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# Efficient catalytic cycloalkane oxidation employing a "helmet" phthalocyaninato iron(III) complex

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We have examined the catalytic activity of an iron(III) complex bearing the

14,28-[1,3-diiminoisoindolinato]phthalocyaninato (diiPc) ligand in oxidation reactions with three substrates (cyclohexane, cyclooctane, and indan). This modified metallophthalocyaninato complex serves as an efficient and selective catalyst for the oxidation of cyclohexane and cyclooctane, and to a far lesser extent indan. In the oxidations of cyclohexane and cyclooctane, in which hydrogen peroxide is employed as the oxidant under inert atmosphere, we have observed turnover numbers of 100.9 and 122.2 for cyclohexanol and cyclooctanol, respectively. The catalyst shows strong selectivity for alcohol (*vs.* ketone) formation, with alcohol to ketone (A/K) ratios of 6.7 and 21.0 for the cyclohexane and cyclooctane and 92% for cyclohexane, based upon the total hydrogen peroxide added. In the catalytic oxidation of indan under similar conditions, the TON for 1-indanol was 10.1, with a yield of 12% based upon hydrogen peroxide. No 1-indanone was observed in the product mixture.

# Introduction

For several years, we have had an interest in a group of modified metallophthalocyaninato complexes in which the 14 and 28 positions on what would otherwise be a normal "flat" phthalocyaninato (Pc) ligand bear connectivities that give rise to chirality. Thus far, we have reported the syntheses and structural characterization for two alkoxy-modified phthalocyaninato complexes of general formula  $[14,28-(RO)_2Pc]Ni(II)$  where R represents Me or Et,<sup>1</sup> and also for three so-called "helmet" metallophthalocyaninato complexes of general formula L(14,28-[1,3-diiminoisoindolinato]phthalocyaninato)M(III).<sup>2</sup> Among this latter group, we have fully characterized examples where M = Fe and L is a mixture of methanol and water (1), where M = Fe and L = 4-hydroxypyridine, and where M = Co and L = methanol. Henceforth, the 14, 28-[1, 3-diiminoisoindolinato]phthalocyaninato ligand will be referred to as "diiPc."

As a class of compounds, the metallophthalocyanines and related derivatives have long provided fertile ground for investigations on many different fronts, in a large part because of their diverse array of optical, electronic, photochemical, magnetic, and catalytic properties.<sup>3</sup> Our current interest, and the subject of this report, is in the area of oxidation catalysis. An examination of the literature reveals several cases where metallophthalocyanine and metallophthalocyanine-like complexes are effective in this role.<sup>4-21</sup> Of particular relevance to the work described in the present paper are a series of peripherally-substituted metallophthalocyanines

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that catalyze the conversion of cyclohexane to cyclohexanone and cyclohexanol, with total turnover numbers (alcohol + ketone) up to 88 and total yields up to  $88\%.^7$ 

In undertaking our study, exploring the potential utility of the modified metallophthalocyanines synthesized in our laboratory as catalysts, we have chosen to focus our attention on 1 in part because of its stability, which is superior to that observed for the alkoxy-modified nickel complexes, and in part because it is far more soluble than its cobalt-containing analogue in solvent systems that are suitable for oxidation experiments. We were also intrigued by some similarities among 1, for which a line drawing is given in Fig. 1, and several non-heme (and nonmetallophthalocyanine) complexes that have been shown to be effective alkane oxidation catalysts.<sup>22-33</sup> A common theme among many of these is the presence of an iron atom coordinated to a tetradentate or pentadentate ligand bearing nitrogen donor atoms, with any remaining metal coordination sites occupied by labile (usually solvent) ligands. Much of the interest in non-heme iron-based catalysis has been driven principally or in part by questions related to the biomimetic relevance of these complexes and mechanistic details regarding their function in catalytic oxidations.<sup>22-38</sup> Our interest, however, derives primarily from a desire to find new oxidation catalysts among the inexpensive and very easily prepared modified metallophthalocyanine complexes that have been discovered during the course of our investigations to date. Alkane oxidation clearly represents, in its own right, an area of vital importance within industrial organic synthesis.<sup>27,33,39-41</sup>

In order to set our results in context with literature reports following from the strong and ongoing interest in non-heme oxidation catalysis that exists at present, we have largely modelled

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**Fig. 1** A line drawing showing an "exploded view" of L(diiPc)Fe(III), **1**, with ligand L omitted for clarity.

the experimental details described below after those set forth fairly recently by Comba<sup>23</sup> and by Que,<sup>24</sup> who have described a series of active, efficient non-heme iron-based oxidation catalysts and probed their mechanisms of function by spectroscopic and theoretical means, in addition to their catalytic behavior.

# Experimental

#### Equipment and materials

All solvents (HPLC grade or higher) were purchased from commercial sources and used without drying or distillation. Iron complex 1 was prepared as we have described previously.<sup>2</sup> All other reagents were obtained from commercial sources in the highest available purity and used as received. All GC-MS analyses were performed on a Varian Saturn 2100D system operating with ultrahigh purity helium carrier gas.

#### Catalyst pre-conditioning

In a typical experiment, a 50 mL Schlenk flask equipped with a magnetic stir bar was charged with 6.5  $\mu$ mol<sup>42</sup> of **1** and attached to the Schlenk line, where an atmosphere of either argon or oxygen was established, depending upon the experiment. After addition with stirring of 6.0 mL of dichloromethane, then 6.0 mL of acetonitrile, the resulting red solution was allowed to stir overnight. Mixed acetonitrile/dichloromethane solvent was necessary due to insufficient solubility of **1** in 100% acetonitrile.

## Oxidation experiments (cyclohexane and cyclooctane)

All reactions were carried out at room temperature. In a typical reaction, a solution containing the pre-conditioned catalyst was treated with substrate (8.33 mmol) and then hydrogen peroxide (0.53 mmol) was added with stirring over the course of 30 min by syringe pump in a volume of 0.6 mL of a solution that had been prepared by diluting 30% aqueous hydrogen peroxide with

acetonitrile. This reaction mixture was stirred for an additional two hours. In experiments involving cyclohexane and cyclooctane substrates, a second aliquot of hydrogen peroxide was added in the same manner as the first, followed by a second two hour stirring period. For indan, only one addition of hydrogen peroxide was made, as extending the reaction time was shown to decrease the yield of desired product and increase by-product formation.

## Analysis of products

Product mixtures were loaded onto very short (3 to 4 cm) silica gel columns and eluted with copious diethyl ether. Products were then quantified by GC-MS using naphthalene as an internal standard on a Varian V-5ms column of dimensions 30 m  $\times$  0.25 mm. Identification of products was made on the basis of retention times and examination of the fragmentation patterns observed in their mass spectra.

# **Results and discussion**

## Oxidation of cyclohexane and cyclooctane

We have found that 1 functions as an active and selective precatalyst for the oxidation of cyclohexane and cyclooctane to the corresponding alcohols, cyclohexanol and cyclooctanol. We refer to 1 as a pre-catalyst because we believe that the ligand L initially present on 1 (a mixture of methanol and water) as it is synthesized is replaced by acetonitrile during the overnight preconditioning period. This pre-conditioning period in the presence of acetonitrile is extremely important in the performance of the (diiPc)Fe moiety as an oxidation catalyst in the systems we have studied. When the oxidation of cyclohexane involving 1 is attempted in 100% dichloromethane, or else in the mixed solvent but without a pre-conditioning period, turnover number (TON) for cycohexanol decrease dramatically, with the formation of ketone decreasing to only trace amounts. Acting upon the expectation that a similar effect would be observed for other substrates, we carried out all cyclooctane and indan oxidations employing 1 with the acetonitrile pre-conditioning period. While we have not directly characterized the version of L(diiPc)Fe(III) where L = acetonitrile, we have observed an apparent slow exchange of the initial methanol and water ligands on 1 for other coordinating solvent ligands in HPLC experiments carried out in conjunction with another project, when coordinating solvents have been included in chromatographic mobile phases. It is reasonable to expect that such a replacement of the L ligands initially present on 1 by acetonitrile, driven by a high concentration of the new ligand, results in a species where L is in a general sense more labile and thus more easily displaced, thus allowing access to the diiPc-coordinated metal center. While it may be expected that reactions carried out in the presence of acetonitrile without a pre-conditioning period could eventually proceed to give product yields that are the same as or similar to those observed with pre-conditioning, we believe that our procedure allows us to be reasonably sure that ligand replacement is complete by the time the oxidation reactions are started. Thus, we are confident that the observed catalytic behavior and necessary reaction times are functions of the inherent properties of the (diiPc)Fe(III) system and not the rate of ligand replacement.

In oxidation experiments carried out under an atmosphere of argon in 50% dichloromethane: 50% acetonitrile solvent, with hydrogen peroxide oxidant and excess cyclohexane substrate following overnight pre-conditioning of the catalyst in the mixed solvent, we have observed the formation of cyclohexanol with a TON of 100.9 and cyclohexanone with TON = 15.1. This corresponds to an alcohol-to-ketone ratio (A/K) of 6.7. While not rivalling the impressive performance of the iron porphyrin complexes described by Groves<sup>43</sup> nearly three decades ago (TON values up to almost 800), the TON for oxidation of cyclohexane to cyclohexanol catalyzed by (diiPc)Fe is higher than has been reported for any other non-porphyrinic (i.e. non-heme-derived) iron catalyst that we are aware of, and the selectivity for formation of alcohol over ketone is high. The yields (based upon total  $H_2O_2$ added) were 64% for cyclohexanol and 9% for cyclohexanone, or a 73% total yield for the oxidized products.

We have observed that (diiPc)Fe catalyzes the oxidation of cyclooctane with results similar to those for cyclohexane substrate under analogous circumstances, where the TON = 122.2 for cyclooctanol and 5.8 for cyclooctanone, corresponding to an alcohol-to-ketone ratio (A/K) of 21.0. As far as we are aware, these numbers significantly surpass those that have been reported in the literature for any other non-heme iron catalyst in the oxidation of cyclooctane. Nam and co-workers have described catalytic systems based upon an iron porphyrin complex that results in the oxidation of cyclooctane to cyclooctanol in up to 60% yield with an A/K up to 10 (and that also results in the conversion of cyclohexane to cyclohexanol in up to 40% yield with an A/K up to 16.5).44 The yields observed for the (diiPc)Fe catalyst (based again upon the total H2O2 added) were 88% for cyclooctanol and 4% for cyclooctanone, giving a 92% total yield for the oxidized products.

When the oxidations of cyclohexane and cyclooctane were carried out under an oxygen (rather than argon) atmosphere we observed significant decreases in TON for the alcohols (to 30.2 for cyclohexanol and 40.4 for cyclooctanol) and in the A/K (2.7 for cyclohexanol and 5.3 for cyclooctanol). In the case of cyclohexane oxidation, TON for the ketone decreased only slightly to 11.1 upon switching to an oxygen atmosphere, whereas TON for cyclooctanol actually increased very slightly, to 7.6. These observations roughly parallel those reported recently by Comba<sup>23</sup> and Que<sup>24</sup> for similar catalytic systems, as discussed below.

#### Oxidation of indan

Oxidations of indan yielded less impressive results, but **1** was nonetheless observed to be a functional pre-catalyst. When the oxidation was carried out under argon, we observed TON = 10.1for 1-indanol, corresponding to a yield of 12% based upon H<sub>2</sub>O<sub>2</sub>. A complex mixture of unidentified by-products was also present in the product mixture. Interestingly, however, we did not observe the formation of any 1-indanone. Upon switching the atmosphere from argon to oxygen, we actually observed a small increase in TON for 1-indanol to 12.3, with the yield rising to 13%. Still, however, no significant 1-indanone formation was observed. These observations stand in contrast to the results for the cyclohexane and cyclooctane systems, suggesting that a different mechanism is probably involved.

# Evaluation of (diiPc)Fe as an oxidation catalyst and comparison to related systems

Our overall results for the oxidation experiments involving cyclohexane, cyclooctane, and indan are summarized in terms of TON and A/K in Table 1. Also included in the Table are values taken from selected literature reports on related catalytic systems for comparative purposes. The results from the present work, when considered in context and examined in terms of observed TON and A/K values and yield of oxidized products based upon total oxidant added, reveal the (diiPc)Fe moiety to be an efficient, reasonably active, and chemoselective oxidation catalyst for cyclohexane and cyclooctane. While conversion of cyclohexane and cyclooctane to the corresponding alcohols and ketones cannot be considered extremely rapid (with reaction times of five hours to completion), oxidation reactions employing 1 as a pre-catalyst do provide turnover numbers and selectivity for formation of alcohol over ketone that compare favorably to reports from the recent literature. Among metallophthalocyanine and metallophthalocyanine-like catalysts, (diiPc)Fe appears to be the most effective in cycloalkane oxidation that has been identified to date. Further, 1 enjoys the advantage of extreme ease of preparation and purification, as it is obtained in crystalline form by one-pot solvothermal syntheses from very inexpensive starting materials and can be used without further purification.

In a real sense, (diiPc)Fe fills a niche within the spectrum of known iron-based oxidation catalysts. Compound 1 can, at least in terms of the iron coordination environment, be viewed as a structural relative of several other non-heme iron-based catalysts that have appeared in the literature in which four or five metal-coordinating nitrogen atoms are observed, along with at least one labile ligand that ultimately allows access to the metal center. Examples include four-and five-coordinate bispidines<sup>22-23</sup> and  $N_4 Py^{24}$  iron complexes for which data is included in Table 1. However, 1 differs from these in at least one clear respect in that all of the metal-coordinating nitrogen atoms in the diiPc ligand are part of the same relatively rigid macrocyclic unit, rather than existing as part of pendant groups attached to some central atom or more complex structural unit. This may account in part for the favorable performance of 1, a complex that we have observed to be almost indefinitely stable as a solid and highly robust in solution, even at high temperature. Results (TON and A/K) taken from some recent reports are presented in entries 7 through 17 in Table 1, revealing both interesting similarities among and some significant differences between the results for 1 (entries 1-4) and those for the related bispidine and N<sub>4</sub>Py complexes (entries 7-17). Probably the most important observation is that all of the complexes referenced in entries 1-17 show good activity in the oxidation of cyclohexane. Beyond this, comparisons of entries 1 with 2, 3 with 4, 9 with 10, 11 with 12, 13 with 14, and 15 with 16 reveal that in oxidation reactions of cycloalkanes the TON for alcohol formation and chemoselectivity for alcohol over ketone are higher under an inert atmosphere but decrease significantly when the reaction conditions are changed to an atmosphere of either  $O_2$  or air in each case involving these related catalysts. We may infer from this observation that (diiPc)Fe and the related species referenced in entries 9-16 probably function in a similar manner in alkane oxidations. As has been described elsewhere, the decrease in alcohol TON and A/K in the presence of significant

Entry	Catalyst/comments	Substrate	Oxidant	Conditions <sup>a</sup>	TON <sup>b</sup> (alcohol)	TON <sup>b</sup> (ketone)	A/K <sup>c</sup>	Ref.
1	L(diiPc)Fe	Cyclohexane	H <sub>2</sub> O <sub>2</sub>	Ar/50% CH <sub>2</sub> Cl <sub>2</sub> 50% MeCN	100.9	15.1	6.7	this work
2	L(diiPc)Fe	Cyclohexane	$H_2O_2$	O <sub>2</sub> /50% CH <sub>2</sub> Cl <sub>2</sub> 50% MeCN	30.2	11.1	2.7	this work
3	L(diiPc)Fe	Cyclooctane	$H_2O_2$	Ar/50% CH <sub>2</sub> Cl <sub>2</sub> 50% MeCN	122.2	5.8	21.0	this work
4	L(diiPc)Fe	Cyclooctane	$H_2O_2$	O <sub>2/</sub> 50% CH <sub>2</sub> Cl <sub>2</sub> 50% MeCN	40.4	7.6	5.3	this work
5	L(diiPc)Fe	Indan	$H_2O_2$	Ar/50% CH <sub>2</sub> Cl <sub>2</sub> 50% MeCN	10.1	0		this work
6	L(diiPc)Fe	Indan	$H_2O_2$	O <sub>2</sub> /50% CH <sub>2</sub> Cl <sub>2</sub> 50% MeCN	12.3	0		this work
7	Tetradentate bispidine Fe complex with chloride	Cyclohexane	ТВНР	Ar/MeCN	55.4	0.1	550	22
8	Tetradentate bispidine Fe complex with bromide	Cyclohexane	ТВНР	Ar/MeCN	56.1	0.4	140	22
9	Tetradentate bispidine Fe complex	Cyclohexane	$H_2O_2$	Ar/MeCN	20.5	13.5	1.5	23
10	Tetradentate bispidine Fe complex	Cyclohexane	$H_2O_2$	O <sub>2</sub> /MeCN	13.2	11.6	1.1	23
11	Pentadentate bispidine Fe complex (isomer $L^2$ in Ref. 23)	Cyclohexane	$H_2O_2$	Ar/MeCN	16.5	7.7	2.1	23
12	Pentadentate bispidine Fe complex (isomer $L^2$ in Ref. 23)	Cyclohexane	$H_2O_2$	O <sub>2</sub> /MeCN	12.1	10.8	1.1	23
13	Pentadentate bispidine Fe complex (isomer $L^3$ in Ref. 23)	Cyclohexane	$H_2O_2$	Ar/MeCN	9.8	9.9	1.0	23
14	Pentadentate bispidine Fe complex (isomer $L^3$ in Ref. 23)	Cyclohexane	$H_2O_2$	O <sub>2</sub> /MeCN	8.9	11.6	0.8	23
15	(N <sub>4</sub> Py)Fe(MeCN)] <sup>2+</sup>	Cyclohexane	$H_2O_2$	Ar/MeCN	18.5	12.9	1.4	24
16	$[(N_4Py)Fe(MeCN)]^{2+}$	Cyclohexane	$H_2O_2$	Air/MeCN	14.9	15.6	0.96	24
17	$[(N_4Py)Fe(MeCN)]^{2+}$	Cyclooctane	$H_2O_2$	Ar/MeCN	2.7	9.0	0.3	24
18	Chlorinated phthalocyaninatoiron(II) complex	Cyclohexane	O <sub>2</sub> /MeCOH <sup>d</sup>	$O_2/CH_2Cl_2$	44	44	1	7
19	Chlorinated phthalocyaninatoiron(II) complex	Indan	O <sub>2</sub> /MeCOH <sup>d</sup>	$O_2/CH_2Cl_2$	166	211	0.79	7
Notes	<sup><math>a</math></sup> Atmosphere and solvent system <sup><math>b</math></sup> T(	ON – moles pro	duct/moles cata	lyst $c \Delta / K = moles alcohol/moles$	les ketone d	MeCOH -	acetalde	hvde

 Table 1
 Catalytic oxidation of cyclohexane, cyclooctane, and indan employing 1 as a pre-catalyst, and data from related catalytic systems employing non-heme iron-based catalysts

amounts of  $O_2$  can very likely be attributed to an aerobic pathway involving  $O_2$  in radical chain processes that compete with alcohol formation.<sup>22–24</sup> It is worthy of note that the decrease in alcohol TON and selectivity with cyclooctane substrate as compared to cyclohexane observed for (N<sub>4</sub>Py)Fe(CH<sub>3</sub>CN) (entries 15 and 17) was not paralleled by **1**. In fact, alcohol TON, alcohol yield, and A/K all increased significantly for the oxidation of cyclooctane catalyzed by (diiPc)Fe relative to the results for cyclohexane, identifying this complex as (to our knowledge) the most active non-heme cyclooctane oxidation catalyst reported to date.

While 1 does serve as a pre-catalyst for indan oxidation, hydroxylating the substrate at the expected benzyllic position to produce 1-indanol, it does not do so with good efficiency, as evidenced by a TON slightly above ten and only a 12% yield based upon  $H_2O_2$ . It is interesting to note that the yield of alcohol in this system did not decrease upon switching from an Ar atmosphere to an  $O_2$  atmosphere; in fact it increased slightly. Further contrast between the cycloalkane and indan oxidations is seen in the lack of any significant ketone formation in the latter, the reason for which we do not yet understand. It should be noted that other metallophthalocyanine systems do function as highly effective oxidation catalysts for indan, especially the chlorinated iron(II) complex referenced in entry 19 of Table 1, which gives turnover numbers of 166 and 179 for 1-indanol and 1-indanone, respectively.<sup>7</sup>

# Conclusion

We have shown that the modified "helmet" metallophthalocyaninato complex **1** is an effective pre-catalyst for cycloalkane oxidation, giving turnover numbers in excess of 100 for conversion of cyclohexane and cyclooctane to the corresponding alcohols. Further, the high A/K ratios observed for the cyclohexane and cyclooctane oxidations catalyzed by (diiPc)Fe reveal excellent chemoselectivity. In these respects, and in light of high yields based on the convenient oxidant  $H_2O_2$ , the (diiPc)Fe system compares quite favorably to many other non-heme iron-based catalysts and also to a variety of "flat" metallophthalocyanines. Complex 1 holds further advantages in that it is very easily prepared, with minimal expense, and it is highly stable. Given the results that have been presented here, the "helmet" metallophthalocyanines currently known and as-of-yet undiscovered present themselves as a ripe area for future study, especially given their chirality and the ultimate possibility that they might catalyze oxidation reactions leading to chiral products in an enantioselective fashion, once the complexes themselves can be obtained in sufficient quantities in enantiopure or significantly enriched form.

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- 42 The pre-catalyst 1 used in this study is prepared in crystalline form, where the composition of the crystals can vary slightly. In the crystallographically determined structure (Ref. 2), ligand L is observed to be a mixture of methanol and water, with two co-crystallized methanol molecules also being present for every complex bearing a methanol ligand, whereas three co-crystallized methanol molecules are present for every complex bearing a water ligand. In a desire to report catalyst performance conservatively in light of this issue, we have calculated TON values based on an assumption that the pre-catalyst has 100% methanol as the L ligand, which along with the two co-crystallized methanol molecules gives a formula weight of 806.65, less than that for the case where L = water and three co-crystallized methanol molecules are present, in which case the formula weight is 824.66. This results in slightly under-reported turnover numbers, assuming a mixture of the two species is actually present, because the number of moles of catalyst actually present in the reaction mixtures will be very slightly less than the number used in TON calculations.
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