Biomimetic organometallic chemistry. Regio- and stereoselectivity in the hydroxylation reaction of cyclohexyltriphenyltin with metalloporphyrins as the biomimetic catalysts and iodosylbenzene as the oxygen transfer agent

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angles of 15 reflections in the range $18° < 2\theta < 24°$. The space group was determined from the systematic absences ($h01$, $l = 2n$; $0k0$, $k = 2n$) and subsequent least-squares refinement.

A total of 5947 reflections were collected. As a check on crystal and electronic stability, two representative reflections were measured every 98 reflections. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ψ scans, were applied to the data. Intensities of equivalent reflections were averaged, and two reflections were rejected because their intensities differed significantly from the average. The agreement factors for the averaging of the 284 observed and accepted reflections was 5.6% based upon intensity and 4.2% based upon F_o.

The structure was solved by the Patterson heavy-atom method. The structure was refined in full-matrix least squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, with a weight w of 1.0 for all observed reflections. All non-hydrogen atoms, except N1, N2, C1, B, and all but Cl1 in the $CHCl_2CHCl_2$ molecules, were refined with anisotropic thermal parameters. One $CHCl_2CHCl_2$ molecule (that containing C47) was situated on a crystallographic inversion center with full occupancy ((*RR,SS*)-**4**/$CHCl_2CHCl_2$ = 1.0/0.5). A second $CHCl_2CHCl_2$ molecule was also found and was assigned an occupancy of 0.2, in accord with the analytical data; this gave satisfactory refinement and reasonable thermal parameters. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[16] Anomalous dispersion effects were included in F_c.[17] The final refinement cycle converged to R and R_w values given in Table I. The highest peak in the final difference Fourier had a height of 1.09 e Å^{-3}, with an estimated error based upon Δf of 0.20.[18] All calculations were performed on a VAX 8300 computer with the SDP/VAX package.[19]

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Supplementary Material Available: A table of anisotropic thermal parameters for (*RR,SS*)-**4**·$(CHCl_2CHCl_2)_{0.7}$ (2 pages); a listing of calculated and observed structure factors for (*RR,SS*)-**4**·$(CHCl_2CHCl_2)_{0.7}$ (11 pages). Ordering information is given on any current masthead page.

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Biomimetic Organometallic Chemistry: Regio- and Stereoselectivity in the Hydroxylation Reaction of Cyclohexyltriphenyltin with Metalloporphyrins as the Biomimetic Catalysts and Iodosylbenzene as the Oxygen Transfer Agent

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The regio- and stereoselectivity in the hydroxylation reaction of cyclohexyltriphenyltin (**1**), with biomimetic catalysts that mimic the active site of cytochrome P-450 monooxygenase enzyme, iron(III), and manganese(III) tetrakis(pentafluorophenyl)porphyrin derivatives [Fe^{III} or $Mn^{III}TF_5PP(Br,OAc)$], was studied with the oxygen transfer agent, iodosylbenzene, and the results were compared to those results previously obtained with the P-450 enzyme from rat liver microsomes. The $Mn^{III}TF_5PP(OAc)$ biomimetic catalyst provided a 22% conversion of **1** to a mixture of *cis*- and *trans*-hydroxycyclohexyltriphenyltin compounds that included the trans-4 (5.9%), **2**; cis-3 (22%), **3**; trans-3 (3.3%), **4**; and trans-2 (68.8%), **5**, isomers. The regiochemistry on a per hydrogen basis shows a C4:C3:C2:C1 ratio of 1:2:6:0 and a high stereoselectivity for equatorial over axial hydroxyl products with a EQ/AX ratio of 29. The corresponding $Fe^{III}TF_5PP(Br)$ catalyst gave the same pattern of hydroxylation as with the above-mentioned Mn catalyst. In comparison to the P-450 enzyme, which had a different regioselectivity ratio on a per hydrogen basis for C4:C3:C2:C1 of 109:7:1:0, the biomimics appear to have less steric requirements at the active site. Mechanistically the tin atom also appears to control the regiochemistry of the hydroxylation reaction by the fact that **3** and **5** are the major hydroxylation products due to a stabilization of radical intermediates on carbons 2 and 3 by the tin–carbon σ bond. As well, the hydroxyl rebound reaction to give products **2–5** also appears to be stereoselective for the sterically more favorable equatorial product.

Introduction

The recent interest in the synthesis of biomimetic catalysts that mimic the biologically important cytochrome P-450 dependent monooxygenase enzyme reaction[1] by converting C–H bonds to C–OH bonds in a regio- and stereoselective manner has led to an enormous number of contributions that have clearly shown similar reactivity to the reactive metal center of that enzyme.[2] While the types

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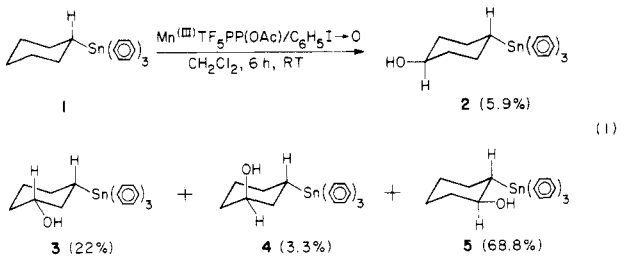
of substrates that have been studied with these biomimics have included alkanes and alkenes, it was surprising, therefore, to discover that no examples of organometallic substrates have been reported with these biomimetic catalysts.

One class of organometallic compounds, the organotins, have been shown to have a wide variety of biological activity[3] and have been studied in depth with a cytochrome P-450 enzyme system from rat liver microsomes.[4] Those studies were unequivocal in determining that the tin atom controlled the regiochemistry when substrate steric effects at the binding site in proximity to the active metal center were not a factor.[4a,b] In addition, those studies clearly were among the first to assign a free radical mechanism to the P-450 enzyme in the conversion of C–H bonds to C–OH bonds, with the tin atom able to stabilize the intermediate carbon radicals that were α and β to it.[4a-d,5]

More importantly, we were also able to study, with the enzyme system, the regio- and stereoselective aspects of this conversion with cyclohexyltriphenyltin (1) and demonstrate that steric effects at the binding site in proximity to the active metal center control the regiochemistry. Thus, we wish to report the first example of the use of an organometallic substrate, 1, with "oxo" metalloporphyrins that have been shown to be biomimetic catalysts for the cytochrome P-450 active metal center, iron(III) or manganese(III) tetrakis(pentafluorophenyl)porphyrin derivatives [$TF_5PP(Br,OAc)$][2b,i,6] in the presence of the oxygen transfer agent, iodosylbenzene, and establish the regio- and stereoselectivity of the hydroxylation reaction, while comparing the results to those found for the enzyme system.

Results and Discussion

Compound 1 and either the Fe^{III} or $Mn^{III}TF_5PP(Br,OAc)$ catalyst were placed in a Schlenk tube in methylene chloride along with the oxygen transfer agent, iodosylbenzene, to form in situ the corresponding "oxo" metalloporphyrin catalyst,[2a-c,i] that converted 1 to a mixture of *cis*-hydroxycyclohexyl- and *trans*-hydroxycyclohexyltriphenyltin compounds (2–5) (~22% based on 1 with the $Mn^{III}TF_5PP(OAc)$ catalyst and represents ~4 turnover numbers) (eq 1).[7] The regiochemistry on a per hydrogen



(1)

basis shows a C4:C3:C2:C1 ratio of 1:2:6:0 and a high stereoselectivity for equatorial over axial hydroxyl products, with a EQ/AX ratio of 29. Compounds **2–5** were separated on a normal-phase silica HPLC column (hexane/THF, 85/15 v/v) and identified by comparison of their HPLC retention times and 200-MHz ^1H NMR and EIMS spectra to those of authentic samples.[7] Several control experiments showed that compounds **2–5** were not formed in the absence of catalyst, although iodosylbenzene did react with 1 to form a small amount (~1–2%) of a triphenyltin derivative (TLC). We also found a small amount of cyclohexene, by capillary GC analysis of the methylene chloride solution, and verified that it emanated from a thermal 1,2-deoxystannylation reaction of **5** in the injection port of the gas chromatograph.[7] Compound **5** also provided a trace amount of cyclohexanone upon reaction with iodosylbenzene in the absence of catalyst, while ketone analogues for compounds **2**, **3**, and **4** were not detected by HPLC using authentic samples as standards.[7]

Table I. Comparison of the Regio- and Stereoselectivity in the Hydroxylation of Compound 1 with $Mn^{III}TF_5PP(OAc)$ and a P-450 Enzyme

compd[a]	$Mn^{III}TF_5PP(OAc)$,[b] %	P-450 enzyme,[c] %
2	5.9	85.6[d]
3	22.0	6.5[e]
4	3.3	3.0
5	68.8	1.6

[a] See eq 1 for structures 2–5. [b] See Experimental Section for reaction conditions. [c] P-450 enzyme from rat liver microsomes (see ref 4). [d] The ketone of 2 was present in 1.9%. [e] The ketone from 3 and 4 was present in 1.4%.

The results in eq 1 were compared to the previously reported enzyme results[4c,d,f] (Table I), and a dramatically different regioselectivity for the enzyme was observed, with 1 as the substrate, that provided on a per hydrogen basis a C4:C3:C2:C1 ratio of 109:7:1:0. As with the biomimetic catalysts, the enzyme also demonstrated an extremely high stereoselectivity for equatorial over axial hydroxyl products with a EQ/AX ratio of 59. Again to reiterate, what is evident is the pronounced regiochemical differences between the enzyme and the biomimics, which obviously reflects the steric requirements of the enzyme system in comparison to the biomimics and provides for the predominant formation of compound **2** rather than **5**. Thus, the concept of shape selectivity, which was recently introduced in several biomimetic catalyst studies, might provide a more realistic model for the binding site of the enzyme system, and future biomimetic studies should utilize this concept.[2f,j]

Mechanistically, the tin atom can be a probe for differentiating free radical versus carbonium ion intermediates for the biomimetic Fe and Mn catalysts used in this study. The formation of *trans*-2-hydroxycyclohexyltriphenyltin (**5**) as the predominant oxidation product further substantiates that a free radical mechanism is operative, as was postulated previously with these biomimics,[2] and that radical stability, via tin–carbon σ bond overlap with the carbon radical p orbital,[4a-d,8] controls product distribution in the absence of stringent steric requirements.[2i] The intermediacy of a carbonium ion β to a tin atom in the biomimetic oxidation would not provide **5**; rather, the elimination of the triphenyltin group and formation of

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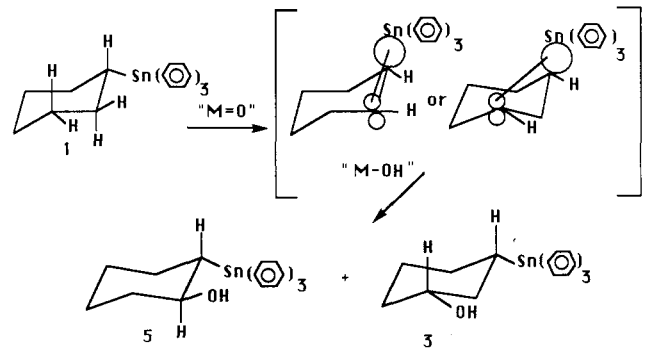
cyclohexene would occur.[7] The formation of a substantial amount of *cis*-3-hydroxycyclohexyltriphenyltin (**3**) might also imply that the carbon–tin σ bond can stabilize a 3-carbon radical by overlap of the p orbital. This possibility is strengthened by the fact that the carbon–tin bond length is ~2.18 Å and the *A* value for a triphenyltin group on a cyclohexyl ring is ~1.5, which allows for an axial conformation population for the tin atom and 1,3 diaxial σ bond–p orbital overlap.[7]

It is also interesting to note that C1 hydroxylation did not appear to occur to any significant extent, since we saw only trace amounts of cyclohexanol, the breakdown product of any 1-hydroxycyclohexyltriphenyltin that might be formed.[4b,c] This latter result may be due to a steric effect of the triphenyltin group in proximity to the oxo metalloporphyrin complex and the fluorine substituents on the meso phenyl groups that prevents close proximity of the C1 hydrogen to the oxo metal center.[2b,f,i,j,6]

The above-mentioned argument on the regioselectivity of the C–H activation reaction, which predominates at the 2- and 3-carbon positions relative to the triphenyltin group in **1**, is further strengthened by the recent results of Nappa and Tolman[2i] on the phenyl-substituted Fe porphyrin catalyzed hydroxylation of methylcyclohexane and *tert*-butylcyclohexane. They show, with the tetra-2-fluorophenyl-substituted Fe porphyrin catalyst, that the regioselectivity ratio for methylcyclohexane (the methyl group has an *A* value of ~1.8 and a C–C bond distance of 1.54 Å), C4:C3:C2:C1, on a per hydrogen basis, is 1:1.5:2:7. If the triphenyltin group has approximately the same steric requirements as the methyl group on a cyclohexane ring (similar *A* values), then the 2-position of compound **1** is three times more reactive than the corresponding 2-position in methylcyclohexane, while the 1-position is unreactive in compound **1** for reasons just mentioned. Nappa and Tolman[2i] also found that by increasing the steric bulk of the cyclohexane substituent from methyl to *tert*-butyl, a dramatic increase in hydroxylation at the 3- and 4-positions was noticed along with a decrease at the 1- and 2-positions; the C4:C3:C2:C1 ratio on a per hydrogen basis being 2.8:4:1:0. Both compound **1** and *tert*-butylcyclohexane show no C1 hydroxylation, while the 2-position in **1** is six times more reactive than the corresponding position in *tert*-butylcyclohexane. Hence, our regiochemical results with **1** clearly are indicative of carbon-tin bond stabilization of intermediate radicals at carbons 2 and 3.

Lastly, the high stereoselectivity for equatorial products by the $Mn^{III}TF_5PP(OAc)$ catalyst (i.e., no *cis*-2-hydroxycyclohexyl- or *cis*-4-hydroxycyclohexyltriphenyltin compounds were detected in the NMR spectra of their trans isomers, **2** and **5**, respectively) suggests that while the formation of the carbon radical may occur from abstraction of either equatorial or axial hydrogens, the hydroxyl rebound reaction to carbon radical to form the sterically more favorable equatorial alcohol, via some radical cage effect, must be extremely selective and the reason for the dominant products observed.[2d,e,i,k] This latter statement is further confirmed by comparing the stereochemistry of the hydroxyl rebound reaction with **1** and *tert*-butylcyclohexane,[2i] i.e., equatorial/axial ratios. Compound **1** had no cis hydroxylation products at carbons 2 and 4 (axial), while *tert*-butylcyclohexane had trans/cis ratios of 2.5 and 2, respectively. More importantly, compound **1** had a cis/trans ratio at carbon 3 of 6.7, while *tert*-butylcyclohexane had a 2.0 ratio. These observations, we believe, are a consequence of the triphenyltin group controlling both the regiochemistry and the stereoselectivity of the hydroxyl rebound reaction as shown in Scheme I.

Scheme I. Proposed Homolytic Mechanism for the Conversion of C–H to C–OH Bonds Using "Oxo" Metalloporphyrin Catalysts with C–Sn Bond Stabilization of Carbon Radical Intermediates, Followed by a Stereoselective OH Rebound Reaction



Conclusions

The biomimetic P-450 model enzymes, substituted metalloporphyrins, which we have used to compare to rat liver microsomes, provide a hydroxylation pattern with compound **1** that has a dramatically different regioselectivity than the enzyme, due probably to the lack of stringent steric requirements at the active putative "oxo" metal site. The tin–carbon σ bond appears to influence the regiochemistry by stabilization of carbon radicals on the 2- and 3-positions, while a high stereoselectivity for equatorial product, as is the case with the enzyme,[4c] coincides with a highly stereoselective hydroxyl rebound reaction to carbon radical. Finally, these metalloporphyrin catalyzed monooxygen transfer reactions offer a facile synthetic entry to hydroxy-substituted organometallic derivatives, a class of compounds not readily available,[7] but of significant interest for their biological properties.[4]

Experimental Section

Materials and Instrumentation. Compounds **1–5** were synthesized previously and reported.[7] The H_2TF_5PP ligand was obtained from Aldrich Chemical Co., while the iron[6] and manganese[2b] complexes of H_2TF_5PP were prepared according to literature methods. The ^1H NMR spectra at 200 MHz, EIMS spectra, and elemental analyses were obtained in facilities located in the Department of Chemistry, University of California, Berkeley. The HPLC separations for **2–5** were obtained on a Beckman/Altex Ternary HPLC system equipped with a rapid-scan UV–vis detector.

A Typical Catalyzed Oxidation Procedure with Cyclohexyltriphenyltin (1). Compound **1** (900 mg, 2.08 mmol), $Mn^{III}TF_5PP(OAc)$ (124 mg, 0.114 mmol), and iodosylbenzene (459 mg, 2.08 mmol) were placed in a 100-mL Schlenk flask under argon. Degassed methylene chloride (40 mL) was transferred to the solids by cannula, and the resulting mixture was stirred for 3 h at ambient temperature. The insoluble iodosylbenzene was apparent during this period, and reaction was allowed to continue for 3 h more. The solution was filtered and analyzed for compounds **1–5** by HPLC (silica, hexane/THF 85:15 v/v: UV detection at 254 nm) to show 75% **1**, 22% **2–5**, and 3% unidentified material. This represents ~4 turnovers of the Mn catalyst. Compound **1** and the $Mn^{III}TF_5PP(OAc)$ catalyst were separated from **2–5** via column chromatography (100% CH_2Cl_2 and then 50–70% Et_2O) on silica gel. Compounds **2–5** were then isolated by preparative HPLC and identified by 200 MHz ^1H NMR and EIMS and were completely consistent with the authentic materials.[7] The corresponding $Fe^{III}TF_5PP(Br)$ also gave similar results, but separation of the catalyst from compound **1** and that of **5** from

iodobenzene by HPLC was difficult and we could not accurately quantify the products **2-5**.

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Registry No. **1**, 20204-06-2; **2**, 64739-02-2; **3**, 64739-01-1; **4**, 65954-06-5; **5**, 64739-04-4; $Mn^{III}TF_5PP(OAc)$, 114634-40-1; $Fe^{III}TF_5PP(Br)$, 36929-15-4; $C_6H_5I(O)$, 536-80-1.

Synthesis, Structure, and Reactions of Rhenium Aminocarbyne Complexes Formed from $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ (R = *t*-Bu or Me) Cations under Reductive Coupling Conditions

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The seven-coordinate $[ReCl_2(CNR)_3(PMePh_2)_2]^+$ cations, R = Me or t-C_4H_9, react with Zn(s) or Al(s) in refluxing THF containing ~1% H_2O to form (alkylamino)carbyne complexes $[ReCl(CNH$-t-$Bu)(CN$-t-$Bu)_2(PMePh_2)_2](SbF_6)$ (**1**) and $[ReCl(CNHMe)(CNMe)_2(PMePh_2)_2](SbF_6)$ (**2**). The structure of **1**, determined by X-ray diffraction, contains a chloride ligand, trans pairs of phosphine and isocyanide ligands, and a Re≡CNHR carbyne unit characterized by a Re—C bond length of 1.82 (1) Å, a C—N distance of 1.30 (1) Å, a Re—C—N angle of 175.7 (9)°, and a C—N—C bend angle of 127.6 (9)°, consistent with considerable Re=C=NHR character. Infrared and ^1H, ^{31}P, and ^{13}C NMR spectroscopic data support the persistence of this structure for both **1** and **2** in solution. Multiple recrystallizations of **2** from THF led to the formation of $[ReCl(CNMe)_3(PMePh_2)_2]$ (**3**) through formal loss of $HSbF_6$. Compound **3** was structurally characterized by X-ray diffraction. It contains two trans phosphine ligands and a meridionally disposed set of three isocyanide ligands, all of which have considerable Re=C=NR character, judging by C—N—C bend angles ranging from 144 (2) to 155 (2)°. Addition of excess zinc to **2** in acetonitrile leads to a similar electron-rich isonitrile complex, $[Re(NCMe)(CNMe)_3(PMePh_2)_2](SbF_6)$ (**5**), in which an acetonitrile solvent molecule replaces the chloride ligand. The structure of **5** is similar to that of **3**, but with less back-donation to the isocyanide ligands judging by the C—N—C angles of 160.4 (5)–178.4 (5)°, owing to the positive charge on the complex. Reaction of $[ReBr_2(CNMe)_3(PMePh_2)_2]^+$ with Zn in refluxing aqueous THF gave only $[ReBr(CNMe)_3(PMePh_2)_2]$ (**4**), which was not protonated. Spectral studies of **3**–**5** established that the solution structures were analogous to those found in the solid state for **3** and **5**. These results are consistent with the following reaction pathway for reductive coupling of isocyanide (and analogous CO) complexes:

$$\{M(CNR)_2X\}^{n+} \xrightarrow[-X^-]{+2e^-} \{M(CNR)_2\}^{(n-1)+} \xrightarrow{H^+} \{M(CNHR)(CNR)\}^{n+} \xrightarrow{HX} \{M(RHNC{\equiv}CNHR)X\}^{n+}$$

In the present instance, the $\{Re(CNHR)(CNR)\}^{2+}$ unit is presumably too stable to form the reductively coupled $\{Re(RHNC{\equiv}CNHR)Cl\}^{2+}$ moiety.

Introduction

Previously we studied reductive coupling of isocyanides in seven coordinate group 16 transition metal complexes to form coordinated bis(alkylamino)acetylenes.[1,2] Analogous reactions of group 15 metal carbonyls produced bis(trialkylsiloxy)-[3] and dihydroxyacetylene[4] complexes. Mechanistic studies of the carbonyl reductive coupling reaction revealed the formation of (trialkylsiloxy)carbyne intermediates that react further with coordinated CO to give the bis(trialkylsiloxy)acetylene complexes.[5]

In the interest of extending the isocyanide reductive coupling chemistry to other metal centers, the system $[ReX_2(CNR)_3L_2]X$ (X = Cl, Br; L = $PMePh_2$, PMe_2Ph; R = Me, *i*-Pr, *t*-Bu, cyclohexyl, benzyl) was investigated. These rhenium(III) cations[6] appeared to be good candidates for reductive coupling. The prototypical compound $[ReCl_2(CN$-t-$Bu)_3(PMePh_2)_2]SbF_6$ is a seven coordinate d^4 complex with capped trigonal prismatic geometry in the solid state and close nonbonded C···C contacts of 2.330 (9) and 2.341 (8) Å.[6] These properties are known to contribute to reductive coupling of isocyanides in several seven coordinate molybdenum(II) and tungsten(II) complexes.[1,2]

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