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Carbaporphyrinoid Chemistry Has a Silver Lining! Silver(III) Oxybenzi-, Oxynaphthi-, Tropi-, and Benzocarbaporphyrins[†]

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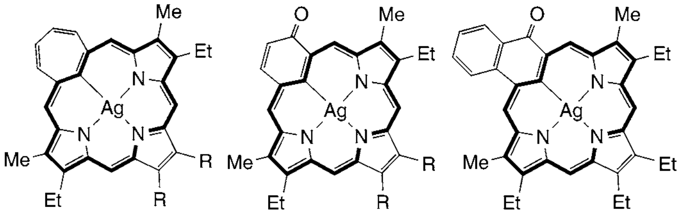
ABSTRACT



Carbaporphyrinoid systems with semiquinone, cycloheptatriene, or indene subunits react under mild conditions with silver(I) acetate to give stable silver(III) organometallic derivatives.

Carbaporphyrinoid systems are porphyrin-like macrocycles with carbocyclic moieties in place of one or more of the pyrrole rings.[1,2] These important porphyrin analogues are closely related to the so-called N-confused porphyrins (NCPs),[3] which have one or more inverted pyrrole subunits. NCPs have been shown to act as dianionic ligands, generating stable organometallic derivatives with Ni^{2+}, Cu^{2+}, Pd^{2+}, etc. (structures **1**, Chart 1)[4] or trianionic ligands (e.g., **2**).[5] Furuta demonstrated that tetraphenylNCP reacted with silver(I) trifluoroacetate to afford **2a**,[5a−c] and related antimony(V) derivatives were later characterized.[5d] Initially, carbaporphyrins[6] and related macrocyclic systems appeared to be poorly suited for metalation reactions.[7] However, azuliporphyrins,[8,9] which possess a CH−N−NH−N arrangement of core atoms, have now been shown to be good “dianionic”

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[†] Part 33 in the Series “Conjugated Macrocycles Related to the Porphyrins”. For Part 32, see: Colby, D. A.; Ferrence, G. M.; Lash, T. D. *Angew. Chem.* **2004**, in press.

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

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

(3) (a) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795. (b) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (c) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779. (d) Liu, B. Y.; Brückner, C.; Dolphin, D. *Chem. Commun.* **1996**, 2141. (e) Geier, G. R., III; Haynes, D. M.; Lindsey, J. S. *Org. Lett.* **1999**, *1*, 1455. (f) Lash, T. D.; Richter, D. T.; Shiner, C. M. *J. Org. Chem.* **1999**, *64*, 7973.

(4) (a) Chmielewski, P. J.; Latos-Grazynski, L.; Schmidt, I. *J. Am. Chem. Soc.* **1996**, *118*, 5690. (b) Furuta, H.; Kubo, N.; Maeda, H.; Ishizuka, T.; Osuka, A.; Nanami, H.; Ogawa, T. *Inorg. Chem.* **2000**, *39*, 5424. (c) Chmielewski, P. J.; Latos-Grazynski, L.; Schmidt, I. *Inorg. Chem.* **2000**, *39*, 5475.

(5) (a) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676. (b) Furuta, H.; Morimoto, T.; Osuka, A. *Org. Lett.* **2003**, *5*, 1427. (c) Maeda, H.; Osuka, A.; Ishikawa, Y.; Aritome, I.; Hisaeda, Y.; Furuta, H. *Org. Lett.* **2003**, *5*, 1293. (d) Ogawa, T.; Furuta, H.; Morino, A.; Takahashi, M.; Uno, H. *Organometallic Chem.* **2000**, *611*, 551.

(6) (a) Lash, T. D.; Hayes, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 840. (b) Lash, T. D.; Hayes, M. J.; Spence, J. D.; Muckey, M. A.; Ferrence, G. M.; Szczepura, L. F. *J. Org. Chem.* **2002**, *67*, 4860. (c) Liu, D.; Lash, T. D. *J. Org. Chem.* **2003**, *68*, 1755. For closely related carbachlorins, see: Hayes, M. J.; Lash, T. D. *Chem. Eur. J.* **1998**, *4*, 508.

(7) (a) Hayes, M. J.; Spence, J. D.; Lash, T. D. *Chem. Commun.* **1998**, 2409. (b) Lash, T. D.; Muckey, M. A.; Hayes, M. J.; Liu, D.; Spence, J. D.; Ferrence, G. M. *J. Org. Chem.* **2003**, 8558.

(8) (a) Lash, T. D.; Chaney, S. T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 839. (b) Graham, S. R.; Colby, D. A.; Lash, T. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1371.

(9) (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.

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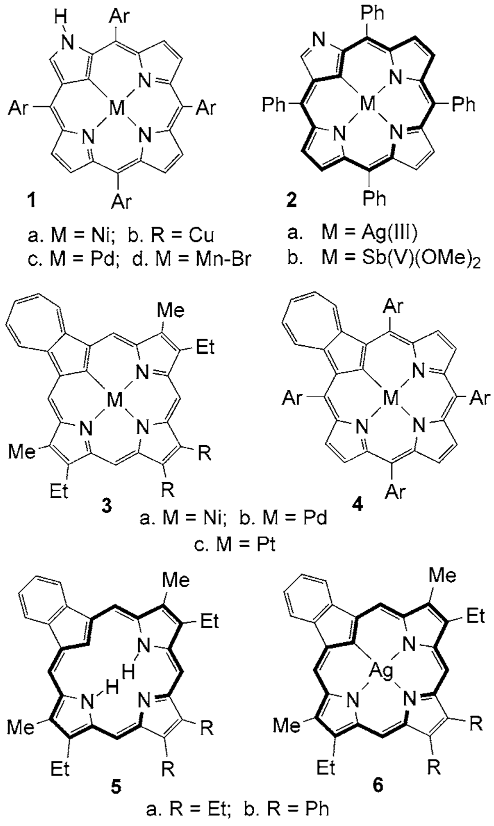
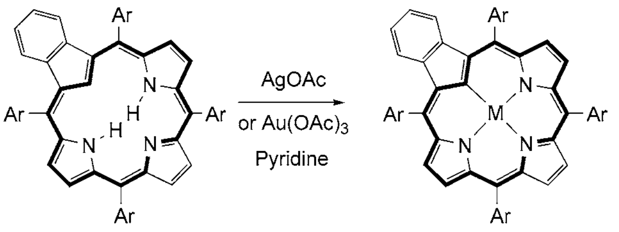
Chart 1



organometallic ligands generating the nickel(II), palladium(II), and platinum(II) complexes **3** and **4**,[10] and related complexes have also been reported for the benziporphyrins.[11,12] In contrast, benzocarbaporphyrins **5**, which have a CH−NH−N−NH core, were subsequently shown to act as trianionic ligands and reacted with silver(I) acetate under very mild conditions to give the silver(III) derivatives **6**.[13,14] Doubly N-confused porphyrins also afford silver(III) derivatives.[15] However, true porphyrins give silver(II) complexes,[16] while the similarly "dianionic" azuliporphyrins fail to react at all with silver salts.[9b] Until recently, silver(III) was considered to be an unusual oxidation state. However, the straightforward syntheses of Ag(III) derivatives of benzocarbaporphyrins and NCPs,[5a,13−15] together with the recent discovery that corroles also readily form Ag(III) complexes,[17] indicate that these species are in fact quite easy to generate. As the field of carbaporphyrinoid chemistry progresses, these organometallic ligands are becoming more accessible for study.[9] Given the relative novelty of the silver(III) complexes and the potential for this type of chemistry to stabilize other metals with unusual oxidation states, we have investigated the ability of other carbaporphyrinoids to form silver(III) derivatives. Our results indicate that the formation of stable Ag(III) organometallic complexes is a general feature for porphyrin analogues with a CH−NH−N−NH arrangement of atoms at the macrocyclic interior.

We have recently developed a direct synthesis of tetraarylazuliporphyrins and related benzocarbaporphyrins **7**.[9] Perhaps unsurprisingly, carbaporphyrins **7** also react with AgOAc to give the silver(III) derivatives **8** (Scheme 1). The best results were obtained in pyridine at room temperature, and following chromatography, the silver(III) complexes were isolated as powders in 80−97% yield. Incorporation of silver into these systems was easily demonstrated by mass spectrometry. As was the case for the "etio" benzocarbaporphyrin chelates **6**,[13] the *meso*-tetraaryl-substituted silver(III) complexes afforded orange-colored solutions and were significantly less polar than the free base carbaporphyrin ligands. The UV−vis spectra for **8** showed a strong Soret band near 450 nm. The porphyrin-like diatropic character of these chelates is also supported by the presence of the pyrrolic protons downfield near 8.7 ppm. The mechanism for the production of silver(III) carbaporphyrins from silver(I) salts remains a matter for speculation. Earlier, we suggested that this occurred via a reductive elimination of H_2.[13] Brückner has proposed[17] that the following disproportionation is taking place to generate silver metal: $3Ag^+ \rightarrow 2Ag^o + Ag^{3+}$. Silver deposits are always observed in our chemistry, and we concede that this explanation is more likely to be correct. The presence of silver at the 3 oxidation state is supported by the diamagnetic nature of the complexes and by cyclic voltammetry.[18] Interestingly, it was also possible to synthesize gold(III) complexes **9** for these *meso*-tetrasubstituted carbaporphyrinoids.[19]

Scheme 1



7 Benzocarbaporphyrins
a. Ar = Ph; b. R = *p*-ClC$_6$CH$_4$

8 M = Ag(III)
9 M = Au(III)

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(10) (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.

(11) (a) Stepien, M.; Latos-Grazynski, L. *Chem. Eur. J.* **2001**, *7*, 5113. (b) Szymanski, J. T.; Lash, T. D. *Tetrahedron Lett.* **2003**, *44*, 8613.

(12) For related organometallic derivatives, see: (a) Liu, D.; Lash, T. D. *Chem. Commun.* **2002**, 2426. (b) Venkatraman, S.; Anand, V. G.; Pushpan, S. K.; Sankar, J.; Chandrashekar, T. K. *Chem. Commun.* **2002**, 462.

(13) Muckey, M. A.; Szczepura, L. F.; Ferrence, G. M.; Lash, T. D. *Inorg. Chem.* **2002**, *41*, 4840.

(14) First disclosure of the synthesis of silver(III) carbaporphyrin **6a**: Lash, T. D. *Book of Abstracts*, 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; Abstract MP-2.

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

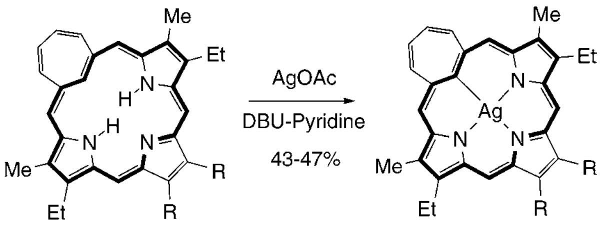
(16) (a) Scheidt, W. R.; Mondal, J. U.; Eigenbrot, C. W.; Adler, A.; Radonovich, L. J.; Hoard, J. L. *Inorg. Chem.* **1986**, *25*, 795. (b) Kadish, K. M.; Lin, X. Q.; Ding, J. Q.; Wu, Y. T.; Araullo, C. *Inorg. Chem.* **1986**, *25*, 3236.

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

(18) Szczepura, L. F.; Colby, D. A.; Lash, T. D. Unpublished work.

Tropiporphyrins **10** can be prepared using the "3 + 1" methodology from 1,3,5-cycloheptatriene-1,6-dicarbaldehyde.[20] This system shows a strong ring current where the interior CH resonates upfield near −7 ppm. However, the *meso*-protons for **10** show up at 8.0 and 9.2 ppm, values that are significantly upfield compared to carbaporphyrins **5**, and this suggests that the geometry of the cycloheptatriene ring significantly distorts the macrocycle and decreases the diatropicity of the tropiporphyrin system.[20a] Tropiporphyrins gave good yields of silver(III) derivatives **11** under basic conditions (DBU in pyridine), and the chelates gave green-colored solutions with weak Soret bands near 440 nm (Scheme 2). The *meso*-protons in the proton NMR spectra for **11** resonated at approximately the same values as those noted for the **10**, indicating that the diatropicity for the silver derivatives was comparable to the corresponding free base structures. However, the cycloheptatrienyl protons are shifted significantly downfield. In **10a**, these protons produce two multiplets at 5.5 and 6.6 ppm, but the related silver(III) derivative **11a** affords the corresponding resonances at 6.9 and 7.2 ppm. These shifts are attributed to a significant change in the conformation for the seven-membered ring on chelation of the silver(III) cation.

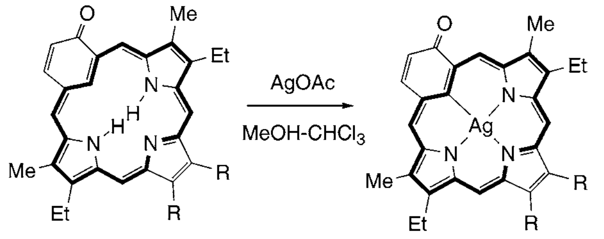
Scheme 2



10 Tropiporphyrin a. R = Et; b. R = Ph **11**

Oxybenziporphyrin **12a**,[21] the first reported example of an aromatic carbaporphyrinoid, has previously been shown to give palladium(II) organometallic derivatives.[22] Under mild conditions, **12a** reacted with excess silver(I) acetate to afford the silver(III) complex **13a** in virtually quantitative yields (Scheme 3). This complex was relatively insoluble in chloroform but gave green solutions and showed a Soret band at 458 nm. The proton NMR spectrum for **13a** in d_4-methanol−CDCl$_3$ showed a strong ring current effect that was comparable to the free base **12a**, and the *meso*-protons resonated downfield as four singlets at 8.69, 9.10, 9.13, and 10.23 ppm (this compares to values of 8.85, 8.98, 8.99, and 10.29 for **12a**[21a,b]). The external protons on the six-membered ring afforded two 1H doublets at 7.32 and 8.44 ppm, compared to values of 7.35 and 8.49 in **12a**.[21a,b] The metalloporphyrinoid methyl groups of **13a** resonated at 3.10 and 3.31 ppm, whereas **12a** gave these resonances at 3.29 and 3.65 ppm. Taken together, the data indicate that the metallo-derivative has slightly diminished diatropic character compared to the free base oxybenziporphyrin. As was the case for all of the silver complexes, the structure of the metalated carbaporphyrinoid was confirmed by mass spectrometry. The molecular ion region for the EI MS showed two peaks with similar intensities at *m/z* 581 and 583 corresponding to the expected ^{107}Ag and ^{109}Ag isotopes (natural abundances of 51.8 and 48.2%, respectively). The related diphenyloxybenziporphyrin **12b** similarly afforded the silver(III) derivative **13b** in >90% yield.

Scheme 3



12 Oxybenziporphyrin a. R = Et; b. R = Ph **13**

Recently, we have shown that 4-methoxy-1,3-naphthalenedicarbaldehyde (**14**) undergoes a "3 + 1" condensation with tripyrrane **15** under standard conditions to give oxynaphthiporphyrin **16** (Scheme 4).[23,24] This new porphyrin analogue system is similar to oxybenziporphyrin **12** but exhibits a slightly enhanced diatropic ring current. The proton NMR spectrum for **16** shows the interior CH at −7.42 ppm (compared to −7.17 ppm for **12**[21]), while the exterior *meso*-protons afford four 1H singlets at 9.27, 9.33, 9.94, and 10.65 ppm. The benzo unit in **16** also gave rise to a series of 1H resonances at 7.73 (t), 7.96 (dt), 8.92 (dd), and 8.96 ppm (d). The free base **16** gives a porphyrin-like UV−vis spectrum and, like **12**, shows two Soret bands (λ_{max} (log ϵ): 431 (5.29) and 450 nm (4.96)) and a series of four Q-bands (λ_{max} 539, 581, 622, and 687 nm) through the visible region. The IR spectrum for **16** (KBr) showed a strong absorption at 1630 cm^{-1}, confirming the presence of a cross-conjugated carbonyl unit. Oxynaphthiporphyrin **16** reacts with AgOAc in methanol−chloroform at room temperature to give the silver complex **17** in excellent yields (Scheme 4). The UV−vis spectrum gave a single Soret band at 456 nm and several ill-defined Q-bands between 500 and 630 nm. The proton NMR spectrum for **17** in CDCl$_3$ showed a decreased ring current compared to **16**, where the exterior *meso*-protons resonated at 8.89, 9.06, 9.14, and 9.90 ppm. This decreased

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(19) Lash, T. D.; Colby, D. A.; Muckey, M. A.; Liu, D.; Ferrence, G. M. *Book of Abstracts*, 225th National Meeting of the American Chemical Society, New Orleans, LA, March, 2003; Abstract INOR 672.

(20) (a) Lash, T. D.; Chaney, S. T. *Tetrahedron Lett.* **1996**, *37*, 8825. (b) Lash, T. D. *Chem. Eur. J.* **1996**, *2*, 1197.

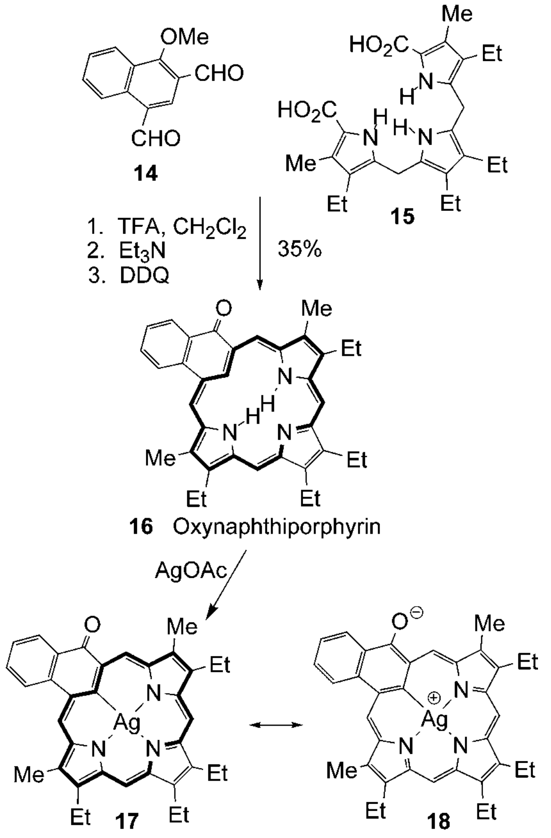
(21) (a) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533. (b) Lash, T. D.; Chaney, S. T.; Richter, D. T. *J. Org. Chem.* **1998**, *63*, 9076. (c) Richter, D. T.; Lash, T. D. *Tetrahedron* **2001**, *57*, 3659. See also: Lash, T. D.; Chaney, S. T. *Chem. Eur. J.* **1996**, *2*, 944.

(22) Stepien, M.; Latos-Grazynski, L.; Lash, T. D.; Szterenberg, L. *Inorg. Chem.* **2001**, *40*, 6892.

(23) Rasmussen, J. M.; Lash, T. D. *Book of Abstracts*, 224th National Meeting of the American Chemical Society, Boston, MA, August, 2002; Abstract CHED 202.

(24) Methyl ether spontaneously cleaves under the reaction conditions. This is in contrast to the behavior of closely related dimethoxybenziporphyrins, which only undergo demethylation in the presence of BBr$_3$ or refluxing HBr−AcOH.[21c]

Scheme 4



diatropic character is also evident from the effects on the peripheral substituents. For instance, the methyl substituents gave rise to two 3H singlets at 2.98 and 3.33 ppm, compared to values of 3.40 and 3.57 in the proton NMR spectrum of **16**. In this system, metalation has a significantly larger effect on the ring current than was the case for the oxybenziporphyrin derivatives possibly due to an increased contribution from canonical forms such as **18**. Silver complex **17** was sufficiently soluble in $CDCl_3$ to give a carbon-13 NMR spectrum. The carbonyl moiety was observed at 191.6 ppm, while the *meso*-carbons gave four separate resonances at 95.8, 95.9, 107.5, and 109.9 ppm. This compares to values of 187.3, 94.2, 94.6, 103.0, and 104.9 ppm, respectively, for the corresponding carbon-13 resonances of the free base oxynaphthiporphyrin **16** in $CDCl_3$. The IR spectrum (KBr) for **17** showed two strong bands at 1642 and 1619 cm^{-1}, in place of the peak at 1630 cm^{-1} that had been observed for **16**. However, the origins of these bands remain to be determined.

Although not every carbaporphyrinoid system can give silver organometallic derivatives, diverse systems with a CH−NH−N−NH macrocyclic core afford stable silver(III) complexes in good to excellent yields. This appears to be a general feature for these macrocycles rather than a special property for N-confused porphyrins and benzocarbaporphyrins. The ability of these important porphyrin analogue systems to stabilize the silver(III) oxidation state suggests that other unusual metalation reactions are likely to be achievable. Now that more direct routes for carbaporphyrinoid syntheses are available,[9,11] these metalation reactions may lead to the development of new catalytic systems.

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Supporting Information Available: Experimental procedures for selected compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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