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Tetraphenyloxybenziporphyrin, a New Organometallic Ligand for Silver(III) and Gold(III)[†]

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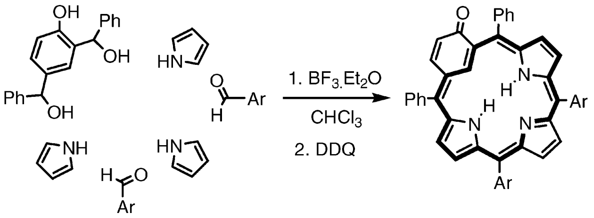
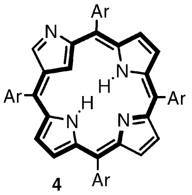
ABSTRACT



Reaction of 4-hydroxyisophthalaldehyde with excess phenyl magnesium bromide gave a dicarbinol and this condensed with pyrrole and aromatic aldehydes in the presence of $BF_3 \cdot Et_2O$ to afford, following oxidation with DDQ, novel tetraarylcarbaporphyrinoids in 10–24% yield. Further reaction with silver(I) acetate or gold(III) acetate gave stable organometallic derivatives that retained the aromatic characteristics of the parent macrocycle.

Oxybenziporphyrin **1** (Scheme 1) was the first reported example of an aromatic carbaporphyrinoid system.[1−3] This porphyrin-like macrocycle was prepared by a “3 + 1” MacDonald-type condensation[4] of a tripyrrane **2** with 4-hydroxyisophthalaldehyde (**3**) in the presence of TFA in dichloromethane, followed by oxidation with DDQ. The benzene unit takes on semiquinoid character in **1**, allowing the macrocycle to have an 18π-electron delocalization pathway.[1,5] Oxybenziporphyrins **1** have been shown to act both as trianionic ligands, giving silver(III) organometallic derivatives in reactions with silver(I) acetate,[6] and as a dianionic ligand for palladium(II) derivatives.[7] Diverse carbaporphyrinoid systems have now been synthesized and many of these form stable organometallic derivatives under mild conditions.[8−11] This chemistry parallels studies on the better known N-confused porphyrins **4** which share the same type of CNNN coordination core.[12,13] However, tripyrranes **2** must be prepared by multistep procedures[14] and this limits the amounts of these porphyrin analogues that are available



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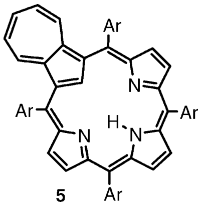

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[†] Part 40 in the series Conjugated Macrocycles Related to the Porphyrins. For Part 39, see: Xu, L.; Ference, G. M.; Lash, T. D. *Org. Lett.* **2006**, *8*, 5113−5116.

(1) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533.

(2) Lash, T. D. *Synlett* **2000**, 279.

(3) Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 2, pp 125−199.

(4) Lash, T. D. *Chem. Eur. J.* **1996**, *2*, 1197.

(5) (a) Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076. (b) Richter, D. T.; Lash, T. D. *Tetrahedron* **2001**, *57*, 3659.

(6) Lash, T. D.; Rasmussen, J. M.; Bergman, K. M.; Colby, D. A. *Org. Lett.* **2004**, *6*, 549.

(7) Stepien, M.; Latos-Grazynski, L.; Lash, T. D.; Szterenberg, L. *Inorg. Chem.* **2001**, *40*, 6892. See also: Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462.

(8) (a) Graham, S. R.; Ferrence, G. M.; Lash, T. D. *Chem. Commun.* **2002**, 894. (b) Lash, T. D.; Colby, D. A.; Graham, S. R.; Ferrence, G. M.; Szczepura, L. F. *Inorg. Chem.* **2003**, *42*, 7326.

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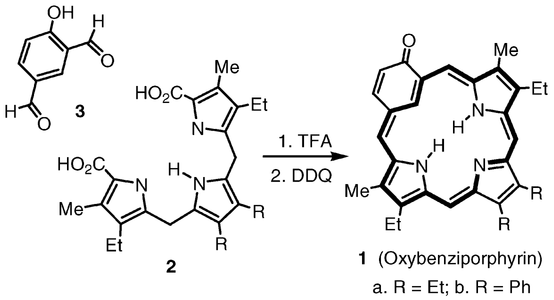
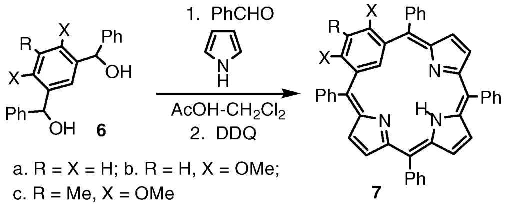
for study. In addition, *meso*-tetraaryl-substituted porphyrinoids may possess greater stability and superior solubility characteristics.[15] Recently, we demonstrated that azuliporphyrins **5** can be synthesized in good yields in a one pot-procedure by reacting azulene with pyrrole and benzaldehyde in the presence of $BF_3{\cdot}Et_2O$ followed by oxidation with DDQ.[15] Oxidative ring contractions with alkaline solutions of *tert*-butyl hydroperoxide gave the related benzocarbaporphyrins.[15] Others have shown that benzene dicarbinols **6** react with pyrrole and benzaldehyde under similar conditions to give tetraphenylbenziporphyrin **7a**,[16] and we have adapted this approach to the synthesis of dimethoxybenziporphyrins **7b** and **7c**.[17] However, no direct routes to the aromatic oxybenziporphyrins have been reported and this has severely limited studies on the chemistry of this important carbaporphyrinoid system.

Scheme 1

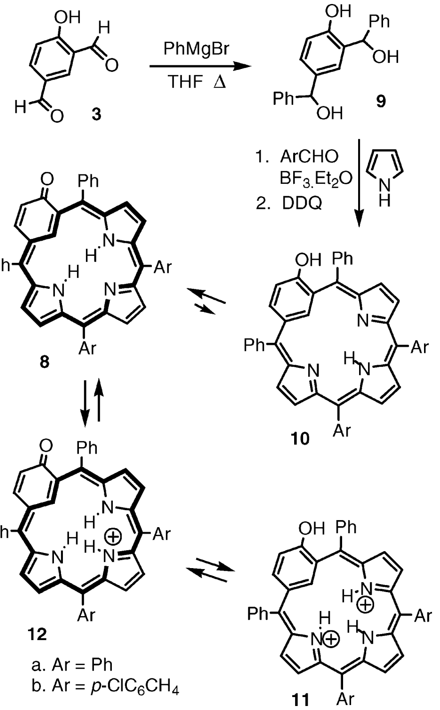


Scheme 2



We now report a straightforward two-step synthesis of tetraphenyloxybenziporphyrin **8** (Scheme 3). Dialdehyde **3** was treated with excess phenylmagnesium bromide in refluxing THF for 2 h, cooled to room temperature, and treated with aqueous ammonium chloride solution to give the dicarbinol **9** in virtually quantitative yields. This was reacted under Lindsey–Rothemund conditions[18,19] with 2 equiv of benzaldehyde and 3 equiv of pyrrole in dichloromethane or chloroform in the presence of $BF_3{\cdot}Et_2O$, followed by oxidation with DDQ. Although **8** was formed with either solvent, superior results were obtained with chloroform. The yield was also dependent on the concentration of catalyst, and better yields were obtained when the amount of $BF_3{\cdot}Et_2O$ was doubled compared to the amounts used to prepare **7b** and **7c**. Catalytic amounts of TFA in place of $BF_3{\cdot}Et_2O$ also gave some product formation, although the yields were low compared to using the Lewis acid catalyst. Under the best conditions, following purification by column chromatography and recrystallization from hexanes, tetraphenyloxybenziporphyrin was isolated as shiny purple crystals in 10–13% yield. Reaction of **9** with 4-chlorobenzaldehyde and pyrrole gave even better results and the related bis(4-chlorophenyl)diphenyloxybenziporphyrin **8b** was isolated in 22–24% yield.

Scheme 3



Oxybenziporphyrin can potentially exist as “keto” or “enol” tautomers **8** and **10**, respectively, but only the former would possess overall aromatic character. Due to the presence of a *meso*-substituent so close to the oxygen atom, this

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(9) (a) Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860. (b) Muckey, M. A.; Szczepura, L. F.; Ferrence, G. M.; Lash, T. D. *Inorg. Chem.* **2002**, *41*, 4840. (c) Lash, T. D.; Colby, D. A.; Szczepura, L. F. *Inorg. Chem.* **2004**, *43*, 5258. See also: Brückner, C. *J. Chem. Educ.* **2004**, *81*, 1665.

(10) Liu, D.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 6079.

(11) (a) Miyake, K.; Lash, T. D. *Chem. Commun.* **2004**, 178. (b) Bergman, K. M.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 7888.

(12) Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10.

(13) Harvey, J. D.; Ziegler, C. J. *Coord. Chem. Rev.* **2003**, *247*, 1.

(14) (a) Sessler, J. L.; Johnson, M. R.; Lynch, V. *J. Org. Chem.* **1987**, *52*, 4394. (b) Lash, T. D. *J. Porphyrins Phthalocyanines* **1997**, *1*, 29.

(15) (a) Colby, D. A.; Lash, T. D. *Chem. Eur. J.* **2002**, *8*, 5397. (b) Lash, T. D.; Colby, D. A.; Ferrence, G. M. *Eur. J. Org. Chem.* **2003**, 4533.

(16) (a) Stepien, M.; Latos-Grazynski, L. *Chem. Eur. J.* **2001**, *7*, 5113. (b) Stepien, M.; Latos-Grazynski, L. *Acc. Chem. Res.* **2005**, *38*, 88.

(17) Szymanski, J. T.; Lash, T. D. *Tetrahedron Lett.* **2003**, *44*, 8613.

(18) Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 1, pp 45–118.

(19) (a) Lindsey, J. S.; Schreiman, I. C.; Hsu, H. C.; Kearney, P. C.; Marguerettaz, A. M. *J. Org. Chem.* **1987**, *52*, 827. (b) Lindsey, J. S.; Wagner, R.W. *J. Org. Chem.* **1989**, *54*, 828. (c) Lindsey, J. S.; MacCrum, K. A.; Tyhonas, J. S.; Chuang, Y.-Y. *J. Org. Chem.* **1994**, *59*, 579. (d) Geier, G. R., III; Lindsey, J. S. *J. Chem. Soc., Perkin Trans. 2* **2001**, 677.

compound cannot be completely planar and this could reduce the favorability of tautomer **8**. Nevertheless, tetraphenyloxybenziporphyrin shows a powerful diamagnetic ring current in its proton NMR spectrum (Figure 1) and the internal CH appears upfield near −3 ppm. As expected, the pyrrolic protons are shifted downfield appearing as a series of doublets or AB quartets between 7.9 and 8.5 ppm. The NMR data are fully consistent with the keto form **8a**, but the magnitude of the ring current is diminished compared to the etio-type system **1**, which shows the internal CH at −7.2 ppm.[1,5] This is due to steric crowding from the *meso*-substituents and similar effects have been noted for tetraarylazuliporphyrins and benzocarbaporphyrins. In addition, alkyl-substituted N-confused porphyrins show a more pronounced diamagnetic ring current in their proton NMR spectra compared to the corresponding *meso*-tetrasubstituted porphyrins.[20,21] The presence of a carbonyl resonance at 180 ppm can be discerned in the carbon-13 NMR spectrum of **8a** in CDCl$_3$, and this is confirmed in the IR spectrum (KBr), which shows a carbonyl absorption at 1615 cm^{-1}. Solutions of oxybenziporphyrins **8** in 1% Et$_3$N−chloroform gave a porphyrin-like UV−vis spectrum with a Soret band at 466 nm, and Q-type absorptions at 567, 716, and 782 nm (Figure 2).

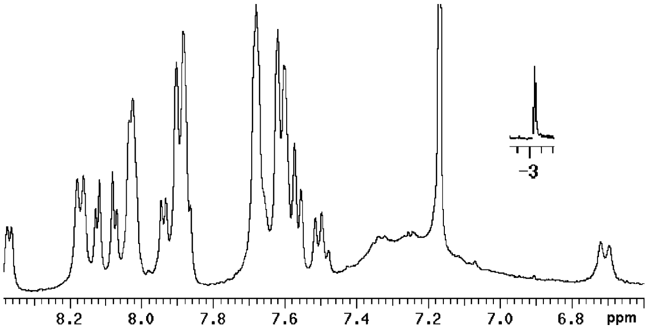


Figure 1. Proton NMR spectrum (400 MHz) of *meso*-tetraphenyloxybenziporphyrin **8a** in CDCl$_3$. The singlet at −3 ppm corresponds to the internal CH.

Addition of one drop of TFA to the NMR solution of **8a** or **8b** in CDCl$_3$ resulted in the formation of a new species that is assigned as the phenolic dications **11**. The proton NMR spectrum of **11a** in TFA−CDCl$_3$ showed the NH resonances at 7.53, 8.86, and 9.20 ppm, while the CH was observed at 4.25 ppm. In addition, the exterior pyrrolic protons were observed between 7.4 and 8.0 ppm. These data indicate that very little of the diatropic character associated with the free base is retained in the dicationic species. The carbon-13 NMR spectra for **11a** also showed the disappearance of the carbonyl resonance. The UV−vis spectra for the diprotonated species also little resembled those of true porphyrins, showing weakened bands in the Soret region at 398 and 479 nm, and a broad band centered near 900 nm (Figure 2). Attempts to observe an intermediary monoprotonated species **12** by proton NMR or UV−vis spectroscopy were unsuccessful.

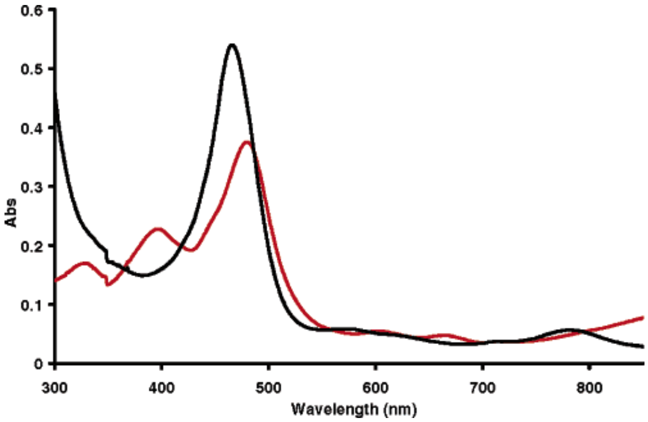
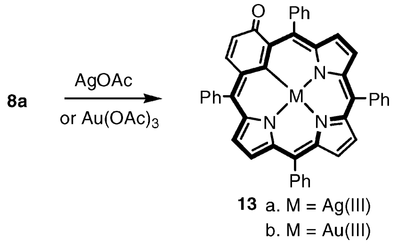


Figure 2. UV−vis spectra of tetraphenyloxybenziporphyrin **8a**: black line, free base in chloroform; red line, dication **11a** in 1% TFA−chloroform.

Oxybenziporphyrins **1** have previously been shown to form silver(III) complexes under mild conditions.[6] Tetraphenyloxybenziporphyrin (**8a**) also reacted with silver(I) acetate in refluxing pyridine to give the silver(III) organometallic derivative **13a** (Scheme 4) in 42% yield. Although silver(III) derivatives are known for many different carbaporphyrinoid systems, few examples of the related gold(III) derivatives have been reported.[9c,22] However, **8a** reacted with gold(III) acetate in pyridine at room temperature to give an excellent yield of the gold(III) porphyrinoid **13b**. The structures of these new metallo-derivatives were confirmed by mass spectrometry and NMR spectroscopy. The silver complex **13a** gave orange solutions and its UV−vis spectrum in chloroform showed the presence of a strong Soret band

Scheme 4



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(20) (a) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973. (b) Morimoto, T.; Taniguchi, S.; Osuka, A.; Furuta, H. *Eur. J. Org. Chem.* **2005**, 3887.

(21) Although the NMR data give valuable insights into the aromatic character of these porphyrin analogues, it is important to note that proton chemical shifts are not always reliable indicators for aromaticity. See: Wannere, C. S.; Corminboeuf, C.; Allen, W. D.; Schaefer, H. F., III; Schleyer, P. v. R. *Org. Lett.* **2005**, *7*, 1457.

(22) Recently, gold(III) organometallic derivatives of hexaphyrins have also been reported. Mori, S.; Osuka, A. *J. Am. Chem. Soc.* **2005**, *127*, 8030.

at 452 nm, followed by three smaller bands at 539, 593, and 641 nm. The spectrum for the gold complex **13b** was very similar, showing a Soret band at 462 nm and smaller absorptions at 533, 587, and 641 nm (Figure 3). Both of the spectra for the metallo-species are far more porphyrin-like than the free base **8a**, suggesting increased aromatic character, and this was confirmed by the NMR data. The proton NMR spectra for **13a** and **13b** showed the presence of strong diatropic ring currents where the pyrrolic hydrogens showed up as a series of resonances between 8.3 and 8.7 ppm, although the downfield shifts were slightly larger for the gold(III) complex (Figure 4). Carbon-13 NMR data showed the presence of a carbonyl resonance for **13a** and **13b** near 200 ppm, while the IR spectra showed peaks at 1653 cm^{-1} confirming the presence of a cross-conjugated carbonyl moiety. These data indicate that these metallo-derivatives are substantially more aromatic than **8a**, although the effect is slightly larger for the gold(III) complex. The free base form **8a** has three internal hydrogens that produce additional steric interactions in addition to those due to the crowded macrocyclic periphery. However, as we have demonstrated previously,[9] the silver(III) and gold(III) cations fit nicely into the macrocyclic cavity and can hold the system in a more planar arrangement that facilitates π-conjugation.

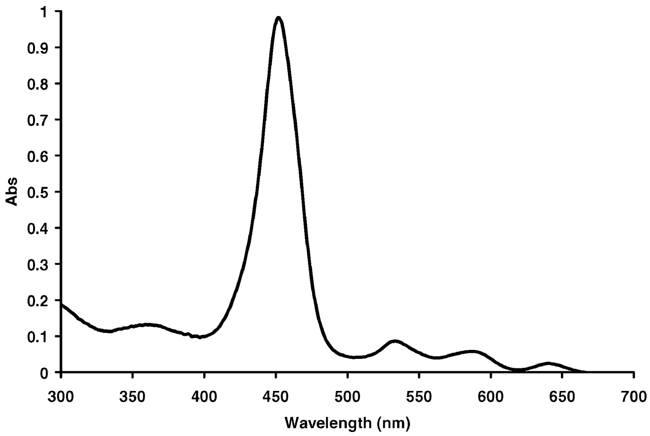

Figure 3. UV−vis spectrum of gold(III) complex **13b** in chloroform showing a porphyrin-like Soret band and three Q-type absorptions.

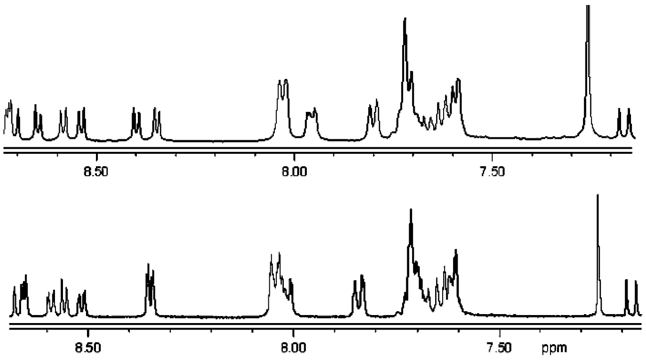

Figure 4. Proton NMR spectra (400 MHz) of metallotetraphenyloxybenziporphyrins **13** in $CDCl_3$: lower spectrum, silver(III) derivative **13a**; upper spectrum, gold(III) complex **13b**. Both spectra show increased diatropic character compared to **8a**, although the gold complex shows slightly larger downfield shifts for the pyrrolic protons.

The direct synthesis of oxybenziporphyrins with Lindsey−Rothemund conditions makes this system far more accessible and will allow the chemistry of this aromatic macrocycle to be further explored. In addition, the ability of this framework to stabilize organometallic derivatives for metals in higher oxidation states may also allow the development of new catalytic systems.

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

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