JOC Article

Regioselective Oxidations of Benzocarbaporphyrins with Ferric Chloride: A Facile Synthesis of Bridged [18]Annulene Ketals with Strong Absorptions in the Far Red and an Unexpected Halogenation Reaction at the Interior Carbon Atom†

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Benzocarbaporphyrins **4** were found to undergo regioselective oxidations with ferric chloride in methanol, ethanol, isopropyl alcohol, or ethylene glycol to give bridged benzo[18]annulene ketal derivatives **5** in excellent yields. These polar derivatives were generally isolated in a monoprotonated form and the corresponding free bases appeared to be relatively unstable. Addition of TFA resulted in the formation of spectroscopically distinct dications. The ketals **5** were highly diatropic in nature, showing the internal alkoxy substituents upfield beyond −1 ppm in their proton NMR spectra. The external *meso*-protons resonated near 10 ppm, confirming the presence of a strong aromatic ring current. The UV−vis spectra for **5** showed a Soret band at 422 nm, and two strong absorptions in the far red at 751 and 832 nm. A carbaporphyrin with a fused acenaphthylene ring was also oxidized with ferric chloride and this produced a ketal derivative with still further bathochromically shifted absorptions particularly for the Soret band. Also, the use of different alcohols in these reactions allows the overall polarity of these ketal products to be controlled and this could have merit in biomedical applications. Reaction of carbaporphyrin **4a** with aqueous ferric chloride afforded the corresponding 21-chloro derivative **20** in good yields, and at longer reaction times a nonaromatic dione was isolated. Aqueous ferric bromide gave a 21-bromocarbaporphyrin product but in this case very poor yields (<10%) were noted. Mechanisms are proposed to explain the formation of these unusual oxidation products. The structure of 21-chlorocarbaporphyrin **20** was further demonstrated by X-ray crystallography. The presence of the interior chlorine atom was found to tilt the indene moiety by 29.59(4)° relative to the [18]annulene macrocyclic ring. The crystal packing for **20** shows offset face-to-face π-stacking interactions that link the porphyrinoid molecules as closely paired dimers.

Introduction

Carbaporphyrinoids are a class of porphyrin analogues where one or more of the usual pyrrole subunits are replaced with carbocyclic rings.[1] These macrocyclic systems have demonstrated many unique chemical and spectroscopic properties that parallel and to a great extent rival those of the better studied N-confused porphyrins (NCPs) (e.g. **1**; Chart 1).[2,3] Examples of carbaporphyrinoids include oxybenziporphyrins (**2**),[4,5] benziporphyrins,[5,6] tropiporphyrins,[7] carbachlorins,[8] and azuliporphyrins (**3**).[9−11] In addition, true carbaporphyrins have been synthesized where cyclopentadiene units have been introduced in place of one or more of the pyrrole moieties.[1,10−16] Carbaporphyrins provide a conceptual link

† Part 27 in the series Conjugated Macrocycles Related to the Porphyrins. For Part 26, see: Jiao, W.; Lash, T. D. *J. Org. Chem.* **2003**, *68*, 3896-3901.

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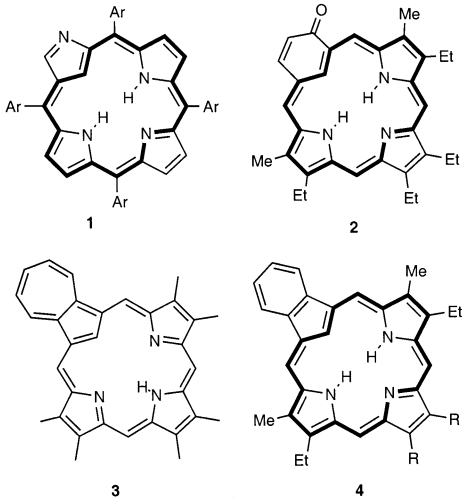
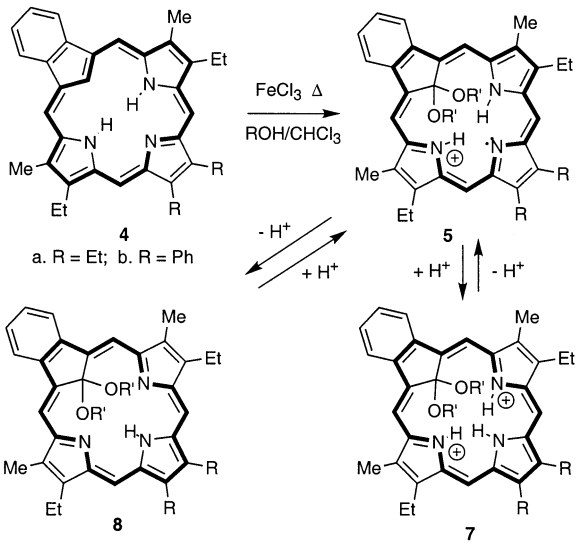
CHART 1



SCHEME 1



For **5**, **7** and **8**: a. R = Et; R' = Me b. R = R' = Et c. R = Et; R' = i-Pr d. R = Et; R' = CH_2CH_2OH e. R = Ph; R' =Me f. R = Ph; R' = Et

between the porphyrins and bridged annulene systems and the aromatic characteristics of these hybrid macrocycles have been the subject of detailed studies.[10−17] For this class of porphyrinoids, benzocarbaporphyrins (e.g. **4**) are by far the easiest to synthesize by the use of established methodologies.[11,12,14,15,18]

Carbaporphyrinoids have at least one internal CH unit, a structural feature also found in the NCPs.[2,3] One of the most appealing aspects of NCP chemistry is the ability of these porphyrin isomers to generate novel organometallic complexes.[3] Indeed, NCPs can act as dianionic or trianionic ligands and have demonstrated other intriguing metal coordination properties.[19] Although our initial studies in the area of carbaporphyrinoid chemistry failed to produce transition metal complexes of this type,[20] we and others have recently achieved the synthesis of stable organometallic products for benzocarbaporphyrins,[21,22] azuliporphyrins,[23,24] oxybenziporphyrins,[25] and benziporphyrins.[6b] However, during the course of our initial investigations into the metalation of benzocarbaporphyrins **4**,[20] we noted that reactions with ferric chloride in the presence of an alcohol solvent resulted in an unprecedented regioselective oxidation at the internal carbon. In this paper, full details of this chemistry are presented, including the isolation and spectroscopic characterization of bridged benzo[18]annulene ketals. In addition, syntheses and the structural characterization of halogenated carbaporphyrin derivatives and a nonaromatic porphyrinoid dione are described.[20,26]

Results and Discussion

In an attempt to metalate carbaporphyrin **4a**, the macrocycle in chloroform was heated with an equal volume of a saturated ferric chloride solution in methanol under reflux for 1 h (Scheme 1). The initially dark brown colored solution quickly turned green and a new chromophore with strong absorptions in the far red was noted. Following column chromatography on alumina, a polar green band was eluted and this was recrystallized from chloroform-hexanes to give dark green crystals in 90% yield. However, fast atom bombardment mass spectrometry showed no incorporation of iron into the product and gave a molecular ion of *m*/*z* 560. High-resolution mass

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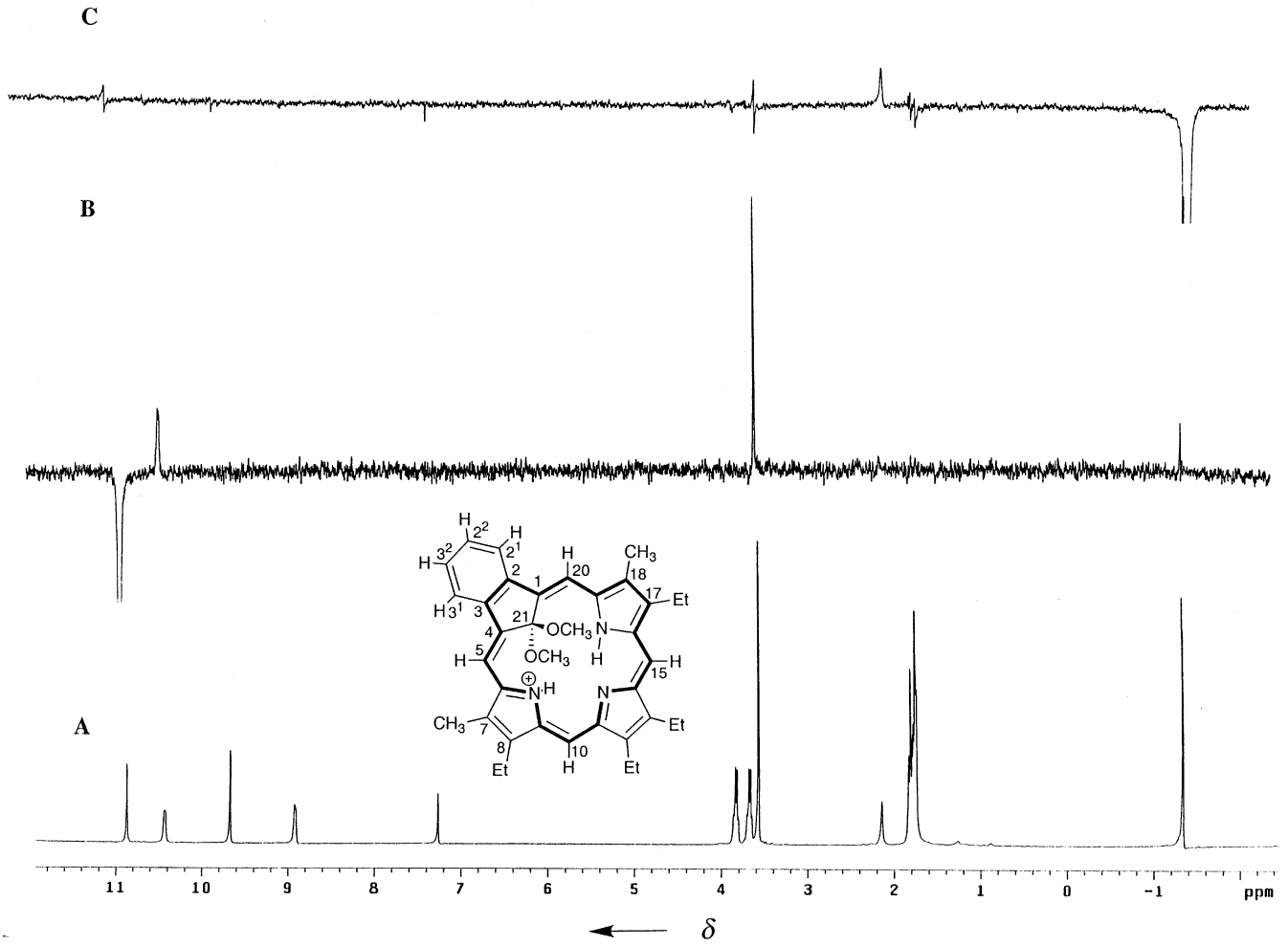

FIGURE 1. (A) Proton NMR spectrum (400 MHz) of dimethoxy ketal **5a** in deuteriochloroform. (B). nOe difference proton NMR spectrum of **5a** resulting from the irradiation of the resonance at 10.9 ppm due to the 5,20-*meso*-protons. This results in an enhancement of the peaks due to the adjacent benzo-2^1,3^1-protons at 10.4 ppm and the 7,18-methyl units at 3.6 ppm. In addition, a weak transannular enhancement of the interior methoxy resonance at −1.3 ppm is evident. (C) nOe difference proton NMR spectrum of **5a** resulting from the irradiation of the peak at −1.3 ppm due to the 21,21-dimethoxy unit. A significant enhancement of the NH resonance at 2.2 ppm is observed.

spectrometry demonstrated that the molecular ion corresponded to the formula $C_{37}H_{42}N_3O_2$, compared to a molecular formula of $C_{35}H_{37}N_3$ for **4a**, and this indicated that an oxidative addition of 2 equiv of methanol had taken place. The proton NMR spectrum for this product showed several unusual features, in particular the presence of a strong 6H singlet at −1.3 ppm (Figure 1A). On the basis of the spectroscopic analyses (vide infra), the oxidation product was identified as the monoprotonated bridged benzo[18]annulene ketal **5a** (Scheme 1). The retention of a plane of symmetry could be deduced from both the proton and carbon-13 NMR spectra for **5a**. In particular, the carbon-13 NMR spectrum showed the presence of the expected 19 resonances, with 5 peaks between 11 and 20 ppm, the methoxy groups at 47.9 ppm, the ketal carbon at 96.9 ppm, and 12 sp^2 resonances in the range of 107−156 ppm. As previously mentioned, the proton NMR spectrum showed the presence of the methoxy substituents as an upfield singlet at −1.3 ppm, unambiguously placing these units within the shielding region for the porphyrinoid macrocycle. The retention of a powerful diamagnetic ring current was confirmed by the presence of two 2H singlets for the *meso*-protons at 9.7 and 10.9 ppm. It was also notable that the ring methyl groups gave a singlet at 3.6 ppm, while the methylene units gave two 4H quartets at 3.7 and 3.8 ppm, values that are comparable to those observed for the same substituents in regular porphyrins or carbaporphyrins such as **4**.[14] The benzo-protons closest to the porphyrinoid ring were downfield shifted from a value of 8.8 ppm in **4a** to 10.5 ppm in **5a**, a result that is consistent with the presence of an 18-π electron delocalization pathway that passes through the benzene ring (shown in bold, Scheme 1). A similar downfield shift is observed for the dications **6** (Chart 2) that can be derived from **4** in 50% TFA−$CDCl_3$ (these have the same type of 18-π electron delocalization pathway).[14,27] Finally, the NH protons of **5a** gave rise to a 2H resonance near 2.2 ppm. The integration confirms that two internal NH protons are present in the isolated product (i.e., that the monoprotonated cation had been isolated). However, the chemical shift for this resonance deserves further discussion. In the absence of any ring current effects, a

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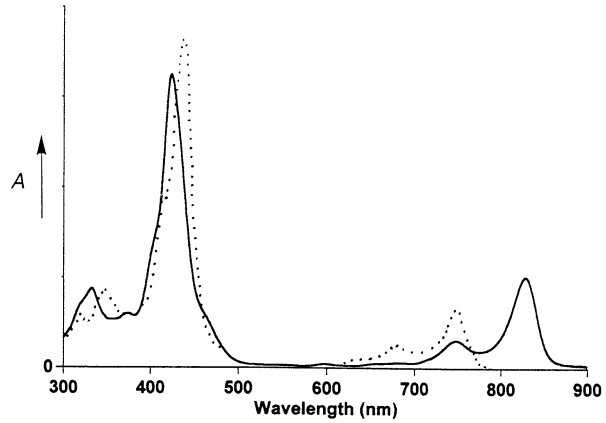
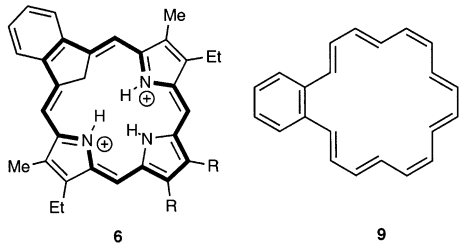


FIGURE 2. Electronic absorption spectra of **5a**: (a) in chloroform (bold line) and (b) dication in 5% TFA−chloroform (dotted line).

CHART 2



6

9

conjugated pyrrole cation NH would resonate at >10 ppm. Hence, the value observed results from opposing factors. While the diatropic ring current leads to an extensive upfield shift for the NH resonance, this is counteracted by the delocalized positive charge and the extensive opportunities for hydrogen bonding interactions that lead to strong downfield shifts. To further confirm the presence of two methoxy groups on the internal carbon, an nOe difference proton NMR study was carried out. Irradiation of the signal at −1.3 ppm resulted in a significant peak enhancement for the NH resonance at 2.2 ppm, confirming that the NH and methoxy protons are in close proximity to one another (Figure 1C). Irradiation of the 10.9-ppm resonance, which corresponds to the *meso*-protons flanking the indene unit, showed an enhancement to the benzo resonance at 10.5 ppm and the methyl signal at 3.6 ppm; in addition, a weak connection was observed to the internal methoxy units (Figure 1B). These data are in complete accord with the proposed structure. Combustion analysis also confirmed that **5a** had been isolated as a hydrochloride salt. Addition of TFA to the NMR tube showed the formation of a new species corresponding to the dication **7a**. The dication was also highly diatropic, showing the methoxy units at −1.0 ppm, while the benzo unit gave two 2H multiplets at 9.1 and 10.1 ppm and the *meso*-protons produced two downfield 2H singlets at 10.0 and 10.7 ppm.

The UV−vis spectrum for **5a** showed a strong Soret band at 422 nm, together with two characteristic absorptions in the far red at 751 and 832 nm (Figure 2). Porphyrinoid systems with long wavelength absorptions in this region are of particular current interest due to their potential value as photosensitizers in photodynamic therapy[28] and viral photoeradication,[29] as well as for a number of other diverse biomedicinal applications.[30] Addition of TFA again generated the dication **7a** and this also showed a strong Soret band (434 nm), as well as a far red absorption near 750 nm. Addition of triethylamine or DBU to solutions of **5a** appeared to lead to decomposition and the free base **8a** could not be observed either by UV−vis or NMR spectroscopy.

As the aromatic delocalization pathway in **5a** is similar to that of benzo[18]annulene (**9**; Chart 2),[31] some comparisons are warranted. The diatropic ring current in **9** is comparatively weak, the interior protons showing up near 5 ppm, and indeed the difference in chemical shifts ($\Delta\delta$) for the internal and external protons is only on the order of 3 ppm. This contrasts to the $\Delta\delta$ for the internal methoxy groups versus the *meso*-protons of >10 ppm (this actually underestimates the differences as the methoxy groups are only indirectly influenced by the diatropic ring current). The increased diatropicity is most likely due to the enhanced charge delocalization that is possible in the fully aromatic macrocycles and indeed this highly aromatic character was also observed for dications **6** for much the same reasons.[14]

Reaction of a chloroform solution of **4a** with saturated solutions of ferric chloride in absolute ethanol occurred more slowly (ca. 16 h under reflux), but again excellent yields of the diethoxy derivative **5b** were obtained. The slower reaction rate may be due to differences in the solubility of ferric chloride in ethanol vs methanol. The spectroscopic properties for **5b** were very similar to **5a**, although it is worth noting that, as expected, the ethoxy groups gave rise to two upfield resonances at −2.37 (6H triplet) and −1.40 ppm (4H quartet). In these studies, the "saturated" solutions were obtained by stirring the alcohol with an excess of ferric chloride. When the solutions were heated to ensure that the maximum amount of $FeCl_3$ had dissolved, and these mixtures used in the oxidation reactions, much poorer yields of **5a** or **5b** were obtained. Further oxidation apparently occurred in these reactions, as additional bands were observed in column chromatography (none of these could be characterized spectroscopically). Due to this complication, the reactions were performed with different amounts of ferric chloride; optimal results were obtained with 500 molar equiv of $FeCl_3$ compared to carbaporphyrin **4a**. Dichloromethane and 1,2-dichloroethane were also found to be suitable cosolvents for these reactions.

The far red absorptions observed for the ketal products **5** could lead to applications and this led us to consider the generality of this chemistry. In principle, other alcohols could be used in these oxidations to produce a variety of products and this would allow the physical properties to be modulated (e.g., the water solubility of the ketals could be enhanced for biological applications). With this in mind, carbaporphyrin **4a** in CH_2Cl_2 was heated with solutions of $FeCl_3$ (500 equiv) in various

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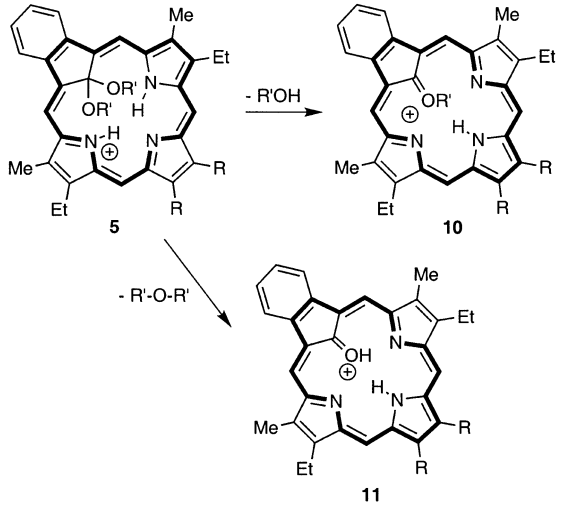
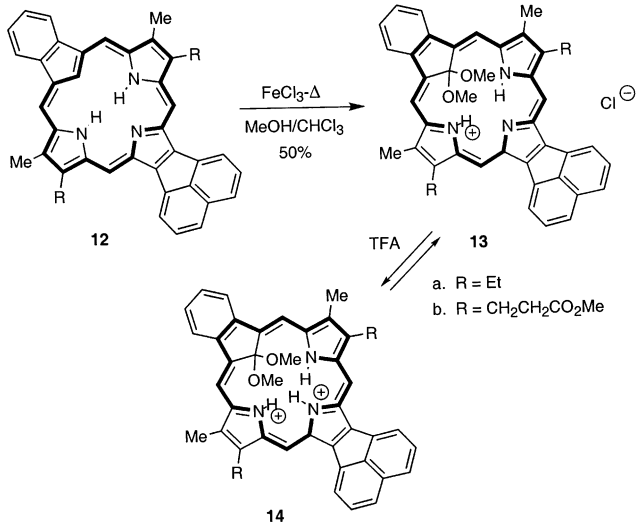
SCHEME 2. Fragmentation Pathways in the EI and FAB Mass Spectra for Ketals 5



SCHEME 3



alcohols. Isopropyl alcohol gave good yields of the diisopropoxy derivative **5c**, while ethylene glycol gave excellent yields of the bis(2-hydroxyethyl) ketal **5d**. However, *tert*-butyl alcohol failed to give any of the corresponding ketal, indicating that the *tert*-butoxy grouping is too sterically demanding to allow this chemistry. In an attempt to introduce chiral moieties at the internal carbon center, menthol and perillyl alcohol were investigated as reagents, but again no product was observed in either case. Diphenylcarbaporphyrin **4b** was reacted with 500 equiv of $FeCl_3$ in MeOH−CH_2Cl_2 and EtOH−CH_2Cl_2, and this also gave the corresponding *gem*-dimethoxy and *gem*-diethoxy derivatives **5e** and **5f**, respectively. Ketals **5c**, **5d**, **5e**, and **5f** gave similar spectroscopic properties to **5a**,**b**. However, unlike **5a**,**b**, solutions of **5c**−**f** showed the reversible formation of a new chromophore in the presence of 5% DBU. This was assigned to the free base forms **8c**−**f**. Even in these cases, solutions of these ketals in 5% DBU or 5% Et_3N degraded on standing. The UV−vis spectra showed broad, less intense absorptions that no longer resembled porphyrinoid systems. For instance, solutions of **5c** in 5% DBU−$CHCl_3$ gave absorption bands at 390 (log ϵ = 4.63) and 550 nm (log ϵ = 4.16). These data suggest that the free base forms more closely resemble benzo[18]annulene, although proton NMR data could not be obtained for the nonprotonated species.

The electron impact MS spectra for ketals **5** are also worthy of note. The parent molecular ion undergoes two principal fragmentation pathways: loss of a molecule of alcohol to give the cation **10**, or elimination of the dialkyl ether unit to produce the protonated ketone **11** (Scheme 2). Similar fragmentations were also observed for FAB MS.

Fusion of acenaphthylene rings to porphyrinoid systems has been shown to induce substantial bathochromic shifts,[32−34] and it was therefore of some interest to see whether the "acenaphthylene effect"[34] is observed for the benzo[18]annulene ketal series. Reaction of acenaphthobenzocarbaporphyrins **12**[14] with $FeCl_3$ in MeOH−$CHCl_3$ gave moderate yields of the corresponding ketals **13** (Scheme 3). Difficulties were obtained in isolating pure samples of these products, which appeared to be significantly less stable than ketals **5**, but this was accomplished for the diester **12b**. The resulting ketal **13b** gave a Soret band at 475 nm (log ϵ = 5.24), and the longer wavelength band appeared at 833 nm; this compares to values of 422 and 832 nm for **5a**. Addition of TFA gave the dication **14b** and this gave major absorptions at 492 and 781 nm, compared to 434 and 749 nm, respectively, in the case of dication **7a**. Hence, pronounced additional shifts are observed particularly in the Soret band region. However, given the difficulties encountered this effect did not warrant further study.

Ferric chloride is a common oxidation agent, and has recently been found to have valuable applications in porphyrin analogue chemistry.[35,36] However, the high degree of selectivity observed in these oxidation reactions is somewhat remarkable. We propose the mechanism detailed in Scheme 4 to account for this chemistry. Ferric chloride would carry out a stepwise removal of 2 electrons from **4** to give the dication **15**. Although **15a** formally possesses antiaromatic character, the canonical form **15b** is essentially a benzo[18]annulene and a preference for this contributor could explain why a regioselective attack by alcohol occurs at the internal carbon to give **16**. Tautomerization would afford the resonance-stabilized cation **17** and subsequent nucleophilic attack would then generate the ketal **18**. This species is potentially antiaromatic, but two additional one-electron oxidations would afford the observed aromatic ketals **5**.

We speculated that reactions of carbaporphyrin **4a** with aqueous ferric chloride would give the related *gem*-diol **19** or the related ketone (Scheme 5). However, reaction of **4a** in chloroform or dichloromethane with aqueous solutions of $FeCl_3$ for 1−3 h gave a totally different product that closely resembled the carbaporphyrin precursor in 84% yield. The proton NMR spectrum

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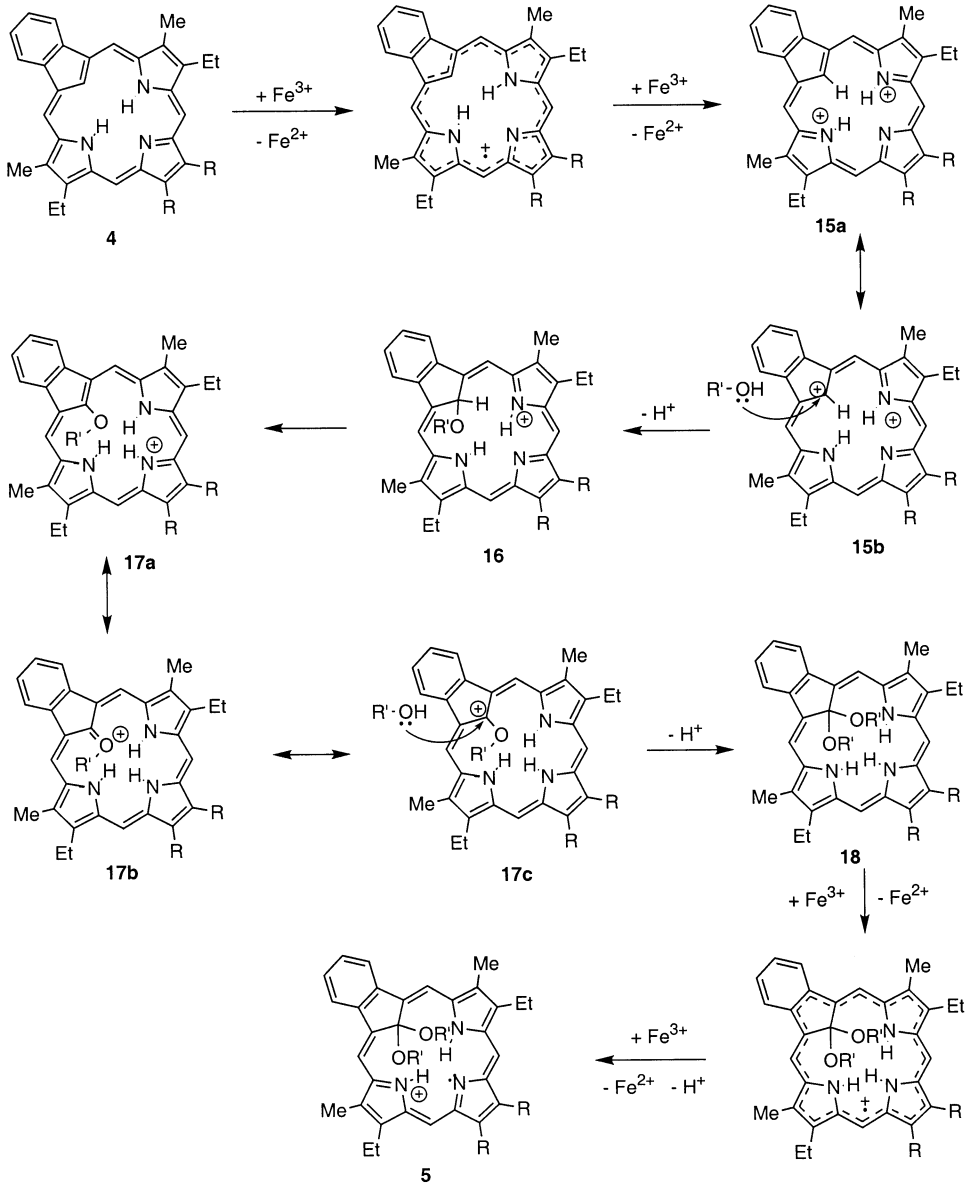
SCHEME 4



for the new compound showed most of the resonances for the parent carbaporphyrin system, but the signal for the inner CH near −7 ppm in **4a** was no longer present. The proton NMR spectrum showed two 2H singlets at 9.75 and 9.91 ppm corresponding to the *meso*-protons, while the porphyrinoid methyl substituents resonated as a 6H singlet at 3.62 ppm. This compares to values of 9.82, 10.10, and 3.68 ppm, respectively, that have previously been reported for **4a**. These values do not significantly differ from one another and this indicates that the product retains diatropic carbaporphyrin characteristics. In addition, proton and carbon-13 NMR spectroscopy demonstrate that the macrocycle still possesses a plane of symmetry. The carbon-13 NMR spectrum in $CDCl_3$ shows the presence of 5 resonances between 11 and 20 ppm for the peripheral substituents, two resonances for the *meso*-carbons at 96.1 and 100.2 ppm, a weak quaternary carbon resonance for C21 at 108 ppm, and 10 additional sp^2 peaks between 120 and 155 ppm. High-resolution EI MS showed that the porphyrinoid has the molecular formula $C_{35}H_{36}ClN_3$, although the classic isotope pattern for chlorine was obscured due to the presence of M^+ and $[M + 1]^+$ peaks. These data unambiguously confirm that the unexpected product is the 21-chlorinated carbaporphyrin **20** (Scheme 5).[37] Hence, a regioselective chlorination reaction has occurred. Although the presence of an internal chlorine atom would be expected to distort the carbaporphyrin ring, the NMR data indicate that the macrocyclic ring current is only slightly diminished.

Further confirmation of the structure of **20** was obtained by single-crystal X-ray diffraction analysis. The macrocycle's tripyrrolic subunit is essentially planar as evidenced by the minimal pyrrole to mean [18]annulene plane tilts of 2.1(1)°, 1.5(1)°, and 5.8(1)°; however, the molecular structure's (Figure 3) most striking feature is

(37) Substitution of NCPs on the interior carbon has also been reported. For example, nitration of TPNCP occurred at C21: Ishikawa, Y.; Yoshida, I.; Akaiwa, K.; Koguchi, E.; Sasaki, T.; Furuta, H. *Chem. Lett.* **1997**, 453.

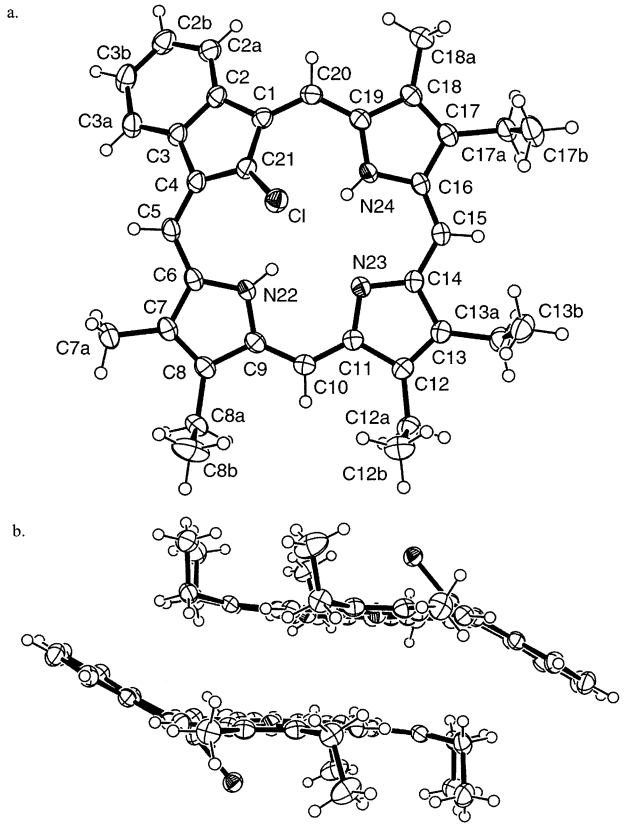
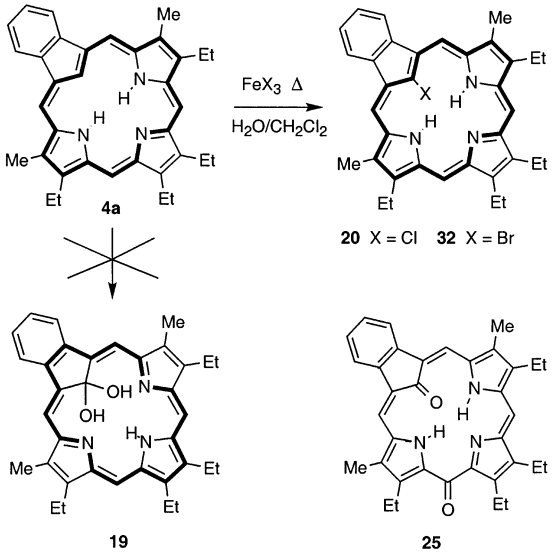


FIGURE 3. Carbaporphyrin **20** showing the atom labeling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 50% probability level. Hydrogen atoms have been drawn arbitrarily small and are not labeled. (a) View perpendicular to the [18]annulene macrocyclic ring. (b) "Side" view showing π-stacked pairs of **20** and illustrating the tilt of the indene units relative to the macrocyclic ring.

SCHEME 5



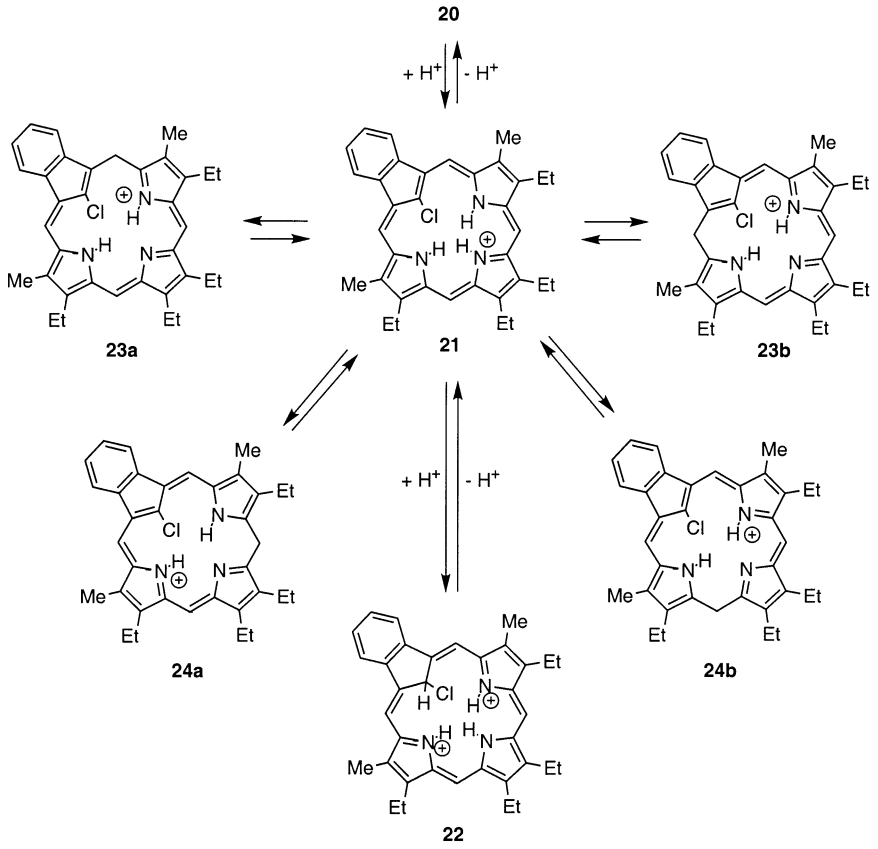
the 29.59(4)° rotation of the indene unit out of the mean [18]annulene plane. This is clearly attributable to the steric requirements of the chlorine atom attached to C21. This contrasts with the closely related free-base benzocarbaporphyrin **4b** which, possessing the smaller hydrogen atom attached to C21, displays a substantially smaller 15.5° rotation of the indene unit out of the mean macrocyclic plane.[14] The chlorine in **20** is forced out of the central cavity due to the van der Waals contact with the two *cis*-pyrrolic hydrogen atoms and lies 2.1382(5) Å from the [18]annulene centroid. The respective Cl−H22 and Cl−H24 distances are 2.54(2) and 2.52(2) Å. The remaining structural parameters are as expected and in close agreement with those observed for **4b**.[14] All C−N bond distances are equivalent with an average length equal to 1.368(3) Å. The C(6)−N(22)−C(9) and C(16)−N(24)−C(19) bond angles, 111.1(2)° and 111.4(2)°, respectively, are similarly equivalent; however, the 104.8(2)° C(11)−N(23)−C(14) bond angle is significantly compressed and may be attributed to the presence of the nonbonding lone pair of electrons on N(23). The chlorinated indene exhibits a 1.742 Å C(21)−Cl bond distance and respective C(1)−C(21)−Cl and C(4)−C(21)−Cl angles equal to 122.5(2)° and 122.4(2)°. The 112.4(2)° C(1)−C(21)−C(4) bond angle is particularly noteworthy. It is the largest internal five-membered ring angle in the structure by a degree and several degrees larger than the internal five-membered C−C−C ring angles, which range between 105.1(2)° and 108.4(2)° with a 107(1)° average. Compound **4b** similarly displayed an enhanced 111.2(3)° C(1)−C(21)−C(4) bond angle.[14] We reasoned that this distortion helps to minimize indene tilt by creating slightly more room in the cavity; this in turn helps to maintain the [18]annulene aromaticity through C21. As the number of structurally characterized carbaporphyrins grows, it may be possible to further substantiate this hypothesis.

The packing of structure **20** (Figure 3b) is also noteworthy in that offset face-to-face π-stacking interactions are observed, linking the molecules into dimers with an interplane separation of 3.27(1) Å and a centroid⋯centroid distance of 4.3334(2) Å (corresponding to an intermolecular lateral displacement of ca. 2.84 Å parallel to the C(21),N(23)-axis). The two molecules are related by a pseudoinversion center and crystallographically by 2-X, 2-Y, 2-Z. The strongest intermolecular contacts (less than 3.5 Å) involve atoms N(22), N(24), C(8), C(9), C(10), C(14), C(15), and C(16) with the shortest interaction, N(22)−C(14), being 3.270(3) Å and orthogonal to the macrocyclic planes. Even with the substantial rotation of the indene out of the macrocyclic plane, the π-stacking interactions are remarkably similar to the typical π-stacking observed in 5,15-diphenylporphyrin.[38]

The UV−vis spectrum of **20** in chloroform shows a Soret band at 434 nm and a series of Q-bands at 521, 560, 608, and 665 nm. This compares to values of 423, 510, 544, 604, and 662 nm, respectively, for **4a**. Small bathochromic shifts of this type are to be expected when a porphyrin-like macrocycle is distorted away from planarity.[39] Addition of TFA gave rise to a new species with Soret bands at 409 and 435 nm, and this was assigned to the monocation **21** (Scheme 6). In 50% TFA−$CHCl_3$, C-protonation leads to the aromatic dication **22** (Scheme 6) with a single Soret band at 437 nm and a moderately strong absorption at 730 nm. These species could also be identified by NMR spectroscopy. The NMR

(38) Bond, A. D.; Feeder, N.; Redman, J. E.; Teat, S. J.; Sanders, J. K. M. *Cryst. Growth Des.* **2002**, *2*, 27.
(39) Shelnutt, J. A.; Song, X.-Z.; Ma, J.-G.; Jai, S.-L.; Jentzen, W.; Medforth, C. J. *Chem. Soc. Rev.* **1998**, *27*, 31.

SCHEME 6

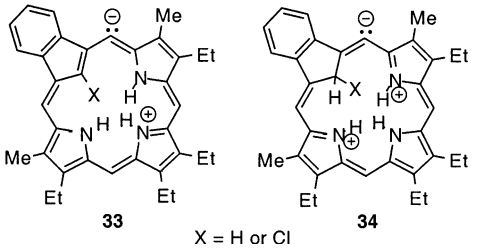


spectrum of **20** in trace TFA−$CDCl_3$ showed three internal NH protons at −5.2 (1H) and −3.4 (2H) ppm, while the *meso*-protons gave rise to two 2H singlets at 9.9 and 10.0 ppm. These data imply a slight enhancement of the diatropic ring current, although the porphyrinoid methyl groups are shifted slightly upfield to 3.5 ppm. The CH_2 component for the ethyl groups produced a complex multiplet, indicating that the methylene protons are diastereotopic, and presumably the conformation of **21** is chiral due to the crowding of the internal substituents. In 50% TFA−$CDCl_3$, the dication **22** showed a strong ring current with the *meso*-protons further downfield at 10.2 and 10.7 ppm. As had been previously observed for the C-protonated dications **6**, the benzo-protons closest to the porphyrinoid ring (2^1,3^1) were strongly downfield shifted to 10.1 ppm, while the remaining 2^2,3^2 protons resonated at 9.05 ppm. These values confirm that the 18-π electron delocalization pathway has been relocated through the benzene ring, as is also the case for ketals **5**. The internal CH is observed upfield at −2.2 ppm, despite the presence of an attached chlorine atom. Further supportive data for **21** were obtained by carbon-13 NMR spectroscopy. However, the carbon-13 spectrum for **22** was not obtained as solutions of the chlorocarbaporphyrin in 50% TFA−$CDCl_3$ proved to be rather unstable and underwent extensive decomposition over the period of several hours.

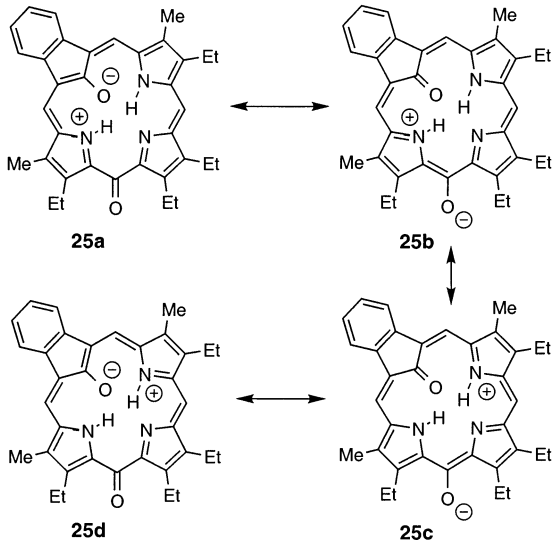
Addition of several drops of deuterated TFA to a solution of **20** in $CDCl_3$ gave a spectrum that primarily corresponded to the monocation **21**. Although the NH protons had obviously undergone deuterium exchange, the rest of the spectrum was unaltered. However, on standing at room temperature for several days, the intensity of the *meso*-proton resonances was significantly reduced. This may be due to the presence of minor C-protonated cations **23** and **24** in equilibrium with the major protonated species (Scheme 6).[40] Similar deuterium exchange processes were previously reported for benzocarbaporphyrins **4**.

When the reaction of **4a** in dichloromethane with aqueous ferric chloride was carried out for 16 h, the yield of **20** was much reduced and a more polar green fraction eluted from the alumina chromatography column. Recrystallization from chloroform−methanol gave the new oxidation product as dark crystals in 22% yield. High-resolution EI MS gave a molecular formula of $C_{35}H_{35}N_3O_2$, demonstrating that the product had incorporated two oxygens while retaining all of the original carbons and

(40) It is conceivable that zwitterionic species such as **33** and **34** (below) are involved in these exchange processes, although C-protonation of the type depicted in Scheme 6 is well established for porphyrinoid systems. For example, see: (a) Jackson, A. H.; Kenner, G. W.; Smith, K. M. *J. Chem. Soc. (C)* **1968**, 294. (b) Lash, T. D.; Armiger, Y. L. S.-T. *J. Heterocycl. Chem.* **1991**, *28*, 965.



SCHEME 7. Dipolar Resonance Contributors for Dione 25



nitrogens. The UV−vis spectrum in chloroform showed broad absorptions at 381 and 609 nm that were not consistent with a porphyrin-like electronic structure. Proton NMR spectroscopy confirmed that the compound was nonaromatic. Three 1H *meso*-proton resonances were observed between 6.9 and 7.2 ppm, values that resemble those reported for acyclic tetrapyrrolic compounds such as a,c-biladienes.[41] In addition, two NH protons were noted as broad 1H singlets at 14.3 and 14.6 ppm. These values not only confirm the absence of a diatropic ring current but also suggest that these protons are in a strongly hydrogen bonding environment. The benzo unit was apparently intact and gave two 2H multiplets at 7.4 and 7.7 ppm. Proton and carbon-13 NMR spectra also showed that the macrocycle has lost its plane of symmetry. The carbon-13 NMR spectrum in TFA−$CDCl_3$ gave 10 resonances between 9 and 19 ppm for the alkyl substituents and 22 peaks for sp^2 carbons between 115 and 152 ppm. In addition, two apparent carbonyl resonances were observed at 173.6 and 197.6 ppm. It was clear from these data that one of the *meso*-carbon bridges had been oxidized to a ketone, and the internal carbon has also undergone a conversion to a carbonyl moiety. These data were consistent with structure **25** (Scheme 5). The keto-bridge cannot be adjacent to the benzo-ring as this would result in a downfield shift of one of the benzene protons. The IR spectrum of **25** showed two low-frequency C=O absorptions at 1574 and 1591 cm^{-1}, as would be expected for carbonyl groups of this type with extensive vinylogous amide characteristics that result in the type of dipolar canonical forms depicted in Scheme 7.[42]

The formation of these products can be rationalized by the mechanism detailed in Scheme 8. Dication **15b** had been postulated as a key intermediate in the formation of ketals **5** (Scheme 4). Nucleophilic attack by chloride would afford **26** and upon loss of a proton this would give the observed chlorocarbaporphyrin **20** (Scheme 8). Although the formation of **20** superficially resembles an electrophilic substitution, the reaction instead involves an oxidative nucleophilic chlorination mechanism. Nucleophilic attack of **15b** by water would lead to the hydroxy cation **27** and this species could delocalize the positive charge through a series of resonance contributors. Further regioselective nucleophilic attack, presumably controlled by steric considerations, would generate a hydroxycarbaphlorin **28**. Two 1-electron oxidations and a deprotonation would afford the diol **29**. Tautomerization and loss of a proton could then yield the oxophlorin **30**, and this could undergo two further 1-electron oxidations to produce, following the loss of two protons, the hydroxyketone **31**. This would undergo a final keto−enol tautomerization to generate the porphyrinoid dione **25**.

Carbaporphyrin **4a** in dichloromethane was also reacted with aqueous ferric bromide and the 21-bromocarbaporphyrin **32** was isolated in 7% yield. Although the result is not synthetically useful, the formation of **32** shows that the chemistry can in principle be extended to other reagents. It is worth noting that the diatropic ring current is not significantly altered by the presence of an internal bromine atom, although the indene ring is likely to be further tilted from the macrocyclic plane to accommodate this bulky moiety.

Conclusions

Benzocarbaporphyrins undergo unique oxidations with ferric chloride in the presence of alcohol solvents to give aromatic ketals that are structurally related to benzo[18]annulene. These show strong absorptions in the far red that could lead to applications in photodynamic therapy. In addition, the versatility of this chemistry allows ketals to be prepared from a variety of alcohols and this provides the means by which the physical properties (e.g., polarity, water solubility) of these molecules can be fine-tuned. Reaction of carbaporphyrin **4a** with aqueous ferric chloride gave good yields of the 21-chloro derivative via an oxidative mechanism, but prolonged reaction times led to further oxidation to produce a nonaromatic dione. These results demonstrate that carbaporphyrins have unique chemical reactivity that can lead to the synthesis of potentially valuable derivatives.

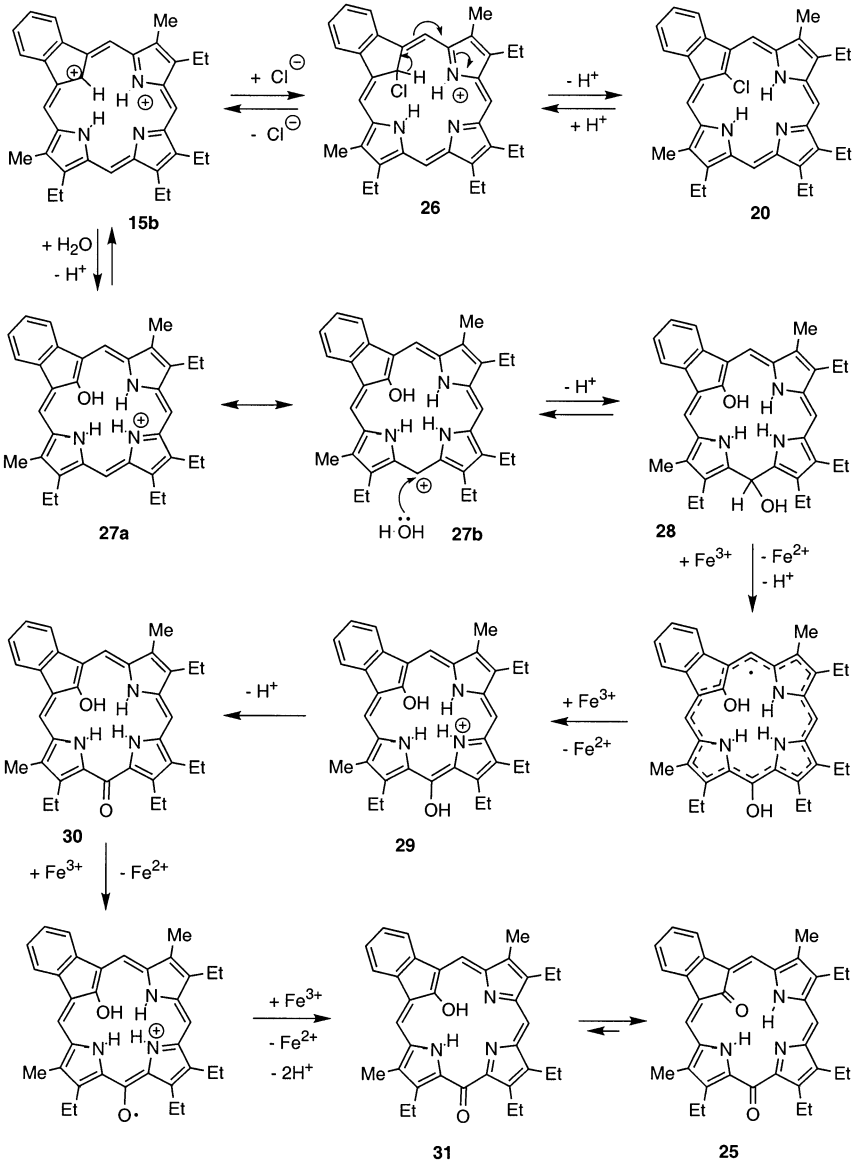
Experimental Section

Carbaporphyrins **4a**, **4b**, and **12** were prepared as described previously.[12,14] Chromatography was performed with Grade 3 neutral alumina or 70−230 mesh silica gel.

8,17-Diethyl-21,22-dihydro-21,21-dimethoxy-7,18-dimethyl-12,13-diphenylbenzo[*b*]-21-carbaporphyrin Hydrochloride (5e). A solution of ferric chloride (3.20 g, 19.7 mmol) in methanol (10 mL) was added to a solution of benzocarbaporphyrin **4b** (20 mg, 0.033 mmol) in dichloromethane (10 mL) and the resulting mixture was heated under reflux for 1 h. The solution was diluted with CH_2Cl_2, washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade III alumina eluting with chloroform and the starting material was collected as a brown fraction. Once the carbaporphyrin fraction had eluted, the column was eluted with 10% methanol/chloroform. Two additional bands moved down the column. The first was a deep blue band, while the second eluted as a green fraction. When the blue fraction was washed with 2 M HCl it turned into a deep green solution that matched the second band. The two fractions were combined, and the solvent was removed under

(41) E.g.: Lash, T. D.; Hall, T.; Mani, U. N.; Jones, M. A. *J. Org. Chem.* **2001**, *66*, 3753.
(42) E.g.: (a) Lash, T. D.; Motta, Y. G. *Heterocycles* **1983**, *20*, 2343. (b) Lash, T. D. *J. Org. Chem.* **1992**, *57*, 4312.

SCHEME 8



reduced pressure. Recrystallization from chloroform/hexanes gave the ketal hydrochloride as green crystals (18 mg, 0.026 mmol, 79%), mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 440 (5.10), 528 (3.69), 566 (3.73), 733 (3.90), 810 (4.40); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 466 (5.18), 613 (3.92), 673 (4.01), 739 (4.31); UV−vis (10% DBU−$CHCl_3$) λ_{max} (log ϵ) 393, 567 nm; ^{1}H NMR ($CDCl_3$/CD_3OD) δ −1.47 (6H, s), 1.32 (6H, t, J = 7.6 Hz), 3.08 (6H, s), 3.29 (4H, q, J = 7.7 Hz), 7.18−7.25 (6H, m), 7.36 (4H, d, J = 6.8 Hz), 8.51−8.54 (2H, m), 9.28 (2H, s), 9.75−7.78 (2H, m), 10.27 (2H, s); ^{1}H NMR (TFA−$CDCl_3$−CD_3-OD) δ −1.44 (6H, s), 1.35 (6H, t, J = 7.8 Hz), 3.10 (6H, s), 3.32 (4H, q, J = 7.7 Hz), 7.20−7.29 (6H, m), 7.39 (4H, d, J = 7.2 Hz), 8.53−8.56 (2H, m), 9.31 (2H, s), 9.76−9.80 (2H, m), 10.27 (2H, s); ^{13}C NMR ($CDCl_3$/CD_3OD) δ 9.9, 16.0, 18.7, 47.3, 97.7, 106.6, 116.7, 123.0, 127.5, 128.2, 131.3, 132.5, 134.0, 134.1, 135.3, 138.4, 138.8, 143.3, 146.1, 146.4, 153.5; EI MS m/z (% rel intensity) 625 (73; $[M - OMe]^+$), 610 (100; $[M - C_2H_6O]^+$); FAB MS m/z (% rel intensity) 656 (5.3), 626 (12), 610 (5.2); HRMS (FAB) m/z calcd for $[C_{45}H_{42}N_3O_2]^+$ 656.3277, found 656.3278.

21,21-Diethoxy-8,17-diethyl-21,22-dihydro-7,18-dimethyl-12,13-diphenylbenzo[*b*]-21-carbaporphyrin Hydrochloride (5f). Benzocarbaporphyrin **4b** (20 mg, 0.033 mmol) in dichloromethane (10 mL) was added to a solution of ferric chloride (3.15 g, 19.4 mmol) in ethanol (10 mL) and the mixture was stirred under reflux for 1 h. The solution was diluted with dichloromethane, washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade III alumina eluting with chloroform, and the residual starting material was collected as a brown fraction. The column was then eluted with 10% methanol/chloroform. Two additional bands, the first blue and the second green, moved down the column. The blue band, when washed with 2 M HCl, turned a deep green color and matched the second band. These two fractions were combined and the solvent was removed under reduced pressure. Recrystallization from chloroform−hexanes gave **5f** (10 mg, 0.014 mmol, 42%) as green crystals, mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 439 (5.20), 593 (3.41), 668 (3.39), 731 (4.06), 807 nm (4.60); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 448 (5.19), 673 (4.00), 738 (4.35); UV−vis (5% DBU−$CHCl_3$) λ_{max} (log ϵ) 396 (4.61), 570 nm (4.21); ^{1}H NMR ($CDCl_3$) δ −2.18 (6H, t, J = 6.8 Hz), −1.16 (4H, q, J = 6.8 Hz), 1.71 (6H, t, J = 7.8 Hz), 2.88 (2H, s), 3.57 (6H, s), 3.63 (4H, q, J = 7.6 Hz), 7.58 (2H, t, J = 7.2 Hz), 7.65 (4H, t, J = 7.4 Hz), 7.80 (4H, d, J = 7.2 Hz), 9.00−9.04 (2H, m), 9.59 (2H, s), 10.40−10.44 (2H, d, m), 10.76 (2H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −1.94 (6H, br), −0.70 (4H, br), 1.65 (6H, t, J = 7 Hz), 2.80 (2H, br s), 3.34 (6H, s), 3.61 (4H,

q, J = 6.8 Hz), 7.74 (6H, br m), 7.81 (4H, br m), 9.00−9.05 (2H, m), 9.8 (2H, s), 10.04−10.08 (2H, m), 10.62 (2H, s); ^{13}C NMR ($CDCl_3$) δ 12.0, 12.3, 17.1, 19.6, 57.1, 95.6, 107.9, 116.7, 125.1, 128.1, 128.9, 132.1, 133.5, 134.9, 135.7, 139.4, 140.7, 144.6, 146.2, 146.4, 153.6; EI MS m/z (% rel intensity) 639 (33; $[M - OEt]^+$), 610 (100; $[M - C_4H_{10}O]^+$); FAB MS m/z (% rel intensity) 684 (53), 639 (47), 610 (53); HRMS (FAB) m/z calcd for $[C_{47}H_{46}N_3O_2]^+$ 684.3590, found 684.3591.

8,12,13,17-Tetraethyl-21,22-dihydro-21,21-dimethoxy-7,18-dimethylbenzo[*b*]-21-carbaporphyrin Hydrochloride (5a). Benzocarbaporphyrin **4a** (21 mg, 0.042 mmol) in chloroform (15 mL) was refluxed with a saturated solution of ferric chloride in methanol (10 mL) for 1 h. The mixture was diluted with equal volumes of chloroform and water. The organic layer was separated and washed with water to remove traces of ferric chloride. The solution was concentrated under reduced pressure and chromatographed on Grade 3 alumina eluting with 1% MeOH−$CHCl_3$. Recrystallization from chloroform−hexane gave the dimethyl ketal **5a** (23.5 mg, 0.0394 mmol, 94%) as green crystals, mp 145−147 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 372 (4.40), 422 (5.06), 751 (4.05), 832 nm (4.55); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 415 (sh) (4.84), 434 (5.12), 633 (3.59), 683 (4.00), 748 (4.39); ^{1}H NMR ($CDCl_3$) δ −1.34 (6H, s), 1.75−1.85 (12H, 2 overlapping triplets), 2.15 (2H, br s), 3.60 (6H, s), 3.68 (4H, q, J = 7.5 Hz), 3.83 (4H, q, J = 7.5 Hz), 8.91−8.95 (2H, m), 9.68 (2H, s), 10.47−10.50 (2H, m), 10.93 (2H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −0.96 (6H, s), 1.76−1.82 (12H, 2 overlapping triplets), 2.11 (3H, br s), 3.38 (6H, s), 3.79 (4H, q, J = 7.5 Hz), 3.87 (4H, q, J = 7.5 Hz), 9.02−9.05 (2H, m), 9.99 (2H, s), 10.05−10.09 (2H, m), 10.64 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.7, 17.3, 18.4, 19.5, 19.6, 47.9, 96.9, 107.4, 112.8, 124.6, 133.2, 135.3, 135.9, 138.6, 139.6, 143.8, 146.0, 147.1, 155.7; FAB MS m/z (% rel intensity) 560 (44; M^+), 529 (100; $[M - OMe]^+$), 514 (60; $[M - C_2H_6O]^+$); HRMS (FAB) m/z calcd for $[C_{37}H_{41}N_3O_2]^+$ 560.3277, found 560.3276. Anal. Calcd for $C_{37}H_{42}ClN_3O_2 \cdot {}^1/_{10}CHCl_3$: C, 73.27; H, 6.98; N, 6.91. Found: C, 73.61; H, 7.02; N, 6.97. This compound consistently analyzed as a partial chloroform solvate even after prolonged drying in a vacuum oven.

21,21-Diethoxy-8,12,13,17-tetraethyl-21,22-dihydro-7,-18-dimethylbenzo[*b*]-21-carbaporphyrin Hydrochloride (5b). The title compound was prepared by the same procedure as **5a** from benzocarbaporphyrin **4a** (21 mg, 0.042 mmol), $CHCl_3$ (15 mL), and EtOH (10 mL) saturated with ferric chloride, although the reflux was carried out for 16 h in this case. Recrystallization from $CHCl_3$−hexane gave the diethoxy compound **5b** (23 mg, 0.037 mmol, 88%) as green crystals, mp 149−151 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 373 (4.45), 422 (5.08), 748 (4.06), 827 nm (4.56); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 416 (sh) (4.86), 436 (5.11), 626 (3.70), 680 (3.97), 748 (4.35); ^{1}H NMR ($CDCl_3$) δ −2.35 (6H, t, J = 6.1 Hz), −1.37 (4H, q, J = 6.1 Hz), 1.77−1.85 (12H, 2 overlapping triplets), 2.41 (2H, br s), 3.59 (6H, s), 3.68 (4H, q, J = 7.7 Hz), 3.83 (4H, q, J = 7.5 Hz), 8.90 (2H, br m), 9.64 (2H, s), 10.47 (2H, br m), 10.90 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.4, 11.7, 17.3, 18.3, 19.5, 19.6, 56.4, 95.3, 107.1, 112.6, 124.5, 133.1, 134.9, 135.5, 139.3, 139.8, 143.8, 145.7, 146.8, 155.7; EI MS m/z (% rel intensity) 541 (32), 514 (97; $[M - C_4H_{10}O]^+$), 512 (100); FAB MS m/z (% rel intensity) 588 (5), 543 (62), 514 (62; $[M - C_4H_{10}O]^+$); HRMS (FAB) m/z calcd for $[C_{39}H_{46}N_3O_2]^+$ 588.3590, found 588.3592. Anal. Calcd for $C_{39}H_{46}ClN_3O_2$: C, 75.04; H, 7.43; N, 6.73. Found: C, 74.80; H, 7.49; N, 6.60.

8,12,13,17-Tetraethyl-21,22-dihydro-21,21-diisopropoxy-7,18-dimethylbenzo[*b*]-21-carbaporphyrin Hydrochloride (5c). Benzocarbaporphyrin **4a** (20 mg, 0.040 mmol) was stirred under reflux in dichloromethane (10 mL) with a solution of ferric chloride (3.30 g, 20.3 mmol) in 2-propanol (10 mL) for 3 h. The solution was diluted with dichloromethane and washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade III alumina eluting with chloroform, and the starting material was collected as a brown fraction. After collection of the starting material, the column was eluted with 10% methanol/chloroform and a deep green band was collected. Recrystallization from chloroform−hexanes afforded the product **5c** as an HCl salt (15 mg, 0.023 mmol, 58%) as dark green crystals, mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 425 (5.03), 751 (4.02), 833 nm (4.56); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 438 (5.06), 685 (4.00), 752 (4.38); UV−vis (5% DBU−$CHCl_3$) λ_{max} (log ϵ) 390 (4.63), 550 nm (4.16); ^{1}H NMR ($CDCl_3$) δ −2.37 (12H, d, J = 6.0 Hz), −1.30 (2H, m), 1.79 (12H, t, J = 7.4 Hz), 2.54 (2H, s), 3.54 (6H, s), 3.67 (4H, q, J = 7.6 Hz), 3.81 (4H, q, J = 7.2 Hz), 8.93 (2H, br m), 9.61 (2H, s), 10.42 (2H, br m), 10.83 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.9, 17.6, 18.5, 19.5, 19.6, 19.7, 64.4, 94.9, 107.8, 112.6, 124.7, 133.2, 134.4, 135.4, 139.1, 141.6, 143.9, 145.6, 146.7, 155.5; EI MS m/z (% rel intensity) 557 (13; $[M - C_3H_7O]^+$), 555 (15), 514 (83; $[M - C_6H_{14}O]^+$), 512 (100); FAB MS m/z (% rel intensity) 616 (5; M^+), 558 (90; $[M - C_3H_6O]^+$), 515 (100; $[M - C_6H_{13}O]^+$); HRMS (FAB) m/z calcd for $[C_{41}H_{50}N_3O_2]^+$ 616.3903, found 616.3920.

8,12,13,17-Tetraethyl-21,22-dihydro-21,21-bis(2-hydroxyethoxy)-7,18-dimethylbenzo[*b*]-21-carbaporphyrin Hydrochloride (5d). A solution of benzocarbaporphyrin **4a** (25 mg, 0.050 mmol) in dichloromethane (10 mL) and a solution of ferric chloride (3.12 g, 19.2 mmol) in ethylene glycol (10 mL) was stirred under reflux for 3 h. The solution was diluted with dichloromethane, washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade III alumina eluting with chloroform and a small amount of starting material was collected as a brown fraction. The column was then eluted with 10% methanol−chloroform, and a deep green band was collected. Recrystallization from chloroform−hexanes afforded **5d** (27 mg, 0.041 mmol, 82%) as shiny blue-green crystals, mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 424 (5.04), 745 (4.04), 824 nm (4.55); UV−vis (10% DBU−$CHCl_3$) λ_{max} (log ϵ) 391 (4.75), 556 (4.08), 684 (3.65); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 435 (5.21), 683 (4.01), 749 (4.39); ^{1}H NMR ($CDCl_3$) δ −1.26 (4H, br), −0.62 (2H, br s), 0.17 (4H, br), 1.77 (6H, t, J = 7.8 Hz), 1.81 (6H, t, J = 7.8 Hz), 2.27 (2H, br s), 3.48 (6H, s), 3.65 (4H, q, J = 7.6 Hz), 3.79 (4H, q, J = 7.6 Hz), 8.80−8.84 (2H, m), 9.68 (2H, s), 10.12−10.16 (2H, m), 10.64 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.6, 17.4, 18.4, 19.7, 19.8, 56.9, 61.9, 95.6, 107.2, 113.2, 124.0, 132.9, 134.8, 135.7, 138.2, 138.9, 143.7, 146.3, 147.6, 156.0; FAB MS m/z (% rel intensity) 621 (10), 620 (5.4; M^+), 561 (34), 560 (93), 559 (92), 558 (20; $[M - C_2H_6O_2]^+$), 516 (30), 515 (78), 514 (100; $[M - C_4H_{10}O_3]^+$); ESI MS: m/z (% rel intensity) 621.3 (7), 620.3 (17; M^+), 561.3 (4), 560.3 (100), 558 (12); HRMS (FAB) m/z calcd for $[C_{39}H_{47}N_3O_4]^+$ 621.3566, found 621.3565. Anal. Calcd for $C_{39}H_{46}ClN_3O_4 \cdot {}^7/_8CHCl_3$: C, 62.96; H, 6.21; N, 5.52. Found: C, 63.12; H, 6.28; N, 5.51.

21,22-Dihydro-21,21-dimethoxy-8,17-bis(2-methoxycarbonylethyl)-7,18-dimethylacenaphtho[*l*]benzo[*b*]-21-carbaporphyrin Hydrochloride (13b). Acenaphthocarbaporphyrin **12b** (11 mg, 0.016 mmol) in chloroform (10 mL) was refluxed with a saturated solution of ferric chloride in methanol (5 mL) for 1 h. The mixture was diluted with equal volumes of chloroform and water. The organic layer was separated and washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on a Grade 3 alumina column eluting initially with dichloromethane and then 7.5% MeOH−CH_2Cl_2. Recrystallization from chloroform−hexane gave the dimethyl ketal **13b** (6 mg, 0.008 mmol, 50%) as green crystals, mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 333 (4.44), 371 (4.44), 475 (5.24), 606 (3.67), 668 (3.45), 752 (3.98), 833 nm (4.51); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 323 (4.33), 368 (4.51), 492 (5.19), 706 (3.92), 781 (4.27); ^{1}H NMR ($CDCl_3$) δ −1.07 (6H, s), 2.78 (2H, br s), 3.28 (4H, t, J = 7.0 Hz), 3.65 (6H, s), 3.74 (6H, s), 4.22 (4H, t, J = 7.0 Hz), 7.95 (2H, t, J = 7.3 Hz), 8.09 (2H, d, J = 7.9 Hz), 8.85 (2H, d, J = 6.7 Hz), 9.91−9.94 (2H, m), 10.26 (2H, s), 10.54−10.57 (2H, m), 10.97 (2H, s); FD MS m/z (% rel intensity) 744 (8.8; M^+), 743 (13), 730 (2.3), 729 (5.9), 728 (4.4), 727 (6.4), 716 (7.7), 715 (24), 714 (64), 713 (100), 712 (7.2), 711 (12), 702 (2.7), 701

(10), 700 (38), 699 (82), 698 (10), 697 (9.1); FAB MS *m/z* (% rel intensity) 746 (13), 745 (15), 744 (17; M^+), 743 (9), 730 (18), 729 (20), 728 (22), 715 (50), 714 (100), 713 (95), 712 (31), 701 (18), 700 (38), 699 (69), 698 (68); ESI MS *m/z* (% rel intensity) 744.2 (100; M^+).

21-Chloro-8,12,13,17-tetraethyl-7,18-dimethylbenzo[*b*]-21-carbaporphyrin (20). A solution of benzocarbaporphyrin **4a** (20 mg, 0.040 mmol) in dichloromethane (10 mL) was vigorously stirred with a solution of ferric chloride (3.25 g, 20 mmol) in water (10 mL) and heated under reflux for 3 h. The solution was diluted with dichloromethane, washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade III alumina, eluting with chloroform, and starting material was collected as an initial brown fraction. A second deep blue fraction moved down the column and was collected. Recrystallization from chloroform/hexanes afforded the 21-chlorocarbaporphyrin **20** (18 mg, 0.034 mmol, 84%) as deep blue crystals, mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 394 (4.63), 421 (4.86), 434 (4.93), 521 (4.03), 560 (4.16), 608 (3.73), 665 (3.13); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 409 (4.90), 435 (4.86), 559 (3.90), 611 (3.99), 663 (3.57), 717 (3.54), 730 (3.58), 717 (3.54); UV−vis (50% TFA−$CHCl_3$) λ_{max} (log ϵ) 437 (5.05), 621 (3.59), 675 (3.93), 730 (4.20); ^{1}H NMR ($CDCl_3$; free base) δ −4.1 (2H, br s), 1.84−1.90 (12H, two overlapping triplets), 3.62 (6H, s), 3.92 (4H, q, J = 7.5 Hz), 4.03 (4H, q, J = 7.6 Hz), 7.45−7.48 (2H, m), 8.21−8.24 (2H, m), 9.75 (2H, s), 9.91 (2H, s); ^{1}H NMR (1% TFA−$CDCl_3$; monocation) δ −5.25 (1H, s), −3.42 (2H, s), 1.71 (6H, t, J = 7.6 Hz), 1.88 (6H, t, J = 7.8 Hz), 3.48 (6H, s), 3.91−4.10 (8H, m), 7.47−7.50 (2H, m), 8.07−8.10 (2H, m), 9.90 (2H, s), 10.00 (2H, s); ^{1}H NMR (50% TFA−$CDCl_3$; dication) δ −2.22 (1H, s), 1.72−1.79 (12H, 2 overlapping triplets), 3.46 (6H, s), 3.90−4.07 (8H, m), 9.04−9.06 (2H, m), 10.09−10.12 (2H, m), 10.25 (2H, s), 10.73 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.7, 17.5, 18.6, 19.7, 20.1, 96.1, 100.2, 108.0, 120.3, 126.2, 131.5, 132.5, 134.5, 135.3, 136.1, 138.2, 144.9, 154.1; ^{13}C NMR (trace TFA−$CDCl_3$) δ 11.8, 16.8, 17.7, 19.9 (2), 93.7, 103.3, 116.9, 121.6, 128.0, 132.7, 133.8, 137.3, 137.5, 139.1, 139.7, 139.9, 141.9; EI MS (70 eV) *m/z* (% rel intensity) 536 (4), 535 (12), 534 (11), 533 (29), 501 (8), 500 (43), 499 (100), 498 (13), 485 (5.5), 484 (13), 267 (M^{2+}, 5.6); FAB MS *m/z* (% rel intensity) 581 (6.5), 580 (18), 579 (9.9), 578 (17), 532 (5.4), 531 (7.9), 530 (12), 501 (26), 500 (66), 499 (58), 498 (57); HRMS (EI) *m/z* calcd for $C_{35}H_{36}ClN_3$ 533.2598, found 533.2603; HRMS (FAB) *m/z* calcd for $C_{35}H_{36}ClN_3$ + H 534.2676, found 534.2674.

Carbaporphyrin Dione (25). A solution of **4a** (20 mg, 0.040 mmol) in dichloromethane (10 mL) was vigorously stirred with ferric chloride (3.26 g, 20.1 mmol) in water (10 mL) and heated under reflux for 16 h. The solution was diluted with dichloromethane and washed with water. The organic solvent was removed under reduced pressure and the residue chromatographed on grade 3 alumina eluting with dichloromethane−hexanes. The first fraction was evaporated under reduced pressure and the residue recrystallized from chloroform−methanol to give chlorocarbaporphyrin **20** (7 mg, 0.013 mmol, 31%) as dark crystals. The second fraction was similarly evaporated and the residue recrystallized from chloroform−hexanes to give the carbaporphyrinoid dione **25** (5 mg, 0.0094 mmol, 22%) as dark crystals, mp >300 °C dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 381 (4.71), 609 (3.98); IR (KBr) $\nu_{C=O}$ 1574, 1591 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13−1.20 (12H, 4 overlapping triplets), 2.20 (3H, s), 2.22 (3H, s), 2.57−2.64 (4H, 2 overlapping quartets), 2.82 (2H, q, J = 7.6 Hz), 2.90 (2H, q, J = 7.6 Hz), 6.91 (1H, s), 7.04 (1H, s), 7.14 (1H, s), 7.40−7.46 (2H, m), 7.69−7.73 (2H, m), 14.27 (1H, s), 14.58 (1H, s); ^{1}H NMR (trace TFA−$CDCl_3$) δ 1.17 (3H, t, J = 7.6 Hz), 1.25−1.33 (9H, 3 overlapping triplets), 2.30 (3H, s), 2.34 (3H, s), 2.78−2.94 (8H, 4 overlapping quartets), 7.41 (1H, s), 7.58 (1H, s), 7.59 (1H, s), 7.66 (1H, t, J = 8 Hz), 7.79 (1H, t, J = 7.2 Hz), 7.99 (1H, d, J = 7.6 Hz), 8.07 (1H, d, J = 8.0 Hz), 10.92 (1H, br s), 13.09 (1H, s), 14.80 (1H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 9.2, 9.4, 14.4, 15.1, 15.6, 17.1, 18.5, 18.7, 18.8, 18.9, 115.2, 119.8, 121.9, 123.3, 124.2, 127.9, 129.0, 129.8, 131.2, 132.1, 132.4, 132.9, 133.9, 135.1, 139.0, 139.2, 140.7, 142.1, 143.6, 149.6, 149.8, 151.7, 173.6, 197.6; HRMS (EI) *m/z* calcd for $C_{35}H_{35}N_3O_2$ 529.2729, found 529.2731.

21-Bromo-8,12,13,17-tetraethyl-7,18-dimethylbenzo[*b*]-21-carbaporphyrin (32). A solution of benzocarbaporphyrin **4a** (10 mg, 0.020 mmol) in dichloromethane (10 mL) was vigorously stirred with a solution of ferric bromide (1.00 g, 3.38 mmol) in water (10 mL) and heated under reflux for 4 h. The solution was diluted with dichloromethane, washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade III alumina, eluting with 4:1 v/v dichloromethane−hexanes to afforded the 21-bromocarbaporphyrin (0.8 mg, 1.4 μmol, 7%). UV−vis ($CHCl_3$) λ_{max} 315, 426, 521, 559, 611, 669 nm; ^{1}H NMR ($CDCl_3$) δ −4.2 (2H, br s), 1.85 (12H, t, J = 7.6 Hz), 3.61 (6H, s), 3.90 (4H, q, J = 7.6 Hz), 4.03 (4H, q, J = 7.6 Hz), 7.44−7.48 (2H, m), 8.21−8.24 (2H, m), 9.74 (2H, s), 9.90 (2H, s); EI MS (70 eV) *m/z* (% rel intensity) 579 (1.5), 578 (1.6), 577 (2.6), 506 (1.5), 505 (4.1), 504 (5.7), 503 (11.5); FAB MS *m/z* (% rel intensity) 581 (6.5), 580 (18), 579 (9.9), 578 (17), 532 (5.4), 531 (7.9), 530 (12), 501 (26), 500 (66), 499 (58), 498 (57); HRMS (FAB) *m/z* calcd for $C_{35}H_{36}BrN_3$ + H 578.2171, found 578.2172.

Crystal Structure Determination of 20. A black prism of approximate dimensions 0.24 × 0.24 × 0.22 mm^3 was mounted on a glass fiber with super-glue and transferred to a Brucker P4/R4/SMART 1000 CCD diffractometer.[43] The X-ray diffraction data were collected at −80 °C, using Mo Kα radiation. Data collection and cell refinement were performed with SMART.[43a] The unit cell parameters were obtained from a least-squares refinement of 8412 centered reflections. The systematic absences indicated the space group $P\bar{1}$ (no. 02).[44] The chlorinated carbaporphyrin **20** was found to crystallize in the triclinic crystal system with the following cell parameters: a = 9.5122(6) Å, b = 12.2836(7) Å, c = 13.3156(8) Å, α = 72.040(1)°, β = 75.555(1)°, and γ = 77.403(1)°, Z = 2. A total of 8081 reflections were collected, of which 5700 were unique, and 4463 were observed $F_o^2 > 2\sigma(F_o^2)$. Data reduction was accomplished with use of SAINT.[43b] The data were corrected for absorption through use of the SADABS procedure.[43c]

Solution and data analysis was performed with the WinGX software package.[45] The structure of **20** was solved by using the direct method program SIR-92[46] and the refinement completed with the program SHELXL-97.[47] With the exception of the two core hydrogen atoms, hydrogen atoms were assigned positions based on the geometries of the attached carbon atoms, and were given thermal parameters of 20% greater than those of the attached atoms. The two core hydrogen atoms, H22, and H24, were located by a difference Fourier and were allowed to freely refine. Full-matrix least-squares refinement on F^2 led to a convergence (shift esd max/min = 0.000/0.000) with R_1 = 0.0499, wR_2 = 0.1271, and a goodness of fit = 1.04 for 4463 data with $F_o^2 > 2\sigma(F_o^2)$. A final difference Fourier synthesis showed features in the range of +0.357 to −0.365 e$^-$/Å^3. An ORTEP[45b] drawing of the refined structure is shown in Figure 3. Complete X-ray structural data have been deposited at the Cambridge Crystallographic Data Center CCDC 209318. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cam-

(43) (a) Brucker *SMART 1000 CCD* software package; Brucker Advanced X-ray Solutions: Madison, WI, 1999. (b) Brucker *SAINT* Integration Software for Single-Crystal Data frames − *h*, *k*, *l*, intensity; Brucker Advanced X-ray Solutions: Madison, WI, 1999. (c) Brucker *SADABS*, Empirical adsorption correction procedures; Brucker Advanced X-ray Solutions: Madison, WI, 1999.

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Supporting Information Available: UV−vis, ^{1}H NMR, ^{13}C NMR, and mass spectra for selected compounds; tables of crystallographic details, atomic coordinates, bond lengths and angles, critical angle planes, torsional angles, anisotropic thermal parameters, and hydrogen atom parameters for carbaporphyrin **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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