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New Riches in Carbaporphyrin Chemistry: Silver and Gold Organometallic Complexes of Benzocarbaporphyrins†

Timothy D. Lash,* Denise A. Colby, and Lisa F. Szczepura

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

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The NH–N–NH–N core of the porphyrin system represents one of the best studied and most versatile platforms for coordination chemistry. However, the replacement of one or more of the interior nitrogens with carbon atoms would be expected to diminish the ability of these systems to form metallo derivatives considerably. Despite this expectation, carbaporphyrinoid systems have been shown to form stable organometallic derivatives. Although azuliporphyrins and benziporphyrins act as dianionic ligands, benzocarbaporphyrins are trianionic ligands. Treatment of five different meso unsubstituted benzocarbaporphyrins and two different meso tetraarylbenzocarbaporphyrins with excess silver(I) acetate afforded 65–97% yields of the corresponding silver(III) organometallic derivatives. The insertion of silver metal was confirmed by mass spectrometry and X-ray crystallography. The UV–vis spectra showed a strong Soret band at wavelengths between 437 and 451 nm, together with a series of Q-type bands at longer wavelengths. The new metallo carbaporphyrins demonstrate the presence of a strong diatropic ring current in their proton NMR spectra, and carbon-13 NMR spectroscopy indicates that the derivatives retain a plane of symmetry. The reaction of meso tetraaryl carbaporphyrins with gold(III) acetate afforded the related gold(III) complexes, and these also showed strongly porphyrin-like aromatic characteristics. The UV–vis spectra for the gold complexes again showed a strong Soret band between 437–439 nm, but a secondary band near 400 nm is somewhat intensified for the gold species compared to the spectra for the related silver(III) meso tetrasubstituted carbaporphyrins. The ring currents observed for the gold(III) complexes by proton NMR spectroscopy were comparable to those of the silver(III) derivatives, implying that both series have similar macrocyclic conformations. Cyclic voltammetry was performed on two different carbaporphyrins, their silver(III) derivatives, and a gold(III) complex. The silver complexes display a reversible cathodic wave that is assigned to the Ag(III/II) couple. However, the gold porphyrinoid gave a value for the reductive wave that could be due to a gold(III/II) couple or a ligand-based process.

Introduction

Carbaporphyrins (**1**) are porphyrin analogues where one of the pyrrolic subunits has been replaced with a cyclopentadiene ring.[1−3] The best studied of these remarkable macrocyclic systems are the benzocarbaporphyrins **2**,[3−6] which are readily available from the "3 + 1" methodology[3,4,7−9] or by oxidative ring contraction of the related azuliporphyrins.[10−14] Many related porphyrinoids have been reported in recent years, including benziporphyrins,[15−19]

* Author to whom correspondence should be addressed. E-mail: tdlash@ilstu.edu.

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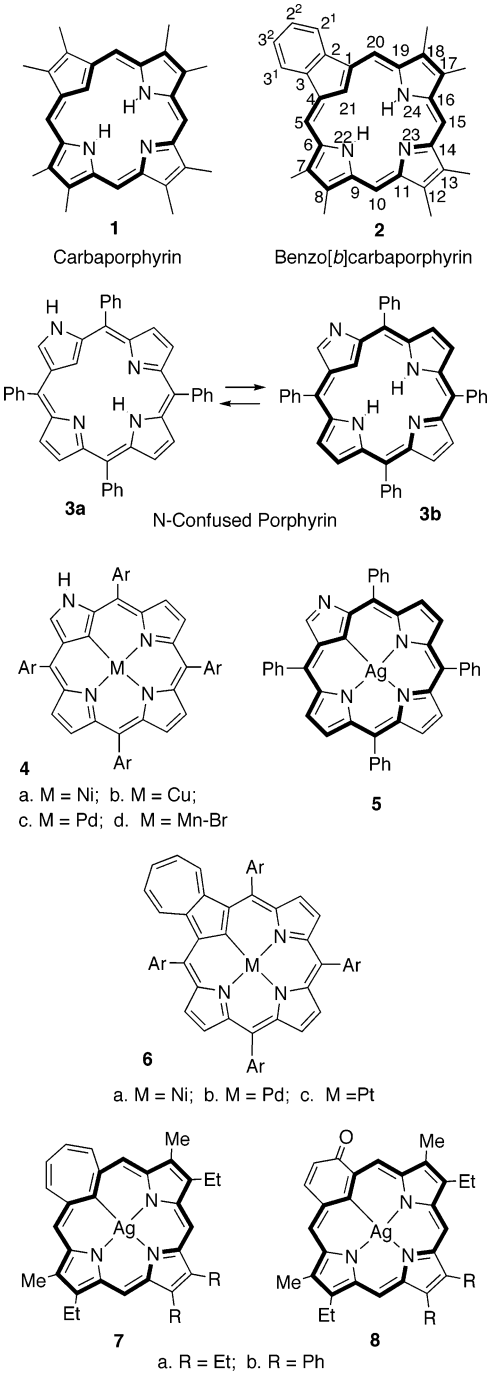
oxybenziporphyrins,[16,17,20] tropiporphyrins,[21] carbachlorins,[22] carbasapphyrins,[23,24] oxa- and thiacarbaporphyrins,[25] and dicarbaporphyrins.[26] All of these species have a carbocyclic ring in place of one or more pyrrole units and have a CH unit lying within the macrocyclic cavity. The latter feature is also found in the so-called N-confused porphyrins **3**,[27−29] which can be considered to be "honorary" carbaporphyrinoids.[2] Porphyrins are extremely versatile ligands because of their NH−N−NH−N core, but the presence of a carbon atom within the macrocyclic cavity would be expected to inhibit the formation of coordination complexes.[5,6] Nonetheless, N-confused porphyrins have been shown to act as both dianionic and trianions ligands,[28−30] readily forming neutral organometallic derivatives with divalent and trivalent metal cations (structures **4** and **5**, respectively).[30,31] Recently, there have been a number of reports on the synthesis of organometallic complexes for a variety of carbaporphyrinoid systems. Of particular note, azuliporphyrins have been shown to form stable nickel(II), palladium(II), and platinum(II) organometallic derivatives such as **6**,[32,33] and similar complexes have been obtained for benziporphyrins[18,19] and oxybenziporphyrins.[34] The formation of stable organometallic derivatives for trivalent metal cations, as exemplified for the silver(III) N-confused porphyrin **4**,[30] demonstrates that systems of this type can stabilize relatively unusual oxidation states.[29,35,36] Indeed, cis doubly N-confused porphyrins have been reported to give silver(III) and copper(III) derivatives,[37] and the recently discovered trans doubly confused system also affords the related copper(III) organometallic complex.[38] In a preliminary communication, we reported the synthesis of silver(III) benzocarbaporphyrins[39,40] and have subsequently shown that many related carbaporphyrinoids with a CH−NH−N−NH core can also generate silver(III) complexes (e.g., **7** and **8**).[35,36] These studies demonstrate that silver(III)

Chart 1



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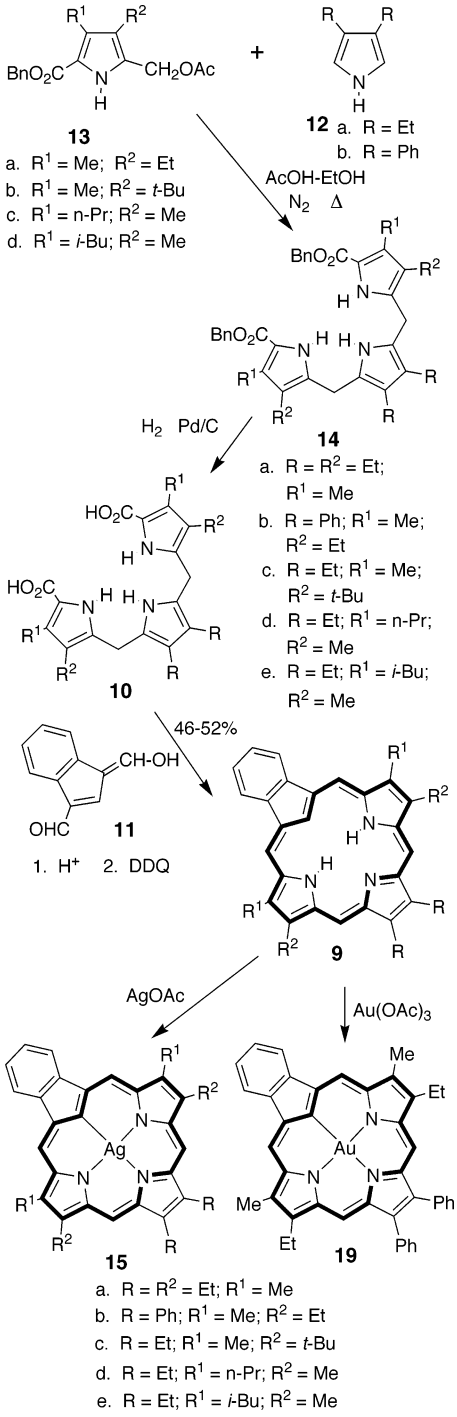
is readily stabilized by diverse carbaporphyrinoid systems. In this paper, we report full details of the synthesis, spectroscopy, and electrochemistry of a series of silver(III) benzocarbaporphyrins.[39,40] In addition, we report the first examples of gold(III) complexes for this class of porphyrin analogues.[41]

Results and Discussion

Our early metalation studies were conducted on meso unsubstituted benzocarbaporphyrins **9**. These porphyrin analogues are easily prepared by the "3 + 1" MacDonald condensation between tripyrranes **10** and diformylindene **11** (Scheme 1).[3,4,7−9] Syntheses of carbaporphyrins **9a**−**c** have been reported elsewhere,[3,4,9] but the dipropyl and diisobutylcarbaporphyrins (**9d** and **9e**) represent new compounds. These were prepared to explore the effect of larger alkyl chains on the solubility of the metalated carbaporphyrins. Reaction of diethylpyrrole (**12a**) with 2 equiv of the known acetoxymethylpyrroles (**13c** and **13d**)[43] in refluxing acetic acid−ethanol[44,45] afforded the new tripyrranes (**14d** and **14e**) in good yields. The benzyl ester protective groups were then cleaved by hydrogenolysis over 10% palladium−charcoal to give the corresponding dicarboxylic acids **10** (quantitative). Reaction of **10d** and **10e** with diformylindene[46] in TFA−dichloromethane, followed by neutralization with triethylamine and oxidation with DDQ, afforded the new carbaporphyrins **9d** and **9e** in 46−52% yield. These new compounds were fully characterized and displayed similar properties to those of previously described benzocarbaporphyrins[3,4] (e.g., strong diatropic ring currents by proton NMR spectroscopy, the presence of a Soret band at ca. 425 nm followed by a series of Q bands in the UV−vis absorption spectra, etc.).

When solutions of carbaporphyrins **9a**−**e** in dichloromethane−methanol were treated with silver(I) acetate, the brown mixtures turned orange over a period of several minutes. Following workup and evaporation of the solvents, we subjected the residues to chromatography on alumina. A deep orange-colored fraction eluted that was considerably less polar than the original carbaporphyrins. Initial studies were carried out on tetraethylbenzocarbaporphyrin **9a**, and following the reaction with excess AgOAc, chromatography and recrystallization from chloroform−methanol, silver(III) complex **15a** was isolated in 83% yield. This derivative gave a porphyrin-like UV−vis spectrum with a strong Soret band at 437 nm followed by a series of Q bands at 482, 518, 555, and 593 nm (Figure 1). The incorporation of silver into this system was easily confirmed by mass spectrometry. Silver exists as two isotopic forms, ^{107}Ag and ^{109}Ag, in near equal natural abundance.[47,48] The EI MS for the organosilver derivative gave the expected isotope pattern with two major

Scheme 1



(40) The synthesis of silver(III) carbaporphyrin **8a** was first disclosed at the *Symposium on Novel Porphyrinoids and their Metal Complexes − Chemistry, Photophysical Properties and Biomedical Aspects*, 37th IUPAC Congress/27th Gesellschaft Deutscher Chemiker General Meeting, Berlin, Germany, August 1999 (Lash, T. D. *Book of Abstracts*, Abstract No. MP-2). Additional results were presented at the following meetings: (a) 221st National ACS Meeting, San Diego, CA, April 2001 (Muckey, M. A.; Lash, T. D. *Book of Abstracts*, ORGN 715); (b) *Recent Advances in Heterocyclic Chemistry: Symposia Honoring Professor B. S. Thyagarajan*, Southwest Regional ACS Meeting, San Antonio, Texas, October 2001. (c) 2nd International Conference on Porphyrins and Phthalocyanines (ICPP-2), Kyoto, Japan, July 2002 (Lash, T. D. *Book of Abstracts*, Abstract No. S-76).

(41) The synthesis of gold(III) tetraarylbenzocarbaporphyrins was first reported at the 225th National Meeting of the American Chemical Society, New Orleans, LA, March 2003 (Lash, T. D.; Colby, D. A.; Muckey, M. A.; Liu, D.; Ferrence, G. M. *Book of Abstracts*, INOR 672).

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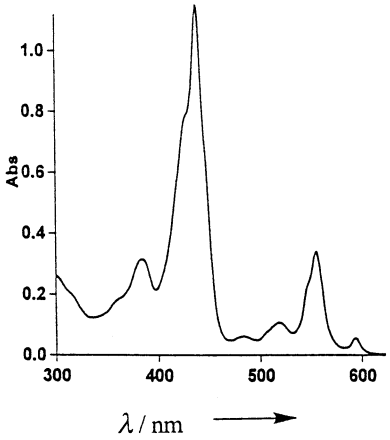

Figure 1. UV−vis spectrum of silver(III) benzocarbaporphyrin **15a** in chloroform.

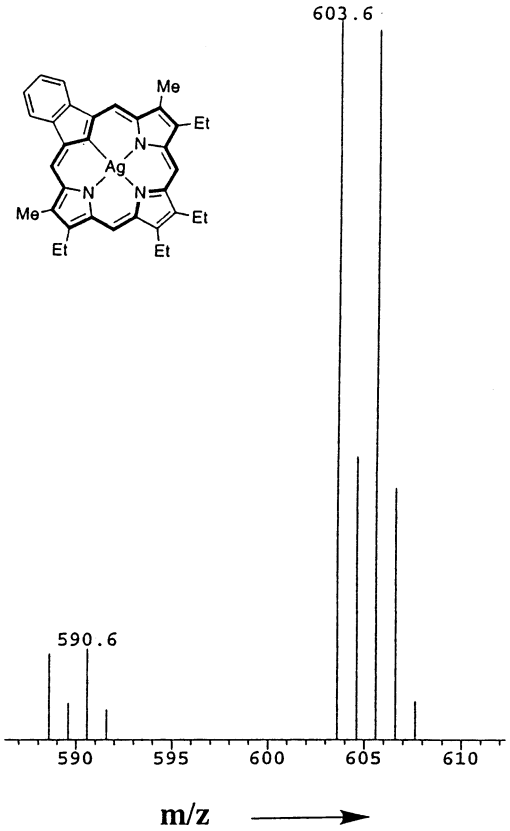

Figure 2. Electron-impact mass spectum (70 eV) of silver(III) benzocarbaporphyrin **15a**, showing the classic silver isotope pattern for the molecular ion at *m*/*z* 603 and 605.

molecular ions at *m*/*z* 603 and 605 (Figure 2). High-resolution MS data also confirmed that the molecular formula corresponded to $C_{35}H_{34}N_3Ag$. Benzylic fragmentation results in the loss of a methyl radical to give a smaller silver isotope pattern at *m*/*z* 588 and 590. These results strongly imply that the macrocycle is intact and that a silver(III) ion has replaced the three internal carbaporphyrin protons. The proton NMR spectrum for **15a** in $CDCl_3$ provides strong supporting evidence for this hypothesis. The spectrum is well resolved and shows the presence of all of the expected proton resonances. The meso protons afford two 2H singlets at 9.89 and 10.06 ppm, whereas the benzo protons gave multiplets at 7.78 and 8.84 ppm. These values are similar to those observed for the parent carbaporphyrin system **9a**, indicating that the macrocycle supports a comparable diatropic ring current, and the simplicity of the spectrum also confirms that the molecule retains a plane of symmetry. The main difference in the spectra of **9a** and **15a** is that the upfield signals corresponding to the internal NH and CH protons are no longer present for the latter species. Silver(III) complexes are diamagnetic, whereas silver(II) is a paramagnetic species, so the absence of line broadening in the proton NMR spectrum of **9a** also provides supporting evidence for the presence of the metal ion in oxidation state III. A carbon-13 NMR spectrum could not be obtained for **15a** because of its low solubility in organic solvents. For this reason, we prepared a series of related silver(III) carbaporphyrins **15b**−**e** in 65−92% yield from the corresponding benzocarbaporphyrins **9b**−**e**. The UV−vis spectra for **15c**−**e** were virtually identical to the spectrum obtained for **15a**; however, diphenyl-substituted system **15b** showed a slightly red-shifted Soret band at 441 nm. The strongest Q band for **15b** was also relatively intense and shifted to a longer wavelength (566 nm for **15b** compared to 555 nm for **15a**). Although the solubilities of **15b**−**e** were somewhat improved compared to those of **15a**, only **15b** gave a good-quality carbon-13 NMR spectrum. These data confirmed that the macrocycle has a plane of symmetry and gives two resonances for the meso carbons at 100.4 and 101.1 ppm. Unfortunately, it was not possible to identify the resonance for the internal carbon atom. The two silver isotopes both have spin values of $I = {}^1/_2$; therefore, they might be expected to produce two doublets for C21,[30,48] but the solubility of **15b** was still not sufficiently improved to allow this signal to be observed. However, it was possible to obtain X-ray-quality crystals of the diphenylcarbaporphyrin complex, and these data confirmed that the silver cation was present within the macrocyclic cavity. The silver complex displays a strikingly planar conformation with only a minor tilting of 5.09° for the indene unit relative to the mean macrocyclic plane. Full details of this structural characterization appeared in the preliminary communication.[39]

Recently, we have obtained meso tetraarylbenzocarbaporphyrins **16** by oxidative ring contraction of the related meso tetraarylazuliporphyrins.[13,14] These new carbaporphyrins were also investigated as potential organometallic ligands. The reaction of **16a** and **16b** with silver(I) acetate afforded good yields of the related silver(III) complexes **17a** and **17b**, respectively. The best results for the meso substituted carbaporphyrins were obtained by using pyridine as a solvent for the metalation reactions. Following chromatography, the pure silver complexes were obtained as orange powders in 80−97% yield. Both metallo carbaporphyrins were isolated as fine powders, and it was not possible to obtain crystals that would be suitable for structural analyses. The UV−vis spectra for both complexes in chloroform were similar with

(47) The natural abundances for ^{107}Ag and ^{109}Ag are 51.82 and 48.18%, respectively. For this reason, the MS isotope patterns for silver-containing compounds are very similar to those observed for bromine derivatives.

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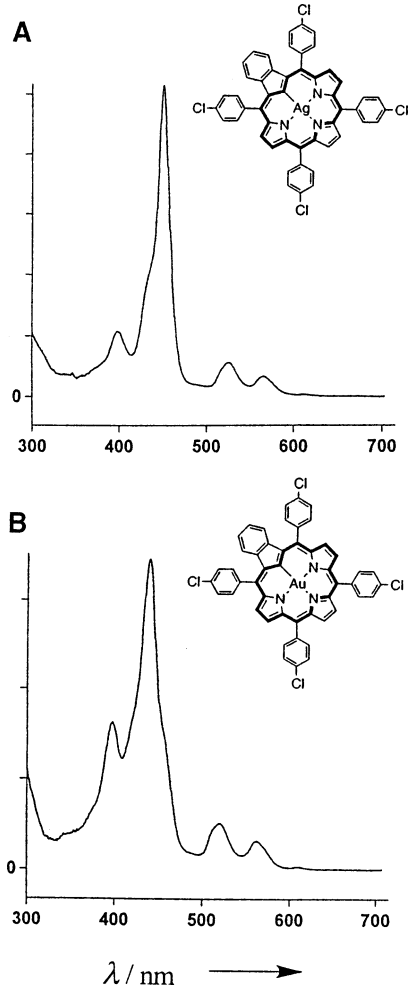

Figure 3. (A) UV−vis spectrum of silver(III) tetrakis(4-chlorophenyl)-carbaporphyrin **17b** in chloroform. (B) UV−vis spectrum of the related gold(III) complex **18b** in chloroform.

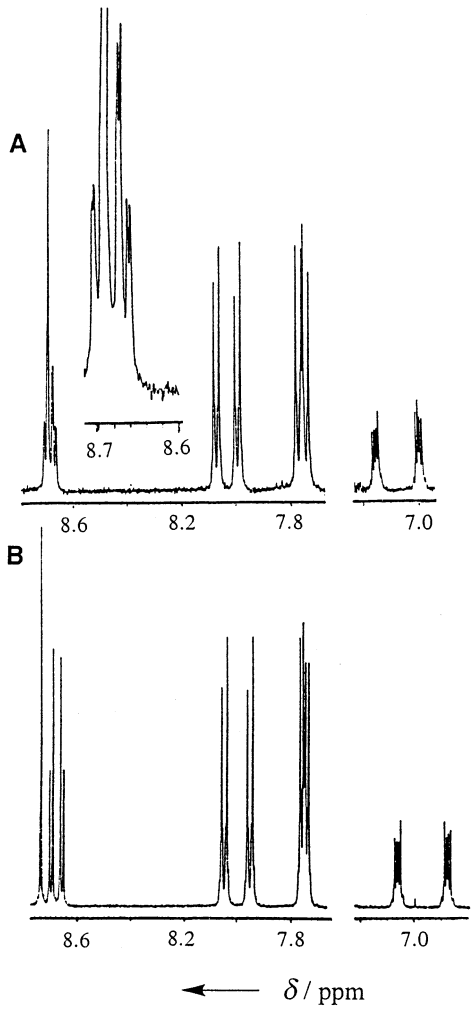

Figure 4. (A) Proton NMR spectrum (400-MHz) of silver(III) tetrakis-(4-chlorophenyl)-benzocarbaporphyrin **17b** in $CDCl_3$. The pyrrolic protons near 8.7 ppm show some fine structure due to transannular coupling to the silver nucleus. (B) Proton NMR spectrum (400-MHz) of the related gold-(III) complex **18b** in $CDCl_3$.

a strong Soret band at 450 nm. A weaker band was observed near 400 nm, and several Q-type bands are present at longer wavelengths (Figure 3A). The proton NMR spectra for the silver complexes were also consistent with the proposed structures, although the tetraphenylcarbaporphyrin derivative showed a considerable overlap of the aromatic resonances. However, tetrakis(4-chlorophenyl)benzocarbaporphyrin complex **17b** gave a particularly well-resolved proton NMR spectrum showing the presence of two sets of para disubstitution patterns for the aryl substituents between 7.7 and 8.1 ppm, whereas the benzo protons gave rise to two 2H multiplets at 7.0 and 7.2 ppm (Figure 4A). The pyrrolic protons produced a singlet that overlapped with an AB quartet that showed additional fine structure near 8.7 ppm. The fine structure associated with the pyrrolic AB quartet is due to transannular coupling from the silver cation. The spectroscopic data indicates that the macrocycle retains a diatropic ring current that is similar to the free base carbaporphyrins **16** and also confirms the presence of a plane of symmetry. Although **17b** was relatively insoluble and gave only a noisy carbon-13 NMR spectrum, a good-quality carbon-13 NMR spectrum could be obtained for **17a**. This showed the presence of the 20 carbon resonances, some of which showed a small degree of long-range coupling from the silver metal. However, as was the case for the meso unsubstituted carbaporphyrin complexes **15**, the internal carbon could not be identified for this system. Silver complexes **17** could not be analyzed by EI or FAB MS but gave good results using field desorption mass spectrometry.

The formation of silver(III) complexes from silver(I) acetate, irrespective of whether the reactions are performed in the presence of air or under a nitrogen atmosphere, deserves further comment. In all of these reactions, the formation of a precipitate or film of metallic silver is always observed. Although we initially speculated that an oxidative elimination might be occurring,[39] it has been suggested that a disproportionation of three silver(I) cations to give two Ag^0 and one Ag^{3+} is involved in the formation of silver(III) corroles ($3Ag^+ \rightarrow 2Ag^0 + Ag^{3+}$),[49] and it is probable that this is the origin of the redox chemistry that occurs in our studies as well.

Although some copper(III) N-confused porphyrin complexes have been reported,[37,38] to our knowledge no examples

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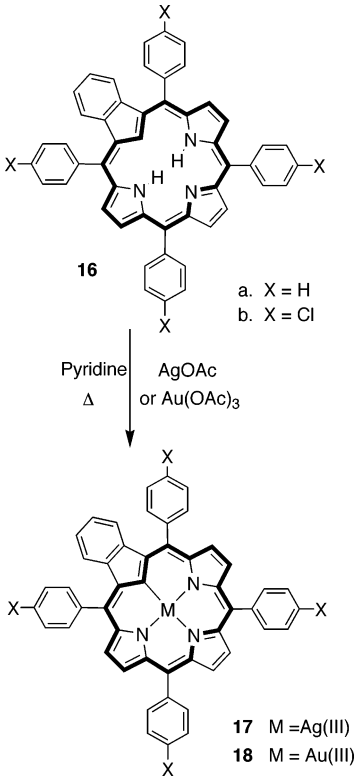
Scheme 2



of gold(III) derivatives have been described. The reaction of **16a** or **16b** with gold(I) iodide in pyridine gave low yields of the corresponding gold complexes **18**, but much better results could be obtained using gold(III) acetate as the reagent. In this case, no change in the metal's oxidation state is required. Under optimized conditions using pyridine as a solvent, we could isolate the gold complexes following column chromatography in 67−83% yield. Again, the gold derivatives were isolated as fine orange powders. The UV−vis spectra for **18a** and **18b** were similar to those of the corresponding silver derivatives, showing a strong Soret band at 437 nm and several Q-type bands between 500 and 610 nm (Figure 3B). A medium-sized band just below 400 nm is also observed in this case. The same absorption is actually present for silver complexes **17** but is considerably weaker for these derivatives. The proton NMR spectra for the gold complexes are also similar to the corresponding silver(III) derivatives. The best data was obtained for [tetrakis(4-chlorophenyl)carbaporphyrinato]gold(III) complex (**18b**), this confirms the presence of both a plane of symmetry and a powerful diatropic ring current (Figure 4B). The aryl substiutents gave rise to the expected signals between 7.7 and 8.1 ppm, whereas the benzo unit produced two 2H multiplets at 6.9 and 7.1 ppm. The pyrrolic protons gave a singlet at 8.74 ppm and two 2H doublets at 8.66 and 8.70 ppm ($J = 4.8$ Hz). The aromatic character of the silver and gold complexes appears to be very similar. This is reasonable given that silver(III) and gold(III) have virtually the same ionic radii,[50] and they presumably allow the porphyrinoid ligands to take on similar conformations. Carbon-13 NMR data was obtained for both gold complexes, but only the more soluble tetraphenyl complex **18a** gave a well-resolved spectrum. In this case, the internal carbon could be identified as a small resonance at 115.8 ppm. As was the case for silver complexes **16**, EI MS could not be obtained for the gold derivatives. The tetraphenyl version **18a** gave adequate FAB MS data, but **18b** could only be characterized using FD MS. All four of the meso substituted complexes (**16a**, **16b**, **18a**, and **18b**) gave clean results by field desorption MS; the poor results using other techniques appear to be due to decomposition during the analyses.

Our attempts to obtain gold(III) complexes for meso unsubstituted benzocarbaporphyrins were far less successful. Trace amounts of metalated products were formed by reacting carbaporphyrins **9** with $Au(OAc)_3$, but these reactions primarily led to the decomposition of the starting material. Product **19** from the reaction of diphenylbenzocarbaporphyrin (**9b**) with gold(III) acetate was isolated as an orange solid in <10% yield. The UV−vis and proton NMR data for complex **19** were similar to that of the related silver complexes **15**, but the low yields obtained for the chemistry prevented further investigations.

All of the silver and gold carbaporphyrins are nonpolar compounds that give deep-orange-colored solutions. The combined spectroscopic data strongly indicate that these complexes must be silver(III) or gold(III) complexes because these are diamagnetic systems that give well-resolved NMR spectra. The R_f values for the derivatives confirm that the metalated products are far less polar than corresponding free base carbaporphyrins **9** and **16**. In addition, the three interior protons residing in the initial carbaporphyrin structures have all been lost and replaced by a single metal ion. Although the overall results cannot be adequately explained unless the metal is in oxidation state III, we performed electrochemical studies to provide further evidence for these assignments. These studies were carried out on free base benzocarbaporphyrins **9b** and **16a**, together with related silver complexes **15b** and **17a** and gold derivative **18a**. These specific samples were primarily selected because of their superior solubility characteristics.

The cyclic voltammograms for the free base carbaporphyrins were measured in dichloromethane under an inert atmosphere. Starting at −0.10 V and scanning to −1.90 V, tetraphenylcarbaporphyrin (**16a**) displays two quasi-reversible cathodic waves at $E_{1/2} = -1.51$ and −1.81 V (Figure 5a). Switching potential experiments verified that the small oxidative waves at −0.53 and −0.16 V are observed only after accessing the waves at −1.51 and −1.81 V, respectively. Scanning from −0.10 to +1.90 V, we observed five oxidative waves at $E_{p,a} = 0.50$ V, $E_{1/2} = 0.62$ V, $E_{p,a} = 1.04$ V, and $E_{1/2} = 1.07$ and 1.80 V. Meso unsubstituted carbaporphyrin **9b** also displays two quasi-reversible cathodic waves when the scan is initiated at 0.0 V, the resting potential, and scanned in the negative direction. These waves appear at $E_{1/2} = -1.58$ and −1.88 V, and the small anodic wave at $E_{p,a} = 0.72$ V is observed only after accessing the wave at −1.58 V. Five oxidative waves are observed between

(50) The ionic radii for four-coordinate square-planar silver(III) and gold(III) are reported to be 0.67 and 0.68 Å, respectively. See Shannon, R. D. *Acta Crystallogr. A* **1976**, *32*, 751−767.

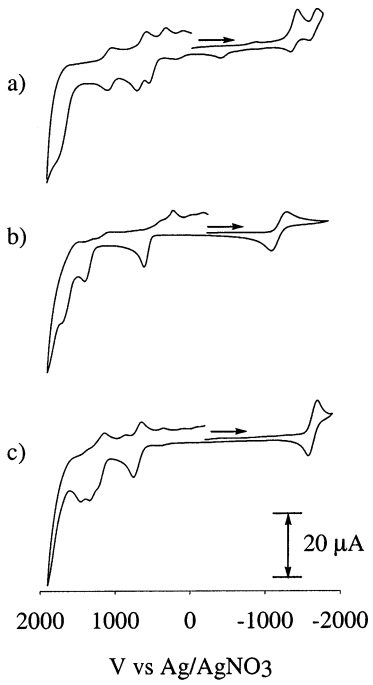


Figure 5. Cyclic voltammograms (200 mV/s) of tetraphenylbenzocarbaporphyrin **16a** (a) and the related silver(III) (b, **17a**) and gold(III) (c, **18a**) complexes in anhydrous dichloromethane, 0.2 M Bu_4NBF_4.

0.0 and 1.90 V. These waves occur at $E_{p,a} = 0.52$ V, $E_{1/2} = 0.76$ V, $E_{p,a} = 1.10$ V, and $E_{1/2} = 1.14$ and 1.65 V. The electrochemical properties displayed by **9b** and **16a** are similar to those previously reported for **9a**,[4] in that two quasi-reversible cathodic waves and five oxidative waves are observed. The oxidative electrochemistry of these free base carbaporphyrins is much more complex than that of free base porphyrins, which typically display two reversible reductive and two reversible oxidative couples. Focusing on the cathodic waves of these carbaporphyrins, we found that there is a noticeable shift in the potentials of the two reductive couples on comparing the voltammograms of compounds **16a**, **9a**, and **9b**. Both reductive couples of **9b** are 70 mV more cathodic than those of **16a**. The reductive couples of **9a** are also shifted in the same direction. However, the shifts for **9a** are much greater; that is, the first and second reductive couples of **9a** are 180 and 230 mV more cathodic than those of **16a**, respectively. Because of the quasi-reversible nature of these waves, it is easier to compare $\Delta E_{1/2}$ values to determine similarities and differences for these three different carbaporphyrins. Specifically, we have looked at the difference between the two quasi-reversible reductive waves ($\Delta E_{1/2}$) as well as the difference between the first reductive and first oxidative waves (HOMO−LUMO gap). Compounds **16a** and **9b** both have $\Delta E_{1/2}$ values of 0.30 V, whereas compound **9a** has a $\Delta E_{1/2}$ value of 0.35 V. These values are all virtually identical to one another but slightly smaller than those for free base porphyrins and metalloporphyrins, which have a $\Delta E_{1/2}$ value of 0.42 ± 0.05 V. However, the HOMO−LUMO gaps ($\Delta E_{1/2}{}^{ox} - \Delta E_{1/2}{}^{red}$) for compounds **16a**, **9a**, and **9b** are 2.02, 2.17, and 2.10 V, respectively. These are all comparable to the gap observed for porphyrins and metalloporphyrins ($\Delta E_{1/2}{}^{ox} - \Delta E_{1/2}{}^{red} = 2.25 \pm 0.15$ V).

The electrochemical properties of metal complexes **15b**, **17a**, and **18a** were also investigated using cyclic voltammetry. Silver complex **17a** was scanned between the limits of +1.90 and −1.90 V versus $Ag/AgNO_3$ (Figure 5b). This compound displays one reversible cathodic wave at $E_{1/2} = -1.14$ V and three irreversible anodic waves at $E_{p,a} = 0.62$, 1.41, and 1.70 V. Accessing these irreversible waves generates numerous cathodic waves that are indicative of a variety of decomposition products. Notably, the reductive wave in **17a** occurs at a potential that is between the first oxidative and first reductive couples of free base carbaporphyrin **16a**, indicating that this wave is metal based and not carbaporphyrin based. Therefore, the wave is assigned to the Ag(III/II) couple. Meso unsubstituted silver complex **15b** similarly shows a quasi-reversible reductive wave ($E_{1/2} = -1.24$ V) between the first reductive wave ($E_{1/2} = -1.58$ V) and the first oxidative wave ($E_{p,a} = 0.52$ V) of free base carbaporphyrin **9b**, again suggesting that the silver ion is in the Ag^{3+} oxidation state. However, the Ag(III/II) redox couple for complex **17a** is 100 mV more positive than that of complex **15b**.

The cyclic voltammogram of gold complex **18a** was qualitatively similar to that of silver(III) carbaporphyrin complexes **15b** and **17a** in that there is one reversible reductive wave and five oxidative waves (Figure 5c). Starting at −0.20 V and scanning in the negative direction, one cathodic wave appears at $E_{1/2} = -1.65$ V. Scanning in the positive direction, we observed the following anodic waves: $E_{1/2} = 0.69$ and 1.18 V and $E_{p,a} = 1.32$, 1.47, and 1.97 V. Gold(III) porphyrin complexes have long been thought of as being electrochemically inert.[51−53] However, a recent electrochemical investigation of [5,10,15,20-tetrakis-(3,5-di-*tert*-butylphenyl)porphyrinato]-gold(III) hexafluorophosphate provided evidence to the contrary. Kadish, Crossley, and co-workers demonstrated that this gold(III) porphyrin complex can be electrochemically reduced to its gold(II) analogue.[54] Thus, the reductive wave observed in complex **18a** could be the gold(III/II) couple. However, in contrast to the silver carbaporphyrin complexes, it is difficult to determine whether the first reductive couple of complex **18a** is metal based or ligand based. In the case of the silver complexes, the first reductive wave appeared at a potential that was between the first oxidative and first reductive wave of the free base carbaporphyrin. However, this is not the case for the reductive wave of **18a**. This single cathodic wave at $E_{1/2} = -1.65$ V appears at a potential that is more negative than the first reductive couple of the free base carbaporphyrin ($E_{1/2} = -1.51$ V). Additional experiments are needed to determine the exact nature of this electrochemical reduction.

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(52) Kadish, K. M.; van Caemelbecke, E.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 8, pp 1−114.
(53) Jamin, M. E.; Iwamoto, R. T. *Inorg. Chim. Acta* **1978**, *27*, 135.
(54) Kadish, K. M.; E. W.; Ou, Z.; Shao, J.; Sintic, P. J.; Ohkubo, K.; Fukuzumi, S.; Crossley, M. J. *Chem. Commun.* **2002**, 356−357.

Conclusions

Benzocarbaporphyrins readily form silver(III) and gold(III) derivatives under mild conditions where the metal ion is bound within the macrocyclic cavity and forms three metal−nitrogen bonds and one metal−carbon bond. These nonpolar diamagnetic complexes were characterized by spectroscopic and mass spectrometric methods, and a silver(III) organometallic derivative was characterized by X-ray crystallography.[39] Electrochemical studies provide additional support for the oxidation states of the metal ions. This study demonstrates that carbaporphyrins can act as superior ligands for the synthesis of organometallic derivatives involving higher oxidation states that compare favorably with the results reported for N-confused porphyrins.

Experimental Section

Carbaporphyrins **9a**−**c** and **16a** and **b** were prepared as described previously.[3,6,9,13,14] NMR spectra were obtained on a Varian Gemini 400-MHz NMR spectrometer and recorded in ppm relative to $CDCl_3$ (residual chloroform at 7.26 ppm in proton NMR and $CDCl_3$ triplet at 77.23 ppm in carbon-13 NMR spectra). UV−vis spectra were recorded on a Varian Cary UV spectrophotometer. EI mass spectral determinations were made at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana−Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

[8,12,13,17-Tetraethyl-7,18-dimethylbenzo[*b*]-21-carbaporphyrinato]silver(III) (15a). A solution of benzocarbaporphyrin **9a** (12 mg) in dichloromethane (10 mL) was added to silver(I) acetate (12 mg) dissolved in methanol (2.5 mL), and the mixture was stirred at room temperature overnight. The mixture was washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane. A deep red−orange fraction was collected and recrystallized from chloroform−methanol to give the silver(III) complex (12 mg, 83%) as red crystals, mp > 300 °C dec; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 384 (4.44), 437 (5.00), 482 (3.76), 518 (3.98), 555 (4.46), 593 (3.70); ^{1}H NMR ($CDCl_3$): δ 1.85 (6H, t, J = 7.6 Hz), 1.90 (6H, t, J = 7.6 Hz), 3.57(6H, s), 4.03 (8H, q, J = 7.4 Hz), 7.78 (2H, m), 8.84 (2H, m), 9.89 (2H, s), 10.06 (2H, s). HRMS (EI): calcd for $C_{35}H_{34}N_3Ag$: *m*/*z* 603.1803; found: 603.1803. Anal. Calcd for $C_{35}H_{34}N_3Ag$: C, 69.54; H, 5.63; N, 6.95. Found: C, 69.02; H, 5.72; N, 6.91.

[8,17-Diethyl-7,18-dimethyl-12,13-diphenylbenzo[*b*]-21-carbaporphyrinato]silver(III) (15b). A solution of diphenylbenzocarbaporphyrin **9b** (12 mg) in dichloromethane (10 mL) was added to silver(I) acetate (12 mg) dissolved in methanol (2.5 mL), and the mixture was stirred at room temperature overnight. The mixture was washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane. A deep red−orange fraction was collected and recrystallized from chloroform−methanol to give the silver(III) complex (13 mg, 92%) as red crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 380 (4.40), 393 (4.43), 441 (5.11), 529 (3.98), 566 nm (4.63); ^{1}H NMR ($CDCl_3$): δ 1.70 (6H, t, J = 7.5 Hz), 3.24 (6H, s), 3.73 (4H, q, J = 7.5 Hz), 7.61 (2H, m), 7.66 (2H, t, J = 7.4 Hz), 7.76 (4H, t, J = 7.4 Hz), 8.05 (4H, d, J = 6.8 Hz), 8.32 (2H, m), 9.22 (2H, s), 9.82 (2H, s); ^{13}C NMR ($CDCl_3$): δ 11.4, 17.3, 20.2, 100.4, 101.1, 119.7, 121.2, 126.4, 127.4, 128.8, 131.9, 132.9, 134.9, 135.1, 135.4, 136.4, 138.6, 140.2, 140.7; HRMS: calcd for $C_{43}H_{34}N_3Ag$: *m*/*z* 699.1787; found: 699.1803. Anal. Calcd for $C_{43}H_{34}N_3Ag\cdot{}^1/_2CHCl_3$: C, 68.72; H, 4.57; N, 5.53. Found: C, 68.96; H, 4.60; N, 5.62.

[8,17-Di-*tert*-butyl-12,13-diethyl-7,18-dimethylbenzo[*b*]-21-carbaporphyrinato]silver(III) (15c). A solution of di-*tert*-butylbenzocarbaporphyrin (**9c)** (12 mg) was reacted with silver(I) acetate (12 mg) under the foregoing conditions. Following chromatography on grade 3 alumina eluting with dichloromethane, the orange product fraction was recrystallized from chloroform−methanol to give the silver(III) complex (9.3 mg, 65%) as orange−red crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 385 (4.40), 440 (4.97), 484 (3.67), 520 (3.96), 556 (4.39), 595 nm (3.78); ^{1}H NMR ($CDCl_3$): δ 1.93 (6H, t, J = 7.6 Hz), 2.43 (18H, s), 3.89 (6H, s), 4.05 (4H, q, J = 7.6 Hz), 7.75−7.78 (2H, m), 8.87−8.90 (2H, m), 10.28 (2H, s), 10.67 (2H, s); ^{13}C NMR ($CDCl_3$): δ 15.6, 18.5, 20.2, 35.8, 37.2, 101.0, 102.4, 120.3, 122.0, 126.7, 132.2, 135.8, 136.1, 136.3, 140.2, 141.3, 145.1; FD MS: *m*/*z* (rel int) 663.1 (9.6), 662.1 (42), 661.1 (100), 660.0 (49), 659.1 (90, M^+). Anal. Calcd for $C_{39}H_{42}N_3Ag\cdot{}^1/_4CHCl_3$: C, 68.27; H, 6.17; N, 6.08. Found: C, 67.96; H, 6.51; N, 5.70.

2,5-Bis(5-benzyloxycarbonyl-3-methyl-4-propyl-2-pyrrolylmethyl)-3,4-diethylpyrrole (14d). A stirred mixture of benzyl 5-acetoxymethyl-4-methyl-3-propylpyrrole-2-carboxylate (**13c**; 2.67 g) and 3,4-diethylpyrrole (**12a**; 0.50 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 in an ice bath. The resulting precipitate was suction filtered, washed with cold ethanol, and dried in vacuo to give the tripyrrane dibenzyl ester (1.96 g; 73%) as an off-white powder, mp 180−181.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 0.79 (6H, t, J = 7.4 Hz), 1.08 (6H, t, J = 7.6 Hz), 1.39 (4H, sextet), 1.89 (6H, s), 2.42 (4H, q, J = 7.5 Hz), 2.61 (4H, t, J = 7.6 Hz), 3.64 (4H, br s), 4.54 (4H, br s), 7.08−7.12 (4H, m), 7.21−7.34 (6H, m), 8.53 (1H, br s), 10.42 (2H, br s); ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ 0.82 (6H, t, J = 7.2 Hz), 1.08 (6H, t, J = 7.4 Hz), 1.43 (4H, sextet), 1.89 (6H, s), 2.42 (4H, q, J = 7.5 Hz), 2.61 (4H, t, J = 7.6 Hz), 3.69 (4H, s), 4.77 (4H, br s), 7.17−7.21 (4H, m), 7.25−7.31 (6H, m), 8.04 (1H, br s), 9.75 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 9.0, 14.4, 16.9, 17.9, 22.5, 24.5, 27.9, 65.8, 116.2, 117.0, 119.4, 122.3, 127.3, 127.5, 128.3, 132.4, 133.1, 136.9, 162.7. Anal. Calcd for $C_{42}H_{57}N_3O_4$: C, 78.95; H, 6.49; N, 5.76. Found: C, 78.98; H, 6.43; N, 5.89.

2,5-Bis(5-benzyloxycarbonyl-4-isobutyl-3-methyl-2-pyrrolylmethyl)-3,4-diethylpyrrole (14e). Benzyl 5-acetoxymethyl-4-methyl-3-isobutylpyrrole-2-carboxylate (**13d**; 1.39 g) was reacted with **12a** (0.25 g) under the foregoing conditions. The tripyrrane (0.84 g, 60%) was isolated as a pink powder, mp 171.5−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 0.72 (12H, d, J = 6.4 Hz), 1.04 (6H, t, J = 7.6 Hz), 1.65−1.76 (2H, m), 1.88 (6H, s), 2.40 (4H, q, J = 7.5 Hz), 2.47 (4H, br d, J = 6 Hz), 3.67 (4H, s), 4.49 (4H, br s), 7.08−7.11 (4H, m), 7.21−7.30 (6H, m), 8.66 (1H, br s), 10.57 (2H, br s); ^{13}C NMR ($CDCl_3$): δ 9.4, 16.4, 16.7, 17.9, 22.6, 22.9, 30.4, 34.5, 65.9, 117.0, 117.4, 120.3, 122.0, 127.9, 128.1, 128.4, 131.9, 132.4, 136.7, 162.4. Anal. Calcd for $C_{44}H_{55}N_3O_4$: C, 76.60; H, 8.03; N, 6.09. Found: C, 76.21; H, 7.87; N, 6.15.

12,13-Diethyl-7,18-dimethyl-8,17-dipropylbenzo[*b*]-21-carbaporphyrin (9d). Tripyrrane dibenzyl ester **14d** (1.50 g) was dissolved in freshly distilled THF (225 mL) in a hydrogenation vessel, methanol (75 mL) and triethylamine (20 drops) were added, and the air was flushed out with a stream of nitrogen. Palladium−charcoal (10%; 200 mg) was added, and the resulting mixture was shaken under a hydrogen atmosphere at 40 psi overnight. The

catalyst was filtered off, and the solvent was removed under reduced pressure. The resulting residue was taken up in 3% aqueous ammonia and neutralized with acetic acid to a litmus end point while maintaining the temperature of the solution between 0 and 5 °C with the aid of a salt−ice bath. The resulting precipitate was suction filtered and washed repeatedly with water to remove all traces of water. After drying overnight in vacuo, the dicarboxylic acid **24b** (1.07 g; 98%) was obtained as a pink powder that was used without further purification. Tripyrrane **24b** (100 mg) was stirred with TFA (2 mL) in a pear-shaped flask for 10 min under nitrogen. The solution was diluted with dichloromethane (38 mL), diformylindene (36 mg) was immediately added, and the solution stirred in the dark under N_2 for an additional 2 h. The solution was neutralized by the dropwise addition of triethylamine, DDQ (50 mg) was added, and the resulting solution was stirred for an additional 1 h. The mixure was washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane, and the product was collected as a brown band. Recrystallization from chloroform−methanol gave the dipropylcarbaporphyrin (57 mg; 52%) as fluffy copper−bronze crystals, mp > 300 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (log ϵ) 376 (4.62), 425 (5.23), 511 (4.25), 545 (4.18), 603 (3.80), 662 nm (3.37); UV−vis (0.05% TFA-$CHCl_3$; monocation): λ_{max} (log ϵ) 401 (4.75), 439 (5.00), 474 (4.51), 548 (4.09), 586 (3.94), 612 nm (3.93); UV−vis (50% TFA−$CHCl_3$): λ_{max} (log ϵ) 344 (4.56), 425 (5.24), 615 (3.92), 668 nm (4.42); ^{1}H NMR (400 MHz, $CDCl_3$): δ −6.84 (1H, s), −4.07 (2H, br s), 1.29 (6H, t, J = 7.4 Hz), 1.85 (6H, t, J = 7.6 Hz), 2.29 (4H, sextet), 3.56 (6H, s), 3.93 (4H, q, J = 7.6 Hz), 4.01 (4H, t, J = 7.8 Hz), 7.74−7.77 (2H, m), 8.81−8.84 (2H, m), 9.73 (2H, s), 10.04 (2H, s);^{1}H NMR (400 MHz, trace TFA−$CDCl_3$; monocation): δ −6.76 (1H, s), −4.52 (1H, br s), −3.09 (2H, br s), 1.19 (6H, t, J = 7.4 Hz), 1.86 (6H, t, J = 7.8 Hz), 2.13 (4H, sextet), 3.55 (6H, s), 4.01 (4H, t, J = 7.4 Hz), 4.10 (4H, q, J = 7.7 Hz), 7.71−7.74 (2H, m), 8.68−8.71 (2H, m), 10.04 (2H, s), 10.29 (2H, s);^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$; dication): δ −5.06 (2H, s), −1.40 (3H, br s), 1.34 (6H, t, J = 7.4 Hz), 1.76 (6H, t, J = 7.6 Hz), 2.28 (4H, sextet), 3.60 (6H, s), 4.04 (4H, t, J = 8 Hz), 4.09 (4H, t, J = 7.8 Hz), 8.96−9.00 (2H, m), 10.17−10.20 (2H, m), 10.54 (2H, s), 11.10 (2H, s); ^{13}C NMR ($CDCl_3$): δ 11.5, 14.7, 18.7, 20.1, 26.2, 28.6, 95.5, 98.8, 109.4, 120.6, 126.5, 131.2, 133.8, 135.1, 136.3, 137.9, 141.5, 144.4, 152.8; ^{13}C NMR ($CDCl_3$, trace TFA−$CDCl_3$; monocation): δ 11.9, 14.6, 17.7, 19.9, 25.8, 28.7, 94.5, 104.6, 119.6, 121.5, 128.1, 134.5, 137.0, 137.6, 138.4, 140.0, 141.1, 141.2, 142.1; HRMS (EI): calcd for $C_{37}H_{41}N_3$, 527.3300; found: 527.3292. Anal. Calcd for $C_{37}H_{41}N_3 \cdot {}^1/_{20}CHCl_3$: C, 83.38; H, 7.75; N, 7.87. Found: C, 83.35; H, 7.76; N, 7.92.

12,13-Diethyl-8,17-diisobutyl-7,18-dimethyl-benzo[*b*]-21-carbaporphyrin (9e). Tripyrrane dibenzyl ester (**14e**) (200 mg) was hydrogenolysed by the procedure described above to give the corresponding dicarboxylic acid **10e** (145 mg, quantitative) as a pink powder. Tripyrrane **10e** (100 mg) was stirred with TFA (2 mL) in a pear-shaped flask for 2 min under nitrogen, the solution was diluted with dichloromethane (200 mL), and diformylindene (33.8 mg) was immediately added. The resulting solution was stirred in the dark under N_2 for an additional 16 h. The mixture was neutralized by the dropwise addition of triethylamine, DDQ (46 mg) was added, and the resulting solution was stirred for an additional 30 min. The mixure was washed with water, and the solvent was removed under reduced pressure. The residue was chromatographed on grade 3 alumina eluting with dichloromethane, and the product was collected as a brown band. Recrystallization from chloroform−methanol gave the diisobutylcarbaporphyrin (50 mg, 46%) as reddish-purple crystals, mp > 300 °C; UV−vis (1% Et_3N−$CHCl_3$): λ_{max} (log ϵ) 377 (4.60), 425 (5.17), 511 (4.25), 545 (4.15), 603 (3.80), 663 nm (3.41); UV−vis (0.05% TFA−$CHCl_3$; monocation): λ_{max} (log ϵ) 395 (4.41), 440 (4.95), 474 (4.48), 549 (4.08), 588 (3.94), 610 nm (3.93); UV−vis (50% TFA−$CHCl_3$): λ_{max} (log ϵ) 345 (4.53), 425 (5.17), 614 (3.94), 669 nm (4.37); ^{1}H NMR (400 MHz, $CDCl_3$): δ −6.79 (1H, s), −4.08 (2H, br s), 1.27 (12H, d, J = 6.4 Hz), 1.85 (6H, t, J = 7.8 Hz), 2.66 (2H, m), 3.56 (6H, s), 3.89−3.97 (8H, m), 7.73−7.77 (2H, m), 8.80−8.83 (2H, m), 9.75 (2H, s), 10.03 (2H, s);^{1}H NMR (400 MHz, trace TFA−$CDCl_3$; monocation): δ −6.73 (1H, s), −4.25 (1H, br s), −2.85 (2H, br s), 1.16 (12H, d, J = 6.8 Hz), 1.87 (6H, t, J = 7.6 Hz), 2.48 (2H, m), 3.56 (6H, s), 3.91 (4H, d, J = 7.6 Hz), 4.10 (4H, q, J = 7.6 Hz), 7.71−7.74 (2H, m), 8.67−8.70 (2H, m), 10.04 (2H, s), 10.28 (2H, s);^{1}H NMR (400 MHz, 50% TFA−$CDCl_3$; dication): δ −5.05 (2H, s), −1.33 (3H, br s), 1.28 (12H, d, J = 6.8 Hz), 1.73 (6H, t, J = 7.8 Hz), 2.59 (2H, m), 3.58 (6H, s), 3.91 (4H, d, J = 7.2 Hz), 4.06 (4H, q, J = 7.6 Hz), 8.95−8.98 (2H, m), 10.13−10.16 (2H, m), 10.49 (2H, s), 11.03 (2H, s);^{13}C NMR ($CDCl_3$): δ 11.8, 18.7, 20.1, 23.5, 32.3, 35.8, 95.6, 99.1, 109.3, 120.6, 126.6, 131.7, 133.7, 135.5, 136.2, 137.2, 141.4, 144.4, 152.8; ^{13}C NMR ($CDCl_3$, trace TFA−$CDCl_3$; monocation): δ 12.2, 17.8, 19.9, 23.3, 32.1, 35.9, 94.7, 104.9, 119.8, 121.5, 128.1, 134.8, 137.0, 137.4, 138.3, 139.1, 141.1, 141.5, 142.2; ^{13}C NMR ($CDCl_3$, 50% TFA−$CDCl_3$; dication): δ 12.1, 17.3, 20.2, 22.8, 32.4, 33.1, 35.8, 108.4, 125.0, 134.8, 140.2, 140.6, 142.4, 145.3, 145.9, 146.7, 151.4, 151.7; HRMS (EI): calcd for $C_{39}H_{45}N_3$, 555.3613; found, 555.3619. Anal. Calcd for $C_{39}H_{45}N_3.0.6CHCl_3$: C, 75.81; H, 7.46; N, 6.70. Found: C, 75.96; H, 7.42; N, 6.71.

[12,13-Diethyl-7,18-dimethyl-8,17-dipropylbenzo[*b*]-21-carbaporphyrinato]silver(III) (15d). A solution of dipropylbenzocarbaporphyrin (**9d**) (12 mg) was reacted with silver(I) acetate under the conditions used to prepare **9a**. Following chromatography on grade 3 alumina eluting with dichloromethane, the orange product fraction was recrystallized from chloroform−methanol to give the silver(III) complex (10.7 mg, 75%) as orange−red crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 383 (4.42), 437 (4.98), 483 (3.71), 518 (3.94), 555 (4.43), 594 nm (3.62); ^{1}H NMR ($CDCl_3$): δ 1.33 (6H, t, J = 7.4 Hz), 1.90 (6H, t, J = 7.6 Hz), 2.29−2.37 (4H, m), 3.63 (6H, s), 4.00−4.08 (8H, overlapping t and q), 7.79−7.82 (2H, m), 8.92−8.95 (2H, m), 10.00 (2H, s), 10.22 (2H, s); HRMS (EI): calcd for $C_{37}H_{38}N_3Ag$, 631.2117; found, 631.2107. Anal. Calcd for $C_{37}H_{38}N_3Ag \cdot {}^1/_8CHCl_3$: C, 68.63; H, 5.93; N, 6.49. Found: C, 68.61; H, 5.90; N, 6.36.

[12,13-Diethyl-8,17-diisobutyl-7,18-dimethyl-benzo[*b*]-21-carbaporphyrinato]silver(III) (15e). The silver complex was prepared from **9e** (12 mg) by the procedure reported above. Recrystallization from chloroform−methanol gave the silver(III) complex (11.9 mg, 83%) as orange−red crystals, mp > 300 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 384 (4.47), 438 (5.03), 483 (3.77), 519 (4.01), 555 (4.49), 594 nm (3.72); ^{1}H NMR ($CDCl_3$): δ 1.30 (12H, d, J = 6.4 Hz), 1.89 (6H, t, J = 7.4 Hz), 2.63−2.73 (2H, m), 3.58 (6H, s), 3.89 (4H, d, J = 7.2 Hz), 4.01 (4H, q, J = 7.4 Hz), 7.79−7.82 (2H, m), 8.88−8.91 (2H, m), 9.94 (2H, s), 10.13 (2H, s); FD MS: m/z (rel int) 663.1 (9.8), 662.0 (40), 661.0 (100, M^+), 660.0 (43), 659.0 (99, M^+). Anal. Calcd for $C_{39}H_{42}N_3Ag$: C, 70.90; H, 6.41; N, 6.36. Found: C, 70.72; H, 6.11; N, 6.09.

[5,10,15,20-Tetraphenylbenzo[*b*]-21-carbaporphyrinato]silver-(III) (17a). Nitrogen was bubbled through a solution of tetraphenylbenzocarbaporphyrin (**16a**) (14.8 mg, 0.0223 mmol) in pyridine (15 mL) for 10 min. Silver acetate (17.4 mg, 0.104 mmol) was added, and the resulting mixture was stirred under nitrogen for 24 h. The solution was diluted with chloroform, washed with water,

the organic layer dried over sodium sulfate, and the solvent removed under reduced pressure. The residue was chromatographed on a silica column eluting with 20% hexanes−dichloromethane, and the metalated product was collected as an orange band. Evaporation of the solvent under reduced pressure gave **17a** (13.7 mg, 0.0178 mmol, 80%) as an orange powder, mp > 350 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 396 (4.57), 450 (5.29), 525 (4.31), 566 (4.09), 610 nm (3.19); ^{1}H NMR ($CDCl_3$): δ 6.91−6.94 (2H, AA′XX′ system), 7.08−7.11 (2H, AA′XX′ system), 7.71−7.86 (12H, m), 8.06−8.09 (4H, m), 8.14−8.18 (4H, m), 8.69−8.73 (6H, m); ^{13}C NMR ($CDCl_3$): δ 120.8, 123.1, 125.1, 125.2, 126.3, 127.2, 127.9, 128.1, 128.2, 128.3, 129.1, 129.7, 132.8, 134.2, 138.5, 138.6, 139.7, 141.9, 142.4, 142.9; FD MS: *m*/*z* (rel int) 771.1 (12), 770.2 (50), 769.2 (100), 768.2 (49), 767 (93).

[5,10,15,20-Tetrakis(4-chlorophenyl)benzo[*b*]-21-carbaporphyrinato]silver(III) (17b). Using the foregoing procedure, **16b** (15.0 mg, 0.0188 mmol) was reacted with silver(I) acetate (22 mg, 0.132 mmol)) in pyridine (15 mL). Following chromatography on silica eluting with 20% hexanes−dichloromethane, we isolated the metalated product **17b** (16.4 mg, 0.0181 mmol, 97%) as an orange powder, mp > 350 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 398 (4.57), 451 (5.25), 526 (4.29), 566 (4.07), 614 nm (3.12); ^{1}H NMR ($CDCl_3$): δ 6.98−7.02 (2H, AA′XX′ system), 7.14−7.17 (2H, AA′XX′ system), 7.74 (4H), 7.77 (4H), 7.99 (4H), 8.07 (4H), 8.66 (2H, dd, $^3J_{HH}$ = 5 Hz, $^4J_{AgH}$ = 1.6 Hz), 8.69−8.71 (4H, s overlapping with dd); ^{13}C NMR ($CDCl_3$): δ 119.7, 122.1, 123.3, 123.8, 125.2, 126.7, 127.6, 128.3, 128.4, 129.2, 129.8, 134.0, 134.9, 135.0, 135.2, 138.6, 139.7, 140.6, 141.2, 141.7; FD MS: *m*/*z* (rel int) 911, 910, 909, 908, 907, 907, 906, 905 (100), 904, 903.

[5,10,15,20-Tetraphenylbenzo[*b*]-21-carbaporphyrinato]gold-(III) (18a). Using the foregoing conditions, **16a** (15.4 mg, 0.0232 mmol) was reacted with gold(III) acetate (33.0 mg, 0.0882 mmol)) in pyridine (15 mL). Following chromatography on silica eluting with 20% hexane−dichloromethane, we obtained gold(III) complex **18a** (13.4 mg, 0.0156 mmol, 67%) as an orange powder, mp > 350 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 395 (4.76), 437 (5.14), 519 (4.28), 561 (4.07), 608 nm (3.03); ^{1}H NMR ($CDCl_3$): δ 6.81−6.85 (2H, AA′XX′ system), 7.00−7.04 (2H, AA′XX′ system), 7.72−7.82 (12H, m), 8.04−8.07 (4H, m), 8.12−8.15 (4H, m), 8.69−8.73 (4H, AB quartet, J = 5 Hz), 8.75 (2H, s); ^{13}C NMR ($CDCl_3$): δ 115.8, 120.2, 125.0, 126.1, 126.2, 127.2, 127.3, 127.7, 127.9, 128.1, 128.2, 128.3, 129.4, 132.6, 134.1, 136.3, 137.8, 138.3, 142.0, 143.1, 143.7; FD MS: *m*/*z* (% rel int) 859, 858, 857 (100); HRMS (FAB): calcd for $C_{49}H_{30}N_3Au$ + H, 858.2183; found, 858.2182.

[5,10,15,20-Tetrakis(4-chlorophenyl)benzo[*b*]-21-carbaporphyrinato]gold(III) (18b). Using the foregoing procedure, **16a** (16.1 mg, 0.0201 mmol) was reacted with gold(III) acetate (28.0 mg, 0.0749 mmol) in pyridine (15 mL). Following chromatography on silica eluting with 20% hexanes−dichloromethane, we isolated gold(III) derivative **18b** (16.7 mg, 0.0168 mmol, 83%) as an orange powder, mp > 350 °C; UV−vis ($CHCl_3$): λ_{max} (log ϵ) 397 (4.81), 439 (5.14), 520 (4.31), 563 (4.09), 612 nm (3.00); ^{1}H NMR ($CDCl_3$): δ 6.86−6.90 (2H, AA′XX′ system), 7.05−7.08 (2H, AA′XX′ system), 7.74 (4H), 7.76 (4H), 7.95 (4H), 8.05 (4H), 8.66 (2H, d, J = 4.8 Hz), 8.70 (2H, 2H, d, J = 4.8 Hz), 8.74 (2H, s); ^{13}C NMR ($CDCl_3$): δ 119.1, 124.9, 125.0, 126.6, 125.5, 127.7, 127.8, 128.1, 128.4, 129.5, 133.7, 135.0, 135.1, 136.2, 138.3, 140.2, 141.3, 143.5; FD MS: *m*/*z* (% rel int) 999.1 (15), 998.1 (28), 997.1 (60), 996.2 (47), 995.2 (100), 994.1 (39), 993.2 (66).

[8,17-Diethyl-7,18-dimethyl-12,13-diphenylbenzo[*b*]-21-carbaporphyrinato]gold(III) (19). The reaction of diphenylbenzocarbaporphyrin **9b** (10 mg) with gold(III) acetate (7 mg) under the foregoing conditions afforded the gold complex (0.9 mg, 7%) as an orange solid, mp > 300 °C; UV−vis $CHCl_3$): λ_{max} (rel int) 375 (0.41), 390 (0.45), 430 (1.00), 452 (0.39), 524 (0.13), 560 (0.41), 594 nm (0.01); ^{1}H NMR ($CDCl_3$): δ 1.74 (6H, t, J = 7.6 Hz), 3.47 (6H, s), 3.86 (4H, q, J = 7.6 Hz), 7.62−7.75 (8H, m), 8.03 (4H, d, J = 7 Hz), 8.62−8.65 (2H, m), 9.90 (2H, s), 9.96 (2H, s); HRMS (FAB): calcd for $C_{43}H_{34}N_3Au$, 789.2418; found, 789.2416.

Cyclic Voltammetry. The electrochemical studies were carried out in anhydrous dichloromethane using a BAS CV-27 potentiostat equipped with an *x*−*y* recorder or a BAS CV-50W. A conventional three-electrode cell consisting of a platinum disk working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ (0.01 M) reference electrode was used. The cyclic voltammograms were run in a 0.2 M Bu_4NBF_4 solution in an inert atmosphere glovebox at a scan rate of 200 mV/s. The scanning limits were +1.7 to −1.9 V versus $Ag/AgNO_3$, and the ferrocene/ferrocenium couple appeared at +0.22 V versus the $Ag/AgNO_3$ reference. All potentials are reported versus the $Ag/AgNO_3$ reference electrode.

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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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