup>13</sup> and roughly parallel the polarizabilities of these ligands. The reaction transferring azide to alkane is the only catalytic process for the incorporation of nitrogen directly into alkanes. Alkanes can be converted into alkyl isocyanates (reaction 15, Table I), but the yields are far lower than for the corresponding azide reactions. The iodination reaction to the best of our knowledge represents the only method in the literature for the direct introduction of iodine into hydrocarbons in any appreciable yield. The reaction of molecular iodine with alkanes is a

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Table III. Catalytic Functionalization of Other Alkane Substrates<sup>a</sup>

no.	catalyst	oxi- dant	X <sup>-</sup> in H <sub>2</sub> O <sup>b</sup>	substrate	product yields <sup>c</sup>					
					(CH <sub>3</sub> ) <sub>3</sub> COH	(CH <sub>3</sub> ) <sub>3</sub> CX	(CH <sub>3</sub> ) <sub>3</sub> CCl	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> X	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl	PhI
1	MnTPPCL	PhIO	Cl <sup>-</sup>	isobutane	14	8		1		94
2	MnTPPCL	OCl <sup>-</sup>	Cl <sup>-</sup>	isobutane	2	9		1		
3	MnTPPN <sub>3</sub>	PhIO	N <sub>3</sub> <sup>-</sup>	isobutane	1	35	<i>d</i>	<1	<i>d</i>	43
4	MnTPPN <sub>3</sub>	OCl <sup>-</sup>	N <sub>3</sub> <sup>-</sup>	isobutane	<1	3	<1	<i>e</i>	<i>e</i>	
					(CH <sub>3</sub> ) <sub>2</sub> CHC(CH <sub>3</sub> ) <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHC(CH <sub>3</sub> ) <sub>2</sub> X	(CH <sub>3</sub> ) <sub>2</sub> CHCH- (CH <sub>3</sub> )CH <sub>2</sub> OH	(CH <sub>3</sub> ) <sub>2</sub> CHCH- (CH <sub>3</sub> )CH <sub>2</sub> X		PhI
5	MnTPPCL	PhIO	Cl <sup>-</sup>	2,3-dimethyl- butane	8	6		<i>e</i>	1	72
6	MnTPPCL	OCl <sup>-</sup>	Cl <sup>-</sup>	2,3-dimethyl- butane	4	8		<i>e</i>	1	
					PhC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OH	PhC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> X	PhCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> OH	PhCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> X		PhI
7	MnTPPCL	PhIO	Cl <sup>-</sup>	<i>tert</i> -butyl- benzene	3	6	2	4		89
8	MnTPPCL	OCl <sup>-</sup>	Cl <sup>-</sup>	<i>tert</i> -butyl- benzene	<i>e</i>	2	<i>e</i>	<i>e</i>		
9	MnTPPN <sub>3</sub>	PhIO	N <sub>3</sub> <sup>-</sup>	<i>tert</i> -butyl- benzene	1	21	<1	10		51

<sup>a</sup> Isobutane reactions run using chlorobenzene as solvent; 2,3-dimethylbutane reactions run using CH<sub>2</sub>Cl<sub>2</sub> as solvent; *tert*-butylbenzene used as solvent and substrate on all *tert*-butylbenzene reactions. Reaction conditions given in the Experimental Section. <sup>b</sup> Aqueous phase not buffered. <sup>c</sup> Based on oxidant. <sup>d</sup> Below detectable limit.

classical case of an endothermic organic reaction ( $\Delta H \sim +15$  kcal/mol). The yields of iodides, e.g., reaction 14, Table I, are anomalously low relative to the yields of azides, bromides, and chlorides primarily because oxidation of the iodide ion in the aqueous phase is competitive with the oxidation of hydrocarbon. The yields for the iodination reactions are far less reproducible than the yields for any of the other reactions and appear to be dependent on stirring rate in a nonlinear manner.

The data in Table I show reactivity ratios for alkane functionalization supported by iodobenzene as a function of the metal that are similar to those seen previously for the one-phase systems (Mn (most effective)  $\gg$  Fe  $\gg$  Cr  $>$  VO (inactive)). Reactions 4–6 are exemplary reactions that illustrate the effect of the pH of the aqueous phase on the alkane functionalization chemistry. Product distributions appear to be little affected by changes in pH except when the aqueous phase is acidic (pH  $<$  3). Under the latter conditions, the brown high-valent MnTPP intermediate species present during catalysis (*vide infra*) are more stable (half-life of days as opposed to hours for the other reactions in Table I) and the yields of functionalized products are low.

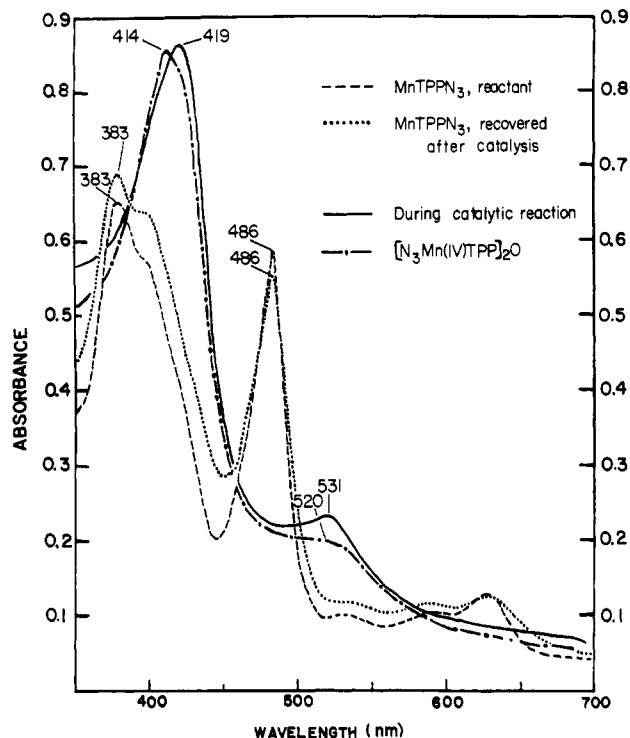
The product balance with regard to the oxidant, iodobenzene, is 70–80% for the azide and bromide reactions and lower for the others. The oxidizing equivalents not accounted for in the products enumerated in Table I are utilized in processes that lead to attack on solvent molecules, the porphyrin ligand, or the iodobenzene generated in situ during the reactions. There is direct or indirect evidence for all three of these side processes. Attack on solvent molecules is supported by the appearance of functionalized solvent molecules or, in the case of reactions run in chlorocarbon solvents, by anomalously high yields of chlorinated products. Reactions run in alkane-chlorocarbon media where only the solvent can supply chlorine show chloroalkane products. Mn<sup>III</sup>TPPX can be recovered after reaction; however, a mass spectrometric analysis of the recovered catalyst shows molecular ions for Mn(TPP-X), implying direct functionalization of the porphyrin ligand periphery during reaction. Regular electron impact mass spectra of manganese(III) porphyrin complexes, XMn<sup>III</sup>(Por), do not show molecular ions but always show large peaks for the Mn<sup>II</sup>(Por) cation radical.<sup>14</sup> The ob-

servation of large peaks for Mn(TPP-X) in the mass spectra of the Mn<sup>III</sup>TPPX complexes recovered after catalytic alkane functionalization and the lack of such peaks in the mass spectra of these complexes prior to reaction strongly suggest that the porphyrin itself is functionalized during these reactions. The relative yields of iodobenzene in all the reactions using iodobenzene as the oxidant provide indirect evidence that attack on iodobenzene can be a significant process. In reactions with reactive substrates, such as hydrocarbons with some tertiary or many secondary C-H bonds (e.g., reactions in Table I), the degree of attack on iodobenzene (or the minimally soluble iodobenzene reactant) is low and a nearly quantitative yield of iodobenzene is recovered after reaction. However, when only molecules of low reactivity are present (e.g., *tert*-butylbenzene—reaction 9, Table III), attack on iodobenzene reflected by lower yields of this product at the termination of the functionalization reactions can be appreciable.

Figure 1 compares the visible spectrum of the Mn<sup>III</sup>T-PPN<sub>3</sub> catalyst before and after reaction with 50 equiv of iodobenzene in cyclohexane-dichloromethane. Under these conditions 25 equiv of cyclohexyl azide and 9 equiv of cyclohexanol (25 and 9 turnovers of the MnTPP moiety respectively) are produced. The spectra clearly show that the Mn<sup>III</sup>TPPX chromophore is still largely intact. However, the two principal absorptions in the visible region, the Soret bands, or bands V and VI using the nomenclature of Boucher<sup>14b</sup> and Gouterman<sup>15</sup> ( $\lambda_{\max} = 383$  and 486 nm), are broadened in the spectra of the recovered material. This is in accord with the presence of several different Mn<sup>III</sup>TPPN<sub>3</sub> complexes with slightly different chromophores in this material. The replacement of the C-H bonds of the porphyrin by C-X bonds would be expected to have a small but discernible effect on the visible spectra of the porphyrin and its metal complexes. Figure 1 also shows the visible spectra of the organic phase during this cyclohexane functionalization reaction and the spec-

(14) Metalloporphyrins are reduced to divalent species in the gas phase: (a) Edwards, L.; Dolphin, D.; Gouterman, M.; Alder, A. D. *J. Mol. Spectrosc.* 1971, 38, 16–32. (b) Boucher, L. J. *Coord. Chem. Rev.* 1972, 7, 311.

(15) Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1.



**Figure 1.** Comparison of the visible spectra of the Mn(III)TPPN<sub>3</sub> catalyst before (---) and after (····) reaction with 50 equiv of iodosylbenzene. Also shown are the visible spectrum obtained during cyclohexane functionalization (—) and the visible spectrum of the purified, characterized dimer complex, [N<sub>3</sub>Mn(IV)TPP]<sub>2</sub>O (— · —). All spectra were recorded in the reaction medium, 1:1 v/v CH<sub>2</sub>Cl<sub>2</sub>-cyclohexane, as ca. 1 mM solutions equilibrated with a second phase of saturated aqueous NaN<sub>3</sub> at 25 °C.

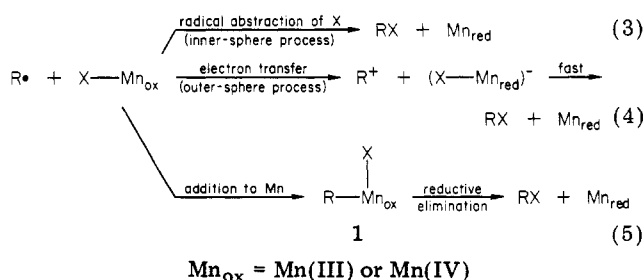
trum of the complex [N<sub>3</sub>Mn<sup>IV</sup>TPP]<sub>2</sub>O that was previously isolated from the one-phase reaction of iodosylbenzene and Mn<sup>III</sup>TPPN<sub>3</sub> in hydrocarbon media and subsequently purified and characterized.<sup>16</sup> It was previously established that manganese(IV) porphyrin complexes, including the [N<sub>3</sub>Mn<sup>IV</sup>TPP]<sub>2</sub>O complex, are capable of activating alkane C-H bonds.<sup>9,10,16</sup> It is apparent that high-valent MnTPP species and not Mn<sup>III</sup>TPPX species are the principal complexes present during catalysis.

Table II summarizes the ability of oxidants other than iodosylbenzene to facilitate alkane functionalization by manganese porphyrin complexes. Aqueous sodium hypochlorite, NaOCl, oxidizes the green Mn<sup>III</sup>TPPX complexes to the brown high-valent species and effects a small degree of alkane functionalization, but is less effective than iodosylbenzene. Control experiments established that both the Mn<sup>III</sup>TPPX and hypochlorite are required for alkane functionalization to occur. A representative alkyl hydroperoxide, *tert*-butyl hydroperoxide (TBHP), was screened for activity. Although some alkane functionalization was detected with this oxidant, there was no apparent oxidation of the Mn<sup>III</sup>TPPX chromophore and the functionalized products likely result from attack on alkane by radicals derived from the hydroperoxide.<sup>17</sup> An exemplary peracid, *m*-chloroperoxybenzoic acid (*m*CPBA), effected immediate oxidation of the Mn<sup>III</sup>TPPX chromophore to a brown high-valent species but produced few functionalized alkane products. The metalloporphyrin was apparently degraded faster than alkane was attacked with

this oxidant. Similar behavior was seen when iodosylbenzene was used as an oxidant under acidic conditions (e.g., reaction 6, Table I). The oxidants periodate, hydrogen peroxide, and persulfate neither oxidized the manganese complex nor led to any discernible alkane functionalization.<sup>18</sup>

Table III summarizes the product distributions obtained from the MnTPP-catalyzed functionalization of the hydrocarbon substrates isobutane, 2,3-dimethylbutane, and *tert*-butylbenzene using iodosylbenzene or hypochlorite as oxidants. Unfortunately these yields do not accurately reflect kinetically controlled product distributions in all cases. A series of control experiments have established that there is no appreciable subsequent reaction of the tertiary azide or the primary or tertiary alcohol products under the reaction conditions, but there is detectable isomerization of the primary chlorides to tertiary chlorides, tertiary chlorides to primary chlorides, and primary azides to tertiary azides under the reaction conditions. A series of reactions were run in the absence of the aqueous phase of NaX, and under these conditions there is no equilibration or subsequent reaction of any of the products. The product distributions obtained from the oxidation of isobutane, dimethylbutane, and *tert*-butylbenzene under these one-phase conditions using iodosylbenzene as an oxidant are very similar to the product distributions in Table III. The product distributions in Table III indicate that long-lived freely diffusing alkyl radicals are precursors to alkyl azide, chloroalkane, and alcohol products under the two-phase conditions required for the catalytic incorporation of X into alkane. The reactions of *tert*-butylbenzene in Table III generating neophyl radical intermediates place an upper limit on the degree of oxidation of the radical intermediates to carbonium ions (ca. 40%). The benzyldimethylcarbinyl products probably arise from 1,2-phenyl migration (neophyl rearrangement) of the intermediate neophyl radicals rather than from oxidation of the neophyl radicals. If all the benzyldimethylcarbinyl products are derived from rearrangement of the long-lived neophyl radicals, then from the known rate constant of the neophyl rearrangement in nonpolar solvents at 25 °C ( $k_r = 59 \text{ s}^{-1}$ ),<sup>19</sup> the half life of the radicals can be calculated to be approximately 4–8 ms.

The product-determining step in these two-phase reactions involves the attack of intermediate radicals on manganese porphyrin complexes in solution. The complexes can be either Mn(III) or Mn(IV) species on the basis of studies of visible spectra.<sup>9,10</sup> Of the three possible product-determining steps shown in eq 3–5, the inner-sphere



mechanism (eq 3) is in best agreement with the observed generation of products as a function of X discussed above. The *tert*-butylbenzene functionalization (reactions 7–9, Table III) rules out eq 4 as the principal product-deter-

(16) Schardt, B. C.; Hollander, F. J.; Hill, C. L. *J. Am. Chem. Soc.* 1982, 104, 3964–3972.

(17) Recent review of metal catalyzed decomposition of peroxides: Sheldon, R. A.; Kochi, J. K. "Metal Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; Chapter 3.

(18) Under basic conditions (pH ca. 9 or greater), S<sub>2</sub>O<sub>8</sub><sup>2-</sup> oxidizes Mn<sup>III</sup>TPPX derivatives to higher valent species: Camenzind, M. J.; Hill, C. L. unpublished work.

(19) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* 1976, 98, 1224–1226.

mining process. Equation 5 involves attack of the radical intermediate at Mn to form a seven-coordinate high-valent Mn species, 1, that subsequently undergoes reductive elimination to form the functionalized product, RX. Although this mechanism cannot be ruled out, it involves a seven-coordinate intermediate, 1, that is unprecedented in metalloporphyrin complexes of first row transition metals. The formation of 1 with tertiary alkyl groups would likely be a high energy process based on steric arguments (two bulky axial ligands on the same side of the metalloporphyrin plane). The rate of the product-determining transfer of X to alkyl radical, at least in the cases where X = N<sub>3</sub> and Br, is very fast. Catalytic bromination in the system MnTPPBr-cyclohexane (CH<sub>2</sub>Cl<sub>2</sub>)/NaBr (H<sub>2</sub>O) produces more alkyl bromide than alcohol even when the reaction is run in the air, despite the fact that the rate of reaction of free alkyl radicals in solution with O<sub>2</sub> is a diffusion-controlled process with effectively no activation energy.<sup>20</sup> Reoxidation of Mn<sub>red</sub> to Mn<sub>ox</sub>, ligation of more X<sup>-</sup> to Mn<sub>ox</sub> at the interface between the organic and aqueous phases, and transport of the new X-Mn<sub>ox</sub> into the organic phase complete the catalytic cycle.

### Conclusions

Systems containing two liquid phases, an organic phase containing the alkane substrate and the Mn<sup>III</sup>TPPX catalyst and an aqueous phase containing the readily available inexpensive sodium salt, NaX, X = N<sub>3</sub>, NCO, Br, Cl, I, in the presence of the oxidant iodosylbenzene, can catalytically produce alkyl azide or halide, RX, and alcohol, ROH, products in good yield based on iodosylbenzene. The cheap oxidant sodium hypochlorite can be substituted for iodosylbenzene, but the yields of functionalized alkane products are substantially lower than when the latter oxidant is used. The MnTPP moiety functions as a catalyst for C-H bond cleavage, for activation of X in transfer to alkyl radical intermediates, and for phase transfer of X<sup>-</sup> from the aqueous phase. The product distributions from all reactions establish that long-lived alkyl radicals are intermediates to all the principal products and the most likely product-determining step involves an inner-sphere transfer of X from Mn to alkyl radical. The radical selectivities seen in these processes largely define the limitations of these processes with regard to their application to synthetic problems.

### Experimental Section

**Instrumentation.** Visible spectra were recorded on a Cary 118 spectrometer. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph coupled with a Hewlett-Packard Model 3390A reporting integrator. Nitrogen was used as the carrier gas with flame ionization detection (FID). A 12-m OV-101 fused silica capillary column

(Hewlett-Packard) was used for separation of the various products through variation of the carrier gas flow and the column temperature. The identity of the products was verified by co-injection with authentic samples and by gas chromatographic-mass spectral (GC/MS) analysis.

**Materials.** The solvents *tert*-butylbenzene, chlorobenzene, and dichloromethane were purified before use by successive treatment with concentrated H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, KOH<sub>aq</sub>, and H<sub>2</sub>O and fractional distillation from P<sub>2</sub>O<sub>5</sub>. Cyclohexane was glass-distilled grade from Burdick and Jackson and used without further purification. 2,3-Dimethylbutane (Aldrich) was treated with concentrated H<sub>2</sub>SO<sub>4</sub> and distilled from P<sub>2</sub>O<sub>5</sub> before use. The complex Mn<sup>III</sup>TPP(OAc) was prepared by the method of Adler et al.<sup>21</sup> and the complexes Mn<sup>III</sup>TPPX, X = Cl, Br, N<sub>3</sub>, NCO, and I, were prepared by ligand exchange with Mn<sup>III</sup>TPP(OAc) by the procedure used by Ogoshi et al. on the corresponding iron complexes.<sup>22</sup> Iodosylbenzene was prepared by literature methods.<sup>23</sup> The oxidants Ca(OCl)<sub>2</sub>, NaOCl, H<sub>2</sub>O<sub>2</sub>, *tert*-butyl hydroperoxide, NaIO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were commercial samples and used without further purification.

**General Procedure for Alkane Oxidation Reactions.** All reactions were run under a nitrogen atmosphere in Schlenk flasks at 25 °C. Solvent, alkane substrate, and the aqueous phase were thoroughly degassed before use. Substrate was always present in at least tenfold excess with an oxidant to catalyst ratio of 10:1. The aqueous phase was composed of a saturated solution of the sodium salt of the transferring anion. Completion of the reaction was indicated by the disappearance of the brown color of the oxidized porphyrin complex and the formation of the green color of the Mn<sup>III</sup>TPPX chromophore. The completed reactions were treated with aqueous Na<sub>2</sub>SO<sub>3</sub> before analysis.

In a typical reaction, 15 mg of the Mn<sup>III</sup>TPPX catalyst and a tenfold excess of oxidant were accurately weighed into a Schlenk flask containing a magnetic stirring bar. The flask was then fitted with a serum stopper and placed under a nitrogen atmosphere. The organic phase, composed of 2 mL of substrate and 3 mL of solvent, was thoroughly degassed and transferred to the reaction vessel via cannula. When the manganese porphyrin catalyst was dissolved, 3 mL of a degassed saturated aqueous solution of NaX was injected into the reaction vessel. After approximately 12 h of reaction time, the reaction mixture was treated with aqueous Na<sub>2</sub>SO<sub>3</sub>, an internal standard was added, and then the organic phase was analyzed by GLPC or GC/MS.

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**Registry No.** MnTPPN<sub>3</sub>, 56413-47-9; MnTPP(OAc), 58356-65-3; MnTPP(Cl), 32195-55-4; MnTPP(Br), 55290-32-9; MnTPP(I), 55290-33-0; MnTPP(NCO), 86549-48-6; FeTPP(Cl), 16456-81-8; FeTPPN<sub>3</sub>, 51455-98-2; CrTPPN<sub>3</sub>, 83438-07-7; VOTPP, 14705-63-6; OCl<sup>-</sup>, 14380-61-1; *t*-BuOOH, 75-91-2; [N<sub>3</sub>MnIVTPP]<sub>2</sub>O, 79775-62-5; iodosylbenzene, 536-80-1; cyclohexane, 110-82-7; isobutane, 75-28-5; 2,3-dimethylbutane, 79-29-8; *tert*-butylbenzene, 98-06-6.

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