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Tropiporphyrins, Cycloheptatrienyl Analogues of the Porphyrins: Synthesis, Spectroscopy, Chemistry, and Structural Characterization of a Silver(III) Derivative†

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Tripyrranes were condensed with 1,3,5-cycloheptriene-1,6-dicarbaldehyde in TFA−CH_2Cl_2 to give, following oxidation with 0.1% aqueous ferric chloride solutions, a series of tropiporphyrins **9**. These cycloheptatrienyl analogues of the porphyrins show strong diatropic ring currents by proton NMR spectroscopy where the internal CH gives a resonance at −7.3 ppm, although the *meso*-protons are not shifted as far downfield as most aromatic porphyrinoid systems. These data indicate that the seven-membered ring distorts the porphyrinoid macrocycle and decreases the overall diatropicity in tropiporphyrins. Addition of trace amounts of TFA to solutions of **9** affords the corresponding aromatic monocations, and at higher acid concentrations a nonaromatic dication is generated. The dication has undergone C-protonation at one of the *meso*-bridges and has lost the plane of symmetry present in the parent system. This species shows significant downfield shifts to the cycloheptatrienyl protons, indicating that this unit has taken on tropylium character. Tropiporphyrin **9a** underwent a Diels−Alder cycloaddition with dimethyl acetylenedicarboxylate in refluxing xylenes to give modest yields of the related adduct. The Diels−Alder adduct **17** showed an increased diatropic ring current where the internal proton shifted beyond −9 ppm, and this indicates that the [18]annulene substructure has flattened out compared to **9a**. Diimide reduction of **9a** afforded a dihydrotropiporphyrin that also showed a stronger ring current. Tropiporphyrins **9** were also shown to react with silver(I) acetate in the presence of DBU in refluxing pyridine to give the corresponding silver(III) organometallic derivatives. The *meso*-protons for these metal complexes give proton NMR chemical shift values similar to those for the parent tropiporphyrins, indicating that the macrocycle is still distorted, but the external olefinic protons are shifted downfield compared to **9**. A diphenyl-substituted silver(III) derivative **18b** was further characterized by X-ray crystallography. This shows that the cycloheptatriene unit takes on a highly twisted geometry that distorts the overall conformation of the porphyrinoid macrocycle.

Introduction

The replacement of one or more pyrrole unit within the porphyrin macrocycle with carbon rings produces a series of carbaporphyrinoid systems with unique chemical and spectroscopic properties.[1,2] The introduction of a cyclopentadiene or indene moiety gives rise to true carbaporphyrins,[3−5] species that retain the full aromatic character of the porphyrin macrocycle. For instance, the proton NMR spectrum of benzocarbaporphyrin **1** (Chart 1) in $CDCl_3$ shows the internal CH upfield at −7 ppm, while the external *meso*-protons give rise to two singlets near 10 ppm.[3,4] The $\Delta\delta$ for the interior vs exterior protons of >17 ppm points to a powerful diatropic ring current even though the indene unit is tilted ca. 15.5° from the mean ring plane.[4] The origin of the diatropic or aromatic character in porphyrin-type systems is often attributed to the presence of an [18]annulene substructure,[5,6] although other interpretations have been put forward.[7] Benzocarbaporphyrins undergo some unusual chemistry, including selective oxidation reactions at the internal carbon,[8] and form stable silver(III) and gold(III) organometallic derivatives (e.g., **2**).[9,10] Azuliporphyrins **3**, where an azulene has formally replaced one of the pyrrole rings, show very different properties and can be considered to

† Part 36 in the series "Conjugated Macrocycles Related to the Porphyrins". For part 35, see: Liu, D.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 6079−6093.

(1) Lash, T. D. *Synlett* **2000**, 279.
(2) Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, pp 125−199.
(3) Lash, T. D.; Hayes, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 840.
(4) Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860. See also: Liu, D.; Lash, T. D. *Chem. Commun.* **2002**, 2426.
(5) Liu, D.; Lash, T. D. *J. Org. Chem.* **2003**, *68*, 1755.
(6) (a) Vogel, E.; Haas, W.; Knipp, B.; Lex, J.; Schmickler, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 406. (b) Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461.
(7) Cyranski, M. K.; Krygowski, T. M.; Wisiorowski, M.; Hommes, N. J. R. van E.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 177.
(8) (a) Hayes, M. J.; Spence, J. D.; Lash, T. D. *Chem. Commun.* **1998**, 2409. (b) Lash, T. D.; Muckey, M. A.; Hayes, M. J.; Liu, D.; Spence, J. D.; Ferrence, G. M. *J. Org. Chem.* **2003**, *68*, 8558.
(9) Muckey, M. A.; Szczepura, L. F.; Ferrence, G. M.; Lash, T. D. *Inorg. Chem.* **2002**, *41*, 4840.

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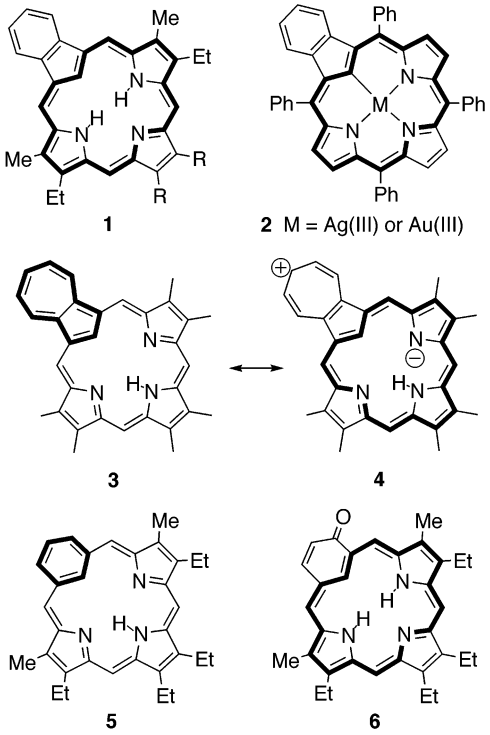
CHART 1



have only borderline aromatic character.[11,12] The azulene effectively disrupts the [18]annulene substructure by introducing cross-conjugation.[11] This factor is mitigated to a certain extent by dipolar canonical forms such as **4** that simultaneously introduce tropylium and carbaporphyrinoid aromatic character (Chart 1). Although this contribution is limited by the associated requirement for charge separation, the diatropic ring current is greatly enhanced in the presence of acid where the resulting dication is stabilized by charge delocalization through this type of resonance contributor.[11] The azuliporphyrins also exhibit remarkable chemical properties, showing oxidative ring contractions to benzocarbaporphyrins[12,13] and the ability to undergo rapid oxidative metalations in the presence of copper(II) acetate.[14] Unlike benzocarbaporphyrins **1**, the azuliporphyrin system **3** acts as a dianionic ligand giving stable nickel(II), palladium(II), and platinum(II) organometallic derivatives.[15] Other carbaporphyrinoid systems include benziporphyrins **5**[16,17] and oxybenziporphyrins **6**.[17−19] The former macrocycle is nonaromatic, but the latter shows a powerful diatropic ring current.[18] Interestingly, tetraphenylbenziporphyrins have been shown to be dianionic ligands,[20] while oxybenziporphyrins can form both palladium(II)[21] and silver(III) derivatives.[10] Hence, carbaporphyrinoids are emerging as an important class of porphyrin analogues that show novel chemical properties and have the potential to find applications in the development of new catalytic systems[22] or as photosensitizers in photodynamic therapy.[23]

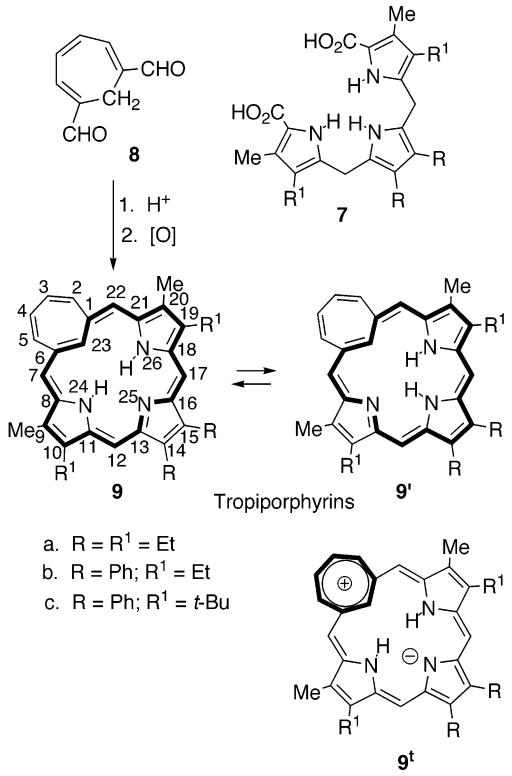
Carbaporphyrinoid systems can be generated by reacting tripyrranes **7**[24,25] with carbocyclic dialdehydes using the MacDonald "3 + 1" methodology.[26] We have previously reported that 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (**8**)[27] reacts with tripyrrane **7a** in the presence of trifluoroacetic acid to give, following oxidation with DDQ, the ususual carbaporphyrinoid system **9**.[28] Although these cycloheptatrienyl porphyrin analogues, which have been named tropiporphyrins, are known to be fully aromatic, few details on this system have been published previously. We now report full details on the synthesis and chemistry of tropiporphyrins and the first X-ray structural characterization of a tropiporphyrin derivative.[28,29]

Results and Discussion

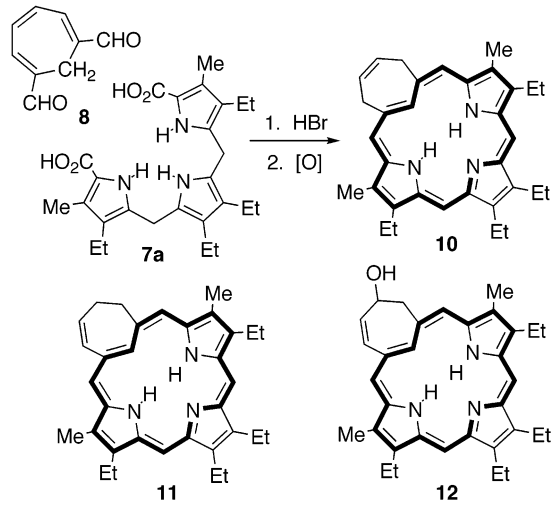
In our initial study, tripyrrane **7a** was condensed with dialdehyde **8** under conventional "3 + 1" conditions to afford tropiporphyrin **9a** in 23% yield (Scheme 1). The reaction was carried out under relatively concentrated conditions (19 mL of CH_2Cl_2 and 1 mL of TFA for every 100 mg of **7a**), and following neutralization with triethylamine the reaction mixture was oxidized with DDQ.[28] Surprisingly, in an independent study using more dilute conditions with HBr as the acid catalyst, Breitmaier and co-workers reported that reaction of **7a** with **8** gave rise to the formation of a complex mixture of carbaporphyrinoid products **10**−**12** (Scheme 2), and only a trace amount of impure **9a** could be isolated.[30] We have now improved upon our initial procedures and find that

(10) Lash, T. D.; Rasmussen, J. M.; Bergman, K. M.; Colby, D. A. *Org. Lett.* **2004**, *6*, 549. See also: Miyake, K.; Lash, T. D. *Chem. Commun.* **2004**, 178.
(11) Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839. (b) Graham, S. R.; Colby, D. A.; Lash, T. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1371.
(12) (a) Colby, D. A.; Lash, T. D. *Chem. Eur. J.* **2002**, *8*, 5397. (b) Lash, T. D.; Colby, D. A.; Ferrence, G. M. *Eur. J. Org. Chem.* **2003**, 4533.
(13) Lash, T. D. *Chem. Commun.* **1998**, 1683.
(14) Colby, D. A.; Ferrence, G. M.; Lash, T. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 1346.
(15) (a) Graham, S. R.; Ferrence, G. M.; Lash, T. D. *Chem. Commun.* **2002**, 894. (b) Lash, T. D.; Colby, D. A.; Graham, S. R.; Ferrence, G. M.; Szczepura, L. F. *Inorg. Chem.* **2003**, *42*, 7326.
(16) Berlin, K.; Breitmaier, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1246.
(17) Lash, T.D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076.
(18) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533.
(19) Richter, D. T.; Lash, T. D. *Tetrahedron* **2001**, *57*, 3659.
(20) (a) Stepien, M.; Latos-Grazynski, L. *Chem. Eur. J.* **2001**, *7*, 5113. (b) Szymanski, J. T.; Lash, T. D. *Tetrahedron Lett.* **2003**, *44*, 8613.
(21) Stepien, M.; Latos-Grazynski, L.; Lash, T. D.; Szterenberg, L. *Inorg. Chem.* **2001**, *40*, 6892. See also: Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462.
(22) For example, Gross, Z.; Simkhovich, L.; Galili, N. *Chem. Commun.* **1999**, 599.
(23) (a) Pandey, R. K.; Zheng, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 6, pp 157−230. (b) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19.
(24) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394.
(25) Lash, T. D. *J. Porphyrins Phthalocyanines* **1997**, *1*, 29.
(26) Lash, T. D. *Chem. Eur. J.* **1996**, *2*, 1197.
(27) Vogel, E.; Deger, H. M.; Sombroek, J.; Palm, J.; Wagner, A.; Lex, J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 41.
(28) Preliminary communication: Lash, T. D.; Chaney, S. T. *Tetrahedron Lett.* **1996**, *37*, 8825.
(29) These results were presented, in part, at the following meetings: (a) 213th National American Chemical Society Meeting, San Francisco, California, April 1997 (Petryka, J. C.; Chaney, S. T.; Lash, T. D. Book of Abstracts, ORGN 298. (b) 5th Chemical Congress of North America, Cancun, Mexico, November 1997 (Lash, T. D.; Chaney, S. T.; Hayes, M. J.; Richter, D. T. Book of Abstracts, Abstract 1154).
(30) Berlin, K.; Steinbeck, C.; Breitmaier, E. *Synthesis* **1996**, 336.

SCHEME 1



SCHEME 2



tropiporphyrin **9a** can be obtained in 38% yield using slightly more dilute conditions with ferric chloride being used as the oxidant.[31,32] Reaction of **8** with tripyrranes **7b** and **7c** gave the related tropiporphyrins **9b** and **9c** under these conditions in 34% and 21% yield, respectively. Tropiporphyrins **9b** and **9c** show properties similar to those of **9a**, although the UV−vis absorptions are shifted to slightly higher wavelengths, and for this reason most of the discussion will focus on the properties of tetraethyldimethyltropiporphyrin **9a**.

The spectroscopic properties of tropiporphyrins **9** differ considerably from other carbaporphyrinoid systems. Although the UV−vis spectrum for **9a** shows a Soret band at 395 nm, this is broadened and weakened compared to other aromatic carbaporphyrinoids (Figure 1). The "Q-bands" are also ill-defined and a very broad weak band extends into the far red region. In the presence of 1% TFA, the reddish-brown solutions associated with the free base tropiporphyrins turn to a bright green, and the resulting species show highly modified UV−vis spectra with a bathochromically shifted Soret band (439 nm for **9a**) and two Q-bands near 600 nm (Figure 1). These spectra were attributed to the monocationic species **13** (Scheme 3). Further addition of TFA to **9a** gave rise to a new species with a weak Soret-like band at 463 nm and a broad absorption that extended beyond 900 nm (Figure 1). This corresponds to a dication **14a**, the structure for which can be deduced from the proton NMR data discussed below. Both protonations are reversible, and tropiporphyrin **9a** is regenerated upon addition of base (e.g., triethylamine).

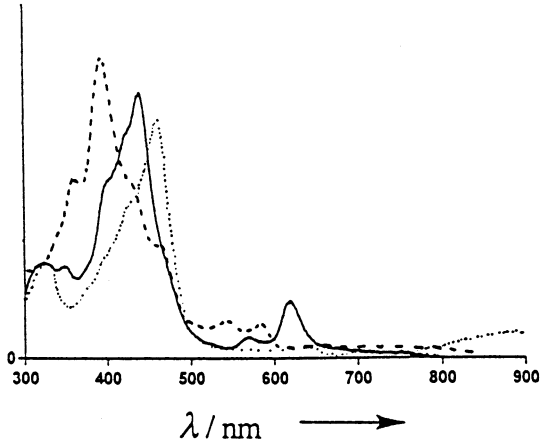
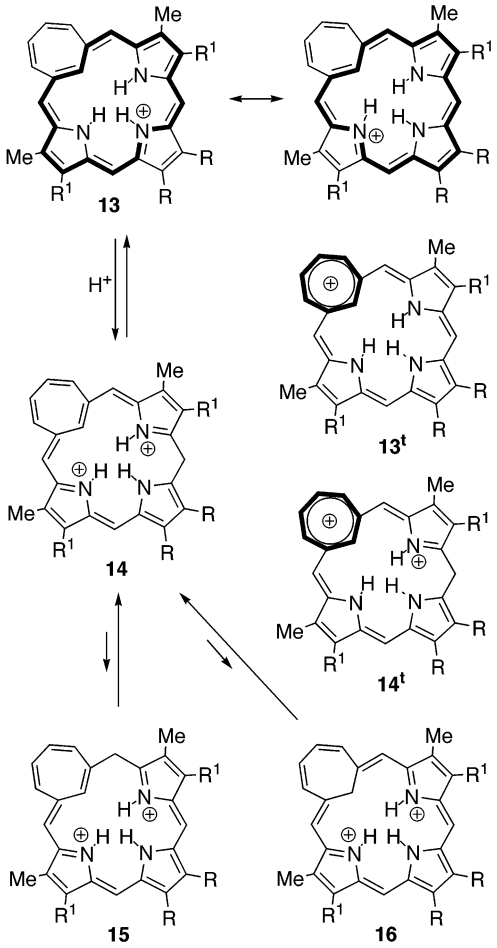


FIGURE 1. UV−vis spectra of tropiporphyrin **9a** (5.97×10^{-5} M): (- - -) free base in 1% triethylamine−chloroform, (—) monocation **13a** in 1% TFA−chloroform, (· · ·) Dication **14a** in 10% TFA−chloroform.

The proton NMR data for tropiporphyrin **9a** is striking in that the internal CH is shifted upfield to −7.3 ppm, and the symmetry of the molecule is evident from the presence of two 2H singlets at 8 and 9 ppm for the four *meso*-protons (Figure 2A). Although it is possible that tropiporphyrins **9** are in equilibrium with tautomers such as **9′**, the NMR data is only consistent with this possibility if the tautomerization occurs rapidly on the NMR time scale. Previous theoretical[33] and spectroscopic studies[4,5] on related systems suggest that carbaporphyrinoids with two internal NHs favor the tautomers where the imine nitrogen is flanked by the NHs to maximize hydrogen bonding interactions, and this is likely to be the case for tropiporphyrins as well. The NH resonances were too broad to identify in most spectra but could be identified in some cases as a very broad peak near −3 ppm. The chemical shift values for the internal protons suggest that the diatropicity of **9** is comparable to that of benzocarbaporphyrins **1**.[3−5] However, although the external *meso*-protons for **1** are present near 10 ppm, these resonances

(31) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973.
(32) Richter, D. T.; Lash, T. D. *Tetrahedron Lett.* **1999**, *40*, 6735.
(33) (a) Ghosh, A.; Wondimagegn, T.; Nilsen, H. J. *J. Phys. Chem. B* **1998**, *102*, 10459. (b) Ghosh, A. *Acc. Chem. Res.* **1998**, *31*, 189. (c) Ghosh, A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 7, pp 1−38.

SCHEME 3



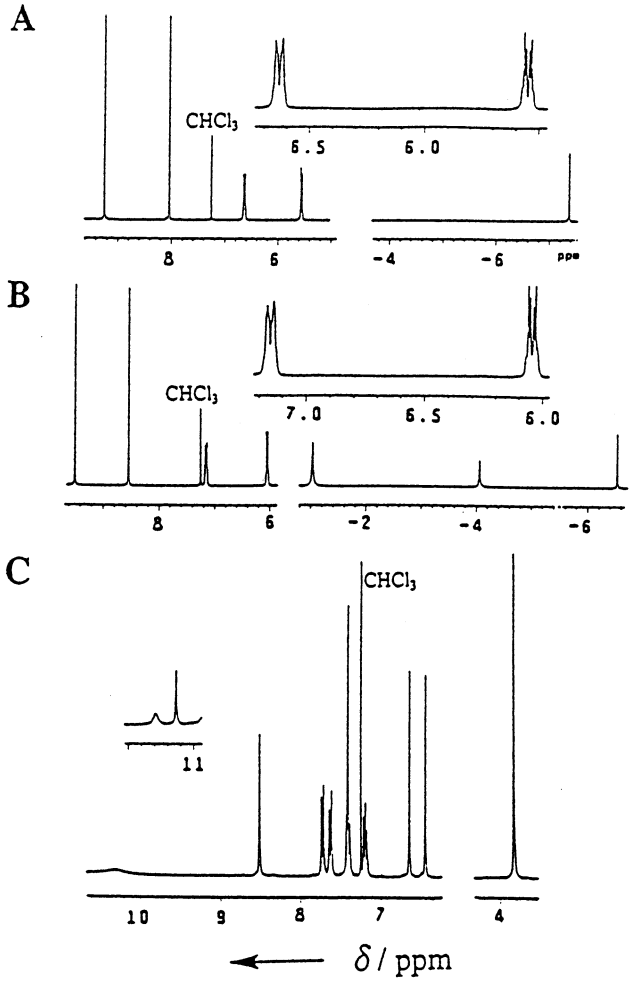


FIGURE 2. Partial 400 MHz proton NMR spectra of tropiporphyrin **9a** at 30 °C. (A) Upfield and downfield regions for the free base form of **9a** in deuteriochloroform. Inset shows an expansion of the resonances for the cycloheptatriene protons. (B) Upfield and downfield regions for the monocation **13a** in trace TFA−$CDCl_3$. Inset shows an expansion of the olefinic protons. (C) Downfield region for the dication **14a** in TFA−$CDCl_3$. This spectrum shows a new CH_2 resonance at 3.8 ppm and has lost the plane of symmetry associated with the free base and monocationic forms of this molecule. The inset shows two of the broad ^1H resonances for the NH protons. This was taken from a different spectrum where this region had not been obscured by the TFA peak.

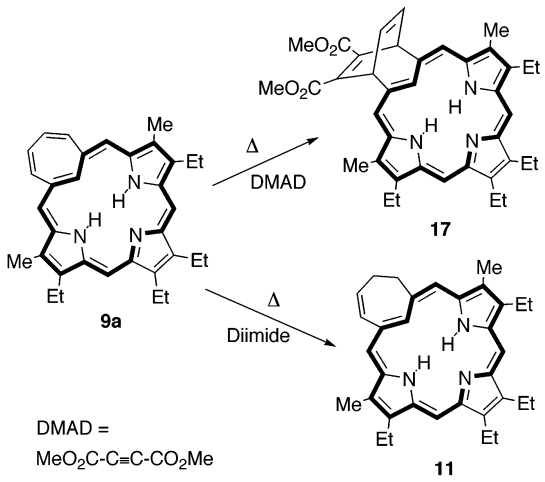
are observed at 8.02 and 9.22 ppm for **9a**. It is evident that the CH=CH−CH=CH unit in **9** plays no role in the aromatic pathways, as this moiety produces two multiplets at 5.5 and 6.6 ppm, values that would be expected for a conjugated diene. It was possible that the tropiporphyrin system could take on tropylium character, as illustrated by structure **9t** (Scheme 1), but this would interrupt the porphyrinoid aromaticity and require charge separation. Certainly, the NMR data are not consistent with the presence of a tropylium character in **9**. The abnormally upfield *meso*-proton resonances for **9a**−**c** are difficult to reconcile with the highly shielded interior CH, but this discrepancy presumably results from the conformation of the tropiporphyrin system. The seven-membered ring would be too strained to be held as a planar unit, and this no doubt disrupts the planarity of the porphyrinoid macrocycle as a whole. Unfortunately, no structural data for free base tropiporphyrins is currently available. However, carbon-13 NMR spectroscopy confirms that the system has a plane of symmetry and shows the *meso*-carbons at 96.0 and 104.9 ppm.

Addition of a trace amount of TFA to a solution of **9a** in $CDCl_3$ gave the dark green monocation **13**, and this retained a strong diatropic ring current (Figure 2B). The internal CH gave a resonance at −6.5 ppm, while the NHs gave two peaks at −4.1 (1H) and −1.4 ppm (2H). The *meso*-protons and the olefinic resonances were all shifted downfield by approximately 0.5 ppm, but this may be due to the positive charge on the system. Although the introduction of tropylium character is more reasonable for the monocation, the retention of an overall aromatic ring current suggests that contributions from **13t** (Scheme 3) are not significant. The methyl substituents also provide a measure of diatropic character in these systems. For most porphyrins, or carbaporphyrins such as **1**, the methyl groups resonate at 3.6 ppm but for free base **9a** or monocation **13a** these appear near 3.2 ppm. Although this represents a significant downfield shift compared to toluene, these values imply that the diatropicity for tropiporphyrins is somewhat reduced compared to that of **1**. Further addition of acid initially gave rise to messy poorly resolved spectra, but when 7−8 drops of TFA were added to the NMR tube, a new species emerged (Figure 2C). This dication showed a complete loss of macrocyclic aromaticity and also no longer re-

tained a plane of symmetry. The data are consistent with the formation of a C-protonated dication **14a** (Scheme 3).[34−36] Three bridging methine units could be identified as 1H singlets at 6.4, 6.6, and 7.4 ppm, while the internal CH was present at 8.5 ppm. The exterior of the cycloheptatrienyl ring produced four resonances at 7.2 (t), 7.4 (t), 7.6 (d), and 7.7 ppm (d). In addition, a new 2H singlet corresponding to the methylene bridge appeared at 3.8 ppm. Several peaks were observed further downfield at >10 ppm that were attributed to NH resonances. The methyl substituents confirmed the loss of overall aromatic character, giving two 3H singlets with chemical shift values of 2.2 and 2.3 ppm. Proton exchange can also be observed at the *meso*-positions for porphyrins,[37] oxophlorins[38,39] and benzocarbaporphyrins.[4] However, the relative ease by which C-protonation occurs in this system provides an additional indication of the reduced aromatic character in the tropiporphyrin system **9**. The downfield shifts for the cycloheptatriene protons also suggests that this species does have significant tropylium character as illustrated by the partial hybrid structure **14**^{t} (Scheme 3). Addition of 7 drops of d-TFA to solutions of **9a** in $CDCl_3$ showed, as expected, the immediate loss of the resonances at 3.8 and 6.4 ppm, as well as the resonances above 10 ppm. However, over a period of 1 h at room temperature, 80% of the signal intensity for the two singlets at 6.6 and 7.4 ppm were also lost. This result indicates that a low concentration of the isomeric dicationic species **15** is present in equilibrium with **14**. Over the period of several days, the resonance at 8.5 ppm corresponding to the internal CH also decreased in intensity, showing that very slow exchange occurs at C-23 as well. This is attributed to the formation of the C-protonated dication **16** at a very low equilibrium concentration. Although structure **16** could potentially take on an antiaromatic 24π electron delocalization pathway, this species is unlikely to retain sufficient planarity to allow for any paratropic character.

The diene component of the tropiporphyrin system represents a unique unit for carbaporphyrinoid structures. As this does not take part in the aromatic delocalization pathway, we speculated that the diene unit might take part in Diels−Alder cycloaddition reactions. Vinyl porphyrins are well-known to undergo this type of chemistry.[40] In our hands, tropiporphyrin **9a** failed to react with maleic anhydride under any of the conditions investigated. However, studies using the more reactive dienophile dimethyl acetylenedicarboxylate (DMAD) were more successful (Scheme 4). Optimal results were obtained when **9a** was reacted with DMAD in refluxing

SCHEME 4



xylenes under nitrogen, and the Diels−Alder adduct **17** was isolated in 13% yield. Lower boiling point solvents such as toluene or dichloroethane gave little or no product, but refluxing in the higher boiling point solvent chlorobenzene resulted in extensive decomposition.

The Diels−Alder adduct **17** gave a far more porphyrin-like UV−vis spectrum with a strong Soret band at 408 nm and a series of four Q-bands extending to 650 nm (Figure 3A). Addition of TFA gave a violet-colored monocation **17**H^+, and this produced a split Soret band at 410 and 432 nm. These results are similar to the data obtained for carbachlorins,[41] and it is noteworthy that both systems share a common chromophore. In addition, the monocations for carbachlorins and tetrapyrrolic chlorins both give split Soret bands.[41,42] The proton NMR spectrum for **17** is particularly noteworthy because it shows a greatly enhanced diatropic ring current (Figure 3B). The internal CH for **17** is shifted upfield beyond −9 ppm, the largest upfield shift ever observed for a non-expanded porphyrinoid system, while the *meso*-protons are shifted downfield toward 10 ppm. The methyl groups also confirm the presence of a stronger aromatic ring current, resonating at 3.6 ppm. The proton NMR spectrum for the monocation **17**H^+ in TFA−$CDCl_3$ showed a similarly strong ring current effect, where the inner CH resonated at −8.5 ppm and the NHs gave peaks at −6.3 (1H) and −4.4 ppm (2H). The *meso*-protons shifted downfield from 9.47 (2H, s) and 9.86 (2H, s) for **17** to values of 9.74 and 10.11 for **17**H^+, although the external cycloheptatriene protons showed relatively small downfield shifts. The carbon-13 NMR spectrum of **17** confirms that it retains a plane of symmetry, and the *meso*-carbons resonated at 95.5 and 104.8 ppm. The addition of DMAD across the diene unit relieves much of the strain associated with the unsaturated seven-membered ring, and this presumably lets the internal CH unit flatten out to produce a stronger ring current within the macrocycle. Unfortunately, X-ray quality crystals could not be obtained to confirm this speculation.

Porphyrins have previously been reduced with diimide to afford chlorins, and this chemistry was attempted for

(34) In contrast, benzocarbaporphyrins,[3−5] dicarbaporphyrins,[35] and carbasapphyrins[36] favor C-protonation on the interior carbon.

(35) Lash, T. D.; Romanic, J. L.; Hayes, M. J.; Spence, J. D. *Chem. Commun.* **1999**, 819.

(36) Lash, T. D.; Richter, D. T. *J. Am. Chem. Soc.* **1998**, *120*, 9965.

(37) Medforth, C. J. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000, Vol. 5, pp 1−80.

(38) Jackson, A. H.; Kenner; G. W.; Smith, K. M. *J. Chem. Soc. C* **1968**, 294.

(39) Lash, T. D.; Armiger, Y. L. S.-T. *J. Heterocycl. Chem.* **1991**, *28*, 965.

(40) (a) Callot, H. J.; Johnson, A. W.; Sweeney, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1424. (b) DiNello, R. K.; Dolphin, D. *J. Org. Chem.* **1980**, *45*, 5196. (c) Pangka, V. S.; Morgan, A. R.; Dolphin D. *J. Org. Chem.* **1986**, *51*, 1094. (d) Cavaleiro, J. A. S.; Jackson, A. H.; Neves, M. G. P. M. S.; Rao, K. R. N. *J. Chem. Soc., Chem. Commun.* **1985**, 776.

(41) Hayes, M. J.; Lash, T. D. *Chem. Eur. J.* **1998**, *4*, 508.

(42) Cavaleiro, J. A. S.; Jackson, A. H.; Ali, S. A. *Tetrahedron Lett.* **1984**, *25*, 229.

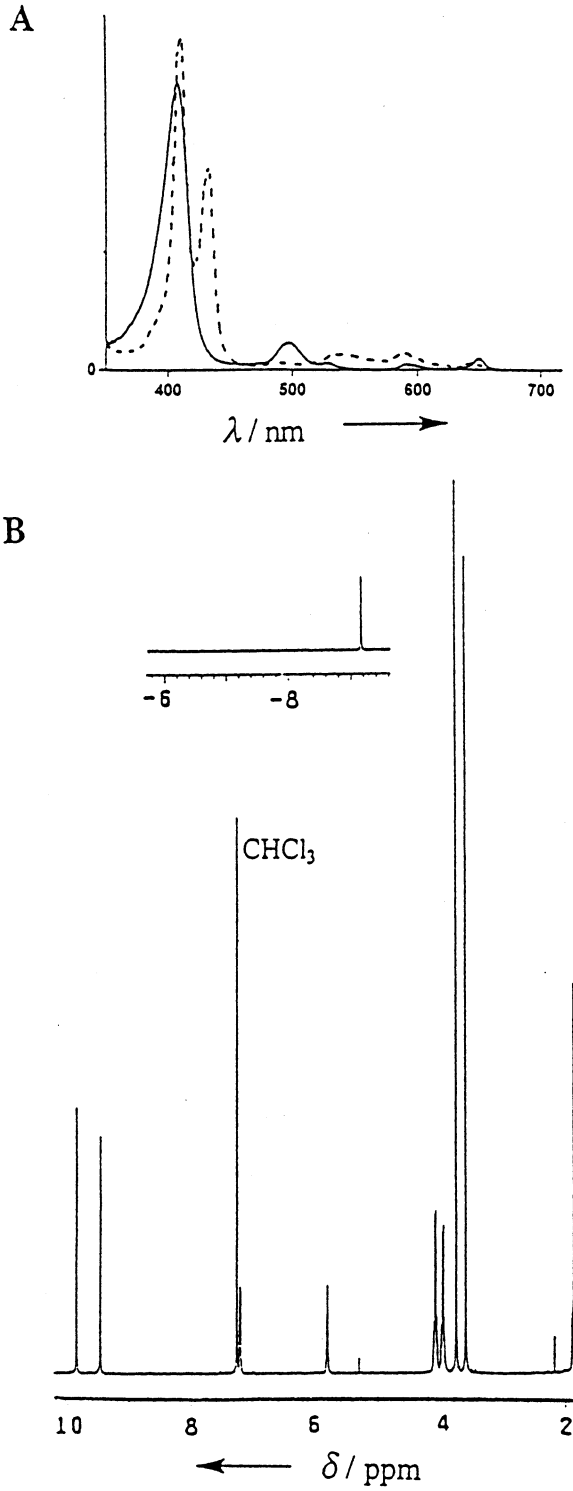
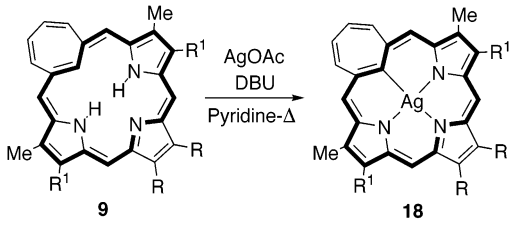


FIGURE 3. (A) UV−vis spectra of the Diels−Alder adduct **17** (9.63×10^{-6} M): (—) free base in 1% triethylamine−chloroform, (- - -) monocation **17**H^+ in 1% TFA−chloroform. (B) 400 MHz proton NMR spectrum for **17** in deuteriochloroform. Inset shows the internal CH resonance at a remarkable upfield value of −9.2 ppm.

tropiporphyrin. Again, we speculated that the diene unit would be more easily reduced than the macrocyclic core, and this proved to be the case. Tropiporphyrin was heated with *p*-toluenesulfonyl hydrazine and potassium carbonate in pyridine, and following workup and chromatography on flash silica, a major pinkish-brown fraction was isolated (Scheme 4). This proved to be the dihydrotropiporphyrin **11**. Again the modified tropiporphyrin showed a larger ring current, where the internal CH resonated upfield at −8.3 ppm, while the *meso*-protons resonated between 9.2 and 9.8 ppm. The methyl resonances were observed as two 3H singlets at 3.57 and 3.58 ppm. These data indicate that the ring current for **11** is not as strong as for **17** but is considerably enhanced compared to that of tropiporphyrin **9a**. This suggests that the internal methine unit cannot flatten out to the same extent as **17**, which is consistent with expectations for the cage-like structure of the Diels−Alder adduct. The UV−vis spectrum of **11** shows a Soret band at 412 nm and four Q-bands extending to 662 nm. The λ_{max} values are similar to those reported previously for **11** by Breitmaier and colleagues,[30] although our sample gave a substantially larger molar extinction coefficient for the Soret band.

SCHEME 5



Carbaporphyrinoid systems can give organometallic derivatives, and we have recently demonstrated that virtually every structure of this type with a CH-NH-N-NH core can give silver(III) derivatives.[9,10] Until recently, silver(III) was considered to be a relatively rare oxidation state but it is now known that N-confused porphyrins,[43] doubly confused porphyrins,[44] corrins,[45] benzocarbaporphyrins,[9] oxybenziporphyrins,[10] oxynaphthiporphyrins,[10] and tropiporphyrins[10] can all give silver(III) derivatives. In most cases, the macrocycles react with silver(I) acetate under mild conditions to give excellent yields of the metal complex; silver metal is formed as a byproduct in this chemistry.[10,45] Tropiporphyrins **9a**−**c** failed to react under the usual conditions but gave a trace amount of product in refluxing pyridine. Under the assumption that base aids metalation by deprotonating one or more of the NHs, DBU was added to the reaction mixtures. Using this strong non-nucleophilic base, the silver(III) complexes **18** were generated in 43−78% yield (Scheme 5). The UV−vis spectra for the metallo-derivatives showed two broad Soret bands near 400 nm and three additional broad absorptions through the visible region (Figure 4A). Although proton NMR spectroscopy demonstrates that the silver derivatives retain a diatropic ring current, this seems to be similar in magnitude to the free base tropiporphyrins. The *meso*-protons for **18a** gave two 2H singlets at 8.0 and 9.1 ppm (Figure 4B), while the methyl groups were observed at 3.1 ppm. Naturally, the internal

(43) (a) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676. (b) Furuta, H.; Morimoto, T.; Osuka, A. *Org. Lett.* **2003**, *5*, 1427. (c) Maeda, H.; Osuka, A.; Ishikawa, Y.; Aritome, I.; Hisaeda, Y.; Furuta, H. *Org. Lett.* **2003**, *5*, 1293.

(44) Araki, K.; Winnischofer, H.; Toma, H. E.; Maeda, H.; Osuka, A.; Furuta, H. *Inorg. Chem.* **2001**, *40*, 2020.

(45) Brückner, C.; Barta, C. A.; Briñas, R. P.; Krause Bauer, J. A. *Inorg. Chem.* **2003**, *42*, 1673.

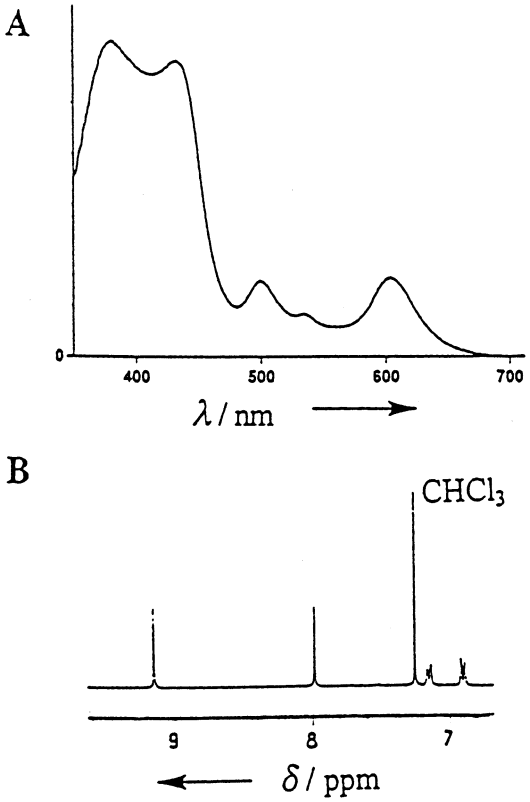


FIGURE 4. (A) UV−vis spectrum of the silver(III) tropiporphyrin complex **18a** (1.84×10^{-5} M) in chloroform. (B) Downfield region of the 400 MHz proton NMR spectrum for **18a** in deuteriochloroform.

CH has now been replaced by the silver cation. Interestingly, the cycloheptatriene protons of **18a** are shifted downfield compared to **9a**, giving rise to two 2H multiplets at 6.9 and 7.2 ppm. This shift is most likely due to a conformation change for this unit rather than increased tropylium character.

Further insights into the preferred conformations for the silver(III) complexes were obtained by single-crystal X-ray diffraction analysis of the diphenyl derivative **18b**. This confirms that the macrocycle is significantly distorted from planarity (Figure 5) as evidenced by the N(24) and N(24′) pyrrole to mean planes twisted 11.57(5)° from the metal coordination sphere defined by C(23), N(24), N(25), and Ag. The 5.65(7)° N(25) pyrrole to metal coordination sphere dihedral angle is less pronounced. The structure is best described as ruffled with the silver(III) ion essentially situated in the center of the macrocyclic cavity. The skeletal atoms lie at 0.223 Å rms distances from the plane defined by the metal coordination sphere, with C6, C7, and C10 having the largest deviations equal to 0.406(2), 0.348(2), and 0.405(2) Å from the plane defined. In contrast, a closely related silver(III) benzocarbaporphyrin displays an extremely planar [18]annulene core with a 0.068 Å rms distance and a maximum deviation equal to 0.188(4) Å from the metal and four coordinated atoms.[9] In **18b**, the cycloheptatriene subunit is severely twisted as evidenced by the substantial 29.9(4)° C5−C4−C4′−C5′ and lesser, yet significant, 4.1(4)° C6−C5−C4−C4′ torsion angles. The abrupt distortions around the carbocyclic ring most likely lead to the decreased diatropicity observed in the proton NMR

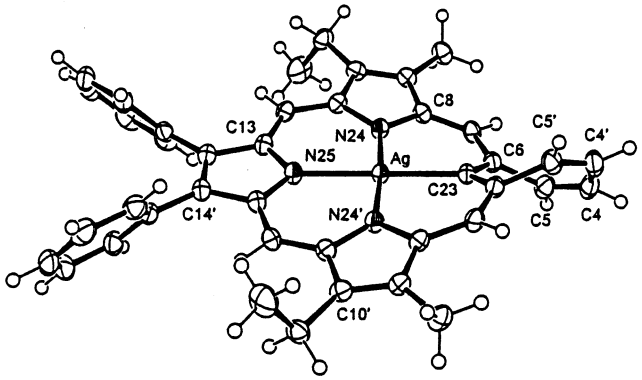


FIGURE 5. ORTEP III drawing (50% probability level, hydrogen atoms drawn arbitrarily small) of silver(III) tropiporphyrin **18b**, depicting the twisted cycloheptatriene subunit. Selected bond lengths (Å): C(23)−Ag 2.126(2), N(24)−Ag 2.052(1), N(25)−Ag 2.136(2), C(6)−C(23) 1.402(2), C(4)−C(4′) 1.440(4), C(4)−C(5) 1.336(3), C(5)−C(6) 1.487(2). Selected bond angles (deg): C(23)−C(6)−C(7) 127.3(2), C(23)−C(6)−C(5) 119.4(2), C(6)−C(5)−C(4) 126.9(2), C(5)−C(4)−C(4′) 124.5(1), C(6)−C(23)−C(6′) 124.5(2), C(8)−N(24)−C(11) 107.0(1), C(13)−N(25)−C(13′) 107.0(2), C(23)−Ag−N(24) 92.13(4), N(24)−Ag−N(25) 87.87(4), C(23)−Ag−N(25) 180, N(24)−Ag−N(24′) 175.73(7). Primed atoms are related by a crystallographic C_2 axis.

spectra for **18** compared to that of silver(III) benzocarbaporphyrins.[9] The metal sits in the expected square planar coordination environment and resides along with C(23) and N(25) on a crystallographic C2 axis of rotation. The metal is centered between the donor ligands with symmetry equivalent Ag−N(24) bond lengths of 2.052(1) Å for the pyrroles *trans* to one another. The longer Ag−C(23) bond length of 2.126(2) Å is consistent with the larger covalent bonding radius of carbon compared to that of nitrogen. The Ag−N(25) bond length of 2.136(2) Å is slightly distended. We have suggested this 0.08 Å increase in bond length may be the result of a small *trans*-effect caused by the more Lewis basic alkenyl C(23) being *trans* to N(25).[15] A similar 0.04 Å increase in bond length is observed for the closely related silver(III) benzocarbaporphyrin.[9]

Conclusions

The first detailed study on the synthesis and chemistry of tropiporphyrins has been completed. The strained unsaturated seven-membered ring in **9** decreases the aromatic character of this porphyrinoid system, although the internal CH still gives an upfield resonance in its proton NMR spectrum beyond −7 ppm. Protonation initially gives an aromatic monocation and then, at higher TFA concentrations, an overall nonaromatic dication. The latter appears to take on significant tropylium character. Two of the seven-membered ring double bonds for **9** do not take part in the aromatic delocalization pathway, and this part of the molecule can act as a diene in Diels−Alder cycloaddition reactions with dimethyl acetylenedicarboxylate. The Diels−Alder adduct **17** shows a much stronger diatropic ring current that is attributed to a flattening out of the [18]annulene substructure. Reduction of tropiporphyrin **9a** with diimide gives a dihydro-derivative that also shows increased diatropicity. Tropiporphyrins also act as trianionic ligands, forming

silver(III) derivatives under basic conditions. One of these silver(III) organometallic complexes was characterized by X-ray crystallography, and these results confirm that the system is highly distorted by the presence of the seven-membered ring within the macrocycle. The results from these studies indicate that tropiporphyrins have a rich chemistry that holds considerable promise for the development of new porphyrinoid systems.

Experimental Section

10,14,15,19-Tetraethyl-9,20-dimethyltropiporphyrin (9a). Tripyrrane dicarboxylic acid **7a** (100 mg) was stirred in TFA (1 mL) under nitrogen for 5 min. The solution was diluted with dichloromethane (400 mL), 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (24 mg) was added, and the reaction mixture was stirred in the dark under nitrogen overnight. The resulting solution was washed with 0.1% ferric chloride solution, and the layers were separated. The organic phase was washed with water, saturated sodium bicarbonate solution, and water, and the solvent was removed under reduced pressure. The residue was chromatographed on Grade 3 alumina eluting with 1% Et_3N in dichloromethane and then on silica eluting with 1% Et_3N in 75/25 dichloromethane−hexanes. Recrystallization from chloroform−hexanes gave the tropiporphyrin (39.6 mg, 38%) as shiny dark purple crystals, mp >300 °C, dec; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 361 (4.71), 395 (4.93), 431 (4.70), 465 (4.46), 542 (3.95), 585 (3,92), 645 (3.37), 737 nm (3.42); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 348 (4.45), 402 (sh, 4.70), 439 (4.88), 569 (3.90), 619 nm (4.26); UV−vis (10% TFA−$CHCl_3$) λ_{max} (log ϵ) 332 (4.42), 463 (4.82), 578 (3.65), 626 (3.76), 865 nm (3.85); ^{1}H NMR ($CDCl_3$; free base) δ −7.45 (1H, s), 1.65−1.75 (12H, m), 3.20 (6H, s), 3.71 (4H, q, J = 8 Hz), 3.78 (4H, q, J = 8 Hz), 5.52−5.55 (2H, m), 6.60−6.63 (2H, m), 8.02 (2H, s), 9.22 (2H, s); ^{1}H NMR (trace TFA−$CDCl_3$; monocation) δ −6.51 (1H, s), −4.12 (1H, br s), −1.38 (2H, br s), 1.51 (6H, t, J = 7.6 Hz), 1.76 (6H, t, J = 7.6 Hz), 3.15 (6H, br s), 3.77 (4H, q, J = 7.6 Hz), 3.89 (4H, br q), 6.05 (2H, br), 7.14 (2H, br), 8.55 (2H, s), 9.49 (2H, s); ^{1}H NMR (7 drops TFA−$CDCl_3$; dication) δ 1.16−1.27 (12H, m), 2.18 (3H, s), 2.28 (3H, s), 2.63−2.77 (6H, m), 2.81 (2H, q, J = 7.8 Hz), 3.82 (2H, s), 6.44 (1H, s), 6.64 (1H, s), 7.17 (1H, t, J = 9.6 Hz), 7.39 (1H, t, J = 9.6 Hz), 7.41 (1H, s), 7.61 (1H, d, J = 10 Hz), 7.70 (1H, d, J = 10 Hz), 8.51 (1H, s), 10.4 (1H, v br), 11.27 (1H, s), 11.6 (1H, v br); ^{13}C NMR ($CDCl_3$; free base) δ 11.6, 17.2, 18.5, 19.6, 19.8, 96.0, 104.9, 126.8, 130.7, 131.3, 133.3, 134.1, 137.0 (2), 142.3, 146.8, 150.3; ^{13}C NMR (trace TFA−$CDCl_3$; monocation) δ 11.8, 16.5, 17.7, 19.6, 20.0, 93.3, 108.9, 131.4, 133.4, 135.7, 136.6, 138.1, 139.9, 140.4, 140.8, 145.9; ^{13}C NMR (8 drops TFA−$CDCl_3$; dication) δ 9.5 (2) 14.5, 15.3, 15.6, 16.3, 17.8, 18.4, 19.2, 37.4, 104.3, 111.8, 120.0, 130.2, 132.3, 136.6 (2), 137.1, 138.8, 139.3, 140.1, 141.2, 144.9, 145.3, 145.9, 147.6, 149.9, 152.0, 154.1, 154.3 161.1, 180.4; EI MS (70 eV) *m/z* (% relative intensity) 476 (46), 475 (100, M^+), 460 (6); HRMS (EI) calcd for $C_{33}H_{37}N_3$ 475.2987, found 475.2982. Anal. Calcd for $C_{33}H_{37}N_3$·0.3$CHCl_3$: C, 78.20; H, 7.35; N, 8.21. Found: C, 78.47; H, 7.68; N, 8.45.

10,19-Diethyl-9,20-dimethyl-14,15-diphenyltropiporphyrin (9b). The diphenyl porphyrinoid was prepared from tripyrrane **7b** (100 mg) and 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (27.8 mg) under the foregoing conditions. The crude product was purified by chromatography on Grade 3 alumina, eluting with 1% Et_3N−dichloromethane, and then by flash chromatography on silica, eluting with 50% dichloromethane−hexanes. Recrystallization from chloroform−hexanes gave the diphenyltropiporphyrin (37.0 mg, 34%) as shiny dark purple crystals, mp >300 °C, dec; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 364 (4.65), 409 (4.99), 435 (4.73), 471 (4.52), 552 (4.08), 598 nm (4.21); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 418 (4.93), 445 (4.88), 580 (3.91), 633 nm (4.31); ^{1}H NMR ($CDCl_3$) δ −7.37 (1H, s), 1.59 (6H, t, J = 7.6 Hz), 3.16 (6H, s), 3.66 (4H, q, J = 7.6 Hz), 5.56−5.60 (2H, m), 6.61−6.65 (2H, m), 7.52 (2H, t), 7.61 (4H, t), 7.86 (4H, d), 7.98 (2H, s), 9.30 (2H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −6.07 (1H, s), −3.43 (1H, br s), −0.83 (2H, br s), 1.43 (6H, t, J = 7.6 Hz), 3.13 (6H, s), 3.66 (4H, q, J = 7.6 Hz), 6.13−6.17 (2H, m), 7.20−7.25 (2H, m), 7.59 (2H, t), 7.66 (4H, t), 7.86 (4H, d), 8.52 (2H, s), 9.48 (2H, s); ^{1}H NMR (7 drops TFA−$CDCl_3$; dication) δ 1.09 (3H, t, J = 7.6 Hz), 1.19 (3H, t, J = 7.4 Hz), 2.14 (3H, s), 2.30 (3H, s), 2.52 (2H, q, J = 7.8 Hz), 2.72 (2H, q, J = 7.6 Hz), 2.81 (2H, q, J = 7.8 Hz), 3.88 (2H, s), 6.40 (1H, s), 6.61 (1H, s), 7.14−7.18 (3H, m), 7.33 (1H, s), 7.37−7.43 (5H, m), 7.58 (1H, d, J = 10 Hz), 7.67 (1H, d, J = 10 Hz), 7.74−7.78 (2H, m), 7.92−7.95 (2H, m), 8.70 (1H, s), 10.70 (1H, s), 10.9 (1H, br), 11.55 (1H, br); ^{13}C NMR ($CDCl_3$) δ 11.6, 17.0, 19.5, 99.4, 104.6, 126.5, 126.8, 128.4, 131.0, 131.5, 132.4, 134.1, 134.5, 137.1, 138.0, 138.1, 141.9, 146.7, 148.9; EI MS (70 eV) *m/z* (% relative intensity) 573 (23), 572 (47), 571 (100, M^+), 556 (4); HRMS (EI) calcd for $C_{41}H_{37}N_3$ 571.2987, found 571.2990. Anal. Calcd for $C_{41}H_{37}N_3$: C, 86.13; H, 6.52; N, 7.35. Found: C, 85.72; H, 6.54; N, 7.44.

10,19-Di-*tert*-butyl-9,20-dimethyl-14,15-diphenyltropiporphyrin (9c). The di-*tert*-butyl porphyrinoid was prepared from tripyrrane **7c** (100 mg) and 1,3,5-cycloheptatriene-1,6-dicarbaldehyde (38.3 mg) under the foregoing conditions. The crude product was purified by chromatography on Grade 3 alumina, eluting with 1% Et_3N−dichloromethane, and then by flash chromatography on silica eluting with 50% dichloromethane−hexanes. Recrystallization from chloroform−hexanes gave the di-*tert*-butyltropiporphyrin (22.2 mg, 21%) as shiny dark purple crystals, mp >300 °C, dec; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 365 (4.60), 410 (4.80), 433 (4.81), 555 (3.99), 597 nm (4.11); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 405 (4.61), 450 (4.90), 575 (3.89), 638 nm (4.21); ^{1}H NMR ($CDCl_3$) δ −6.91 (1H, s), 2.03 (18H, s), 3.43 (6H, s), 5.72−5.77 (2H, m), 6.66−6.70 (2H, m), 7.50 (2H, t), 7.59 (4H, t), 7.84 (4H, d), 8.09 (2H, s), 9.81 (2H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −5.92 (1H, s), −3.42 (1H, br s), −1.07 (2H, br s), 1.94 (18H, s), 3.27 (6H, s), 6.06−6.10 (2H, m), 7.07−7.11 (2H, m), 7.56 (2H, t), 7.62 (4H, t), 7.80 (4H, d), 8.45 (2H, s), 9.91 (2H, s); ^{13}C NMR ($CDCl_3$) δ 14.8, 34.2, 36.0, 103.2, 103.8, 125.6, 126.9, 128.3, 130.8, 131.6, 132.4, 134.0, 134.4, 137.1 (2), 142.3, 146.5, 148.9; HRMS (EI) calcd for $C_{45}H_{45}N_3$ 627.3613, found 627.3614. Anal. Calcd for $C_{45}H_{45}N_3$·0.2$CHCl_3$: C, 83.30; H, 6.99; N, 6.45. Found: C, 83.12; H, 7.06; N, 6.45.

Diels−Alder Adduct 17. Tropiporphyrin **9a** (13.5 mg) was dissolved in xylenes (20 mL), 2 drops of dimethyl acetylenedicarboxylate were added, and the solution was refluxed under nitrogen overnight. The resulting dark brown solution was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was chromatographed on grade 3 alumina, eluting with 75/25 dichloromethane−hexanes. A greenish fraction was collected and recrystallized from chloroform−hexanes to give the Diels−Alder adduct (2.3 mg, 13.5%) as purple crystals, mp >300 °C, dec; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 408 (5.09), 497 (4.06), 533 (3.59), 592 (3.41), 649 nm (3.69); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 410 (5.16), 432 (4.95), 538 (3.84), 589 (3.86), 640 nm (3.45); ^{1}H NMR ($CDCl_3$) δ −9.17 (1H, s), 1.80 (6H, t, J = 7.6 Hz), 1.86 (6H, t, J = 7.6 Hz), 3.61 (6H, s), 3.76 (6H, s), 3.97 (4H, q, J = 7.6 Hz), 4.09 (4H, q, J = 7.6 Hz), 5.80 (2H, t, J = 4 Hz), 7.19 (2H, dd, J = 3.4, 5 Hz), 9.47 (2H, s), 9.86 (2H, s); ^{1}H NMR (TFA−$CDCl_3$) δ −8.55 (1H, s), −6.29 (1H, s), −4.39 (2H, br s), 1.58 (6H, t, J = 7.6 Hz), 1.83 (6H, t, J = 7.6 Hz), 3.45 (6H, s), 3.80 (6H, s), 4.00−4.13 (8H, m), 5.81 (2H, t, J = 4 Hz), 7.31 (2H, m), 9.74 (2H, s), 10.11 (2H, s); ^{13}C NMR ($CDCl_3$) δ 12.0, 17.6, 18.7, 19.9, 20.1, 52.5, 53.5, 95.5, 104.8, 109.9, 128.7, 132.2, 132.3, 133.1, 134.2, 137.0, 141.0, 143.5, 151.0, 167.4; EI MS (70 eV) *m/z* (% relative intensity) 619 (10), 618 (39), 617 (100, M^+), 558 (28, $[M - CO_2Me]^+$), 475 (14, $[M - MeO_2C-C{\equiv}C-CO_2Me]^+$); HRMS (EI) calcd for $C_{39}H_{43}N_3O_4$ 617.3254, found 617.3254.

10,14,15,19-Tetraethyl-2,3-dihydro-9,20-dimethyltropiporphyrin (11). A stirred mixture of tropiporphyrin **9a** (22.4 mg), potassium carbonate (57.3 mg), and *p*-toluenesulfonyl

hydrazine (15.6 mg) in pyridine (5 mL) was heated on an oil bath under nitrogen at 105 °C for 2 h. After this time, a solution of *p*-toluenesulfonyl hydrazine (15 mg) in pyridine (1 mL) was added dropwise, and the resulting mixture was heated under nitrogen at 105 °C for a further 2 h. A further portion of *p*-toluenesulfonyl hydrazine (15 mg) in pyridine (1 mL) was added, and the mixture was stirred for a further 2.5 h under the same conditions. The mixture was removed from the oil bath, a mixture of benzene (12.5 mL) and water (6 mL) was added, and the resulting mixture was heated for an additional 1 h at 105 °C. The solution was cooled to room temperature, and the organic phase was separated. The organic phase was washed with 3 M hydrochloric acid, water, saturated sodium bicarbonate solution, and water. The solution was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on flash silica, eluting with dichloromethane, and the product was collected as a brownish-pink solution. Recrystallization from chloroform−hexanes gave the dihydrotropiporphyrin (8.7 mg, 39%) as shiny purple crystals, mp 295 °C, dec; UV−vis (1% Et_3N−$CHCl_3$) λ_{max} (log ϵ) 412 (5.20), 502 (4.08), 534 (3.92), 603 (3.54), 662 nm (3.70); UV−vis (1% TFA−$CHCl_3$) λ_{max} (log ϵ) 415 (5.22), 438 (5.01), 536 (3.89), 599 (4.00), 655 nm (3.70); ^{1}H NMR ($CDCl_3$) δ −8.29 (1H, s), 1.81 (6H, t, J = 7.6 Hz), 1.86 (6H, t, J = 7.6 Hz), 3.41−3.44 (2H, m), 3.57 (3H, s), 3.58 (3H, s), 3.97 (4H, q, J = 7.6 Hz), 4.09 (4H, q, J = 7.6 Hz), 4.59−4.62 (2H, m), 6.85−6.92 (1H, m), 7.91 (1H, d, J = 11.6 Hz), 9.23 (1H, s), 9.43 (1H, s), 9.80 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.9, 12.0, 17.5, 18.7, 19.9, 20.1, 29.9, 32.5, 43.3, 94.7, 94.9, 107.1, 109.5, 114.5, 130.4, 131.9, 132.1, 132.4, 134.4, 136.4, 136.5, 136.6, 136.9, 138.2, 143.2, 143.3; EI MS (70 eV) *m/z* (% relative intensity) 479 (16), 478 (41), 477 (100, M^+), 462 (6.7, $[M - CH_3]^+$); HRMS (EI) calcd for $C_{33}H_{39}N_3$ 477.3144, found 477.3130.

[10,14,15,19-Tetraethyl-9,20-dimethyltropiporphyrinato]silver(III) (18a). Silver(I) acetate (11.0 mg) was added to a solution of 10,14,15,19-tetraethyl-9,20-dimethyltropiporphyrin (8.8 mg) and DBU (3 drops) in pyridine (15 mL), and the mixture was stirred overnight in the dark at room temperature. The mixture was diluted with chloroform and washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica flash column eluting with dichloromethane. A green fraction was collected and recrystallized from chloroform−hexanes to give the silver(III) complex (5.1 mg, 47%) as dark crystals, mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 381 (4.53), 432 (4.50), 499 (3.91), 533 (3.69), 604 nm (3.92); ^{1}H NMR ($CDCl_3$) δ 1.67 (6H, t, J = 7.6 Hz), 1.76 (6H, t, J = 7.6 Hz), 3.19 (6H, s), 3.69−3.78 (8H, m), 6.89−6.92 (2H, m), 7.13−7.17 (2H, m), 7.99 (2H, s), 9.16 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.5, 17.1, 18.1, 19.7, 20.1, 95.4, 100.8, 120.7, 128.5, 135.4 (2), 136.9, 139.9, 142.6, 143.0, 143.1, 144.4 (2); EI MS (70 eV) *m/z* (% relative intensity) 582 (18), 581 (54, $^{109}AgM^+$), 580 (19), 579 (59, $^{107}AgM^+$), 566 (8), 564 (8, $[M - CH_3]^+$), 475 (100); HRMS (EI) calcd for $C_{33}H_{34}N_3Ag$ 579.1804, found 579.1801. Anal. Calcd for $C_{33}H_{34}N_3Ag$: C, 68.28; H, 5.90; N, 7.24. Found: C, 68.20; H, 5.86; N, 7.09.

[10,19-Diethyl-9,20-dimethyl-14,15-diphenyltropiporphyrinato]silver(III) (18b). Silver(I) acetate (12.4 mg) was added to a solution of 10,19-tetraethyl-9,20-dimethyl-14,15-diphenyltropiporphyrin (8.8 mg) and DBU (3 drops) in pyridine (15 mL), and the mixture was stirred overnight in the dark at room temperature. The mixture was diluted with chloroform and washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica flash column eluting with dichloromethane. A green fraction was collected and recrystallized from chloroform−hexanes to give the silver(III) complex (3.8 mg, 43%) as dark crystals, mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 390 (4.89), 445 (4.88), 506 (4.29), 543 (4.28), 599 nm (4.19); ^{1}H NMR ($CDCl_3$) δ 1.56 (6H, t, J = 7.6 Hz), 3.18 (6H, s), 3.57 (4H, q, J = 7.6 Hz), 6.93−6.96 (2H, m), 7.17−7.21 (2H, m), 7.53 (2H, tt), 7.61 (4H, t), 7.85 (4H, dd), 8.01 (2H, s), 9.23 (2H, s); ^{13}C NMR ($CDCl_3$) δ 11.5, 16.8, 20.0, 98.8, 100.5, 121.8, 127.3, 128.6, 132.2, 135.5, 135.6, 136.1, 136.6, 140.7, 141.4, 141.8, 143.5, 145.3, 145.4; EI MS (70 eV) *m/z* (% relative intensity) 678 (9), 677 (21, $^{109}AgM^+$), 676 (9), 675 (20, $^{107}AgM^+$), 571 (69); HRMS (EI) calcd for $C_{41}H_{34}N_3Ag$ 675.1803, found 675.1793.

[10,19-Di-*tert*-butyl-9,20-dimethyl-14,15-diphenyltropiporphyrinato]silver(III) (18c). Silver(I) acetate (7.8 mg) was added to a solution of 10,19-tetraethyl-9,20-dimethyl-14,15-diphenyltropiporphyrin (7.4 mg) and DBU (3 drops) in pyridine (15 mL), and the mixture was stirred overnight in the dark at room temperature. The mixture was diluted with chloroform and washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on a silica flash column eluting with dichloromethane. A green fraction was collected and recrystallized from chloroform−hexanes to give the silver(III) complex (6.7 mg, 78%) as shiny purple crystals, mp >300 °C; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 388 (4.60), 448 (4.58), 511 (3.99), 547 (3.92), 607 nm (3.89); ^{1}H NMR ($CDCl_3$) δ 1.96 (18H, s), 3.36 (6H, s), 6.87−6.91 (2H, m), 7.09−7.11 (2H, m), 7.51 (2H, t), 7.61 (4H, t), 7.85 (4H, d), 7.83 (2H, s), 9.65 (2H, s); ^{13}C NMR ($CDCl_3$) δ 14.9, 34.3, 36.4, 98.8, 101.8, 122.2 (2), 127.3, 128.6, 128.7, 132.1, 135.8, 136.4, 136.3, 141.3, 141.4, 144.4, 150.8; HRMS (EI) calcd for $C_{45}H_{42}N_3Ag$ 731.2430, found 731.2437.

Crystal Structure Determination of 18b. X-ray quality crystals were obtained by slow diffusion of hexanes into a dichloroethane solution of **18b**. A black prism thereby obtained of approximately 0.59 × 0.22 × 0.20 mm^3 was affixed to a glass fiber with Paratone-N and transferred to a CCD diffractometer. The X-ray diffraction data were collected at −80 °C using Mo Kα (λ = 0.71073 Å) radiation. Data collection and cell refinement were performed using SMART.[46a] The unit cell parameters were obtained from a least squares refinement of 5939 centered reflections. The silver(III) complex **18b** was found to crystallize in the monoclinic crystal system with the following unit cell parameters: a = 16.2839(7) Å, b = 14.8351(6) Å, c = 13.8730(6) Å, β = 114.104(1)°, Z = 4. The systematic absences were ambiguous and indicates the space group to be either *Cc* (No. 9) or *C*2/*c* (No. 15).[47] The latter was selected on the basis that it is of higher symmetry and the refined crystal structure displays reasonable structural parameters.[48] A total of 11164 reflections were collected, of which 3145 were unique, and 3050 were observed $F_o^2 > 2\sigma(F_o^2)$. Limiting indices were as follows: $-20 \le h \le 20$, $-18 \le k \le 18$, $-17 \le l \le 17$. Data reduction was accomplished using SAINT.[46b] The data were corrected for absorption through use of the SADABS procedure.[46c]

Solution and data analysis were performed using the WinGX software package.[49] The structure of **18b** was solved by the Patterson method using the program DIRDIF-99,[50] and the refinement was completed using the program SHELX-97.[51] All non-hydrogen atoms were refined isotropically. Hydrogen atoms were assigned positions on the basis of the geometries of their attached carbon atoms and were given thermal parameters of 20% greater than those of the attached atoms. Full-matrix least squares refinement on F^2 led to convergence, $(\Delta/\sigma)_{max}$ = 0.0020, $(\Delta/\sigma)_{mean}$ = 0.0000, R_1 = 0.0217 and wR_2 =

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

(47) McArdle, P. *J. Appl. Crystallogr.* **1996**, *29*, 306.

(48) Marsh, R. E. *Acta Crystallogr., Sect. B* **2004**, *60*, 252.

(49) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(50) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. *The DIRDIF-99 Program System*; Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

(51) Sheldrick, G. M. *SHELX-97*; *Programs for Crystal Structure Analysis*, Release 97-2; Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

0.0588 for 3050 data with $F_o^2 > 2\sigma(F_o^2)$ using zero restraints and 205 parameters. A final difference Fourier synthesis showed features in the range of $\Delta\rho_{max} = 0.387$ e$^-$/Å^3 to $\Delta\rho_{min} = -0.256$ e$^-$/Å^3, which were deemed of no chemical significance. The molecular diagram was prepared using ORTEP-3.[52]

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

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(52) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.