Synthesis and Reactivity of N-Methyl and N-Phenyl meso-Unsubstituted N-Confused Porphyrins†

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Condensations of 1-methyl and 1-phenyl-2,4-pyrroledicarbaldehydes with a tripyrrane in TFA—dichloromethane, followed by oxidation with aqueous FeCl₃, gave novel cross-conjugated meso-unsubstituted N-confused porphyrins (NCPs; 12). These porphyrin analogues showed significant diatropic ring currents that were enhanced upon protonation. Reactions with nickel(II) acetate in refluxing DMF, or palladium(II) acetate in acetonitrile, gave good yields of the corresponding nickel(II) or palladium(II) organometallic derivatives 18 and 19. These complexes were stable and the proton NMR spectra showed slightly increased downfield shifts to the external protons. Addition of TFA resulted in C-protonation at the internal carbon to give aromatic cations that showed the inner CH resonance between −2.5 and −4.0 ppm. The nickel(II) cations 20a and 20b slowly underwent demetalation but the related palladium cations 20c and 20d were quite robust and showed no loss of palladium after 1 week at room temperature. Reaction of NCPs 12 with silver(I) acetate gave silver(III) derivatives 21a and 21b where an oxidation had occurred at C-3 to afford a lactam unit. The silver complexes showed strong diatropic ring currents and porphyrin-like UV—vis spectra with a Soret band near 430 nm. N-Methyl NCP 21a also reacted with gold(III) acetate to give the gold(III) NCP 21c, albeit in low yield, and this species showed similar spectroscopic properties to silver(III) NCP 21a. Syntheses of N-phenyl NCP 12b were accompanied by the formation of the 3-oxo derivative 15b, and the related N-methyl product 16a could also be obtained when the reaction mixtures were oxidized with silver(I) acetate under acidic conditions. The proton NMR spectra for these aromatic NCPs in CDCl₃ show the internal CH shifted upfield to near −6.5 ppm, while the external meso-protons are strongly deshielded giving 4 singlets between 9 and 10 ppm. This study demonstrates that meso-unsubstituted NCPs have unusual reactivity and unique spectroscopic properties, and these results complement and extend the work on the much better known meso-tetraaryl NCPs.

Introduction

N-confused porphyrins (NCPs; 1) were first reported as byproducts in Rothemund-type syntheses by two independent groups in 1994.¹,² These tetrapyrrolic macrocycles differ from true porphyrins by having an inverted pyrrole moiety and a CNNN arrangement of core atoms.³ NCPs immediately aroused a great deal of interest due to their aromatic character, the presence of relatively long wavelength UV—vis absorptions, and their ability to generate organometallic derivatives under mild conditions.⁴ NCPs have two major tautomeric forms, 1 and 2, that differ in energy by approximately 5 kcal/mol.⁵ The fully aromatic tautomer 1 is favored in organic solvents such as chloroform and the proton NMR spectrum for NCPs in CDCl₃

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with Ni(II), Pd(II), and Pt(II), and in this respect have comparable reactivity to NCP tautomer 2. In contrast, benzo-carbaporphyrins 6 and related carbaporphyrinoids act as trianionic ligands, readily forming silver(III) and gold(III) complexes, and therefore mirror the properties of aromatic NCP tautomer 1.

The development of a high yielding procedure for synthesizing meso-tetrasubstituted NCPs opened up the field and has allowed detailed investigations into the reactivity of these porphyrin isomers. However, far less work has been conducted on the synthesis and reactivity of meso-unsubstituted NCPs. The first synthesis of meso-unsubstituted NCPs made use of a MacDonald “2 + 2” procedure, but this method was not suitable for larger scale reactions. Porphyrin analogues like 5 and 6 were synthesized by a “3 + 1” methodology by reacting tripyrranes with aromatic dialedehydes. However, initial attempts to prepare NCPs 8 by reacting 2,4-pyrorotedialdehydes 9 with tripyrranes under a variety of conditions afforded mediocre yields of porphyrinoid products (Scheme 1). In these reactions, the macrocyclic product is generated as a dihydro derivative and an oxidation step is required to generate the final product. In most of the early studies, DDQ was used for the dehydrogenation step, but this gave very poor results for NCPs. Eventually, washing the reaction solutions with dilute aqueous solutions of ferric chloride was found to be a

shows the presence of a strong diatropic ring current where the internal CH resonates at -N ppm, while the external pyryllic protons give rise to a series of peaks between 8.5 and 9.0 ppm. However, in polar aprotic solvents such as DMF and DMSO, the cross-conjugated tautomer 2 predominates and surprisingly this form has been characterized by X-ray crystallography. Although the diatropicity of 2 is much reduced, the internal CH is still shifted upfield to 0.76 ppm in proton NMR spectra run in d$_6$-DMF. The less aromatic tautomer of the NCPs can be trapped by methylation on the external nitrogen. In addition, NCPs form metalloc-derivatives that are derived from tautomer 2 with divalent metal cations such as nickel(II) and palladium(II). On the other hand, tautomer 1 can act as a trianionic ligand and form stable organometallic derivatives with metals in higher oxidation states such as silver(III). In parallel with these studies, the synthesis and metalation of carbaporphyrinoids such as 5 and 6 have been reported. Azuliporphyrins 5 act as diatomic ligands giving stable organometallic derivatives of Nickel, Pd(II), and Pt(II). and in this respect have comparable reactivity to NCP tautomer 2. In contrast, benzo-carbaporphyrins 6 and related carbaporphyrinoids act as trianionic ligands, readily forming silver(III) and gold(III) complexes, and therefore mirror the properties of aromatic NCP tautomer 1.

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superior oxidation protocol for these syntheses and under optimized conditions up to 61% yield of NCPs 8 could be isolated, although 3-unsubstituted NCP 8c was only obtained in 16% yield. More recently, a synthesis of fully unsubstituted NCP has also been completed. It is noteworthy that the meso-unsubstituted NCPs show significantly larger diatropic ring currents and the internal CH for NCPs 8 in CDCl₃ was observed near -6.3 ppm. The increased diatropicity in 8 can be ascribed to a flattening out of the macrocycle due to the relief of steric congestion caused by meso-aryl substitution. NCP 8a was shown to react with nickel(II) acetate in DMF at 145 °C to give the nickel(II) complex 10, but this metallo-derivative was somewhat unstable and showed little aromatic character. Addition of TFA to an NMR solution of 10 in CDCl₃ gave a surprising result where C-protonation at position C-21 occurred to generate an aromatic species 11. The proton NMR spectrum showed the internal CH resonance at -4.93 ppm, and the meso-protons shifted from 7.83–8.68 ppm in 10 to 9.37–10.01 ppm for 11. This phenomenon was subsequently demonstrated for Ni(II) and Cu(II) complexes derived from meso-tetraaryl NCPs as well.

As the field of N-confused porphyrin chemistry has developed, remarkable reactivity features, such as the formation of N-fused porphyrins, have been discovered and a profusion of unusual coordination complexes have been described. Nevertheless, very little work has so far been conducted on meso-unsubstituted NCPs. These versions of NCPs have the potential to extend the reactivity studies while complementing the results obtained for other carboxyporphyrinoid systems such as 5 and 6. In this paper, we describe rational "3 + 1" syntheses of N-methyl and N-phenyl NCPs 12 and provide details on the oxidation and metalation of these new porphyrinoids.

Results and Discussion

The synthesis of N-substituted NCPs 12 by the "3 + 1" methodology required the availability of pyrrole dialdehydes 13a and 13b. For this work, we adapted procedures developed by Anderson et al. for the synthesis of 2,4-pyrroledicarbaldehydes. N-Methylpyrrole had previously been shown to react with the Vilsmeier reagent to give an imine salt 14a and this further reacts with dichloromethyl methyl ether, aluminum chloride and nitromethane to afford, following hydrolysis, the required dialdehyde 13a (Scheme 2). N-Phenylpyrrole was shown to react similarly to give 1-phenyl-2,4-pyrroledicarbaldehyde in 75% yield. Tripyrrane 7 was treated with TFA, diluted with dichloromethane, and diahlyde 13a was added. After stirring the mixture for 16 h at room temperature, the solution was oxidized by shaking it with 0.1% aqueous ferric chloride solution in a separatory funnel for 5 min. The crude product was purified by column chromatography on grade 3 basic alumina and recrystallized from chloroform-hexanes to give N-methyl NCP 12a in 39% yield (Scheme 3). Reaction of N-phenylpyrrole dialdehyde 13b with 7 afforded the corresponding N-phenyl NCP 12b together with an oxidation product 15b. Following careful chromatography on grade 2 neutral alumina, 13b and 15b were isolated in 17 and 12% yields, respectively. The formation of lactam-like confused porphyrinoids is well precededent in the literature. A plausible mechanism involves initial addition of water to the protonated NCP to give hemiaminal 16, followed by oxidation to give the oxo-derivative 15 (Scheme 4). As expected, NCPs 12 showed intermediary diatropic character.

In the proton NMR spectrum for N-methyl tetraphenyl NCP 17 in CDCl₃, the internal CH is reported to show up at 0.98 ppm and the NH gives rise to a peak at 3.43 ppm. However, in the proton NMR spectrum for 12a, the 21-CH gave rise to a singlet near 1.5 ppm and the NH showed up as a broad peak at

(28) These results were presented, in part, at the following meeting: 233rd National American Chemical Society Meeting, Chicago, IL, March 2007 (Von Ruden, A. L.; Lash, T. D. Book of Abstracts, ORGN 192).
(31) Halide anion binding has recently been demonstrated for a protonated meso-unsubstituted 3-oxoNCP. See: Furuta, H.; Nanami, T.; O’Kraǐ, L.; Morimoto, T.; Ogawa, T.; Král, V.; Sessler, J. L.; Lynch, V. Chem. Asian J. 2008, 3, 592–599. We thank a referee for bringing this paper to our attention.
2.75 ppm (Figure 1). A D$_2$O shake showed exchange of the NH but the 21-CH resonance also sharpened and shifted slightly upfield (Figure 1C). A similar effect was previously noted for substituted azuliporphyrins.\(^{32}\) The reduced diatropic shift for the 21-CH resonance in 12a compared to 17 was unexpected, as the decrease in macrocyclic planarity due to the presence of meso-substituents would be likely to lead to downfield shifts for both the NH and 21-CH resonances. However, computational studies show that the molecular orbitals for meso-tetraphenyl NCP differ significantly from unsubstituted NCP,\(^{33}\) and DFT calculations indicate that “contributions from the $\pi$ electrons of the phenyl ring are significant” for NCPs 1 and 2.\(^ {34}\) Therefore, these subtle interactions are likely to be responsible for the small upfield shifts of the inner protons for 17 compared to 12a. The N-phenyl NCP 12b showed the 21-CH resonance at 2.06 ppm and the NH was identified as a broad peak near 3.9 ppm. The meso-protons for 12b gave rise to 4 singlets between 7.90 and 8.52 ppm, whereas the equivalent resonances for 12a showed up between 8.00 and 8.50 ppm. Apart from the meso-proton that is adjacent to the phenyl group, the resonances for 12a are further upfield and taken together the diatropic character of 12b is significantly reduced compared to 12a. The [18]annulene model for porphyrinoid aromaticity continues to provide valu-
able insights into these types of effects. The N-substituted NCPs are cross-conjugated but it is noteworthy that an 18 \pi electron delocalization pathway is present in dipolar resonance contributors like 12\textsuperscript{z} (Scheme 3). The required electron-donation from the confused pyrrolic nitrogen is clearly aided by the more electron-donating methyl group in 12a compared to the phenyl unit in 12b. This trend has also been observed for tert-butyl and phenyl substituted azuliporphyrins 5 (Scheme 5).\textsuperscript{39} The azulene moiety in 5 is electron-donating and gives the azuliporphyrins a degree of aromatic character due to zwitterionic resonance contributors 5\textsuperscript{z} which combine trypylium character with a carbaporphyrin-like 18\pi electron delocalization pathway. Although the shifts for 5 are not as large as those observed for NCPs 12, the internal CH is still shifted upfield to approximately 3 ppm. In the tert-butylazuliporphyrin 5a, the 21-CH gave a resonance at 2.9 ppm but the less electron-donating phenyl moiety in 5b decreased the contribution of canonical form 5\textsuperscript{z} and gave this singlet at 3.3 ppm. Observations of this type further emphasize the close relationship of the NCPs, azuliporphyrins and other carbaporphyrinoid systems.

Addition of TFA to NMR solutions of 12a in CDCl\textsubscript{3} gave the corresponding dication 12aH\textsubscript{2}\textsuperscript{z+}, and this showed a greatly increased diatropic ring current by proton NMR spectroscopy. The 21-CH resonance shifted upfield to \(-2.8\) ppm and two broad peaks were observed at 0.9 (1H) and 1.1 ppm (2H) for the three NHs (Figure 2). The increased diatropic character is due to the increased favorability of resonance structures like 12\textsuperscript{z} which are no longer hampered by charge separation but instead aid in charge delocalization. Nevertheless, the presence of an electron-donating methyl group is beneficial. This explains why the shifts for N-phenyl NCP dication 12bH\textsubscript{2}\textsuperscript{z+} are decreased compared to 12aH\textsubscript{2}\textsuperscript{z+}, and the 21-CH now gives a signal at \(-2.05\) ppm that is weakly coupled to the C-3 doublet (\(J = 1\) Hz) at 8.96 ppm, while the NH resonances are observed at 0.9 (1H) and 1.9 ppm (2H). This effect is also evident in the downfield shifts for the meso-protons, which show up as 4 singlets between 9.06 and 9.72 ppm for 12aH\textsubscript{2}\textsuperscript{z+}, while three of these values are shifted upfield to between 8.94 and 9.06 ppm for 12bH\textsubscript{2}\textsuperscript{z+}. Only the resonance for the meso-proton next to the phenyl moiety is an outlier, giving rise to a singlet at 9.70 ppm. Dication 17H\textsubscript{2}\textsuperscript{z+} in excess TFA-CDCl\textsubscript{3} is reported to give a resonance for the 21-CH at \(-1.57\) ppm and three peaks for the NHs at 2.05, 2.91 and 3.25 ppm, so in this case the meso-tetraphenylNCP shows decreased diatropicity. This can be attributed to the crowding due to the presence of four hydrogen atoms in the macrocyclic cavity exacerbating the steric effects due to the meso-substituents.

The UV-vis spectra for 12a showed two moderate absorption bands at 409 and 420 nm and weaker broadened absorptions over the visible region (Figure 3). Addition of TFA generated dication 12aH\textsubscript{2}\textsuperscript{z+} and gave a stronger Soret band at 427 nm with a shoulder at 453 nm and a series of Q bands between 500 and 800 nm. PhenylNCP 12b showed a similar spectrum for the free base, with a weakened Soret-like band at 420 nm, but this again showed a more intense absorption band at 431 nm for the dication 12bH\textsubscript{2}\textsuperscript{z+}.

Metalation of the new NCPs 12 was investigated using nickel(II) and palladium(II) acetate (Scheme 6). The best results for incorporating nickel(II) were obtained by refluxing 12a or 12b with Ni(OAc)\textsubscript{2} in DMF. The earlier work on the synthesis of 10 had to be carried out at 145 \degree C because extensive decomposition occurred at the slightly higher boiling temperature of DMF. However, better yields of nickel(II) derivatives were obtained under the higher temperature conditions, and following column chromatography on basic alumina and recrystallization, the nickel derivatives 18 were isolated in 76–90% yield. Reactions of 12 with Pd(OAc)\textsubscript{2} were carried...
out in refluxing acetonitrile and the palladium(II) complexes \(19\) were isolated in 58–63% yield. Unlike the moderately unstable nickel(II) complex \(10\), the new nickel and palladium derivatives were robust and stable in solution for prolonged periods of time. The proton NMR spectra for derivatives were robust and stable in solution for prolonged periods in \(\text{CDCl}_3\). The chemical shifts are shifted slightly downfield for the phenyl series. The chemical shifts were similar for the methyl and phenyl series.

The formation of silver derivatives was also investigated (Figure 5). As had been observed previously for metalated azuliporphyrins, \(13,31,39\) but the \(N\)-methyl and \(N\)-phenyl complexes were very similar in each case. For instance, nickel derivative \(18b\) gave a spectrum with two bands at 327 and 406 nm, together with a shoulder at 454 nm and a prominent peak at 557 nm. Palladium complex \(20b\) gave a more complex spectrum with three stronger peaks in the Soret region and a broad band between 500 and 600 nm, that corresponds to the aromatic cation \(20b\) (Figure 5A). In the case of \(19b\), addition of TFA gave bright green solutions of stabilizatowards the product due to the presence of a more electron-donating substituent. The protonation of \(18\) and \(19\) is reversible, but in the case of nickel(II) derivatives \(20a\) and \(20b\) slow demetalation occurs over a period of several hours to give the NCP dications \(12H_2^{2+}\). However, the palladium complexes showed little sign of decomposition even after a week at room temperature. The nickel derivatives showed larger upfield shifts for the 21-CH resonance than for the palladium cations, but the downfield signals for the palladium cations were more deshielded. In the methyl series, nickel(II) derivative \(20a\) gave an upfield resonance at \(-4.01\) ppm, compared to \(-2.97\) ppm for palladium complex \(20c\). However, the five downfield singlets for \(20c\) fell into the range of 9.56–10.42 ppm compared to 9.41–10.19 ppm for \(20a\). These data show that the palladium cations are more diatropic than the nickel species, and the differences in the chemical shifts for the 21-CH resonance can be attributed to the higher electronegativity of Pd compared to Ni. The phenyl substituted cations \(20b\) and \(20d\) showed a decreased upfield shift for the 21-CH resonance and a decreased downfield shift for the \(meso\)-proton resonances due to the reduced electron-donating capabilities of the phenyl substituent.

The UV–vis spectra of the nickel(II) derivatives \(18\) and palladium(II) complexes \(19\) differed considerably from one another (Figure 5), as had been observed previously for metalated azuliporphyrins, \(13,31,39\) but the \(N\)-methyl and \(N\)-phenyl complexes were very similar in each case. For instance, nickel derivative \(18b\) gave two stronger absorptions at 342 and 406 nm, together with a shoulder at 454 nm and a prominent peak at 557 nm. Palladium complex \(20b\) gave a more complex spectrum with three stronger peaks in the Soret region and a series of smaller bands between 500 and 750 nm. Addition of TFA to \(18a\) gave a spectrum with two bands at 327 and 406 nm, and a broad band between 500 and 600 nm, that corresponds to the aromatic cation \(20b\) (Figure 5A). In the case of \(19b\), addition of TFA gave bright green solutions of \(20d\) that showed a strong broad band at 437 nm and weaker broad absorptions between 500 and 650 nm (Figure 5B). Again the methyl and phenyl substituted versions for each metal gave similar UV–vis absorption spectra.
systems\textsuperscript{14–16} easily form silver(III) derivatives, although porphyrins generally afford silver(II) complexes.\textsuperscript{40} N-Methyl NCP 12a was treated with 3 equiv of silver(I) acetate at room temperature in dichloromethane and following workup and purification gave a metallo-porphyrinoid product in 65% yield. The complex was only sparingly soluble in organic solvents and it was not possible to obtain a carbon-13 NMR spectrum. However, the proton NMR spectrum in CDCl\textsubscript{3} showed only the 3H singlets corresponding to the two methyl groups, and it was not possible to obtain a carbon-13 NMR spectrum. In this case, the product was sufficiently soluble to obtain carbon-13 NMR data in CDCl\textsubscript{3}, and a resonance for the carbonyl unit was identified at 169.5 ppm. The IR spectrum showed that a prominent absorption was present at 1677 cm\textsuperscript{-1}, confirming the presence of a carbonyl moiety. These data indicate that the product is the silver(III) lactam-type NCP 21a, and that the silver acetate had acted as an oxidant as well as a source of silver ions. This is consistent with the observation that the o xo-derivative 15b was formed as a byproduct in the synthesis of NCP 12b (Scheme 3). N-Phenyl NCP 12b also reacted with silver(I) acetate to give silver(III) complex 21b. In this case, the product was sufficiently soluble to obtain carbon-13 NMR data in CDCl\textsubscript{3}, and a resonance for the carbonyl unit was identified at 169.5 ppm. The UV–vis spectrum of 21b was slightly red-shifted compared to 21a, and showed a strong Soret band at 432 nm.

As silver(I) acetate is acting as an oxidant during metalation, we speculated that it could be used under acidic conditions to prepare the free base porphyrinoid 15a (Scheme 3). Tripyrrane 7 was reacted with dialdehyde 13a in the presence of TFA in dichloromethane and then treated with AgOAc. Following column chromatography and recrystallization, lactam 15a was isolated in 11% yield. The oxo-species was very aromatic by proton NMR spectroscopy, although like its silver(III) derivative 15a had poor solubility characteristics. The proton NMR spectrum of 15a in CDCl\textsubscript{3} showed the internal CH strongly shifted upfield to $-6.63$ ppm, while the NHs gave a broad 2H signal centered on $-3.9$ ppm. The meso-protons produced four 1H singlets in the downfield region at 9.06, 9.64, 9.73, and 9.83 ppm (Figure 7). The presence of a porphyrin-like aromatic ring current was also supported by the downfield shifts for the peripheral substituents and the pyrrolic methyl groups gave two 3H singlets at 3.47 and 3.50 ppm. These data show that the silver complex has taken on a fully aromatic carbaporphyrinoid structure unlike the nickel and palladium complexes 18 and 19, respectively. The UV–vis spectrum for the silver complex (Figure 6) showed the presence of a strong Soret band at 429 nm and a series of Q-type bands that confirm that this species has porphyrin-like aromatic characteristics. Nevertheless, the external hydrogen on the confused pyrrole unit has been lost and HR MS demonstrated that an oxygen atom had been incorporated and that the molecular formula was $C_{31}H_{34}N_{4}OAg$. The IR spectrum showed that a prominent absorption was present at $1677$ cm$^{-1}$, confirming the presence of a carbonyl moiety. These data indicate that the product is the silver(III) lactam-type NCP 21a, and that the silver acetate had acted as an oxidant as well as a source of silver ions. This is consistent with the observation that the o xo-derivative 15b was formed as a byproduct in the synthesis of NCP 12b (Scheme 3). N-Phenyl NCP 12b also reacted with silver(I) acetate to give silver(III) complex 21b. In this case, the product was sufficiently soluble to obtain carbon-13 NMR data in CDCl\textsubscript{3}, and a resonance for the carbonyl unit was identified at 169.5 ppm. The UV–vis spectrum of 21b was slightly red-shifted compared to 21a, and showed a strong Soret band at 432 nm.

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at –3.85, –3.16, and –2.43 ppm. The meso-protons are strongly shifted into the downfield region showing four 1H singlets at 9.55, 9.89, 10.08, and 10.20 ppm, and the methyl substituents are also still strongly deshielded giving rise to two 3H singlets at 3.44 and 3.49 ppm.

In previous studies on the metalation of carbaporphyrinoid systems, we have demonstrated that gold(III) derivatives of tetraaryl benzocaraporphyrins \textsuperscript{22} can easily be prepared using gold(III) acetate as a reagent. A meso-unsubstituted benzocaraporphyrin gold(III) complex was also isolated but very poor yields were obtained in this case. \textsuperscript{14} Attempts to prepare gold(III) NCPs from \textsuperscript{12a} and \textsuperscript{12b} gave poor results as well, but the reaction of \textsuperscript{12a} with Au(OAc)\textsubscript{3} in refluxing pyridine did give an 8\% yield of the gold complex \textsuperscript{21c}. The chemical shifts in the proton NMR spectrum of \textsuperscript{21c} in CDCl\textsubscript{3} were very similar to those obtained for silver(III) complex \textsuperscript{21a}, and the UV–vis spectrum of \textsuperscript{21c} was also comparable, although the Soret band was split into two peaks at 419 and 436 nm. Interestingly, the synthesis of a gold(III) complex of tetraphenyl NCP (4b) has only accomplished very recently. \textsuperscript{42} The complex, which is reported to have unique luminescence properties, had to be prepared from a brominated intermediate rather than directly from tetraphenyl NCP. \textsuperscript{42}

Conclusions

Two examples of cross-conjugated N-confused porphyrins were prepared by the “3 + 1” methodology using N-methyl

UV-vis (CHCl3): λmax (logε) 340 (4.95), 405 (4.95), 418 (infl, 4.89), 453 (sh, 4.55), 516 (4.15), 558 (4.51), 710 (3.77), 772 nm (3.70); UV-vis (5% TFA-CHCl3): λmax (logε) 324 (4.84), 407 (4.99), 540 nm (4.43); 1H NMR (CDCl3): δ 1.51–1.56 (6H, m), 1.59–1.64 (6H, m), 2.91 (3H, s), 2.92 (3H, s), 3.32–3.45 (8H, m), 4.46 (3H, s), 8.37 (1H, s), 8.41 (1H, s), 8.45 (1H, s), 8.52 (1H, s), 8.59 (1H, s); 1H NMR (TFA-CDCl3): δ -4.01 (1H, br s), 1.63–1.69 (6H, m), 1.72–1.77 (6H, m), 3.20 (3H, s), 3.21 (3H, s), 3.60–3.74 (8H, m), 5.11 (3H, s), 9.41 (1H, s), 9.45 (1H, s), 9.61 (1H, s), 9.98 (1H, s), 10.19 (1H, s); 13C NMR (CDCl3): δ 10.9, 11.0, 16.4, 16.8, 17.36, 17.43, 19.2, 19.36, 19.41, 35.0, 95.4, 95.9, 101.9, 111.6, 115.5, 123.9, 134.1, 136.8, 137.8, 140.0, 140.7, 142.9, 144.1, 144.4, 144.8, 148.6, 149.8, 151.3, 153.1; HR MS (EI): Calcd for C31H34N4Ni: 520.2137 Found: 520.2133. Anal. calcd for C31H34N4Ni·1/5CHCl3: C, 68.73; H, 6.32; N, 10.27. Found: C, 68.77; H, 6.56; N, 9.99.

[8,12,13,17-Tetraethyl-2,7,18-trimethyl-2-aza-21-carbaporphyrinato]palladium(II) (19a). Palladium(II) acetate (26.9 mg; 0.12 mmol) was added to a solution of 2-methyl N-confused porphyrin (20 mg; 0.043 mmol) in dichloromethane (40 mL), and the solution was stirred under reflux for 30 min. The solution was washed with water, and the organic layer separated and evaporated to dryness. The residue recrystallized from chloroform-methanol to yield the palladium(II) complex (43.0 mg; 0.076 mmol; 63%) as dark purple crystals, mp 104.2, 113.4, 120.8, 131.4, 135.6, 136.5, 139.1, 140.1, 142.1, 143.5, 145.1, 146.8, 148.3, 148.6; HR MS (EI): Calcd for C31H34NiPd·1/5CHCl3: C, 63.20; H, 5.81; N, 9.45. Anal. calcd for C31H34NiPd·1/5CHCl3: C, 63.40; H, 5.97; N, 9.07.

Silver(III) Complex of 2-Methyl-3-oxo-N-confused Porphyrin (21a). Three equivalents of silver(I) acetate (21.5 mg; 0.13 mmol) were added to a solution of 2-methyl N-confused porphyrin (20 mg; 0.043 mmol) in dichloromethane (40 mL), and the solution was stirred at room temperature overnight under nitrogen. The solution was washed with water, and the organic layer was separated and evaporated to dryness. The purple residue was chromatographed on grade 3 basic alumina, eluting with chloroform, and afforded a dark red band. The solvent was evaporated to dryness and the residue recrystallized from chloroform-methanol to yield the silver(III) complex (16.4 mg; 0.028 mmol; 65%) as greenish metallic crystals, mp 113.4, 120.8, 131.4, 135.6, 136.5, 139.1, 140.1, 142.1, 143.5, 145.1, 146.8, 148.3, 148.6; HR MS (EI): Calcd for C31H34NiPd: 568.1818 Found: 568.1813. Anal. calcd for C31H34NiPd·1/2CHCl3: C, 63.20; H, 5.81; N, 9.45. Found: C, 63.40; H, 5.97; N, 9.07.

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Supporting Information Available: Experimental procedures for compounds 12b, 13a, 13b, 15a, 15b, 18b, 19b, 21b, and 21c, and MS, UV-vis, 1H NMR, and 13C NMR spectra for selected compounds, are provided. This material is available free of charge via the Internet at http://pubs.acs.org.