JOC Article

O-Confused Oxaporphyrin—An Intermediate in Formation of 3-Substituted 2-Oxa-21-Carbaporphyrins

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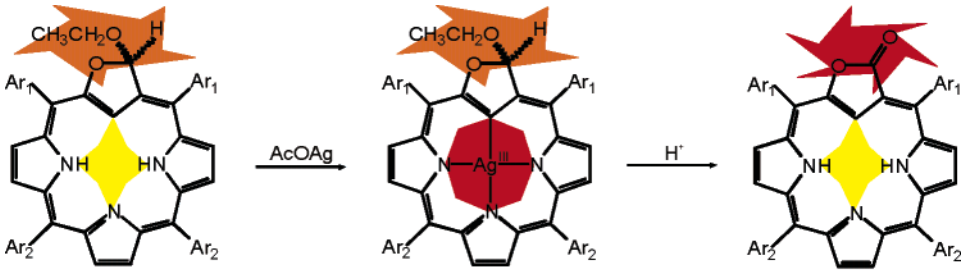

Ar_1 = Ph, Ar_2 = *p*-Tol

A condensation of 2,4-bis(phenylhydroxymethyl)furan with pyrrole and *p*-toluylaldehyde in the presence of ethanol formed 5,20-diphenyl-10,15-di(*p*-tolyl)-2-oxa-3-ethoxy-3-hydro-21-carbaporphyrin [(H,EtO)*OCPH*]H_2. The new carbaporphyrinoid has ^{1}H NMR features of an aromatic molecule, including the upfield shift of the inner H(21) atom (−5.48 ppm). Addition of acid removes the ethoxy substituent and converts [(H,EtO)*OCPH*]H_2 into the dication of "true" *O*-confused oxaporphyrin $\{[(H)OCPH]H_3\}^{2+}$ via an exocyclic C(3)−O bond cleavage followed by an elimination of the ethoxy group as determined by ^{1}H NMR. Addition of ethanol, water, or pyrrole converts $\{[(H)OCPH]H_3\}^{2+}$ into [(H,EtO)*OCPH*]H_2, [(H,OH)*OCPH*]H_2, or pyrrole appended *O*-confused porphyrin [(H,pyrrole)-*OCPH*]H_2, respectively. The reaction of [(H,OEt)*OCPH*]H_2 with silver(I) acetate yields a stable Ag(III) complex [(H,OEt)OCP]Ag^{III} substituted at the C(3) position by the ethoxy group and hydrogen. Coordination through the nitrogen donors is reflected by the presence of $^{107/109}$Ag scalar splitting seen for the selected *β*-H pyrrolic signals. Addition of TFA to [(H,OEt)OCP]Ag^{III} produces a weakly aromatic *O*-confused porphyrin complex $\{[(H)OCP]Ag^{III}\}^+$. In the course of this reversible process the tetrahedral−trigonal rearrangements originate at the C(3) atom but extend its consequences on the whole structure. Insertion of silver into the hydroxy analogue of [(H,OEt)-*OCPH*]H_2, i.e., [(H,OH)*OCPH*]H_2, was accompanied by ligand oxidation, yielding carbaporpholactone which contains the lactone functionality instead of the regular furan moiety embedded in the carbaporphyrin ligand of [(O)*OCP*]Ag^{III}. The structure was determined by X-ray crystallography. The macrocycle is only slightly distorted from planarity, and silver(III) is located in the NNNC plane.

Introduction

Inverted porphyrins (*N*-confused porphyrins) 5,10,15,-20-tetraaryl-2-aza-21-carbaporphyrin ((CTPPH)H_2)[1,2] and their derivatives revealed a remarkable tendency to stabilize peculiar organometallic compounds.[3−6] The ability of carbaporphyrinoids to coordinate metal ions and form metal−carbon bonds extends beyond the family of 2-aza-21-carbaporphyrins[3,4,6−10] as demonstrated by extensive studies on the coordination properties of 6,11,-

(1) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 779.
(2) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767.
(3) Latos-Grażyński, L. Core Modified Heteroanalogues of Porphyrins and Metalloporphyrins. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds. Academic Press: New York, 2000; pp 361−416.
(4) Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10.
(5) Furuta, H.; Maeda, H.; Osuka, A. *Chem.Commun.* **2002**, 1795.
(6) Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1.
(7) Stępień, M.; Latos-Grażyński, L. *Chem. Eur. J.* **2001**, *7*, 5113.
(8) Stępień, M.; Latos-Grażyński, L.; Lash, T. D.; Szterenberg, L. *Inorg. Chem.* **2001**, *40*, 6892.

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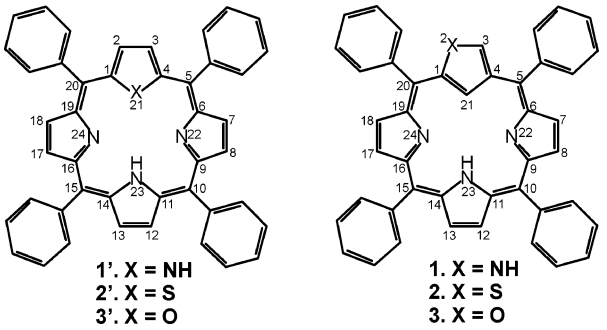
SCHEME 1. Heteroatom-Confusion Concept



16,21-tetraarylbenziporphyrin,[11] 8,19-dimethyl-9,13,14,-18-tetraethyl-oxybenziporphyrin,[10] azuliporphyrins,[12] and benzocarbaporphyrin.[13] Recently, we reported on 5,10,-15,20-tetraphenyl-*p*-benziporphyrin (TP*p*BPH)H—isomeric to 5,10,15,20-tetraphenyl-*m*-benziporphyrin—with the benzene ring linked at the para positions.[9] Significantly, *p*-benziporphyrin forms a complex with cadmium(II) and nickel(II) to reveal an unprecedented η^2 Cd(II)—arene and η^2 Ni(II)—arene interaction.[14,15]

In constructing a nontrivial macrocyclic environment for organometallic chemistry the heteroatom (X-confusion) confusion concept (Scheme 1), originally exemplified by a porphyrin (2-aza-21-carbaporphyrin) couple (Scheme 1, X = NH),[1,2] could be applied. Thus, interchanging a heteroatom with a β-methine group transforms the regular porphyrin (i.e., **1′**−**3′**) into "confused" isomer and produces the carbaporphyrins (**1**−**3**), which, while porphyrin-like in character, are expected to have fundamentally different electronic and coordination properties.

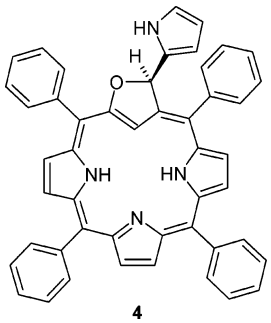
Previously, following such a strategy we characterized 5,10,15,20-tetraphenyl-2-thia-21-carbaporphyrin **2**,[16,17] and 5,20-diphenyl-10,15-di(*p*-tolyl)-2-oxa-21-carbaporphyrin with appended pyrrole ring **4** [(H,pyr)*OCPH*]H_2, formally considered as a product of 2-oxa-3-(2′-pyrrolyl)-5,10,15,20-tetraphenyl-21-carbaporphyrin hydrogenation (Scheme 2).[18]

Here we describe the synthesis and spectroscopic characterization of 2-oxa-21-carbaporphyrin derivatives without appended pyrrole linked to the C(3) carbon including the inherently reactive "true" *O*-confused 2-oxa-21-carbaporphyrin **3** [(H)*OCPH*]H.

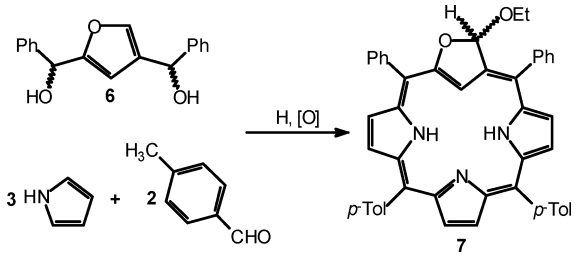
Results and Discussion

Synthesis of *O*-Confused Oxacarbaporphyrins. The procedure applied to synthesize 5,10,15,20-tetraaryl-2-oxa-21-carbaporphyrin followed the methodology previously utilized for the synthesis of heteroporphyrins[19] including 5,10,15,20-tetraphenyl-2-thia-21-carbaporphyrin **2**[16] and 5,20-diphenyl-10,15-di(*p*-tolyl)-2-oxa-21-carbaporphyrin with appended pyrrole **4**.[18]

SCHEME 2. Pyrrole Appended *O*-Confused Porphyrin



SCHEME 3. Synthetic Route



The synthesis of 2,4-bis(phenylhydroxymethyl)furan **6** (Scheme 3), which is a necessary synthon to introduce the inverted furan ring into a porphyrin-like skeleton, was described previously.[18] Originally the condensation of 2,4-bis(phenylhydroxymethyl)furan **6** with pyrrole and *p*-toluylaldehyde (1:3:2 molar ratio) via a one-pot, two-step, room-temperature synthesis was expected to yield 5,20-diphenyl-10,15-di(*p*-tolyl)-2-oxa-21-carbaporphyrin **3** (Scheme 3). Contrary to expectation, the condensation did not stop at the intended **3** but the pyrrole addition product **4** was obtained in a relatively high yield (ca. 10%).[18]

In these studies the condensation, described above, was purposely directed toward formation of 2-oxa-21-carbaporphyrin derivatives, which do not contain appended pyrrole. We recognized the fact that a suitable nucleophile, capable of competing efficiently for the C(3) position of **3** with the ubiquitous condensation substrate (pyrrole), is necessary. Eventually the acquired substituent should be readily converted into a good leaving group contrary to the appended pyrrole of **4**. Previously we found that the silver(III) complexes of **4** [(H,pyr)*OCP*]Ag^{III} undergo facile ethoxy substitution at C(3) to form [(C_2H_5O,pyr)-*OCP*]Ag^{III}, which can be reversed after acidification. The reversible addition/elimination at the macrocycle periphery was also recently reported for *N*-confused porphyrins.[20] Consequently, ethanol has been chosen as the perspective nucleophilic agent capable of fulfilling the conditions outlined above. Several condensations with various ethanol concentrations allowed isolation of [(H,EtO)*OCPH*]H_2 (**7**) apart from previously characterized **4** as the second macrocyclic product. After chromato-

(9) Stępień, M.; Latos-Grażyński, L. *J. Am. Chem. Soc*. **2002**, *124*, 3838.
(10) Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462.
(11) Stępień, M.; Latos-Grażyński, L. *Acc. Chem.Res.* **2005**, *38*, 88.
(12) Graham, S. R.; Ferrence, G. M.; Lash, T. D. *Chem. Commun.* **2002**, 894.
(13) Muckey, M. A.; Szczepura, L. F.; Ferrence, G. M.; Lash, T. D. *Inorg. Chem.* **2002**, *41*, 4840.
(14) Stępień, M.; Latos-Grażyński, L.; Szterenberg, L.; Panek, J.; Latajka, Z. *J. Am. Chem. Soc*. **2004**, *126*, 4566−4580.
(15) Hung, C.-H.; Chang, F.-C.; Lin, C.-Y.; Rachlewicz, K.; Stępień, M.; Latos-Grażyński, L.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **2004**, *43*, 4118, 4120.
(16) Sprutta, N.; Latos-Grażyński, L. *Tetrahedron Lett*. **1999**, *40*, 8457.
(17) Szterenberg, L.; Sprutta, N.; Latos-Grażyński, L. *J. Inclusion Phenom*. **2001**, *41*, 209.
(18) Pawlicki, M.; Latos-Grażyński, L. *Chem. Eur. J*. **2003**, *9*, 4650.
(19) Ulman, A.; Manassen, J. *J. Am. Chem. Soc.* **1975**, *97*, 6540.
(20) Chmielewski, P. J. *Org. Lett.* **2005**, *7*, 1789.

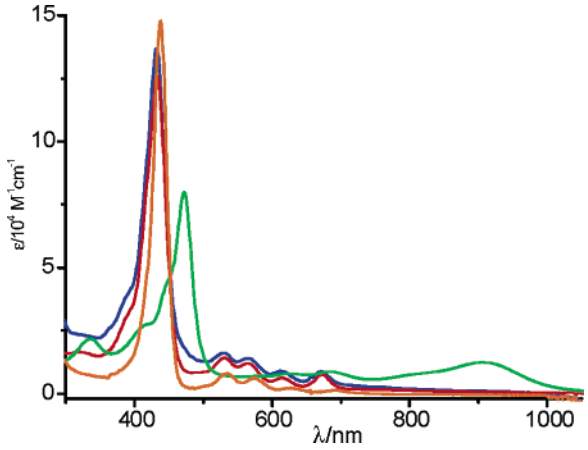


FIGURE 1. Electronic spectra of **7** (red), **8** (blue), **3**-H_2 (green), and **11** (orange) in dichloromethane.

graphic workup the yield of **7** is 5%, which is comparable with the yield of **4** obtained in the course of the same condensation. Eventually we found that the concentration of ethanol used to stabilize chloroform as the solvent is practically optimal for the outcome. The identity of **7** was confirmed by a combination of NMR spectroscopies, including NOESY, HMQC, and HMBC experiments, and high-resolution mass spectrometry.

Spectroscopic Characterization of 7. The electronic spectra of **7** demonstrate a Soret band (433 nm) accompanied by a set of Q-bands in the 500−800 nm region (Figure 1). The spectroscopic pattern is typical for aromatic carbaporphyrinoids.

All pyrrole resonances are downfield shifted due to the ring current effect. The peculiar position of the methine H(3) resonance at 7.46 ppm has been noted. Complete assignments of all ^{1}H NMR resonances for **7**, shown in Figure 2, have been obtained by 2D ^{1}H NMR COSY and NOESY experiments using the unique NOE correlation between H(3)−ortho-H(5-phenyl) as a starting point. The H(3) hydrogen is bound to the tetrahedral carbon atom, but its strongly downfield shift is caused by the combination of two effects: substitution by two oxygen atoms and the deshielding contribution of the ring current effect. At the same time the ^{13}C chemical shift of C(3) (109.1 ppm) is consistent with the tetrahedral hybridization. The diagnostic set of two complex multiplets at 3.84 and 3.55 ppm has been assigned to the ethoxy methylene group (Figure 2, trace A, inset). The strong difference of the chemical shifts detected for the two methylene multiplets is due to the diastereotopic effect as the chiral center is created on the tetrahedral hybridized C(3) atom.

Essentially **7** demonstrates aromaticity due the typical 18π electron delocalization pathway (Scheme 3). The strongly upfield positions of the H(21) (−5.49 ppm) and inner NH −2.82, −3.07 223 K) resonances are readily accounted for by the ring current effect.

"True" *O*-Confused Oxaporphyrin−Awaited Crucial Intermediate. Addition of TFA or DCA to a dichloromethane solution of **7** yields a UV−vis electronic spectrum that is completely different from that of the macrocyclic substrate (Figure 1, green). Although several bands in the region typically assigned to the Soret-like band of aromatic carbaporphyrinoids could be found, their low extinction coefficients, ca. $\epsilon = 8 \times 10^3$, imply

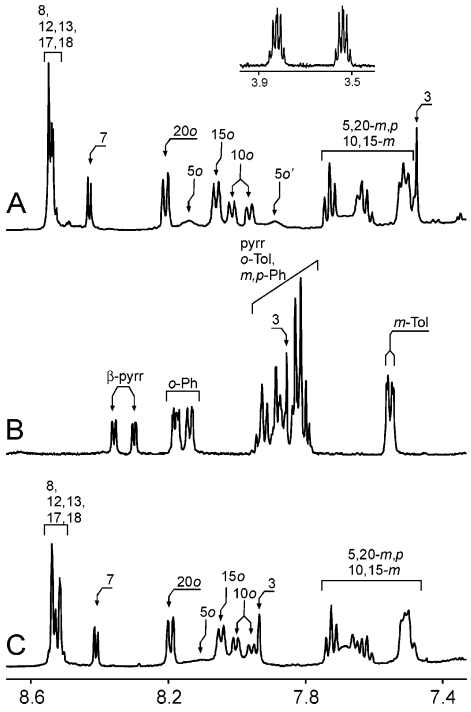


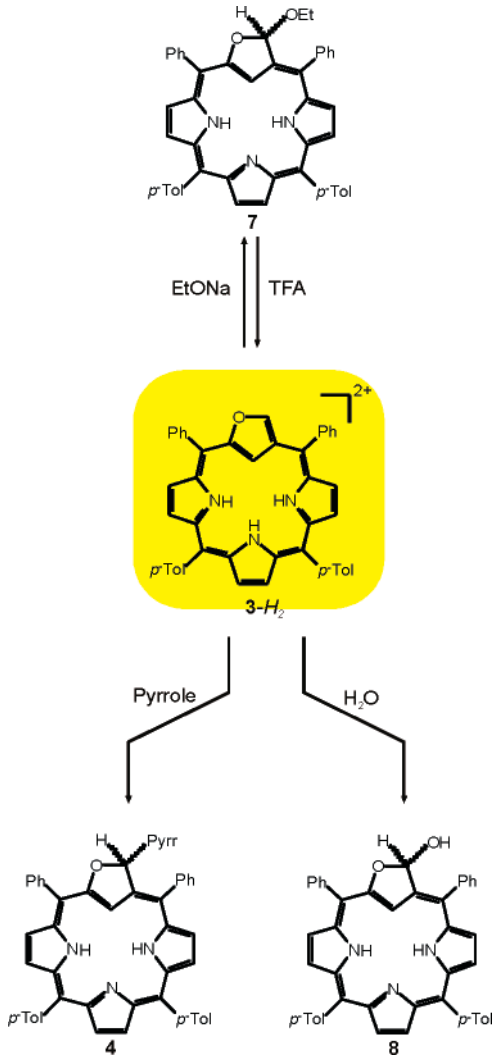
FIGURE 2. ^{1}H NMR spectra of (A) **7** (chloroform-*d*, 298 K), (B) **3**-H_2 (chloroform-*d*, 298 K), and (C) **8** (chloroform-*d*, 298 K) Peak labels follow systematic position numbering of the macrocycle or denote proton groups: *o*, *m*, *p* = ortho, meta, and para positions of *meso*-phenyl or *meso*-*p*-tolyl rings. The diastereotopic splitting of the $-CH_2-$ resonances of 3-ethoxide is shown in trace A, inset.

lowering of the aromatic character of the ligand in the formed species.

^{1}H NMR spectroscopic titration of **7** with TFA carried out in $CDCl_3$ at 298 K demonstrated a separate set of resonances assigned directly to the dicationic form of **3**, i.e., **3**-H_2 (Figure 2, Scheme 4). A new aromatic carbaporphyrinoid **3**-H_2 has been formed via an exocyclic C(3)−O bond cleavage, followed by protonation of the ethoxy group and elimination of ethanol. In the course of this reversible process the tetrahedral−trigonal rearrangements originate at the C(3) atom but extend its consequences on the whole structure. The "true" *O*-confused oxaporphyrin **3** has been trapped for the very first time although in its diprotonated (dicationic) form **3**-H_2. The diastereotopically split ethoxy methylene multiplet of **7** has been replaced by a quartet of the free ethanol. Importantly, 1 equiv of ethyl alcohol was released as confirmed by careful integration of alcohol resonances with respect to those of **7**. Addition of sodium ethoxide to a solution of **3**-H_2 reverses the course of the process (Scheme 4) yielding **7**. The biphasic equilibration of the $CDCl_3$ solution of **3**-H_2 with H_2O (D_2O) has readily afforded the new aromatic species **8** [(H,OH)*OCP*H]H_2 resembling **7** structurally but with a hydroxy substituent at the tetrahedral C(3) atom. ^{1}H NMR parameters of **8** resemble those of **7**.

At the synthetic stage two different pathways may lead to formation of **4**[18] and **7**. The first involves addition of ethanol or pyrrole to the already preformed *O*-confused 2-oxa-21-carbaporphyrin **3**. Alternatively, attack of pyrrole on the furan at either the precursor or the porphyrinogen stage can take place. The reversibility of the

SCHEME 4. Reactivity of "True" Oxacarbaporphyrin Dication

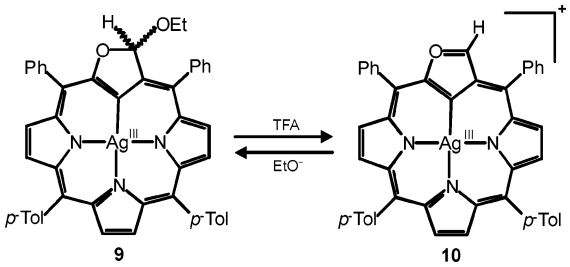


ethanol addition at the *O*-confused oxaporphyrin oxidation level is consistent with the first pathway. Significantly, addition of pyrrole, followed by ^{1}H NMR, quantitatively converts **3**-H_2 to **4**. Thus, "true" *O*-confused oxaporphyrin can be considered to be a common intermediate in the formation of **4**, **7**, and **8**.

The ^{1}H NMR spectrum of **3**-H_2 (Figure 2, trace B) shows three AB patterns located according to the COSY map (8.32, 7.82 (^3J = 4.9 Hz); 8.27, 7.85 (^3J = 4.9 Hz); 7.82, 7.79 (^3J = 4.9 Hz)) and assigned to three pyrrole rings. The inverted furan ring contributes with a 3-H resonance at 7.83 ppm, i.e., upfield regarding the position of the furan fragment of regular oxaporphyrin (9.13 ppm)[21] but downfield with respect to the furan resonance of **6** (6.07 ppm). The NH resonance gave three slightly broadened singlets at 5.32, 5.10, and 4.37 ppm at 298 K, i.e., upfield with respect to the NH-unsubstituted pyrrole resonance. The unique inner 21-CH resonance of the inverted furan ring is located at 1.32 ppm, i.e., upfield with respect to the corresponding 3-H resonance of furan (6.07 ppm).[18] The diagnostic shift difference between the

(21) Chmielewski, P. J.; Latos-Grażyński, L.; Olmstead, M. M.; Balch, A. L. *Chem. Eur. J.* **1997**, *3*, 268.

SCHEME 5. Reactivity of Silver(III) Complexes



outer and inner furan resonances (6.51 ppm) reflects their location in the deshielding (3-H) and shielding (21-H) zones of the macrocycle diatropic ring current.

One can consider the ^{1}H NMR shifts of the internally located CH proton and the peripheral pyrrole resonances as a convenient spectroscopic criterion of aromaticity. The following porphyrinoids have a relatively small degree of aromaticity: 2-*N*-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (21-CH, 0.98 ppm; pyrrole, 7.96−7.48 ppm),[22] 2-*N*-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (pyrrole, 7.91−7.27 ppm),[22] azuliporphyrin (internal CH, 1.5 ppm),[23] and 5,10,15,20-tetraphenyl-3-thia-21-carbaporphyrin (21-CH, 4.76 ppm; pyrrole, 7.54−7.15 ppm).[16] In the limiting case of *m*-benziporphyrin the strong aromatic structure of benzene completely blocks a π delocalization pathway for the entire macrocycle (22-H 7.33; pyrrole 7.19, 6.52, 6.74).[7] Thus, **3**-H_2 can be classified as a borderline case of the carbaporphyrinoid aromaticity. The furan subunit attenuates conjugative pathways in **3**-H_2, providing, however, the very efficient 18π delocalization path for 21-oxaporphyrin,[21] which is due to the difference of an orientation of the furan moiety in the macrocyclic structure.

Formation and Characterization of [(H,OEt)*OC*P]-Ag^{III}. Reaction of silver(I) acetate with **7** in chloroform/acetonitrile mixture results in formation of [(H,OEt)-*OC*P]Ag^{III} **9** (Scheme 5). Compound **9** sustained the chromatographic purification to give the overall 75% yield of insertion. The electronic absorption spectrum [(H,OEt)-*OC*P]Ag^{III} (Figure 3) with its intense Soret-like band (431 nm) and a set of bands in the Q region (500−800 nm) is consistent with the fact that **9** conserves the aromatic character of the chromophore seen for **7** (Figure 1, red line).

The ^{1}H NMR spectra of **9** bear strong resemblance to the spectrum of the free ligand **7**, proving that the macrocyclic frame of **7** is conserved in **9**. Due to the coordination the H(21) and two inner NH resonances seen for **7** are absent in the spectrum of **9**. Consequently, the diagnostic set of two complex multiplets at 3.83 and 3.65 ppm has been assigned to the ethoxy methylene group (Figure 4, trace A, inset). The strong difference of the chemical shifts detected for the two methylene multiplets is due to the diastereotopic effect as the chirality center is created on the tetrahedral hybridized C(3) atom. The structurally informative H(3) resonance for **9** was identified at 7.87 ppm (^{13}C 111.4 ppm).

Coordination through the nitrogen donors in **9** is reflected by the presence of $^{107/109}$Ag scalar splitting seen

(22) Chmielewski, P. J.; Latos-Grażyński, L.; Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690.
(23) Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839.

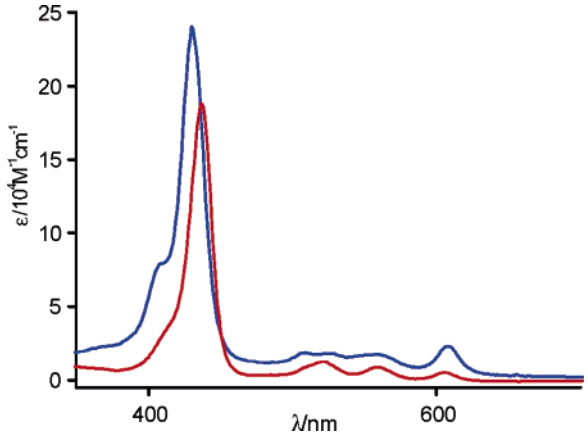


FIGURE 3. Electronic spectra of silver complexes **9** (blue) and **12** (red) in dichloromethane.

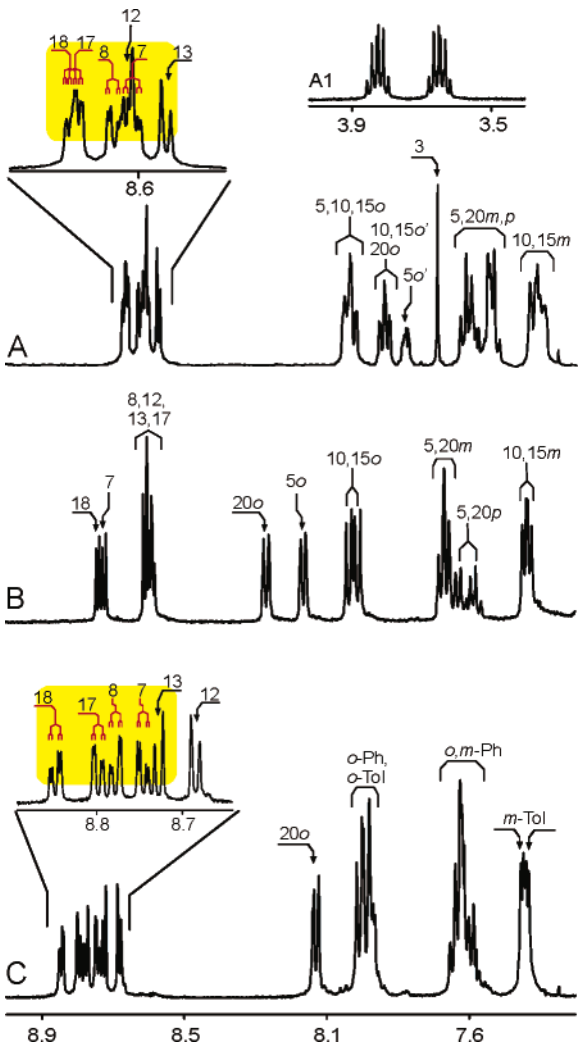
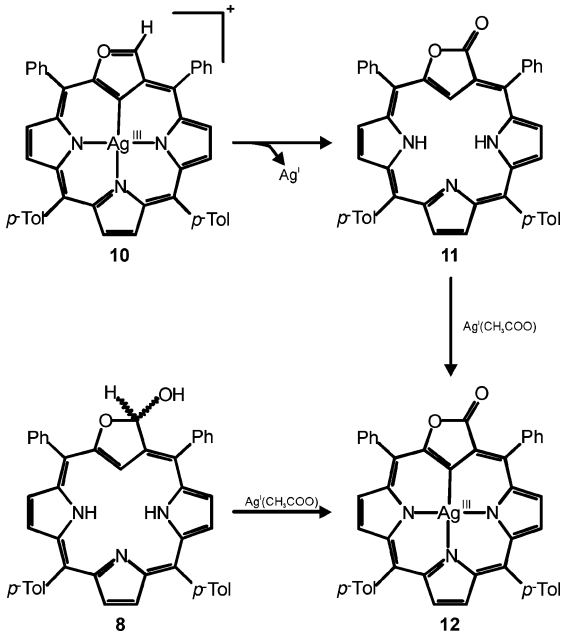


FIGURE 4. ^{1}H NMR spectra (A) **9** (chloroform-*d*, 298 K), (B) **11** (chloroform-*d*, 298 K). The scalar couplings between the β-H resonances and $^{107/109}$Ag are presented. The diastereotopic splitting of the $-CH_2-$ resonances of 3-ethoxide is shown in trace A, inset.

for the H(7), H(8), H(17), and H(18) β-H pyrrolic signals. In each case the coupling constant $^4J_{AgH} = 1.5$ Hz (Figure 4, trace A, inset A1). Such a coupling has not been

SCHEME 6. Formation of the Lactone Derivative



detected for the H(12), H(13) resonances of the central pyrrole ring. The spectroscopic parameters of **9** resemble those determined for the pyrrole-appended counterpart [(EtO,pyr)*OC*P]Ag^{III} reported previously.[18]

The ^{1}H NMR titration readily transforms [(H,OEt)-*OC*P]Ag^{III} **9** into the aromatic complex {[(H)*OC*P]Ag^{III}}$^+$ **10** via an exocyclic C(3)−O bond cleavage, which involves protonation of ethoxy oxygen followed by ethanol elimination (Scheme 5) as seen already for the **7**−**3**-H_2 couple of free ligands. Formally complex **10** can be produced by direct insertion of silver(III) cation into **3** with replacement of H(21) and inner NH protons. Addition of sodium ethoxide in ethanol to the solution of {[(H)*OC*P]Ag^{III}}$^+$ **10** recovers starting [(H,OEt)*OC*P]Ag^{III} **9**. Following the marked changes seen in the electronic spectra the ^{1}H NMR chemical shifts of **10** reflect the smaller aromaticity in comparison to **9,** resembling the properties of **3**-H_2 The fine structure of β-H resonances due to coupling with $^{107/109}$Ag seen for parent **9** has been conserved at **10**.

Carbaporpholactone−Carbaporphyrinoid Incorporating Lactone Functionality. {[(H)*OC*P]Ag^{III}}$^+$ **10**, generated as described above, quantitatively transforms into carbaporpholactone **11** (298 K, $CDCl_3$). Originally the progress of the reaction was followed by ^{1}H NMR to be modified eventually into the synthetic procedure. The total conversion requires 12 h. The electronic spectrum of **11** (Figure 1) with its intense Soret-like band (438 nm) and a set of bands in the Q region reflect the aromatic character of the new ligand. The ^{1}H NMR spectrum of **11** (Figure 4, trace B) shows three AB patterns assigned to three pyrrole rings at the position expected for aromatic carbaporphyrinoid. The characteristic resonance reflecting the presence of the carbonyl group has been identified in the ^{13}C NMR spectrum at 167.4 ppm. Presumably the Ag(III) species **10** undergoes reversible binding of the water molecule at C(3). This step is followed by an intramolecular two-electron oxidation step to yield, after extrusion of Ag(I), the carbaporpholactone **11** (Scheme 6).

Reaction of silver(I) acetate with **11** in chloroform/acetonitrile mixture produces the four-coordinate silver(III) complex [(O)OCP]Ag^{III} **12**. The identical species has been formed once macrocycle **8** has been used as a substrate (Scheme 6). The insertion process is accompanied by a ligand oxidation step. Namely, the hemiacetal structure in **8** has been oxidized by excess silver salt into a lactone one as seen in **12**. Presumably this process involves three steps: insertion of silver, intramolecular oxidation to form lactone accompanied by extrusion of silver(I), followed by insertion of silver(III). The acetal structure, encountered in **7**, efficiently protects this molecular fragment against oxidation in analogous insertion processes. The silver insertion product **9** preserves the original acetal unit.

Thus, in the indirect route the new carbaporphyrinoid that embeds the lactone moiety has been obtained. The macrocycle of **11** is formally formed by replacement of one pyrrole ring of regular porphyrin with properly oriented cyclic lactone—furanone. The structure of **11** is related to porpholactone, which was formally derived by transformation of one pyrrole ring of a porphyrin macrocycle to an oxazolone.[24−27]

The electronic spectrum of [(O)*OC*P]Ag^{III} **12** (Figure 3) with its intense Soret-like band (437 nm in CH_2Cl_2) and a set of bands in the Q region reflect the aromatic character of the new ligand. The ^{1}H NMR spectrum of **12** (Figure 4, trace C) shows three AB patterns assigned to three pyrrole rings at positions expected for an aromatic carbaporphyrinoid resembling that of **11**. The fine structure of β-H resonances due to coupling with $^{107/109}$Ag seen for parent **11** has been detected as well. The characteristic resonance reflecting the presence of the carbonyl group has been identified in the ^{13}C NMR spectrum at 167.9 ppm.

Crystal Structure of 12. The structure of **12** has been determined by X-ray crystallography. The perspective views of the molecule are shown in Figure 5. The macrocycle is only slightly distorted from planarity as seen in Figure 5.

The Ag−N and Ag− C distances (Ag−C(21) 2.013(5), Ag−N(22) 2.020(4), Ag−N(23) 2.038(4), Ag−N(24) 2.039(4)) are comparable to those in other silver(III) carbaporphyrinoids: silver(III)-inverted porphyrin [Ag−N(22), 2.06(2); Ag−N(23), 2.08(2); Ag−N(24), 2.03(2); Ag−C(21), 2.04(2)];[28] silver(III) benzocarbaporphyrin [Ag−N(22), 2.038(4); Ag−N(23), 2.084(4); Ag−N(24), 2.046(4); Ag−C(21), 2.015(4)],[13] silver(III) double *N*-confused porphyrin [Ag−C(21), 2.011(7); Ag−C(22), 1.987(2); Ag−N(23), 2.064(5); Ag−N(24), 2.047(7)].[29]

Comparison of the structural data of silver(III) (NNNC) carbaporphyrinoids shows that silver(III)−carbon(sp^2) bond lengths are very similar despite the different nature of the carbon donor bearing ring related to *N*-confused pyrrole, substituted *O*-confused furan, or indene.

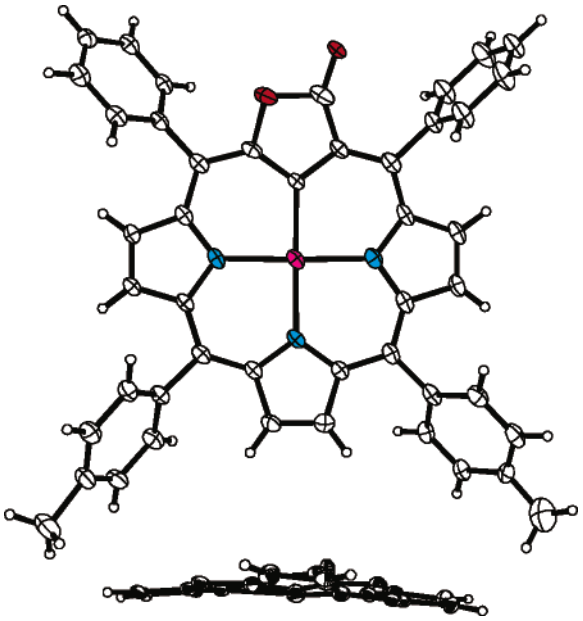


FIGURE 5. Crystal structure of **12** (top, perspective view; bottom, side view with phenyl groups omitted for clarity). The thermal ellipsoids represent 30% probability.

TABLE 1. Crystal Data for [(O)*OC*P]Ag^{III} with Refinement Details

compound	[(O)*OC*P]Ag^{III} **12**
crystals grown by	slow diffusion of MeOH into toluene solution
cryst habit	red block
formula	$C_{46}H_{30}N_3O_2Ag$
fw	768.63
a, Å	9.873(2)
b, Å	13.001(3)
c, Å	15.530(3)
α, deg	73.36(3)
β, deg	72.13(3)
γ, deg	85.90(3)
V, Å^3	1817.5(6)
Z	2
D_{calcd}, g·cm^{-3}	1.405
cryst syst	triclinic
space group	*P*-1
μ, mm^{-1}	0.598
abs corr	not applied
T, K	100(2)
θ range	$3.64 \le \theta \le 28.50$
hkl range	$-13 \le h \le 13$ $-17 \le k \le 10$ $-20 \le l \le 20$
reflns	
measured	7998
unique, $I \ge 2\sigma(I)$	5477
params/restraints	512/0
S	1.035
R1	0.0639
wR2	0.1802

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Conclusion

In the present work we have described the synthesis and reactivity of "true" *O*-confused oxaporphyrin and its

(24) Crossley, M. J.; King, L. G. *J. Chem. Soc., Chem. Commun.* **1984**, 920.
(25) Gouterman, M.; Hall, R.; Khalil, G. E.; Martin, P. C.; Shankland, E. G.; Cerny, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 3702.
(26) Jayaraj, K.; Gold, A.; Austin, R. N.; Ball, L. M.; Terner, J.; Mandon, D.; Weiss, R.; Fischer, J.; DeCian, A.; Bill, E.; Müther, M.; Schünemann, V.; Traütwein, A. X. *Inorg. Chem.* **1997**, *36*, 4555.
(27) McCarthy, J. R.; Jenkins, H. A.; Brückner, C. *Org. Lett.* **2003**, *5*, 19.
(28) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676.
(29) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc.* **2000**, *122*, 803.

derivatives. The molecules have been constructed applying the heteroatom confusion concept. Thus, interchanging of an oxygen atom with a β-methine group of furan transforms 5,10,15,20-tetraaryl-21-oxaporphyrin into 2-oxa-5,10,15,20-tetraaryl-21-carbaporphyrin. Inherent reactivity of the furan ring allowed stabilization of targeted *O*-confused oxaporphyrin only in the dicationic form as trapped by ^{1}H NMR spectroscopy. Of particular importance is the fact that the inherently reactive "true" 2-oxa-21-carbaporphyrin may serve as a fundamental intermediate to construct a stable related derivative fine-tuned at the C(3) position. For instance, a coupled insertion and oxidation process using the product of addition of a water molecule to *O*-confused oxaporphyrin yielded the silver(III) complex of carbaporphyrinoid, which embeds the lactone functionality.

Experimental Section

Materials. 3-Furaldehyde, phenyl Grignard reagent, *s*-butyllithium, and *n*-butyllithium have been used as received. 2,4-Bis(phenylhydroxymethyl)furan has been obtained as previously described.[18]

5,20-Diphenyl-10,15-ditolyl-2-oxa-3-ethoxy-3-hydro-21-carbaporphyrin, 7. In a round-bottom flask 2,4-bis(phenylhydroxymethyl)furan was dissolved in chloroform stabilized with about 0.75% ethanol (150 mL). To the solution pyrrole (209 μL, 3 mmol) and *p*-toluylaldehyde (234 μL, 2 mmol) were added, and the resulting mixture was degassed with N_2 for an additional 30 min. After that time $BF_3{\cdot}Et_2O$ (120 μL) was added, and the obtained solution was stirred for the next hour with protection from the light. The resulting orange mixture was oxidized with DDQ (681 mg, 3 mmol) and immediately dried with a vacuum rotary evaporator. The dark residue was dissolved in freshly distilled dichloromethane and chromatographed with basic alumina (GII). The fast moving fraction was collected and chromatographed again with silica gel (40, Mesh 35−70). The chloroform fraction was collected and separated by column chromatography (Al_2O_3, GII). Expected product was eluted as a fast moving brown-yellow band. Recrystallization with CH_2Cl_2/MeOH gave 40 mg of **7** (yield 5%).

^{1}H NMR (500.13 MHz, $CDCl_3$): 8.55−8.50 (m, 5H), 8.41 (d, 1H, ^3J = 4.6 Hz), 8.19 (d, 2H, ^3J = 7.6 Hz), 8.04 (d, 2H, ^3J = 7.6 Hz), 8.00 (d, 1H, ^3J = 7.6 Hz), 7.95 (d, 1H, ^3J = 7.6 Hz), 7.88 (bs), 7.72 (t, 2H), 7.69−7.56 (m, 3H), 7.5 (m, 4H), 7.46 (s, 1H), 3.82 (m, 1H), 3.54 (m, 1H), 2.66 (s, 3H), 2.65 (s, 3H), 1.05 (t, 3H), −5.49 (s, 1H). ^{13}C NMR (126.7 MHz, $CDCl_3$): 158.0, 153.7, 153.3, 140.0, 139.8, 139.7, 139.1, 138.9, 138.8, 137.7, 137.6, 135.8, 135.1, 134.8, 134.7, 134.5, 134.46, 133.0, 132.8, 128.2, 128.0, 127.9, 127.7, 126.6, 125.5, 124. 0, 123.8, 121.3, 120.6, 115.2, 109.1, 106.7, 105.9, 65.4, 21.9, 21.9, 15.5. UV−vis (λ_{max}[nm], log ϵ): 433 (5.10), 531 (4.15), 567 (4.08), 615 (3.80), 672 (3.89). HRMS (ESI, *m/z*): 690.3115 (690.312 calcd for $C_{48}H_{39}N_3O_2 + H^+$).

[(H,OH)*OC*PH]H$_2$, 8. To a solution of 10 mg of **7** dissolved in 20 mL of freshly distilled dichloromethane concentrated TFA (10 μL) was added. Then the resulting mixture was washed with water, and the organic phase, containing **8** as a dicationic form, was neutralized with Et_3N and chromatographed with basic alumina (GII). Expected product was eluted with a chloroform. Crude product was crystallized with CH_2Cl_2/hexane mixture.

^{1}H NMR (500.13 MHz, $CDCl_3$): 8.55−8.48 (m, 5H), 8.41 (d, 1H, ^3J = 4.6 Hz), 8.20 (d, 2H, ^3J = 7.9 Hz), 8.04 (d, 1H, ^3J = 7.9 Hz), 8.00 (m, 1H), 7.96 (d, 1H, ^3J = 8 Hz), 7.93 (s, 1H), 7.76−7.59 (m, 8H), 7.54−7.46 (m, 6H), 2.66 (s, 2 × 3H), 1.21 (t, 3H), −5.50 (s, 1H). ^{13}C NMR (126.7 MHz, $CDCl_3$): 157.2, 153.7, 153.2, 140.6, 140.2, 139.8, 139.64, 139.6, 139.1, 138.7, 137.8, 137.7, 135.9, 135.2, 134.9, 134.7, 134.6, 134.5, 133.0, 132.7, 131.3, 129.2, 128.3, 128.1, 128.0, 126.7, 126.6, 124.1, 124, 121.4, 120.7, 115.1, 113.8, 106.9, 105.4, 103.9, 21.9, 21.9. UV−vis (λ_{max}[nm], log ϵ): 432 (5.14), 530 (4.21), 565 (4.14), 613 (3.96), 673 (3.95). HRMS (ESI, *m/z*): 662.2812 (662.2802 calcd for $C_{46}H_{35}N_3O_2 + H^+$).

[(H,OEt)*OC*P]Ag^{III}, 9. A 15 mg (0.022 mmol) amount of **7** was dissolved in 20 mL of chloroform, and 146 mg of silver(I) acetate in acetonitrile (20 mL) was added. The mixture was stirred for about 1 h, and the solvent was removed using a vacuum rotary evaporator. Recrystallization of the remaining solid from chloroform/methanol (50/50 v/v) gave 14 mg of **9**, yield 75%.

^{1}H NMR (500.13 MHz, $CDCl_3$): 8.67 (dd, 1H, ^3J = 4.9 Hz, $^4J_{Ag}$ = 1.1 Hz), 8.66 (d, 1H, ^3J = 4.6), 8.62 (dd, 1H, ^3J = 4.9 Hz, $^4J_{Ag}$ = 1.5 Hz), 8.61 (d, 1H, ^3J = 4.9), 8.60 (dd, 1H, ^3J = 4.6, $^4J_{Ag}$ = 1.5 Hz), 8.57 (d, 1H, ^3J = 4.9), 8.03 (m, 4H), 7.94 (m, 2H), 7.88 (m, 1H), 7.79 (s, 1H), 7.73−7.67 (m, 3H), 7.66−7.61 (m, 4H), 7.55−7.47 (m, 5H), 3.84 (m, 1H), 3.65 (m, 1H), 2.67 (s, 3H), 2.66 (s, 3H), 1.09 (t, 3H). ^{13}C NMR (125.77 MHz, $CDCl_3$): 149.8, 142.6, 142.5, 140.7, 139.4, 139.31, 139.29, 138.8, 138.4, 137.86, 137.84, 137.2, 136.7, 135.5, 134.6, 134.0, 133.98, 133.95, 131.0, 129.8, 129.77, 129.2, 128.7, 128.5, 128.1, 128.07, 127.9, 127.8, 127.7, 127.2, 125.6, 125.5, 121.9, 121.8, 118.2, 64.8, 21.9, 21.9, 15.5. UV−vis (λ_{max}[nm], log ϵ): 430(5.38), 508-(4.27), 526(4.26), 558(4.24), 608(4.36). HRMS (*m/z*) $[M]^+$ 793.1841 (793.1853 calcd for $[C_{48}H_{36}N_3O_2Ag]^+$).

[(O)*OC*PH]H$_2$, 11. A 15 mg (0.019 mmol) amount of **9** was dissolved in 20 mL of freshly distilled CH_2Cl_2. To the resulting mixture TFA (1 μL) was added and mixed for an additional 12 h. Then the solvent was removed under reduced pressure, and the remaining solid was dissolved in freshly distilled dichloromethane and chromatographed with basic alumina (GII). Expected product was eluted as a fast moving brown-yellow fraction. The process is quantitative.

^{1}H NMR (500.13 MHz, $CDCl_3$): 8.74 (d, 1H, ^3J = 4.6 Hz), 8.72 (d, 1H, ^3J = 4.6), 8.62−8.56 (m, 4H), 8.27 (m, 2H), 8.16 (m, 2H), 8.04 (d, 2H, ^3J = 8.0), 8.01 (d, 2H, d, 2H, ^3J = 8.0), 7.77 (m, 4H), 7.72 (m, 1H), 7.69 (m, 1H), 7.55−7.51 (m, 4H), 2.67 (s, 6H), − 5.12 (s, 1H). ^{13}C NMR (125.77 MHz, $CDCl_3$): 167.5, 156.0, 155.0, 145.9, 139.2, 139.0, 138.7, 138.6, 138.4, 137.8, 137.6, 137.1, 137.0, 137.9, 135.1, 134.6, 134.5, 134.4, 134.2, 133.9, 130.9, 128.8, 128.3, 128.2, 128.0, 127.9, 127.2, 126.9, 126.1, 125.8, 121.4, 120.9, 119.7, 118.8, 111.3, 21.5, 21.5. UV−vis (λ_{max}[nm], log ϵ): 438(5.17), 534(3.91), 574(3.79), 627(3.36), 690(3.17). HRMS (*m/z*) $[M + H]^+$ 660.2676 (660.2646 calcd for $[C_{46}H_{33}N_3O_2 + H]^+$).

[(O)*OC*P]Ag^{III}, 12. *Route A.* A 15 mg (0.023 mmol) amount of **11** was dissolved in 20 mL of $CHCl_3$ stabilized with amylene. A 146 mg amount of silver(I) acetate dissolved in 20 mL of freshly distilled acetonitrile was added, and the resulting mixture was mixed for an additional 30 min without heating, The solvent was removed under reduced pressure. The remaining solid was dissolved in toluene and chromatographed on a silica gel (mesh 35−70) column. The red band, eluted with toluene, was collected and evaporated. Recrystallization from $CHCl_3$/MeOH gave 14 mg of **12**, yield 75%.

Route B. A 15 mg (0.023 mmol) amount of **8** was dissolved in 20 mL of $CHCl_3$ stabilized with amylene. A 146 mg amount of silver(I) acetate dissolved in 20 mL of freshly distilled acetonitrile was added, and the resulting mixture was refluxed for an additional 30 min. The solvent was removed under reduced pressure. The remaining solid was dissolved in toluene and chromatographed on a silica gel (mesh 35−70) column. The red band, eluted with toluene, was collected and evaporated. Recrystallization from $CHCl_3$/MeOH gave 14 mg of **12**, yield 75%.

^{1}H NMR (500.13 MHz, $CDCl_3$): 8.85 (dd, 1H, ^3J = 4.9 Hz, $^4J_{Ag}$ = 1.5 Hz), 8.79 (dd, 1H, ^3J = 4.9, $^4J_{Ag}$ = 1.5 Hz), 8.77 (dd, 1H, ^3J = 4.9 Hz, $^4J_{Ag}$ = 1.1 Hz), 8.74 (dd, 1H, ^3J = 4.9, $^4J_{Ag}$ = 1.5 Hz), 8.72 (d, 1H, ^3J = 4.9), 8.68 (d, 1H, ^3J = 4.9), 8.13 (d, 1H, ^3J = 7.8 Hz), 8.03−7.96 (m, 3H), 7.76−7.66 (m, 5H), 7.56−7.51 (m, 4H), 2.69 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (125.77 MHz,

$CDCl_3$): 167.9, 140.0, 139.7, 139.5, 139.2, 139.1, 139.0, 138.8, 138.4, 138.3, 138.1, 137.4, 136.5, 134.2, 134.17, 132.8, 131.3, 130.6, 130.4, 129.4, 129.2, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.2, 125.3, 122.9, 122.3, 114.9, 110.9, 21.9, 21.9. UV−vis (λ_{max}[nm], log ϵ): 437(5.27), 522(4.10), 558(3.96), 605(3.73). HRMS (*m/z*) $[M]^+$ 764.6319 (764.6328 calcd for $[C_{46}H_{30}N_3O_2Ag]^+$).

***O*-Confused Porphyrin Dication 3-H_2.** ^{1}H NMR ($CDCl_3$, 298 K): 8.36 (d, 1H, ^3J = 4.9 Hz), 8.30 (d, 1H, ^3J = 4.9 Hz), 8.18 (m, 2H), 8.14 (m, 2H), 7.95−7.78 (m, 15H), 7.55 (m, 4H), 5.46 (s, 1H), 5.25 (s, 1H), 4.61 (s, 1H), 2.62 (s, 6H), 1.18 (s, 1H). UV−vis (λ_{max}[nm], log ϵ): 335(4.34), 412(4.43), 445(4.63), 472(4.90), 576(3.84), 624(3.90), 685(3.94), 807(3.89), 907(4.09).

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded at 500.13 and 125.7 MHz, respectively. Absorption spectra were recorded on a diode array spectrometer. Mass spectra were recorded using the electrospray and liquid matrix secondary-ion mass spectrometry techniques.

X-ray Data Collection and Refinement. Crystals of **12** were prepared by diffusion of methanol into the toluene solution contained in a thin tube. Data were collected at 100 K and corrected for Lorentz and polarization effects. No absorption correction was applied. Crystal data are compiled in Table 1.

The structure was solved by direct methods with SHELXS-97 and refined by the full-matrix least-squares method using SHELXL-97 with anisotropic thermal parameters for the non-H atoms. Scattering factors were those incorporated in SHELXS-97.[30] The structure contains a disordered molecule of toluene which could not be resolved.[30]

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Supporting Information Available: Tables of crystal data, bond lengths, angles, anisotropic thermal parameters (cif file). This material is available free of charge via the Internet at http://pubs.acs.org.

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(30) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.