JOC Article

Oxybenziporphyrins, Oxypyriporphyrins, Benzocarbaporphyrins, and Their 23-Oxa and 23-Thia Analogues: Synthesis, Spectroscopic Characterization, Metalation, and Structural Characterization of a Palladium(II) Organometallic Derivative†

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A series of nine porphyrin analogues have been synthesized using the "3 + 1" variant on the MacDonald condensation. Tripyrrane-type systems with a centrally unsubstituted pyrrole, furan, or thiophene ring were prepared using conventional methods, and these were condensed with indene-1,3-dicarbaldehyde, 5-formylsalicylaldehyde, or 3-hydroxy-2,6-pyridinedicarbaldehyde in the presence of TFA to generate benzocarba-, oxybenzi-, and oxypyriporphyrins, respectively. The furan-containing analogues proved to be highly basic and could only be isolated as the corresponding hydrochloride salts. All nine analogue systems showed porphyrin-like UV−vis spectra with one or two Soret absorptions near 400 nm and a series of weaker bands at longer wavelengths. These systems also showed large diatropic ring currents by proton NMR spectroscopy that were comparable to true porphyrins. In the presence of trace amounts of TFA, benzocarbaporphyrin **12** formed a monocation, and in 50% TFA a C-protonated dication was generated. The 23-oxacarbaporphyrin **14** gave a monocation in chloroform, although the free base was generated in 5% Et_3N−chloroform. In 50% TFA−$CHCl_3$, **14** afforded a mixture of mono- and diprotonated species. Thiacarbaporphyrin **15** also formed a monocation in the presence of TFA, but C-protonation was relatively disfavored for this system. Nonetheless, in the presence of TFA-*d*, **12**, **14**, and **15** all showed rapid exchange of the internal NH and CH protons. Carbaporphyrin **12** also showed slow exchange at the *meso*-positions, but this process was not observed for its heteroanalogues **14** and **15**. Protonation studies were also conducted for oxybenziporphyrins and oxypyriporphyrins **16**−**21**. Oxacarbaporphyrin **14** was shown to be a superior organometallic ligand and afforded good yields of the related nickel(II) and palladium(II) derivatives under mild conditions. A low yield of the platinum(II) complex could also be isolated. All three complexes retained their aromatic character, although the Pd(II) derivative appeared to possess a slightly larger diatropic ring current. The palladium(II) complex **27** was further characterized by X-ray crystallography. The macrocyclic core was shown to be highly planar where the dihedral angles of the component pyrrole, furan and indene rings relative to the mean [18]annulene plane were all ≤2.1°.

Introduction

Carbaporphyrinoid systems,[1,2] porphyrin analogues where one or more of the pyrrole units have been replaced by carbocyclic rings, were first investigated in the mid-1990s.[3−12] These relatively new porphyrin-like macrocycles show unusual chemical properties, including the formation of stable organometallic derivatives[13−17] and unprecedented oxidation reactions.[18,19] Porphyrins and carbaporphyrins (e.g., **1**) are fully aromatic species that

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† Conjugated Macrocycles Related to the Porphyrins. 35. For part 34, see: Lash, T. D.; Colby, D. A.; Szczepura, L. F. *Inorg. Chem.* **2004**, *43*, 5258−5267.

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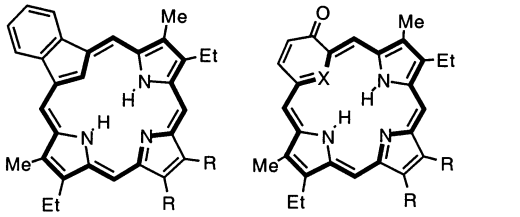
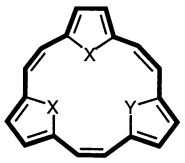
CHART 1





possess many similar spectroscopic properties.[6] The electronic absorption spectra are dominated by a strong Soret band (molar absorptivity ca. 2×10^5) near 400 nm, followed by a series of weaker Q-bands through the visible region.[1,2] These systems also exhibit very strong diatropic ring currents in their proton NMR spectra where the external bridging methine (*meso*) protons are typically shifted downfield to ca. 10 ppm, while the internal NHs resonate near −4 ppm.[20] In addition, the internal CH of **1** is shifted further upfield to −7 ppm.[6] Protons on the pyrrole units are typically shifted to near 9 ppm, and even methyl substituents at these positions are abnormally downfield shifted to approximately 3.6 ppm.[20] Related macrocyclic systems include the oxybenziporphyrins **2a**[3] and their pyridone analogues, the oxypyriporphyrins **2b**,[21] and these also exhibit porphyrin-like aromatic character (Chart 1).

Although the introduction of a five-membered carbon ring, a semiquinone unit or a pyridone moiety as a component of the porphyrinoid ring system does not unduly diminish the aromatic properties of carbaporphyrins, oxybenziporphyrins or oxypyriporphyrins, respectively, it is less clear what effect further modifications will have on the properties of these macrocycles.[1,2] Core modified porphyrins where one or more of the nitrogen atoms have been replaced by oxygen, nitrogen, selenium, or tellurium have been known since the late 1960s,[22] although research on these systems has intensified in recent years due in part to their unique coordination chemistry,[23] as well as their promise as photosensitizers in photodynamic therapy.[24,25] The early studies on heteroanalogues of this type were directed at gaining an understanding of what factors govern the aromatic properties of the porphyrins.[22] It is now known that even when all four pyrrole units are replaced with furan, thiophene, or selenophene rings, the resulting dicationic macrocycles retain aromatic character.[26,27] It remains less clear how the replacement of pyrrole rings with furan or thiophene in porphyrin analogues will alter the chemical and spectroscopic properties of these systems. While furan units will cause a pronounced electronic effect due to the presence of an electronegative oxygen atom, thiophene rings may be disruptive due to steric crowding from the larger sulfur atom. The arrangement of core atoms in carbaporphyrins and oxybenziporphyrins is more crowded than true porphyrins due to the presence of a third hydrogen atom,[6] and additional steric interactions with core sulfur atoms could lead to considerable distortion of the macrocycle. This concept was recognized by Badger for a series of bridged [18]annulenes **3**.[28] The trifuran **3a** and the related monothiophene **3b** showed overall aromatic character, whereas the di- and trithiophene derivatives **3c** and **3d** are nonplanar species that are nonaromatic by proton NMR spectroscopy. Hence, when steric interactions reach a critical point the aromaticity of the macrocycle will be compromised. These considerations prompted us to consider the synthesis of analogues that possess a furan or thiophene ring in addition to the carbocyclic or pyridone subunits found in **1** and **2**. The result of additional core modification should considerably alter the properties of the carbaporphyrinoid systems and provide further insights into the factors influencing the aromatic properties and spectroscopy of these analogues. Furthermore, carbaporphyrins and oxybenziporphyrins readily form organometallic derivatives[13,14,16] and the presence of an oxygen or sulfur atom in place of a nitrogen would inevitably alter the metalation properties of the resulting hybrid porphyrinoids. In this paper, full details of the synthesis, spectroscopy, and protonation of a matched set of highly modified porphyrin analogues are reported. This is the first time that a complete series of porphyrin analogues of this type have been studied and contrasted, and for this reason the results provide fundamental insights that will be of crucial value in future investigations.[29,30]

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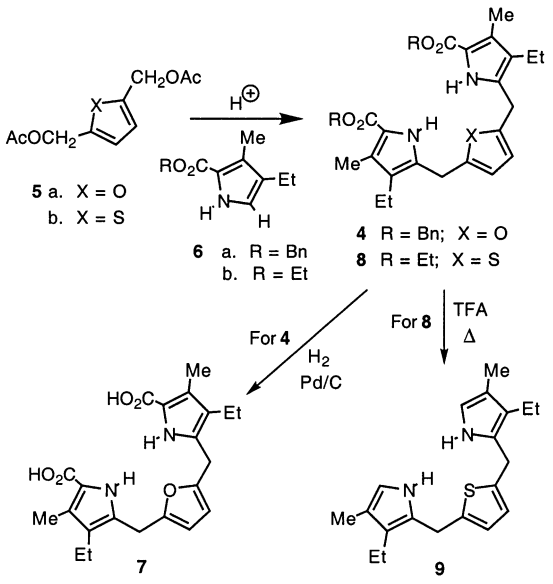
SCHEME 1



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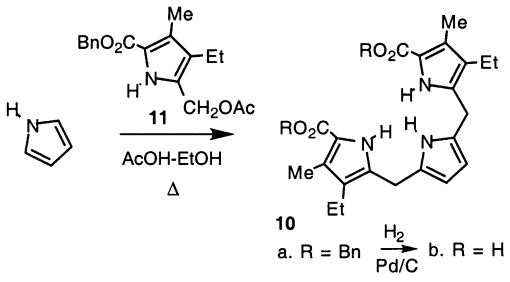

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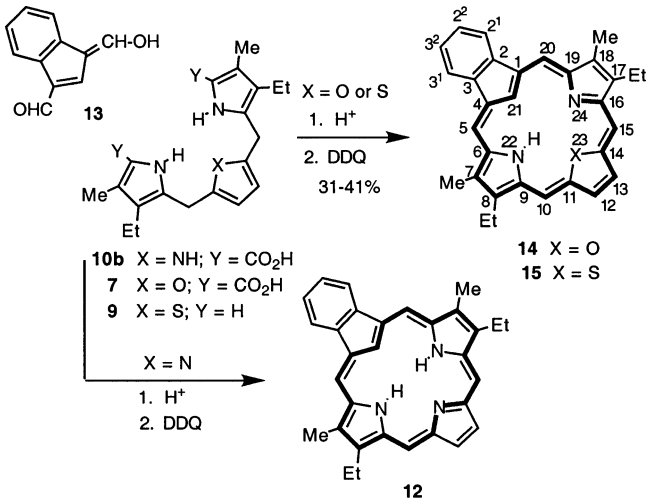

Results and Discussion

Synthesis of Mixed Porphyrin Analogues. Earlier syntheses of carbaporphyrinoid systems have relied on a "3 + 1" version of the MacDonald condensation.[31] This methodology involves the condensation of a tripyrrane with a dialdehyde, followed by an oxidation step, to generate the macrocyclic system. To use this strategy in the synthesis of porphyrin analogues with furan and thiophene subunits, tripyrrane-type systems with furan and thiophene components were required. Similar compounds have been used in the synthesis of oxa- and thiaporphyrins, as well as in the preparation of heterosapphyrins and related expanded porphyrin systems.[32,33] The furan tripyrrane analogue **4** was prepared in moderate yield by reacting bis(acetoxymethyl)furan **5a** with α-unsubstituted pyrrole **6a** in refluxing acetic acid (Scheme 1). The dibenzyl ester could then easily be hydrogenolysed over 10% palladium-charcoal to afford the dicarboxylic acid **7**. The palladium catalysts used to cleave benzyl esters are incompatible with sulfur containing compounds, so thiatripyrrane **8** was prepared as a diethyl ester. Condensation of bis(acetoxymethyl)thiophene **5b** with α-free pyrrole **6b** in the presence of a catalytic amount of *p*-toluenesulfonic acid in refluxing ethanol gave the required tripyrrane analogue in 51% yield (Scheme 1). The ester moieties were cleaved with concomitant decarboxylation in TFA at 60 °C to give the terminally unsubstituted thiatripyrrane **9**. This species is rather unstable and must be immediately used for macrocycle synthesis. To provide a matched set of macrocyclic systems, a tripyrrane **10a** was also synthesized where the central pyrrole unit was unsubstituted (Scheme 2). Previously, porphyrin analogues with alkyl groupings on this ring had been investigated, and it was possible that the presence of these substituents could alter the properties of the macrocyclic products. Pyrrole was found to react with 2 equiv of acetoxymethylpyrrole **11** in refluxing acetic acid−ethanol[34] to give the tripyrrane **10a** in 87% yield. Hydrogenolysis of the benzyl esters afforded the related dicarboxylic acid **10b** in quantitative yield.

Benzocarbaporphyrin **12** was obtained in 54% yield by reacting tripyrrane **10b** with indene dicarbaldehyde **13** in TFA−dichloromethane, followed by oxidation with DDQ, chromatography on alumina, and recrystallization from chloroform−methanol (Scheme 3). Dialdehyde **13** reacted similarly with **7** to afford the oxacarbaporphyrin **14** in 41% yield, although in this case it was convenient to isolate the porphyrinoid as a hydrochloride salt. Indene dialdehyde **13** also reacted with thiatripyrrane **9** to give 21-carba-23-thiaporphyrin **15** in 31% yield (Scheme 3). Oxybenziporphyrin and oxypyriporphyrin analogues **16**−**18** and **19**−**21**, respectively, were prepared similarly by reacting the tripyrranes **10b**, **7**, or **9** with 5-formylsalicylaldehyde (**22**) or 3-hydroxy-2,6-pyridinedicarbaldehyde (**23**) under conventional "3 + 1" conditions (Scheme 4). Good yields of macrocyclic products were obtained using tripyrrane **10b** or oxatripyrrane **7** (31−52%), but the thiatripyrrane **9** afforded relatively poor yields of thiaoxybenziporphyrin **18** (15%) and thiaoxypyriporphyrin **21** (10%), possibly caused by deleterious steric interactions due to the presence of a larger sulfur atom. As was the case for 21-carba-23-oxaporphyrin **14**, the furan-containing porphyrinoids **17** and **20** were found to be relatively basic and were most easily isolated as the corresponding hydrochloride salts.

Carbaporphyrins and Heteroanalogues. As has been observed for related benzocarbaporphyrins,[6] the

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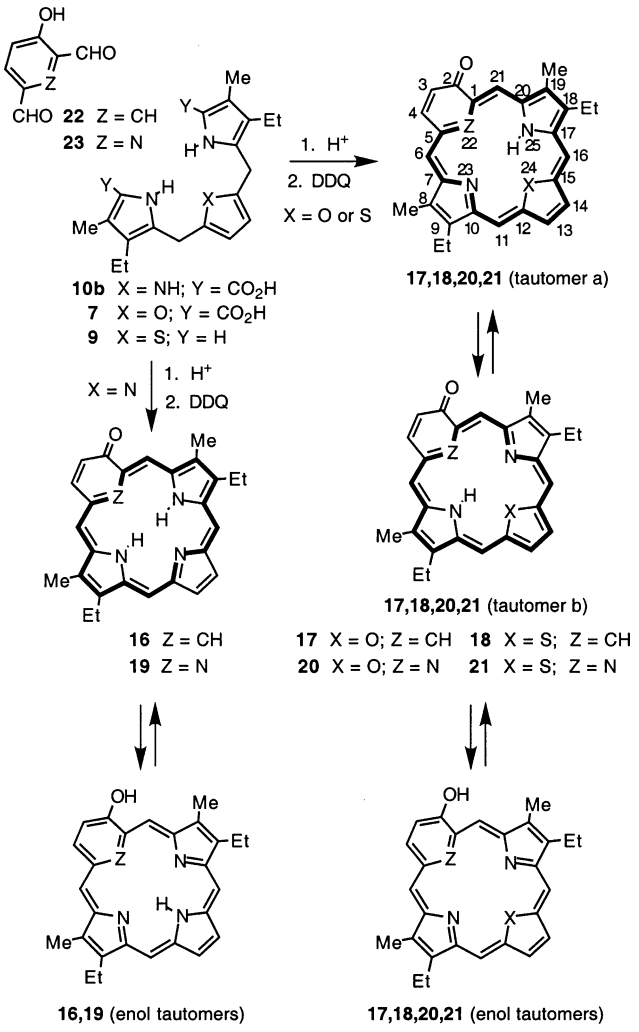
SCHEME 4



electronic absorption spectrum of **12** in $CHCl_3$ shows a strong Soret-type band at 423 nm and a series of Q-bands at 513, 546, 601, and 663 nm (Figure 1). Oxacarbaporphyrin **14** was isolated in a monoprotonated form, but the UV−vis spectrum of the free base could be observed in 5% Et_3N−chloroform. This showed a broader Soret band at 428 nm, with a secondary absorption at 371 nm, and Q-like bands are present between 500 and 700 nm. The free base spectrum of thiacarbaporphyrin **15** was remarkably similar, although the Soret band at 431 nm was intermediary in appearance between **12** and **14** (Figure 1). It should be noted that carbaporphyrins are known to favor a tautomer with the two NHs flanking the carbocyclic ring,[6,36] but this type of structure is not possible for porphyrinoids **14** and **15** (Scheme 3). Hence, these macrocycles have a decreased symmetry compared to **12**. Addition of trace amounts of TFA to solutions of **12** resulted in the formation of a monocation **12**H^+ (Scheme 5) that shows a complex series of absorptions. In 50% TFA−chloroform, a new species assigned as the C-protonated dication **12**H_2^{2+} is generated (Scheme 5), and this shows a Soret band at 423 nm and two

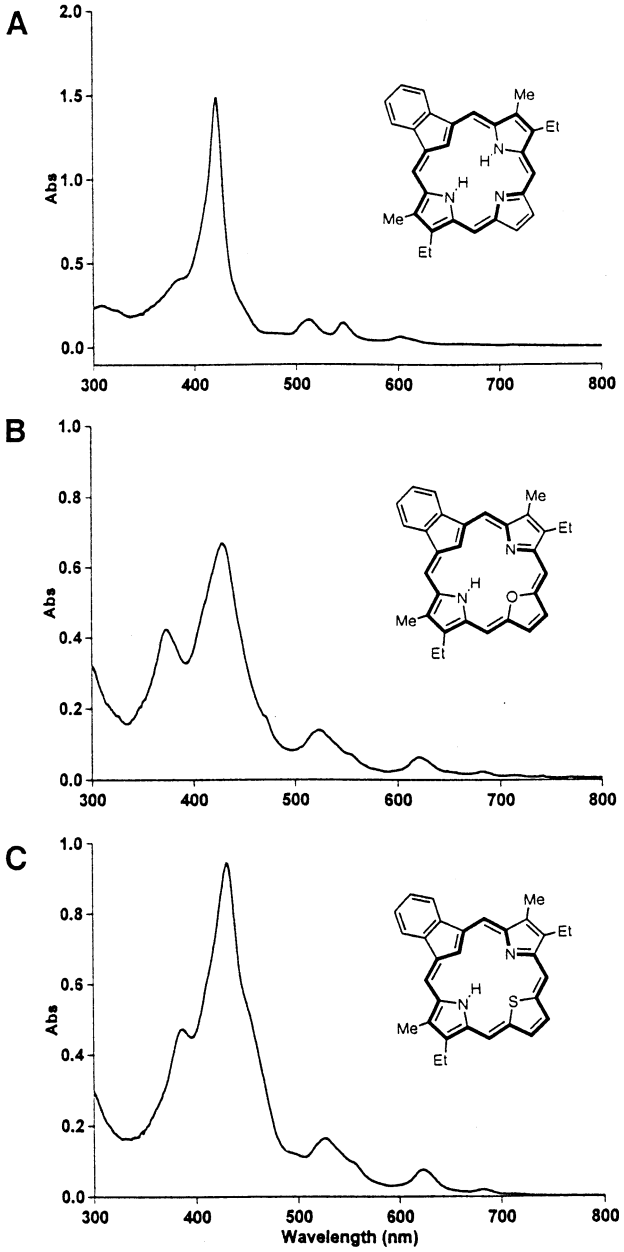


FIGURE 1. UV−vis spectra of free base benzocarbaporphyrins: (A) **12** in chloroform, (B) oxacarbaporphyrin **14** in 5% Et_3N−$CHCl_3$, (C) thiacarbaporphyrin **15** in chloroform.

additional absorptions at 597 and 649 nm. Oxacarbaporphyrin hydrochloride **14**·HCl in chloroform shows a complex series of absorption bands; in the presence of trace amounts of TFA the spectrum is essentially unchanged. Hence, the predominant species present in these solutions was assigned as the monocation **14**H^+. As the concentration of TFA was increased, the spectra evolved to show the presence of a new species that was assigned as the dication **14**H_2^{2+}. In 50% TFA−chloroform, this conversion appeared to be incomplete suggesting that C-protonation is less favored for **14** compared to **12**. This is undoubtedly due to the decreased ability of oxygen compared to nitrogen to stabilize the second positive charge. Thiacarbaporphyrin **15** also gave rise to a new species in the presence of trace amounts of TFA that was assigned as monocation **15**H^+. However, the spectrum

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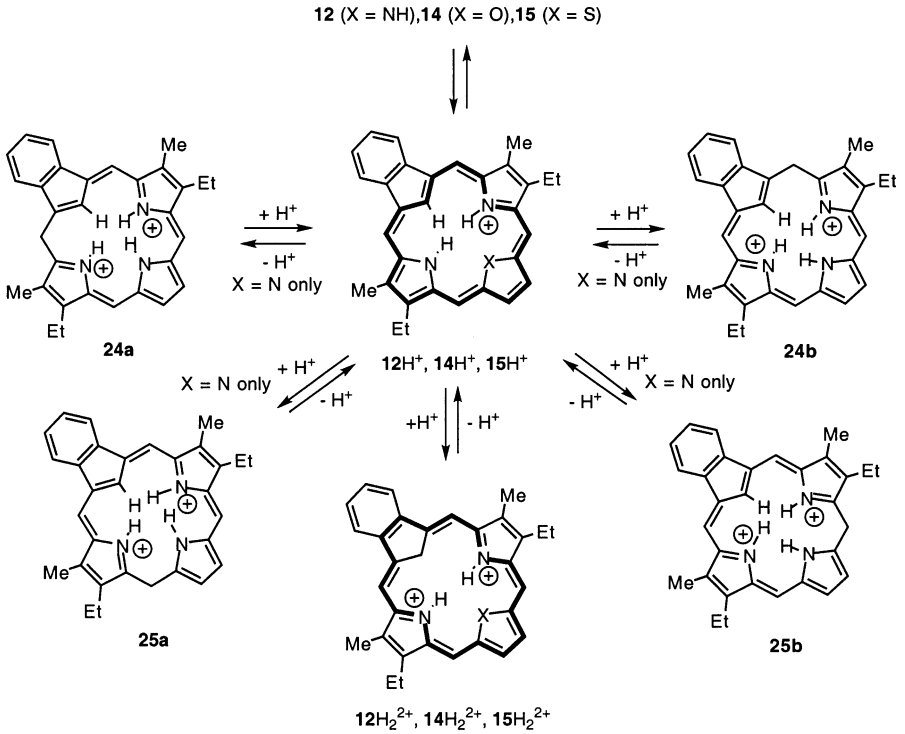
SCHEME 5



remained virtually unchanged as the concentration of TFA was increased and apart from a shoulder showing up at 460 nm, the monocation **15**H$^+$ appeared to be the main species present in solution even in 50% TFA−chloroform.

The proton NMR spectra of **12**, **14**, and **15** all show strong diatropic ring currents. The free base forms of **12** and **15** gave comparable shifts for the protons at the macrocyclic periphery. The *meso*-protons gave two 2H singlets at 10.20 and 10.34 ppm for **12** and 10.20 and 10.41 ppm for **15**, while the 12,13-protons for **12** and **15** resonated at 9.46 and 9.89 ppm, respectively. In addition, the methyl substituents gave rise to a 6H singlet near 3.5 ppm in both cases. The internal CH was shifted upfield to −7.0 ppm for **12** but appeared at −5.5 ppm for **15**. These differences could be due to a number of factors, including steric crowding within the macrocyclic cavity, and in any case some minor shifts for these resonances can be observed with sample concentration. For **15**, the apparent symmetry of the molecule is retained indicating that proton exchange between the two internal nitrogen atoms must be occurring rapidly. The proton NMR spectrum for the free base form of oxacarbaporphyrin **14** was obtained in pyridine-d_5. This showed a broad resonance near −5 ppm for the internal CH, while the furan protons gave a 2H resonance at 9.93 ppm and the *meso*-protons produced two 2H singlets at 10.35 and 10.57 ppm. In $CDCl_3$, the proton NMR spectrum for **14**.HCl in $CDCl_3$ corresponded to the monocation **14**H$^+$, and this species showed the internal CH as an 1H singlet at −6.45 ppm while the NHs gave rise to a broad 2H resonance at −1.53 ppm (Figure 2B). In addition, the furan protons afforded a 2H singlet at 9.78 ppm, and the *meso*-protons produced two 2H singlets at 10.08 and 10.32 ppm. Addition of trace amounts of TFA to solutions of **12** or **15** in $CDCl_3$ afforded the corresponding monocations. Carbaporphyrin monocation **12**H$^+$ gave a 1H singlet for the internal CH at −7.04 ppm, while the NHs produced two resonances at −4.69 (1H) and −3.58 ppm (2H). The two pyrrolic protons gave a 2H singlet at 9.46 ppm, while the *meso*-protons produced two additional 2H singlets at 10.20 and 10.34 ppm (Figure 2A). These data suggest that **12**H$^+$ has slightly greater diatropic character than **14**H$^+$. However, addition of one drop of TFA to a solution of **14**·HCl in $CDCl_3$ produced an upfield shift for the interior CH resonance to −6.91 ppm, while the *meso*-protons shifted downfield to values similar to those for **12**H$^+$. Therefore, although solvent effects appear to be playing a significant role, no differences in the diatropicity of **12**H$^+$ and **14**H$^+$ can be discerned from these data. The monocation of the sulfur analogue **15**H$^+$ gave the inner CH resonance at −7.45 ppm, a 2H resonance for the NHs at −5.86 ppm, and showed the exterior thiophene and *meso*-protons as three 2H singlets at 10.10, 10.21, and 10.71 ppm, respectively. These values do suggest a small increase in ring current, although again these results must be interpreted with caution. In 50% TFA−$CDCl_3$, benzocarbaporphyrin **12** generates the dication **12**H_2^{2+} (Scheme 5), and this shows a 2H singlet for the internal CH_2 at −4.78 ppm, while the *meso*-protons are shifted further downfield to 10.46 (2H, s) and 10.94 ppm (2H, s). In this species, the 18π electron delocalization pathway is relocated through the benzene ring, and this leads to a significant downfield shift for the benzo-proton resonances from 7.7 and 8.7 ppm in the case of monocation **12**H$^+$, to 8.9 and 10.1 ppm in dication **12**H_2^{2+}. Oxacarbaporphyrin gave a poor quality spectrum in 50% TFA−$CDCl_3$ that appeared to correspond to a mixture of species, although the monocation still predominated. On the other hand, thiacarbaporphyrin **15** gave a clear proton NMR spectrum in 50% TFA−$CDCl_3$, but this only showed the presence of the monocation **15**H$^+$.

Carbaporphyrins show proton exchange with TFA-*d* at the internal CH and more slowly at the *meso*-positions.[6b,18b]

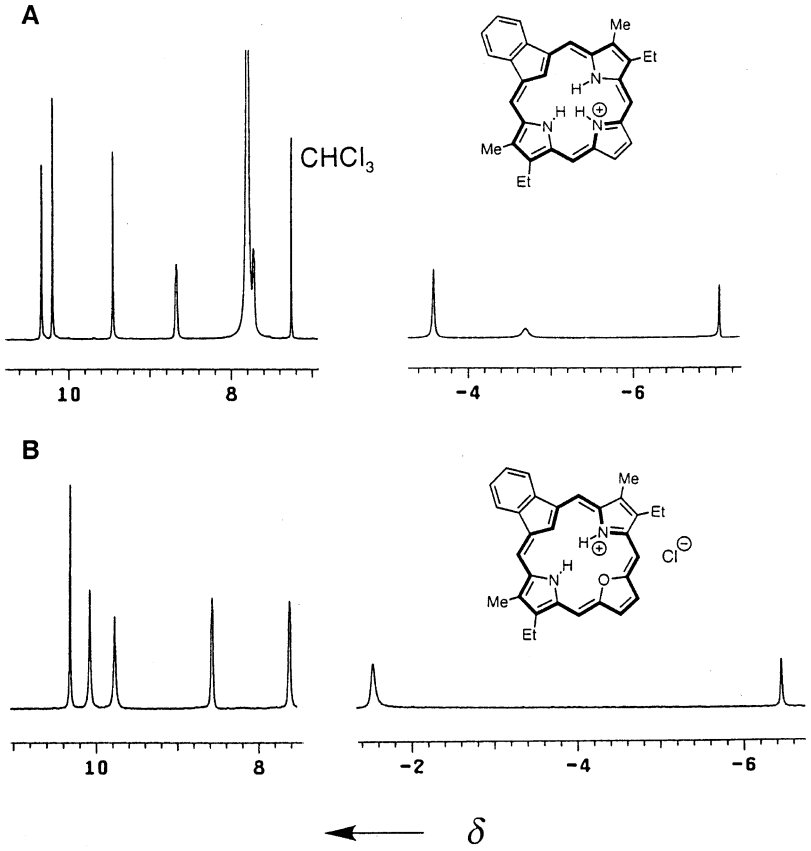


FIGURE 2. 400 MHz proton NMR spectra of benzocarbaporphyrin monocations: (A) **12**H^+ in TFA−$CDCl_3$, (B) **14**H^+ in $CDCl_3$.

Addition of 3 drops of TFA-*d* to a solution of **12** in $CDCl_3$ showed immediate loss of signal intensity for the 21-CH and NH resonances. Over a period of several days at room temperature, significant exchange is also observed for the *meso*-protons as well. We have proposed that monocation **12**H^+ and dication **12**H_2^{2+} are in equilibrium with low concentrations of C-protonated dications such as **24** and **25** (Scheme 5), or possibly related monocations, and these species facilitate slow exchange at the *meso*-positions.[6b] Addition of TFA-*d* to NMR solutions of **14**·HCl also showed an immediate disappearance of the C-21 and NH resonances, confirming that the dication **14**H_2^{2+} was present in equilibrium with the monocation, but no loss of intensity for the *meso*-protons was observed after 1 week at room temperature. Thiacarbaporphyrin **15** also showed immediate loss of signal for the 21-CH and NH resonances but no exchange at the *meso*-carbons. This result indicates that the sulfur system can generate low concentrations of **15**H_2^{2+}. It is interesting that *meso*-proton exchange is only possible for the tripyrrolic macrocycles. This may be due to the greater ability of nitrogen to stabilize positive charge compared to oxygen or sulfur. However, no exchange could be observed for the protons at positions 12 and 13 in any of these systems.

Oxybenziporphyrins and Heteroanalogues. Oxybenziporphyrins can potentially exist in keto or enol forms,[3] but the keto tautomers are favored for both the tripyrrolic macrocycle **16** and the new oxa- and thia-versions **17** and **18** (Scheme 4). In the favored tautomeric forms, the porphyrinoid system can take on a porphyrin-like 18π electron delocalization pathway, but in the process the benzene unit loses its aromatic character. Several keto tautomers are possible for **16**, although the form with NHs at positions 23 and 25 is believed to be the most favorable (Scheme 4).[3,16] For heteroanalogues **17** and **18**, this type of tautomer is precluded by the presence of an O or S at position 24, and these systems may exist as a mixture of tautomers a and b (Scheme 4). The cross-conjugated carbonyl stretch in these macrocycles is easily identified in the IR spectra (KBr), giving rise to strong bands for **16**, **17**, and **18** at 1627, 1625, and 1624 cm^{-1}, respectively.

The UV−vis spectrum of **16** in chloroform shows two Soret bands at 426 and 450 nm, followed by a series of Q-bands extending to 701 nm (Figure 3). Addition of trace amounts of TFA to a solution of **16** gives a monocation **16**H^+ but at higher concentrations a dication **16**H_2^{2+} is generated (Scheme 6). The dication shows weakened absorptions at 348 and 430 nm, and a series of Q-like bands at 558, 604, 710, and 775 nm, and appears to take on more "enol" character that decreases the porphyrin-type aromaticity of the system. The 23-oxaoxybenziporphyrin **17** was isolated as a hydrochloride salt, and this showed a strong Soret band at 424 nm ($\log \epsilon = 5.19$), a secondary absorption at 478 nm ($\log \epsilon = 4.83$), and four poorly defined Q-bands. In 5% Et_3N−$CHCl_3$, the free base form of **17** was generated, and this showed a broadened Soret band at 416 nm ($\log \epsilon = 4.95$), followed by a series of bands through the visible region (Figure 3). In 5% TFA−chloroform, dication **17**H_2^{2+} was formed, and this gave a UV−vis spectrum that closely resembled the one obtained for **16**H_2^{2+} suggesting that this species has also diminished porphyrinoid aromaticity. Broadened Soret-

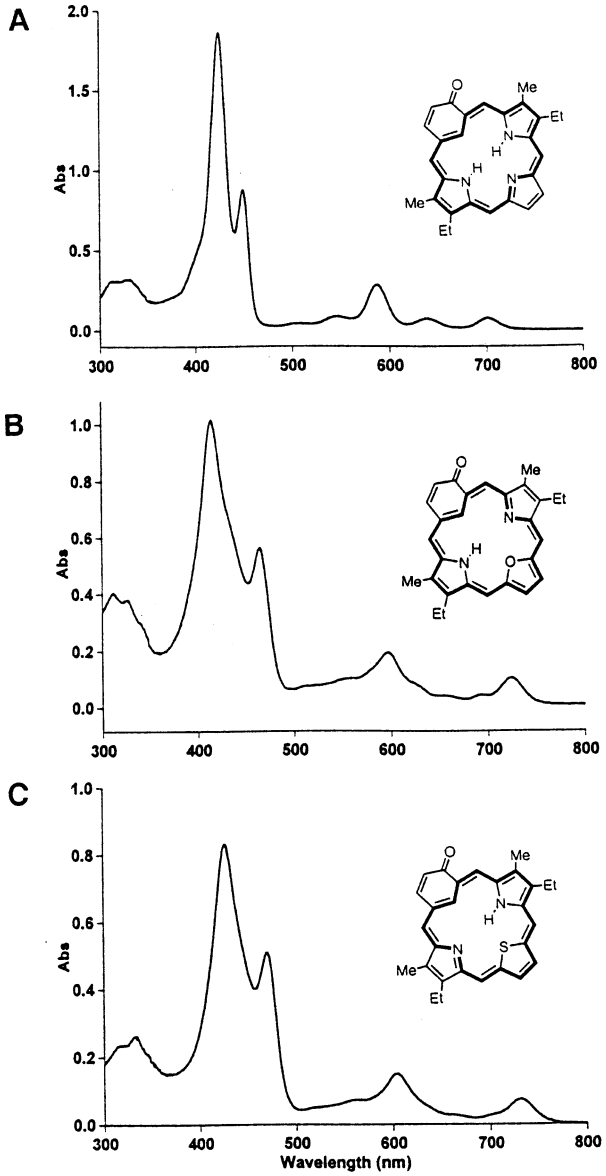
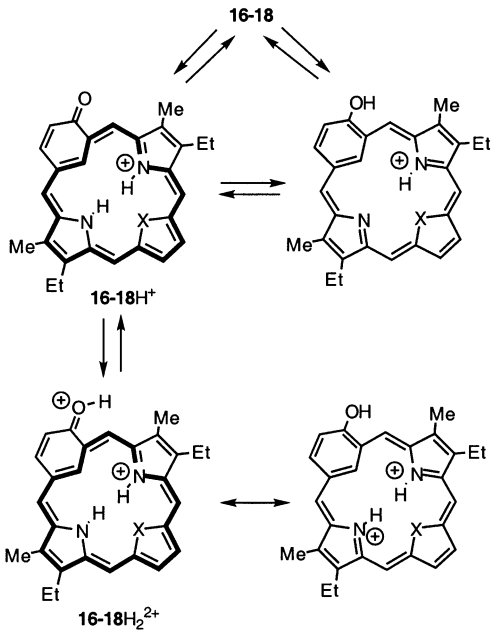


FIGURE 3. UV−vis spectra of free base oxybenziporphyrins: (A) **16** in chloroform, (B) oxaoxybenziporphyrin **17** in 5% Et_3N−$CHCl_3$; (C) thiaoxybenziporphyrin **18** in chloroform.

like absorptions were present at 348 and 423 nm, and a series weaker bands were noted at 556, 600, 653, and 719 nm. Free base thiaoxybenziporphyrin **18** also showed two Soret bands at 427 and 471 nm, although these absorptions and the weaker bands through the rest of the visible region were broader than those seen for **16** and **17** (Figure 3). Addition of TFA showed a gradual change in the UV−vis spectra resulting in a spectrum corresponding to the dication **18**H_2^{2+} in 50% TFA−$CHCl_3$. The diprotonated thia-analogue spectrum was very similar to the spectra for **16**H_2^{2+} and **17**H_2^{2+}, showing a Soret-like band at 441 nm, and again the data suggest a decrease in aromatic character in the diprotonated system due to phenolic resonance contributors (Scheme 6).

The proton NMR spectrum of oxybenziporphyrin **16** confirmed the presence of a potent diatropic ring current. The internal CH resonated at −7.11 ppm while the NHs gave rise to a broad peak near −3.5 ppm. Unlike the

SCHEME 6



benzocarbaporphyrins discussed in the previous section, oxybenziporphyrins **16**−**18** have no plane of symmetry, and for this reason the *meso*-protons afford four 1H singlets at 9.20, 9.32, 9.37, and 10.46 ppm (the latter resonance corresponds to the proton closest to the carbonyl unit). The pyrrole protons have sufficiently distinct chemical shifts to couple and produce an AB quartet near 8.9 ppm. Protonation leads to a pronounced decrease in the diatropic ring current, and in 50% TFA−$CDCl_3$ the internal CH resonance shifts downfield to 1.20 ppm, while the *meso*-protons undergo an upfield shift to give four 1H resonances at 8.27, 8.31, 8.93, and 9.54 ppm. 24-Oxaoxybenziporphyrin **17** gave a satisfactory proton NMR spectrum in pyridine-d_5 that was assigned to the free base. The internal CH gave a broad resonance at −4.5 ppm, while the external *meso*-protons gave the expected series of 1H singlets at 9.77, 9.82, 9.97, and 10.86 ppm. The furan protons afforded a poorly resolved AB quartet near 9.6 ppm. The spectrum for **17**·HCl in $CDCl_3$ corresponded to the monocation **17**H^+. In this case, the inner CH resonated at −5.23 ppm and the NHs give rise to two 1H peaks at 0.40 and 0.52 ppm. The diatropic ring current for **17**H^+ was confirmed by the presence of four 1H singlets for the *meso*-protons that are downfield at values of 9.71, 9.76, 9.82, and 10.84 ppm. However, addition of TFA led to a decrease in ring current in accord with the UV−vis data. In 50% TFA−$CDCl_3$, the dication showed the interior CH at 1.33 ppm, while the *meso*-protons shifted upfield to values of 8.33, 8.36, 9.06, and 9.68 ppm. As was the case for the tripyrrolic oxybenziporphyrin **16**, **17**H_2^{2+} is believed to have taken on a greater amount of phenolic character. Similar trends are observed for thiaoxybenziporphyrin **18**. In $CDCl_3$, the free base gave the internal CH resonance at −5.80 ppm, while the NH produced a broad 1H resonance at −4.24 ppm. As would be expected for this asymmetrical aromatic porphyrinoid, the *meso*-protons gave four 1H singlets downfield at 9.25, 9.85, 9.93, and 10.59 ppm. The thiophene protons were also shifted downfield to give a 2H AB quartet near 9.5 ppm. Addition of 1 drop of TFA

to the NMR tube produced the corresponding monocation **18**H^+, and this showed enhanced diatropicity with the inner CH resonance appearing at −4.63 ppm while the *meso*-protons shifted slightly further downfield to give four 1H singlets at 9.92, 10.35, 10.46, and 10.96 ppm. Further addition of acid again leads to a decrease in the aromatic ring current that was associated with the formation of the dication **18**H_2^{2+}. In 50% TFA−$CDCl_3$, the inner CH shifted downfield to give a 1H doublet (J = 2 Hz) at 0.45 ppm while the *meso*-protons shifted upfield to give 1H resonances at 9.27, 9.32, 9.33, and 10.09 ppm. Although dication **18**H_2^{2+} retains a larger ring current than **16**H_2^{2+} or **17**H_2^{2+}, the same general trends are seen in all three systems. Carbon-13 NMR spectroscopy also helped to confirm the structural identity of these macrocycles, and in particular all three systems showed a resonance near 180 ppm corresponding to the cross-conjugated carbonyl moiety. All three oxybenziporphyrins showed a strong molecular ion by EI MS where the principal fragmentation observed was loss of methyl, i.e., benzylic cleavage.

Oxypyriporphyrins and Heteroanalogues. Oxypyriporphyrins can exist as pyridone or hydroxypyridine tautomers,[21] but like the oxybenziporphyrin series the carbonyl porphyrin-like forms are favored for **19**, **20**, and **21** (Scheme 4). The IR spectra for these three systems gave strong absorptions at 1634, 1638, and 1636 cm^{-1} for **19**, **20**, and **21**, respectively. These values are approximately 10 cm^{-1} higher in frequency than those for the oxybenziporphyrin series **16**−**18**. Tripyrrolic oxypyriporphyrins also favor the tautomer with the internal NH protons on positions 23 and 25 as this minimizes steric repulsion and maximizes hydrogen-bonding interactions.[3b,21,37] Naturally, this type of tautomer is not possible for **20** or **21** when an oxygen or sulfur atom resides at position 24, and these systems, in common with the related heterooxybenziporphyrins **16** and **17**, may exist as a mixture of tautomers a and b (Scheme 4). Solutions of oxypyriporphyrin **19** in chloroform gave porphyrin-like UV−vis spectra with two Soret bands at 420 and 438 nm and a series of broad Q-bands between 500 and 660 nm (Figure 4). Addition of TFA produces a new species that can be assigned to dication **19**H_2^{2+} (Scheme 7), and this shows two Soret bands at 425 and 441 nm together with four smaller Q-bands at 568, 595, 619, and 647 nm. Oxaoxypyriporphyrin **20**·HCl in 5% Et_3N−chloroform shows a spectrum for the free base with two broad Soret bands at 406 and 452 nm and four Q-bands between 500 and 700 nm (Figure 4). In chloroform, a UV−vis spectrum was obtained that appeared to show the presence of two species, tentatively assigned as monocation **20**H^+ and dication **20**H_2^{2+} (Scheme 7). A strong band is present at 413 nm, together with two similar absorption at 448 and 454 nm and smaller bands near 600 nm. In 0.01% TFA−chloroform, the band at 448 nm increased in intensity relative to its neighbor at 454 nm. In 5% TFA−$CHCl_3$, only the band at 448 remained; in addition, a Soret band was present at 414 nm and several broad Q-bands were observed near 600 nm. In 50% TFA, a new species appeared to be present in solution in equilibrium with **20**H_2^{2+} that was associated with the appearance of a band at 438 nm, and this is possibly due to the presence of a triprotonated species. The free base for thiaoxypyriporphyrin **21** showed a broad Soret band at 424 nm, together with a shoulder near 450 nm, and this region of the spectrum somewhat resembled the free base form of **20**. However, the longer wavelength region was far more complex showing at least seven Q-like bands between 500 and 710 nm (Figure 4). Addition of TFA induced a gradual change in the UV−vis spectrum associated with the formation of the dication **21**H_2^{2+}. In 5% TFA−$CHCl_3$, this showed two Soret bands at 430 and 463 nm, and two broadened weaker absorptions at 601 and 644 nm.

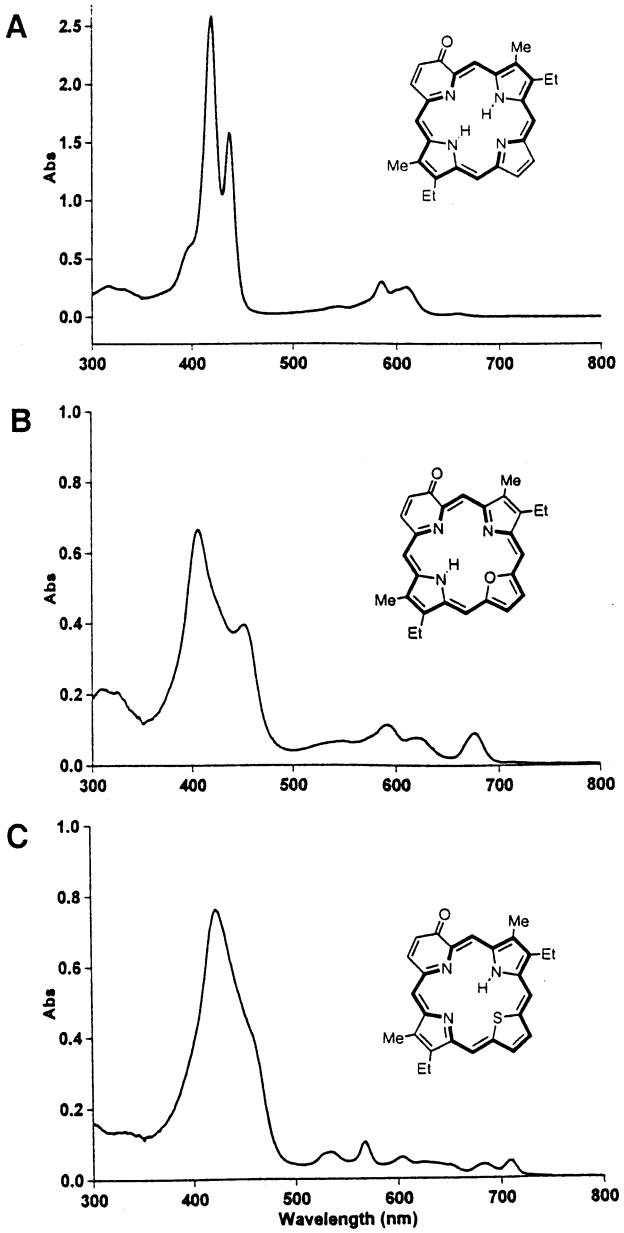
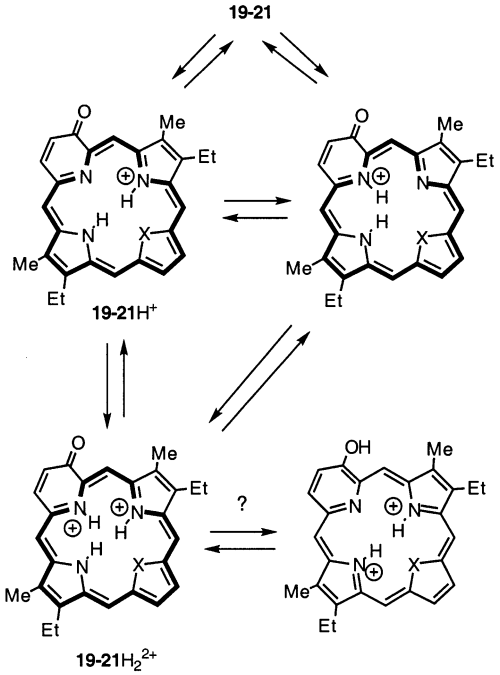


FIGURE 4. UV−vis spectra of free base oxypyriporphyrins: (A) **19** in chloroform, (B) oxaoxypyriporphyrin **20** in 5% Et_3N−$CHCl_3$, (C) thiaoxypyriporphyrin **21** in chloroform.

Proton NMR spectroscopy confirmed the aromatic character of oxypyriporphyrins **19**−**21**. In $CDCl_3$, the free base form of **19** showed two singlets near −4.3 ppm for the internal NHs, while the *meso*-protons were shifted downfield to give a series of 1H singlets at 10.39, 10.66,

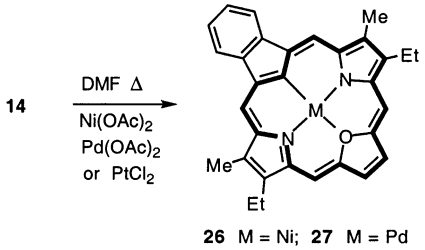
(37) Schönemeier, T.; Breitmaier, E. *Synthesis* **1997**, 273.

SCHEME 7



10.67, and 11.26 ppm. The pyrrolic protons gave rise to an AB quartet near 9.6 ppm. These data indicate that **19** has a stronger diatropic ring current than oxybenziporphyrin **16**, which is consistent with previous observations for these systems. The presence of two NH resonances also indicates that proton exchange is slow compared to regular porphyrin systems. The strong ring current is retained for the dication **19**H_2^{2+} in TFA−$CDCl_3$. Oxaoxypyriporphyrin in trace TFA−$CDCl_3$ gave a spectrum for the cation **20**H^+ that showed two broad resonances for the NHs near −4.7 ppm. Many of the resonances were somewhat broadened, possibly due to aggregation effects. In 50% TFA−$CDCl_3$, a higher quality spectrum of dication **20**H_2^{2+} was obtained that showed the *meso*-protons as four 1H singlets near 10 ppm, while an NH resonance was present at −1.4 ppm. The proton NMR spectrum for the free base form of thiaoxypyriporphyrin **21** in $CDCl_3$ showed the *meso*-protons downfield near 10 ppm, although the NH resonance could not be observed. However, the aromatic ring current was confirmed by the deshielding effects on the alkyl side chains. For instance, the methyl substituents gave two 3H singlets at 3.33 and 3.44 ppm. Nevertheless, addition of 1 drop of TFA produced a monocation **21**H^+ that showed an enhanced diatropic ring current where the *meso*-protons gave four 1H singlets at 10.41, 11.22, 11.28, and 11.64 ppm, while the methyl groups gave two singlets at 3.78 and 3.81 ppm. Dication **21**H_2^{2+} in 50% TFA−$CDCl_3$ showed a slightly reduced ring current where the *meso*-protons gave four singlets between 10.5 and 11.6 ppm. The NH resonances could not be observed for **21**H^+ or **21**H_2^{2+}. Carbon-13 spectra also supported the stuctures for **19**−**21**, and the carbonyl resonances could be identified in each case between 180 and 190 ppm. EI mass spectrometry for **19** and **21** showed a strong molecular ion and a significant fragment ion at [M − 28] corresponding to loss of CO. Unfortunately, oxaoxypyriporphyrin **20**·HCl failed to give satisfactory MS data by EI or FAB MS. However, a clear mass spectrum of this system could be obtained using FD MS.

SCHEME 8



Metalation of 21-Carba-23-oxabenzo[*b*]porphyrin 14. A particularly exciting aspect of carbaporphyrinoid systems that has emerged over the past few years is their ability to form organometallic derivatives. This chemistry complements work on the N-confused porphyrins,[23,38,39] which also exhibit the ability to form complexes of this type. Benziporphyrins[17] and azuliporphyrins[15] have been shown to form stable nickel(II), palladium(II), and platinum(II) derivatives, while benzocarbaporphyrins, tropiporphyrins, oxybenziporphyrins, and oxynaphthiporphyrins all favor the formation of silver(III) derivatives.[13,14] Oxybenziporphyrins also afford palladium(II) complexes[16] and, therefore, show the ability to bind metals at two different oxidation states. We considered the oxacarbaporphyrin system **14**, and the related oxaoxybenziporphyrin macrocycle **17**, to have the potential to give interesting organometallic chemistry. In particular, **14** has been shown to be a good organometallic ligand for divalent cations from group 10.

Benzocarbaporphyrins have a CH−NH−N−NH core that must lose three protons to accommodate a metal ion and appear to be best suited to act as a trianionic ligand. Hence, this system forms stable silver(III) and gold(III) derivatives but does not form complexes with Ni^{2+} or Pd^{2+}.[14] However, oxacarbaporphyrin **14** has a CH−NH−O−N arrangement of core atoms and would seem better suited to act as a dianionic ligand. Hence, although **14** failed to react with AgOAc to give a silver complex, this system readily formed nickel(II) or palladium(II) complexes (Scheme 8).

When **14** was heated with nickel(II) acetate or palladium(II) acetate in DMF, the corresponding metallo derivatives **26** and **27** were formed in good yields. Platinum(II) chloride also reacted with **14**, but only low yields of the platinum(II) complex **28** could be isolated. The UV−vis spectra for the metal complexes gave multiple absorptions and differed considerably from one another (Figure 5). The strongest absorption in each case resembled a Soret band but was comparatively blue shifted appearing at 392, 378, and 380 nm for **26**, **27**, and **28**, respectively. The spectrum for the palladium complex **27** showed considerable fine structure that was distorted or broadened in the spectra for the other two complexes. Palladium(II) is a good fit for the macrocyclic cavity, and this complex may be more planar than the nickel(II) derivative where distortions are necessary to provide better bonding interactions with the metal cation.

(38) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795.
(39) (a) Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1. (b) Ghosh, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1918.

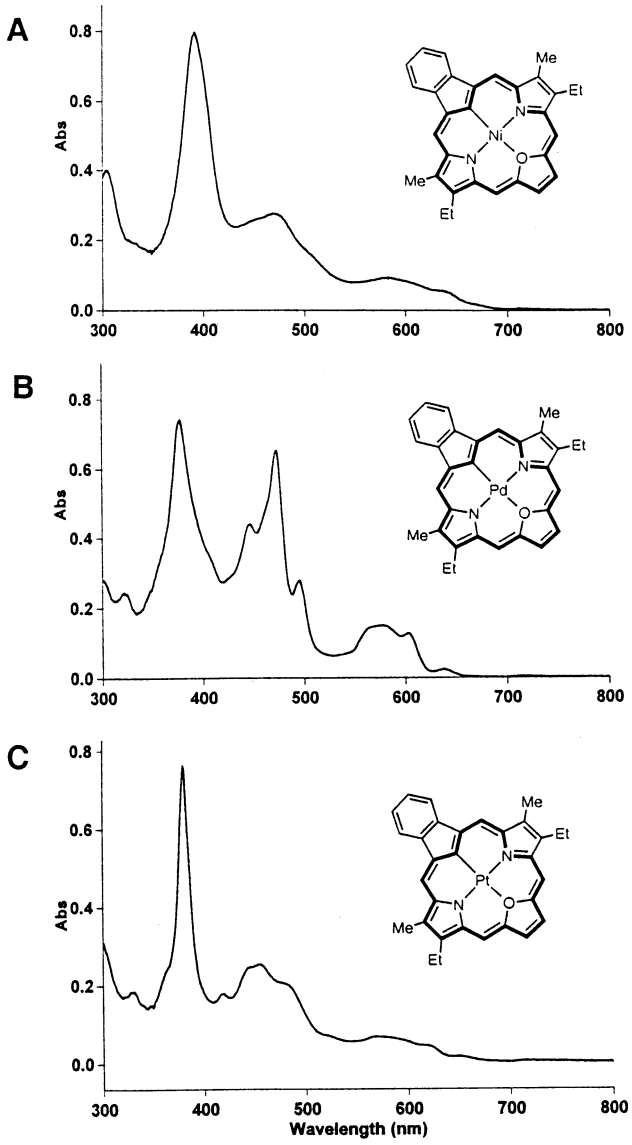


FIGURE 5. UV−vis spectra of free base metallooxabenziporphyrins: (A) nickel(II) complex **26** in chloroform, (B) palladium(II) complex **27** in chloroform, (C) platinum(II) complex **28** in chloroform.

This suggestion is supported by the proton NMR data for these complexes, where **27** shows a slightly larger ring current (Figure 6) than **26**. Specifically, the furan protons resonate at 9.49 ppm, while the *meso*-protons gave two 2H singlets at 9.89 and 10.02 ppm. The equivalent peaks were observed at 9.39, 9.75, and 9.87 ppm for nickel complex **26** and 9.49, 9.82, and 9.90 for the platinum derivative **28**. The UV−vis and proton NMR data for **28** appear to be intermediary between **26** and **27**, but in this case distortions to the macrocyclic system are unlikely to be a factor. The covalent radii for Pd^{2+} and Pt^{2+} are virtually identical and as a consequence the X-ray structures for the palladium(II) and platinum(II) derivatives of octaethylporphyrin are nearly indistinguishable.[40] Hence, further studies will be required to fully understand the observed spectroscopic properties for these organometallic derivatives. All three metalated products were only sparingly soluble in organic solvents, and it was not possible to obtain carbon-13 NMR data. However, the structures were supported by high-resolution MS data.

The structure and planar conformation of **27** was supported by single-crystal X-ray diffraction analysis. This represents the first structurally characterized oxacarbaporphyrin complex. As expected, **27** has a near-planar macrocyclic core (Figure 7) as evidenced by the distances (0.03(2) Å rms; C(12), 0.0822(1) Å max) skeletal atoms lie from the plane defined by Pd(1)C(21)N(22)O(23)N(24) and by the pyrrole, furan, and indene to mean [18]annulene plane dihedral angles of 1.5(3)°, 1.0(3)°, 2.1(4)°, and 0.2(2)°. The palladium(II) ion is centered between the donor ligands with equivalent *trans*-Pd−N bond lengths of 2.018(5) and 2.022(6) Å. These values fall within the typical 2.012 ± 0.018 Å range reported for palladium coordinated porphyrin-type macrocycles.[41] The packing for structure **27** is also noteworthy in that offset face-to-face π-stacking interactions are observed, linking the molecules into chains separated by interplane distances of 3.37(1) and 3.45(1) Å. Pairs of molecules separated by 3.37(1) Å are related to one another crystallographically by 2-X, -Y, 2-Z and display a Pd···Pd distance of 4.620(1) Å (corresponding to an intermolecular lateral displacement of ca. 3.15 Å), while pairs of molecules separated by 3.45(1) Å are related by 1-X, -Y, 2-Z and display a Pd···Pd distance of 5.199(1) Å (ca. 3.89 Å intermolecular lateral displacement). At least eight less than 3.5 Å intermolecular separations between framework atoms exist in each π-stacked pairs of molecules. These π-stacking interactions are remarkably similar to the π-stacking observed in 5,15-diphenylporphyrin.[42]

During the course of these investigations, a synthesis of dimesityl oxaoxybenziporphyrin **29** was reported (Scheme 9).[43] This compound gave the related palladium(II) complex on heating with $PdCl_2$ in benzonitrile. We also investigated the metalation of the related porphyrinoid **17**, but in our hands we were unable to isolate the palladium complex. Nonetheless, porphyrin analogues with a CH−NH−O−N core do appear to show some promise in the synthesis of organometallic derivatives.

Conclusions

The synthesis of a matched set of porphyrin analogues by the "3 + 1" version of the MacDonald condensation has been completed. Although all nine macrocyclic systems retain strong diamagnetic ring currents by proton NMR spectroscopy, the spectroscopic properties of these molecules show significant variations. In addition, protonation studies show considerable differences for these macrocycles and the basicities are considerably enhanced for the oxa-derivatives. Of particular significance, oxa-

(40) (a) Milgrom, L. R.; Sheppard, R. N.; Slawin, A. M. Z.; Williams, D. J. *Polyhedron* **1988**, *7*, 57. (b) Stolzenberg, A. M.; Schussel, L. J.; Summers, J. S.; Foxman, B. M.; Petersen, J. L. *Inorg. Chem.* **1992**, *31*, 1678.

(41) Bruno, I. J.; Cole, J. C.; Edgington, P. R.; Kessler, M.; Macrae, C. F.; McCabe, P.; Pearson, J.; Taylor, R. *Acta Crystallogr.* **2002**, *B58*, 389. A CSD search returned 11 hits for tetrapyrrole palladium complexes with CR bridges at the alpha carbon; from these hits 60 Pd−N (palladium to pyrrole) distances were averaged).

(42) Bond, A. D.; Feeder, N.; Redman, J. E.; Teat, S. J.; Sanders, J. K. M. *Cryst. Grow. Des.* **2002**, *2*, 27.

(43) Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462.

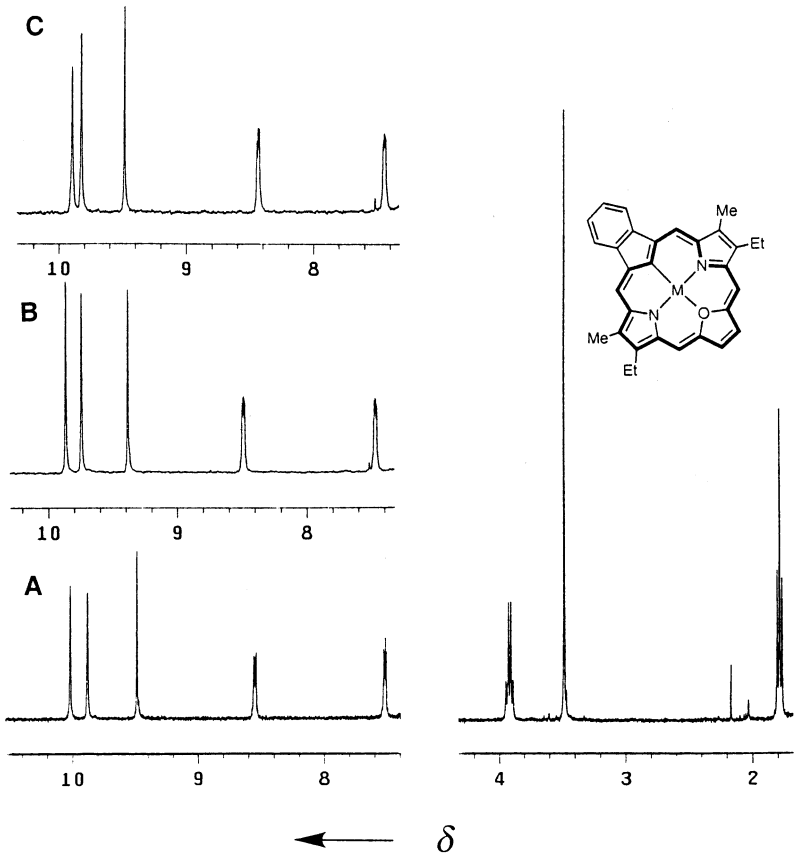


FIGURE 6. (A) 400 MHz proton NMR spectrum of palladium(II) oxacarbaporphyrin **27** in $CDCl_3$. (B) Downfield region for the 400 MHz proton NMR spectrum of nickel(II) complex **26** in $CDCl_3$. (C) Downfield region for the 400 MHz proton NMR spectrum of platinum(II) complex **28** in $CDCl_3$.

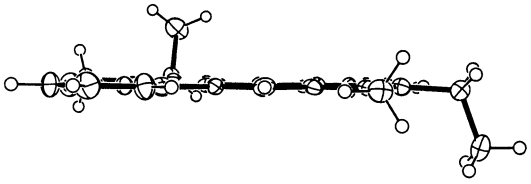
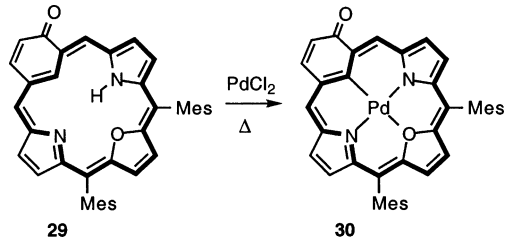


FIGURE 7. Molecular structure (50% probability level) of complex **27** depicting the planar conformation.

SCHEME 9



carbaporphyrin **14** was shown to be a excellent ligand for synthesizing organometallic derivatives. However, unlike benzocarbaporphyrins **1**, which favor the formation of silver(III) or gold(III) derivatives, **14** readily forms complexes with Ni(II), Pd(II), and Pt(II) ions. X-ray crystallography shows that the palladium(II) complex derived from **14** is a highly planar structure, where the metal cation is centrally situated within the macrocyclic cavity. Overall, mixed heterocarbaporphyrinoid systems show considerable promise for further investigation and the metalloderivatives may find applications in the development of novel catalytic systems.

Experimental Section

2,5-Bis(5-benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)pyrrole (10a). A stirred mixture of benzyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate[44] (**11**, 2.56 g) and pyrrole (0.30 g) in acetic acid (2 mL) and ethanol (30 mL) was heated under reflux under a nitrogen atmosphere for 16 h. The solution was cooled to room temperature and further chilled with the aid of an ice bath, and the resulting precipitate was suction filtered, washed with cold ethanol, and dried in vacuo overnight. The tripyrrane dibenzyl ester (2.02 g; 87%) was obtained as an off-white powder: mp 195−196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (6H, t, J = 7.6 Hz), 2.25 (6H, s), 2.34 (4H, q, J = 7.6 Hz), 3.60 (4H, br s), 4.39 (4H, br s), 5.88 (2H, s), 7.03 (4H, m), 7. 24 (6H, m), 9.14 (1H, br s), 11.10 (2H, br s); ^{13}C NMR ($CDCl_3$) δ 11.2, 15.9, 17.3, 24.5, 65.5, 105.1, 117.4, 123.6, 126.8, 126.9, 127.5, 128.4, 132.9, 137.1, 162.9; EI MS m/z (rel int) 578 (40), 577 (100, M^+), 469 (66); HRMS (EI) calcd for $C_{36}H_{39}N_3O_4$ m/z 577.2940, found 577.2938. Anal. Calcd for $C_{36}H_{39}N_3O_4 \cdot {}^1/_4H_2O$: C, 74.27; H, 6.84; N, 7.22. Found: C, 74.00; H, 6.76; N, 7.27.

2,5-Bis(5-benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)furan (4). 2,5-Bis(acetoxymethyl)furan (**5a**, 0.212 g) and benzyl 4-ethyl-3-methylpyrrole-2-carboxylate[45] (**6a**, 0.486 g) were dissolved in acetic acid (100 mL), and the mixture was refluxed under a nitrogen atmosphere for 24 h.

(44) Johnson, A. W.; Kay, I. T.; Markham, E.; Price, R.; Shaw, K.B. *J. Chem. Soc.* **1959**, 3416.

(45) Lash, T. D.; Bellettini, J. R.; Bastian, J. A.; Couch, K. B. *Synthesis* **1993**, 170.

The mixture was diluted with chloroform (200 mL) and washed with water and saturated sodium bicarbonate. The organic layer was evaporated on a rotary evaporator and the residue chromatographed on grade 3 alumina eluting with 10% hexanes−dichloromethane. A yellow fraction was collected and recrystallized from chloroform−hexanes to give the tripyrrane analogue (129 mg, 22%) as pale yellow crystals: mp 196−197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (6H, t, J = 7.6 Hz), 2.29 (6H, s), 2.40 (4H, q, J = 7.6 Hz), 3.84 (4H, s), 5.28 (4H, s), 5.90 (2H, s), 7.36 (10H, m), 8.56 (2H, br s); ^{13}C NMR (DMSO-d_6, 50 °C) δ 11.0, 15.7, 17.2, 25.2, 65.1, 107.2, 116.9, 124.0, 126.8, 128.4 (2), 129.1, 130.6, 137.7, 152.1, 161.2; EI MS *m*/*z* (rel int) 579 (33), 578 (77, M^+), 487 (13), 470 (43), 443 (38), 379 (37), 335 (100); HRMS (EI) calcd for $C_{36}H_{38}N_2O_5$ *m*/*z* 578.2781, found 578.2785. Anal. Calcd for $C_{36}H_{38}N_2O_5 \cdot H_2O$: C, 72.46; H, 6.75; N, 4.70. Found: C, 72.40; H, 6.44; N, 4.90.

2,5-Bis(5-carboxy-3-ethyl-4-methyl-2-pyrrolylmethyl)-furan (7). The foregoing dibenzyl ester (600 mg) was placed in a hydrogenation vessel and dissolved in THF (200 mL, freshly distilled from CaH_2), methanol (100 mL), and triethylamine (20 drops). The air was displaced with nitrogen, 10% Pd/C (200 mg) was added, and the resulting mixture was shaken under hydrogen at room temperature and a pressure of 40 psi for 16 h. The catalyst was removed by suction filtration and the solvent evaporated under reduced pressure. The residue was taken up in 3% aqueous ammonia solution, cooled in an ice−salt bath, and neutralized by the dropwise addition of acetic acid while maintaining the temperature of the mixture between 0 and 5 °C. The mixture was allowed to stand at 0 °C for 1 h, and the precipitate was suction filtered and washed well with water to remove all traces of acetic acid. After drying in vacuo overnight, the dicarboxylic acid (391 mg, 95%) was obtained as a pink powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (6H, t, J = 7.6 Hz), 2.31 (6H, s), 2.44 (4H, q, J = 7.6 Hz), 3.90 (4H, s), 6.05 (2H, s), 8.55 (2H, br s); ^{13}C NMR ($CDCl_3$) δ 10.5, 15.6, 17.4, 25.3, 108.0, 117.5, 124.4, 128.8, 129.8, 151.0, 166.9. Anal. Calcd for $C_{22}H_{26}N_2O_5$: C, 66.32; H, 6.58; N, 7.03. Found: C, 66.32; H, 6.96; N, 6.98.

2,5-Bis(5-ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)thiophene (8). *p*-Toluenesulfonic acid monohydrate (50 mg) was added to a solution of 2,5-bis(acetoxymethyl)-thiophene[46] (**6a**, 1.14 g) and ethyl 4-ethyl-3-methylpyrrole-2-carboxylate[47] (**6b**, 1.81 g) in ethanol and the mixture refluxed under a nitrogen atmosphere for 16 h. The volume was reduced to ca. 25 mL on a rotary evaporator and the remaining solution cooled in an ice bath for 1 h. The resulting precipitate was suction filtered and washed with a small amount of cold ethanol to give the title product (1.19 g, 51%) as pale brown crystals: mp 197−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (6H, t, J = 7.6 Hz), 1.33 (6H, t, J = 7.2 Hz), 2.28 (6H, s), 2.42 (4H, q, J = 7.6 Hz), 4.01 (4H, s), 4.27 (4H, q, J = 7.2 Hz), 6.61 (2H, s), 8.45 (2H, br s); ^{13}C NMR (DMSO-d_6) δ 11.0, 15.2, 15.9, 17.4, 26.5, 59.5, 117.1, 123.3, 124.8, 126.2, 132.6, 141.8, 161.6; EI MS *m*/*z* (rel int) 471 (33), 472 (100, M^+), 424 (81); HRMS (EI) calcd for $C_{26}H_{34}N_2O_4S$ *m*/*z* 470.2239, found 470.2244. Anal. Calcd for $C_{26}H_{34}N_2O_4S$: C, 66.35; H, 7.28; N, 5.95. Found: C, 65.83; H, 7.14; N, 5.72.

8,17-Diethyl-7,18-dimethylbenzo[*b*]-21-carbaporphyrin (12). Dibenzyl ester **10a** (1.30 g) was placed in a hydrogenation vessel and dissolved in THF (200 mL, freshly distilled from CaH_2), methanol (65 mL), and triethylamine (26 drops). The air was displaced with nitrogen, 10% Pd/C (200 mg) was added, and the resulting mixture was shaken under hydrogen at room temperature and a pressure of 40 psi for 16 h. The catalyst was removed by suction filtration and the solvent evaporated under reduced pressure. The residue was taken up in 3% aqueous ammonia solution, cooled in an ice−salt bath, and neutralized by the dropwise addition of acetic acid while the temperature of the mixture was maintained between 0 and 5 °C. The mixture was allowed to stand at 0 °C for 1 h, and the precipitate was suction filtered and washed well with water to remove all traces of acetic acid. After drying in vacuo overnight, tripyrrane **10b** (878 mg, 98%) was obtained as a pale purple powder. The crude dicarboxylic acid was used without further purification.

Tripyrrane **10b** (100 mg) was stirred with TFA (1 mL) under nitrogen for 10 min. The solution was diluted with dichloromethane (19 mL), and 1,3-diformylindene[48] (**13**, 43 mg) was added immediately. The resulting mixture was stirred under nitrogen for 2 h. The solution was neutralized by the dropwise addition of triethylamine, DDQ (58 mg) was added, and the resulting mixture stirred at room temperature for 1 h. The solution was washed with water, evaporated under reduced pressure, and the residue chromatographed on grade 3 alumina eluting with dichloromethane. Recrystallization from chloroform−methanol gave the carbaporphyrin (60 mg, 54%) as purple crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 423 (5.08), 513 (4.13), 546 (4.08), 601 (3.72), 663 nm (3.23); UV−vis (0.01% TFA−$CHCl_3$; monocation) λ_{max} (log ϵ) 392 (sh, 4.64), 424 (4.84), 435 (4.85), 473 (4.31), 548 (4.01), 588 (3.89), 610 (3.81), 671 nm (3.47); UV−vis (50% TFA−$CHCl_3$; dication) λ_{max} (log ϵ) 340 (4.48), 423 (5.15), 597 (3.90), 649 nm (4.31); ^{1}H NMR (400 MHz, $CDCl_3$) δ −7.03 (1H, s), −4.20 (2H, br s), 1.86 (6H, t, J = 7.6 Hz), 3.65 (6H, s), 4.07 (4H, q, J = 7.6 Hz), 7.74−7.77 (2H, m), 8.82−8.85 (2H, m), 9.26 (2H, s), 9.88 (2H, s), 10.12 (2H, s); ^{1}H NMR (400 MHz, 3 drops TFA−$CDCl_3$, monocation) δ −7.04 (1H, s), −4.69 (1H, br s), −3.58 (2H, s), 1.73 (6H, t, J = 7.6 Hz), 3.58 (6H, s), 4.06 (4H, q, J = 7.6 Hz), 7.71−7.74 (2H, m), 8.67−8.69 (2H, m), 9.46 (2H, s), 10.20 (2H, s), 10.34 (2H, s); ^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$, dication) δ −4.78 (2H, s), −1.08 (3H, br s), 1.76 (6H, t, J = 7.6 Hz), 3.55 (6H, s), 3.98 (4H, q, J = 7.6 Hz), 8.90−8.95 (2H, m), 9.31 (2H, s), 10.06−10.12 (2H, m), 10.46 (2H, s), 10.94 (2H, s); ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.7, 16.7, 20.0, 97.7, 104.1, 118.8, 121.6, 128.5, 135.3, 137.6, 137.9, 138.6, 141.9, 142.0, 142.3; HRMS (EI) calcd for $C_{31}H_{29}N_3$ *m*/*z* 443.2361, found 443.2358. Anal. Calcd for $C_{31}H_{29}N_3 \cdot {}^1/_2H_2O$: C, 82.27; H, 6.68; N, 9.28. Found: C, 82.00; H, 6.44; N, 9.20.

8,17-Diethyl-7,18-dimethylbenzo[*b*]-21-carba-23-oxaporphyrin Hydrochloride (14). Dipyrrolylfuran dicarboxylic acid (**7**, 100 mg) was stirred with TFA (1 mL) under nitrogen for 10 min. The solution was diluted with dichloromethane (19 mL), and 1,3-diformylindene[48] (**13**, 43 mg) was added immediately. The resulting mixture was stirred under nitrogen for 2 h. The solution was neutralized by the dropwise addition of triethylamine, DDQ (58 mg) was added, and the resulting mixture was stirred at room temperature for 1 h. The solution was washed with water and evaporated under reduced pressure, and the residue was chromatographed on grade 3 alumina eluting initially with dichloromethane and then with chloroform. A green fraction was collected, and this was washed first with saturated sodium carbonate solution and then with 10% hydrochloric acid. The organic solution was evaporated under reduced pressure and the residue recrystallized from chloroform−methanol to give the oxacarbaporphyrin (50 mg, 41%) as dark green crystals: mp >300 °C; UV−vis (5% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 371 (4.65), 428 (4.85), 521 (4.15), 521 (4.15), 619 (3.81), 677 (3.40), 709 nm (3.16); UV−vis ($CHCl_3$) λ_{max} (log ϵ) 391 (4.79), 426 (4.70), 441 (4.70), 484 (4.47), 606 (4.01), 671 nm (3.19); UV−Vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 324 (4.31), 392 (4.86), 407 (4.77), 446 (4.61), 479 (4.36), 574 (3.96), 609 nm (4.10);^{1}H NMR (400 MHz, pyridine-d_5, 50 °C) δ −4.96 (1H, br s), 1.71 (6H, t, J = 7.6 Hz), 3.45 (6H, s), 3.89 (4H, q, J = 7.6 Hz), 7.75−7.78 (2H, m), 8.92−8.95 (2H, m), 9.93 (2H, s), 10.35 (2H, s), 10.57 (2H, s); ^{1}H NMR (400 MHz, $CDCl_3$) δ −6.45 (1H, s), −1.53 (2H, br s), 1.79 (6H, t, J = 7.2 Hz), 3.56 (6H, s), 4.00 (4H, q, J = 7.2 Hz), 7.61−7.65 (2H, m), 8.57−8.61 (2H, m), 9.78 (2H, s), 10.08 (2H, s), 10.32 (2H, s);

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^{1}H NMR (400 MHz, 1 drop TFA−$CDCl_3$) δ −6.91 (1H, s), −4.37 (2H, br s), 1.80 (6H, t, J = 7.2 Hz), 3.65 (6H, s), 4.10 (4H, q, J = 7.2 Hz), 7.72−7.76 (2H, m), 8.66−8.70 (2H, m), 9.98 (2H, s), 10.29 (2H, s), 10.42 (2H, s); ^{13}C NMR (TFA−$CDCl_3$) δ 11.8, 17.1, 19.9, 94.9, 105.1, 122.0, 128.8, 129.1, 129.6, 135.5, 137.0, 140.1, 140.6, 140.9, 142.6, 153.2; HRMS (EI) calcd for $C_{31}H_{28}N_2O$ *m*/*z* 444.2202, found 444.2206.

8,17-Diethyl-7,18-dimethylbenzo[*b*]-21-carba-23-thiaporphyrin (15). 2,5-Bis(5-ethoxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)thiophene (**8**, 100 mg) was dissolved in TFA (20 mL) and the solution heated under nitrogen at 60 °C for 4 h. The solution was diluted with chloroform (50 mL) and washed with water (50 mL) and saturated sodium bicarbonate solution (50 mL). The organic phase was concentrated on a rotary evaporator to give **9** as a viscous red oil. TFA (2 mL), dichloromethane (200 mL), and 1,3-diformylindene[48] (**13**, 38 mg) were added, and the resulting solution was stirred under nitrogen at room temperature for 2 h. The solution was neutralized by the dropwise addition of triethylamine, DDQ (51 mg) was added, and the mixture was stirred for a further 1 h at room temperature. The solution was washed with water and evaporated under reduced pressure and the residue chromatographed on grade 3 alumina eluting with dichloromethane. The product fraction was collected and washed with a saturated sodium carbonate solution. Recrystallization from chloroform−hexanes gave the thiacarbaporphyrin (30 mg, 31%) as dark brown crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 387 (4.60), 431 (4.89), 527 (4.14), 623 (3.80), 683 nm (3.22); UV−vis (0.01% TFA−$CHCl_3$) λ_{max} (log ϵ) 428 (4.86), 617 (4.09), 667 nm (3.50); ^{1}H NMR (400 MHz, $CDCl_3$) δ −5.49 (1H, s), −4.30 (1H, br s), 1.81 (6H, t, J = 7.6 Hz), 3.48 (6H, s), 3.89 (4H, q, J = 7.6 Hz), 7.74−7.77 (2H, m), 8.85−8.88 (2H, m), 9.89 (2H, s), 10.20 (2H, s), 10.41 (2H, s); ^{1}H NMR (400 MHz, 1 drop TFA−$CDCl_3$) δ −7.45 (1H, s), −5.86 (2H, br s), 1.81 (6H, t, J = 7.6 Hz), 3.55 (6H, s), 4.02 (4H, q, J = 7.6 Hz), 7.81−7.84 (2H, m), 8.66−8.70 (2H, m), 10.10 (2H, s), 10.21 (2H, s), 10.71 (2H, s); ^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$) δ −6.69 (1H, s), −5.34 (2H, s), 1.94 (6H, t, J = 7.2 Hz), 3.76 (6H, s), 4.23 (4H, q, J = 7.6 Hz), 7.88−7.92 (2H, m), 8.86−8.90 (2H, m), 10.40 (2H, s), 10.67 (2H, s), 11.10 (2H, s); ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.6, 17.0, 20.1, 105.0, 108.1, 122.1, 129.7, 135.8, 137.2, 138.5, 141.1, 141.4, 141.5, 144.8; HRMS (EI) calcd for $C_{31}H_{28}N_2S$ *m*/*z* 460.1973, found 460.1967. Anal. Calcd for $C_{31}H_{28}N_2S\cdot{}^1/_4H_2O$: C, 80.05; H, 6.17; N, 6.02. Found: C, 79.92; H, 6.01; N, 6.07.

9,18-Diethyl-8,19-dimethyl-2-oxybenziporphyrin (16). Tripyrrane **10b** (200 mg) was stirred with TFA (2 mL) under nitrogen for 10 min. The solution was diluted with dichloromethane (38 mL), and 5-formylsalicylaldehyde (**22**, 76 mg) was added immediately. The resulting mixture was stirred under nitrogen for 2 h. The solution was neutralized by the dropwise addition of triethylamine, DDQ (116 mg) was added, and the resulting mixture was stirred at room temperature for 1 h. The solution was washed with water and evaporated under reduced pressure, and the residue was chromatographed on grade 3 alumina eluting initially with dichloromethane and then with chloroform. Recrystallization from chloroform−methanol gave the oxybenziporphyrin (80 mg, 38%) as purple crystals: mp >300 °C; IR (KBr) $\nu_{C=O}$ 1627 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 426 (5.24), 450 (4.91), 546 (3.90), 587 (4.42), 638 (3.83), 701 nm (3.85); UV−vis (0.01% TFA−$CHCl_3$) λ_{max} (log ϵ) 425 (5.21), 451 (4.78), 588 (4.26), 633 (3.93), 695 nm (3.81); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 317 (4.42), 348 (4.68), 430 (4.86), 558 (3.83), 604 (4.26), 710 (3.83), 775 nm (3.98); ^{1}H NMR (400 MHz, $CDCl_3$) δ −7.11 (1H, s), −3.56 (2H, br s), 1.72−1.79 (6H, 2 overlapping triplets), 3.41 (3H, s), 3.53 (3H, s), 3.84−3.92 (4H, 2 overlapping quartets), 7.41 (1H, d, J = 9.6 Hz), 8.67 (1H, d, J = 9.6 Hz), 8.92−8.94 (2H, AB quartet, J = 4.4 Hz), 9.20 (1H, s), 9.32 (1H, s), 9.37 (1H, s), 10.46 (1H, s); ^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$) δ 1.20 (1H, s), 1.46 (6H, t, J = 7 Hz), 3.00 (3H, s), 3.01 (3H, s), 3.30−3.36 (4H, 2 overlapping quartets), 5.18 (1H, br s), 5.23 (1H, br s), 7.62 (1H, d, J = 9 Hz), 8.27 (1H, s), 8.31 (1H, s), 8.35−8.40 (2H, AB quartet, J = 5.2 Hz), 8.66 (1H, d, J = 9 Hz), 8.93 (1H, s), 9.54 (1H, s); ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.3, 11.4, 15.4, 15.5, 19.0, 96.9, 98.5, 115.5, 118.4, 121.4, 123.5, 123.8, 126.0, 133.0, 133.8, 140.5, 141.5, 145.2, 146.5, 146.8, 148.3, 150.2, 151.8, 153.8, 176.4; HRMS (EI) calcd for $C_{28}H_{27}N_3O$ *m*/*z* 421.2154, found 421.2150. Anal. Calcd for $C_{28}H_{27}N_3O\cdot H_2O$: C, 76.51; H, 6.42; N, 9.56. Found: C, 76.41; H, 6.53; N, 9.17.

9,18-Diethyl-8,19-dimethyl-24-oxa-2-oxybenziporphyrin Hydrochloride (17). The title compound was prepared from **10b** (100 mg) and 5-formylsalicylaldehyde (**22**, 38 mg) by the procedure described for **14**. The crude product was chromatographed on a grade 3 alumina column eluting initially with dichloromethane and then with chloroform. A green fraction was collected, and this was washed first with saturated sodium carbonate solution and then 10% hydrochloric acid. Recrystallization from chloroform−hexanes gave the oxaoxybenziporphyrin (60 mg, 52%) as dark green crystals: mp >300 °C; IR (KBr) $\nu_{C=O}$ 1625 cm^{-1}; UV−vis (5% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 416 (4.95), 466 (4.70), 597 (4.23), 724 nm (3.96); UV−vis ($CHCl_3$) λ_{max} (log ϵ) 424 (5.19), 478 (4.83), 592 (3.99), 639 (4.24), 680 nm (3.85); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 348 (4.72), 423 (4.87), 556 (3.79), 600 (4.11), 653 (3.80), 719 nm (3.79); ^{1}H NMR (400 MHz, $CDCl_3$) δ −5.23 (1H, s), 0.40 (1H, br s), 0.52 (1H, br s), 1.64−1.69 (6H, 2 overlapping triplets), 3.38 (3H, s), 3.47 (3H, s), 3.79−3.88 (4H, 2 overlapping quartets), 7.32 (1H, d, J = 9.2 Hz), 8.63 (1H, d, J = 9.2 Hz), 9.51 (1H, d, J = 3.6 Hz), 9.59 (1H, d, J = 3.6 Hz), 9.71 (1H, s), 9.76 (1H, s), 9.82 (1H, s), 10.84 (1H, s); ^{1}H NMR (400 MHz, pyridine-d_5) δ −4.5 (1H, br s), 1.30−1.39 (6H, 2 overlapping triplets), 2.99 (3H, s), 3.06 (3H, s), 3.44 (2H, q, J = 7.6 Hz), 3.52 (2H, q, J = 7.6 Hz),7.35 (1H, d, obscured by pyridine peak), 8.74 (1H, d, J = 9.6 Hz), 9.54−9.61 (2H, poorly resolved AB quartet), 9.77 (1H, s), 9.82 (1H, s), 9.97 (1H, s), 10.86 (1H, s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (1H, s), 1.45−1.50 (6H, 2 overlapping triplets), 3.03 (3H, s), 3.04 (3H, s), 3.35 (4H, q, J = 7.3 Hz), 5.46 (1H, s), 5.58 (1H, s), 7.67 (1H, d, J = 8.8 Hz), 8.33 (1H, s), 8.36 (1H, s), 8.69 (1H, d, J = 8.8 Hz), 8.72−8.77 (2H, AB quartet, J = 5 Hz), 9.06 (1H, s), 9.68 (1H, s); ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.3, 11.5, 15.5, 15.6, 18.8 (2), 95.2, 96.5, 120.0, 120.8, 121.6, 123.6, 124.0, 128.3, 133.9, 135.0, 139.5, 140.3, 140.8, 140.9, 145.2, 146.1, 149.1, 150.7, 151.1, 156.9, 161.0, 177.2; HRMS (EI) calcd for $C_{28}H_{26}N_2O_2$ *m*/*z* 422.1994, found 422.1992.

9,18-Diethyl-8,19-dimethyl-24-thia-2-oxybenziporphyrin (18). The title compound was prepared from thiatripyrrane diethyl ester **8** (100 mg) and 5-formylsalicylaldehyde (**22**, 32 mg) by the procedure described for **15**. The crude product was chromatographed on a grade 3 alumina column eluting with dichloromethane. The product fraction was washed with saturated sodium carbonate solution and recrystallized from chloroform−hexanes to give the thiaoxybenziporphyrin (14 mg, 15%) as dark green crystals: mp >300 °C; IR (KBr) $\nu_{C=O}$ 1624 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 353 (4.27), 427 (4.93), 471 (4.72), 605 (4.19), 733 nm (3.88); UV−vis (0.01% TFA−$CHCl_3$) λ_{max} (log ϵ) 319 (4.40), 330 (4.40), 440 (4.91), 492 (4.50), 606 (4.06), 726 nm (3.79); UV−vis (50% TFA−$CHCl_3$) λ_{max} (log ϵ) 358 (4.54), 441 (4.86), 577 (3.64), 624 (3.91), 730 nm (3.74); ^{1}H NMR (400 MHz, $CDCl_3$) δ −5.80 (1H, s), −4.24 (1H, br s), 1.67−1.74 (6H, 2 overlapping triplets), 3.25 (3H, s), 3.37 (3H, s), 3.65−3.75 (4H, 2 overlapping quartets), 7.40 (1H, d, J = 9.2 Hz), 8.68 (1H, d, J = 9.2 Hz), 9.25 (1H, s), 9.50 (1H, d, J = 4 Hz), 9.55 (1H, d, J = 4 Hz), 9.85 (1H, s), 9.93 (1H, s), 10.59 (1H, s); ^{1}H NMR (400 MHz, 1 drop TFA−$CDCl_3$) δ −4.63 (1H, s), 1.69−1.75 (6H, 2 overlapping triplets), 3.45 (3H, s), 3.49 (3H, s), 3.85−3.93 (4H, 2 overlapping quartets), 7.68 (1H, d, J = 8.8 Hz), 8.97 (1H, d, J = 8.8 Hz), 9.80−9.87 (2H, AB quartet, J = 5 Hz), 9.92 (1H, s), 10.35 (1H, s), 10.46 (1H, s), 10.96 (1H, s); ^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$) δ 0.45 (1H, d, J = 2 Hz), 1.54−1.59 (6H, 2 overlapping triplets), 3.14 (3H, s), 3.15 (3H, s), 3.43−3.49 (4H, 2 overlapping quartets), 3.6 (2H, v br), 7.84 (1H, d, J = 8.8 Hz), 8.96 (1H, dd, ^4J = 2 Hz, ^3J = 2 Hz,

9 Hz), 9.09−9.14 (2H, AB quartet, J = 5.6 Hz), 9.27 (1H, s), 9.32 (1H, s), 9.33 (1H, s), 10.09 (1H, s); ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.7, 11.8, 16.2, 16.3, 19.6, 108.9, 111.1, 119.0, 119.8, 125.1, 125.6, 127.9, 138.3, 139.0, 139.5, 139.8, 142.4, 142.5, 142.9, 145.5, 147.4, 148.9, 149.9, 151.5, 152.5, 185.9; HRMS (EI) calcd for $C_{28}H_{26}N_2OS$ m/z 438.1766, found 438.1768.

9,18-Diethyl-8,19-dimethyl-2-oxypyriporphyrin (19). The oxypyriporphyrin was prepared from tripyrrane **10b** (200 mg) and 3-hydroxy-2,6-pyridinedicarbaldehyde[21] (**23**, 76 mg) by the procedure described for **16**. The crude product was chromatographed on grade 3 alumina, eluting first with dichloromethane and then with chloroform. Recrystallization from chloroform−methanol afforded the title porphyrin analogue (65 mg, 31%) as purple crystals: mp >300 °C; IR (KBr) $\nu_{C=O}$ 1634 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 420 (5.27), 438 (5.06), 545 (3.79), 586 (4.34), 609 (4.26), 660 nm (3.30); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 425 (5.27), 441 (5.15), 568 (3.91), 595 (3.94), 619 (3.88), 647 nm (4.14); ^{1}H NMR (400 MHz, $CDCl_3$) δ −4.33 (1H, s), −4.29 (2H, s), 1.76−1.85 (6H, 2 overlapping triplets), 3.46 (3H, s), 3.63 (3H, s), 3.93−4.04 (4H, 2 overlapping quartets), 7.85 (1H, d, J = 9.6 Hz), 9.10 (2H, s), 9.12 (1H, d, J = 9.6 Hz), 9.29 (1H, s), 9.68 (1H, s), 9.71 (1H, s), 10.84 (1H, s); ^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$) δ 1.74 (6H, t, J = 7.6 Hz), 3.57 (3H, s), 3.60 (3H, s), 4.06 (4H, q, J = 7.6 Hz), 8.87 (1H, d, J = 9.6 Hz), 9.61−9.65 (2H, AB quartet, J = 4.8 Hz), 10.05 (1H, d, J = 9.6 Hz), 10.39 (1H, s), 10.66 (1H, s), 10.67 (1H, s), 11.26 (1H, s); ^{13}C NMR ($CDCl_3$) δ 11.4, 11.8, 17.3, 19.6, 19.7, 99.9, 100.3, 103.0, 107.7, 131.2, 134.8, 135.0, 135,1, 135.7, 137.2, 137.7, 138.1, 138.4, 139.4, 139.9, 144.0, 145.8, 155.2, 155.6, 184.9; ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.9, 12.1, 16.5 (2), 20.1, 101.9, 104.4, 104.6, 105.7, 131.3, 133.1, 135.2, 136.1, 139.1, 140.3, 142.7, 143.8, 143.9, 144.9, 145.3, 145.5, 180.0; HRMS (EI) calcd for $C_{27}H_{26}N_4O$ m/z 422.2107, found 422.2109. Anal. Calcd for $C_{27}H_{26}N_4O\cdot{}^1/_3CHCl_3$: C, 71.01; H, 5.70; N, 12.12. Found: C, 71.12; H, 6.05; N, 11.68.

9,18-Diethyl-8,19-dimethyl-24-oxa-2-oxypyriporphyrin Hydrochloride (20·HCl). The title compound was prepared from **7** (100 mg) and 3-hydroxy-2,6-pyridinedicarbaldehyde[21] (**23**, 38 mg) by the procedure described for **14**. The crude product was chromatographed on a grade 3 alumina column eluting initially with dichloromethane and then with chloroform. A green fraction was collected, and this was washed first with saturated sodium carbonate solution and then 10% hydrochloric acid. Recrystallization from chloroform−hexanes gave the oxaoxypyriporphyrin (53 mg, 40%) as dark green crystals: mp >300 °C; IR (KBr) $\nu_{C=O}$ 1638 cm^{-1}; UV−vis (5% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 406 (4.78), 452 (4.56), 591 (4.01), 621 (3.85), 676 nm (3.92); UV−vis (0.01% TFA−$CHCl_3$) λ_{max} (log ϵ) 424 (5.19), 478 (4.83), 590 (4.00), 638 (4.25), 627 nm (3.87); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 414 (4.99), 448 (4.94), 586 (3.96), 627 nm (4.22); ^{1}H NMR (400 MHz, TFA−$CDCl_3$) δ −4.75 (1H, br s), −4.70 (1H, br s), 1.89 (6H, br m), 3.76 (6H, br s), 4.22 (4H, br m), 7.37 (1H, br), 8.27 (1H, br), 10.27 (1H, br s), 10.37 (1H, br), 10.42 (1H, br), 10.68 (1H, br s), 10.76 (1H, br s), 11.34 (1H, s); ^{13}C NMR (6 drops TFA−$CDCl_3$) δ 12.1, 16.9, 20.0, 97.1, 97.7, 111.6, 116.6, 132.2, 133.3, 133.8, 138.3, 139.3, 140.4, 141.1, 142.1, 142.5, 143.9, 144.8, 144.9, 149.4, 155.7, 156.1, 185.0; FD MS m/z (rel int) 425 (54), 424 (100, [M + H]$^+$), 423 (53, M$^+$); FAB MS m/z (rel int) 425 (100).

9,18-Diethyl-8,19-dimethyl-24-thia-2-oxypyriporphyrin (21). The title compound was prepared from thiatripyrrane diethyl ester **9** (100 mg) and 3-hydroxy-2,6-pyridinedicarbaldehyde[21] (**23**, 32 mg) by the procedure described for **15**. The crude product was chromatographed on a grade 3 alumina column eluting with dichloromethane. The product fraction was washed with saturated sodium carbonate solution and recrystallized from chloroform−hexanes to give the thiaoxypyriporphyrin (9 mg, 10%) as dark green crystals: mp >300 °C; IR (KBr) $\nu_{C=O}$ 1636 cm^{-1}; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 424 (4.86), 535 (3.85), 568 (3.99), 604 (3.75), 683 (3.56), 709 nm (3.66); UV−vis (5% TFA−$CHCl_3$) λ_{max} (log ϵ) 430 (5.00), 463 (4.88), 601 (3.98), 644 nm (4.07); ^{1}H NMR (400 MHz, $CDCl_3$) δ −4.89 (1H, v br), 1.74−1.80 (6H, 2 overlapping triplets), 3.33 (3H, s), 3.44 (3H, s), 3.75−3.85 (4H, 2 overlapping quartets), 8.07 (1H, d, J = 9.2 Hz), 9.33 (1H, d, J = 9.2 Hz), 9.43 (1H, s), 9.87−9.92 (2H, AB quartet, J = 4.4 Hz), 10.37 (1H, s), 10.39 (1H, s), 10.80 (1H, s); ^{1}H NMR (400 MHz, 1 drop TFA−$CDCl_3$) δ 1.92−1.97 (6H, 2 overlapping triplets), 3.78 (3H, s), 3.81 (3H, s), 4.20−4.27 (4H, 2 overlapping quartets), 8.33 (1H, d, J = 8.8 Hz), 9.73 (1H, d, J = 8.8 Hz), 10.37−10.41 (2H, m), 10.41 (1H, s), 11.22 (1H, s), 11.28 (1H, s), 11.64 (1H, s); ^{13}C NMR (3 drops TFA−$CDCl_3$) δ 11.8, 11.9, 17.1, 20.2, 111.0, 111.1, 111.8, 115.2, 130.6, 133.3, 137.8, 138.2, 139.7, 140.6, 141.2, 142.3, 142.9, 144.2, 146.3, 146.6, 147.1, 147.8, 148.5, 150.4, 187.0; HRMS (EI) calcd for $C_{27}H_{25}N_3OS$ m/z 439.1718, found 439.1722.

[8,17-Diethyl-7,18-dimethylbenzo[*b*]-21-carba-23-oxaporphyrinato]nickel(II) (26). A mixture of oxacarbaporphyrin **14** (20 mg) and nickel(II) acetate (12 mg) in DMF (20 mL) was heated for 1 h at 120−130 °C. The mixture was diluted with chloroform and washed with water. The organic solvents were removed under reduced pressure, and the residue was chromatographed on a silica gel column eluting with dichloromethane. Recrystallization from chloroform−hexanes gave the nickel(II) derivative (11 mg, 53%) as black crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 392 (4.87), 470 (4.41), 580 nm (3.94); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (6H, t, J = 7.6 Hz), 3.41 (6H, s), 3.83 (4H, q, J = 7.6 Hz), 7.47 (2H, m), 8.49 (2H, m), 9.39 (2H, s), 9.75 (2H, s), 9.87 (2H, s); HRMS (EI) calcd for $C_{31}H_{26}N_2ONi$ m/z 500.1399, found 500.1405.

[8,17-Diethyl-7,18-dimethylbenzo[*b*]-21-carba-23-oxaporphyrinato]palladium(II) (27). A mixture of oxacarbaporphyrin **14** (20 mg) and palladium(II) acetate (10 mg) in DMF (20 mL) was heated for 1 h at 120−130 °C. The mixture was diluted with chloroform and washed with water. The organic solvents were removed under reduced pressure, and the residue was chromatographed on a silica gel column eluting with 50% dichloromethane−chloroform. Recrystallization from chloroform−hexanes gave the palladium(II) complex (16 mg, 70%) as black crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 322 (4.30), 378 (4.77), 447 (4.54), 473 (4.71), 496 (4.34), 576 (4.07), 603 (4.00), 639 nm (3.28); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (6H, t, J = 7.6 Hz), 3.49 (6H, s), 3.92 (4H, q, J = 7.6 Hz), 7.52 (2H, m), 8.55 (2H, m), 9.49 (2H, s), 9.89 (2H, s), 10.02 (2H, s); HRMS (EI) calcd for $C_{31}H_{26}N_2OPd$ m/z 548.1080, found 548.1074.

[8,17-Diethyl-7,18-dimethylbenzo[*b*]-21-carba-23-oxaporphyrinato]platinum(II) (28). A mixture of oxacarbaporphyrin **14** (20 mg) and platinum(II) chloride (12 mg) in DMF (20 mL) was heated for 3 h at 120−130 °C. The mixture was diluted with chloroform and washed with water. The organic solvents were removed under reduced pressure, and the residue was chromatographed on a silica gel column eluting with dichloromethane. Recrystallization from chloroform−hexanes gave the platinum(II) complex (1.5 mg, 5%) as dark crystals: mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (rel int) 349 (0.20), 380 (1.00), 419 (0.23), 454 (0.33), 569 nm (0.09);^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (6H, t, J = 7.6 Hz), 3.45 (6H, s), 3.89 (4H, q, J = 7.6 Hz), 7.43−7.46 (2H, m), 8.42−8.45 (2H, m), 9.49 (2H, s), 9.82 (2H, s), 9.90 (2H, s); HRMS (EI) calcd for $C_{31}H_{26}N_2O^{195}Pt$ m/z 637.1693, found 637.1688.

Crystal Structure Determination of 27. X-ray data were collected with a Bruker P4/R4/SMART 1000 diffractometer using Mo Kα radiation (λ = 0.710 73 Å) at −80 °C. Data collection and cell refinement were performed using SMART.[49a] Data reduction was accomplished using SAINT.[49b] Empirical absorption correction was performed on the data though use of the SADABS procedure.[49c] Solution and data analyses were

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

performed using the WinGX software package.[50] The structure was solved using the direct methods program SIR-92.[51] Remaining atoms were located using difference Fourier syntheses and full-matrix least-squares refinement on F^2 leading to convergence using SHELXL-97.[52] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were assigned positions based on the geometries of their attached carbon atoms, and were given isotropic thermal parameters of 20% greater than their parent carbon atoms.

X-ray quality crystals were obtained by slow diffusion of hexanes into a chloroform solution of **27**. A purple needle thereby obtained of approximately 0.18 × 0.05 × 0.04 mm^3 was mounted on a glass fiber with Paratone-N and transferred to the diffractometer. Limiting indices were as follows: $-11 \leq h \leq 12$, $-20 \leq k \leq 20$, $-13 \leq l \leq 18$. The structure was refined to convergence, $(\Delta/\sigma)_{max} = 0.000$; a final difference Fourier synthesis showed features in the range $\Delta\rho_{max} = 0.650$ e $Å^{-3}$ to $\Delta\rho_{min} = -0.543$ e $Å^{-3}$ and were deemed to have no chemical significance.

Complete X-ray structural data has been deposited at the Cambridge Crystallographic Data Centre, CCDC no. 233162. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; URL, http://www.ccdc.cam.ac.uk).

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Supporting Information Available: UV−vis, ^{1}H NMR, ^{13}C NMR, and mass spectra for selected compounds. X-ray data for compound **27**. This material is available free of charge via the Internet at http://pubs.acs.org.

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