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Silver(III) Carbaporphyrins: The First Organometallic Complexes of True Carbaporphyrins[†]

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Reaction of carbaporphyrins **1** with silver(I) acetate in methanol–CH_2Cl_2 gave excellent yields of the related silver(III) complexes **6**. These nonpolar organometallic compounds retain fully aromatic properties as judged by UV–vis and NMR spectroscopy and were further characterized by X-ray crystallography and cyclic voltammetry.

Carbaporphyrins (e.g., **1**) are porphyrin-like systems where one or more of the pyrrolic nitrogens have been replaced by carbon atoms.[1−3] In the case of monocarbaporphyrins **1**, the inner macrocyclic cavity contains a CH, two pyrrole type NH's, and a pyrroline nitrogen atom. Similar CNNN coordination centers are found in N-confused porphyrins,[4] benziporphyrins,[5] tropiporphyrins,[6] and azuliporphyrins.[7] Although the formation of organometallic derivatives for N-confused porphyrins has been well established,[4a,8−10] the synthesis of stable organometallic derivatives for benziporphyrins[11] and azuliporphyrins[12] has been accomplished only very recently. The organometallic chemistry of these systems has captured a great deal of interest[13] due to the possibilities of stabilizing unusual oxidation states and producing novel catalytic systems. N-Confused porphyrins show the ability to act as both dianionic ligands (coordination to nickel(II), palladium(II), etc., to give chelates of structural type **2**)[4a,8,9] and trianionic ligands.[10] Azuliporphyrins show a similar ability to act as dianionic ligands and indeed form stable Ni(II) and Pd(II) complexes **3** under mild conditions.[12] However, up to this point true carbaporphyrins (e.g., **1**) have failed to produce metallo derivatives. Attempts to react **1a** with the salts of many transition block elements have previously failed to produce metalloporphyrinoid products, although carbaporphyrins **1** reacted with ferric chloride in refluxing alcohol−chloroform mixtures to afford the unusual benzo[18]annulene ketals **4** in high yields (Chart 1).[14] Carbaporphyrins have three internal hydrogen atoms, but divalent metal cations can effectively replace only two protons upon forming a neutral complex. In N-confused porphyrins the extra proton can be relocated onto the external nitrogen atom,[4a] while the macrocyclic cavity of azuliporphyrins starts off with only two inner hydrogen atoms.[7,12] In order to form neutral organometallic derivatives of **1**, it would be necessary to introduce a trivalent metal cation. Recently, Furuta reported that tetraphenyl N-confused porphyrin reacts with silver(I) trifluoroacetate to afford the silver(III) derivative **5**, thereby demonstrating that the N-confused porphyrins can act as trivalent as well as divalent ligands.[10] We now report that this type of chemistry also occurs for carbaporphyrins and that the carbaporphyrin

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[†] Part 22 of the series Conjugated Macrocycles Related to the Porphyrins. Part 21: Reference 1.

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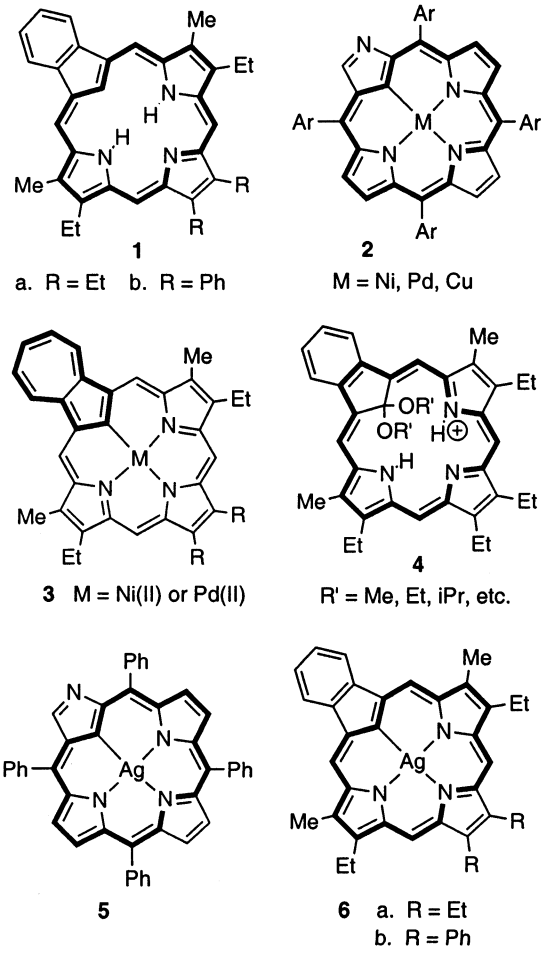
Chart 1



nucleus can parallel the trianionic chemistry exhibited by N-confused porphyrins.

Initial attempts to react carbaporphyrin **1a** with silver(I) trifluoroacetate were unsuccessful. However, reaction of **1a** with silver(I) acetate in methanol−dichloromethane at room temperature afforded good yields (>80%) of a metallo derivative **6a** (Chart 1). Presumably the more basic acetate anion aids in the metalation process by deprotonating an NH unit. The complex proved to be very nonpolar in comparison to the parent ligand and eluted from a grade III alumina column with dichloromethane as a deep orange colored fraction. The UV-vis spectrum shows a strong Soret band at 437 nm and a series of weaker bands at 482, 518, 555, and 593 nm. The proton NMR spectrum of the sparingly soluble complex also confirmed porphyrin-like character showing the *meso*-protons downfield at 9.89 and 10.06 ppm due to a strong diatropic ring current. The structure was confirmed by high-resolution EI MS and combustion analysis. The presence of the two silver isotopes (^{107}Ag and ^{109}Ag) in roughly equal abundance provided an additional vivid confirmation of the proposed structure by producing two molecular ions at m/z 603 and 605.

Diphenylcarbaporphyrin **1b** was also reacted with silver(I) acetate to give the related complex **6b**. The UV−vis spectrum was slightly modified compared to **6a**, showing the Soret band red shifted to 441 nm, and the proton NMR spectrum again demonstrated the presence of a powerful diatropic ring current. Silver complex **6b** was further characterized by MS and combustion analysis and proved to be sufficiently soluble to run a carbon-13 NMR spectrum. Due to the plane of symmetry, 16 sp^2 and 3 sp^3 carbon resonances are to be expected in addition to the Ag−C unit. All 19 of these resonances were observed, and, of particular note, the *meso*-carbons appeared at 100.4 and 101.2 ppm. Unfortunately, the sample was still insufficiently soluble to allow the internal carbon atom to be identified. This carbon should be coupled to the two different silver isotopes (both spin $I = {}^1/_2$) to give two doublets. Although the equivalent carbon could be located for the N-confused chelate **5** at 138.97 ppm,[10] the internal carbons for a related Ag(III) doubly confused porphyrin were not observed.[15]

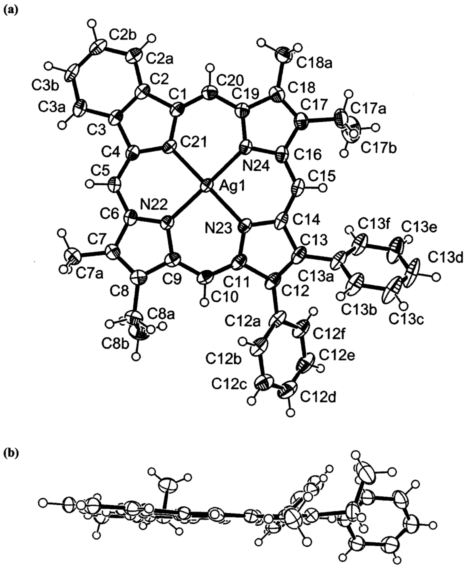


Figure 1. (a) Aerial view ORTEP drawing (50% probability level) of **6b**, with hydrogen atoms drawn arbitrarily small. Selected bond lengths (Å) and angles (deg): Ag(1)−C(21) 2.015(4), Ag(1)−N(22) 2.038(4), Ag(1)−N(23) 2.084(4), Ag(1)−N(24) 2.046(4), C(1)−C(21) 1.414(6), C(4)−C(21) 1.405(6); C(1)−C(21)−C(4) 110.9(4), C(1)−C(21)−Ag(1) 124.6(3), C(4)−C(21)−Ag(1) 124.4(3), C(21)−Ag(1)−N(23) 179.2(2), C(21)−Ag(1)−N(24) 89.3(2), N(22)−Ag(1)−N(24) 178.7(2), N(22)−Ag(1)−C(21) 89.6(2). (b) Edge view ORTEP drawing of **6b**.

Dark purple single-crystal prisms of **6b** were grown by diffusion of methanol into a $CHCl_3$ solution, and the molecular structure was confirmed by X-ray crystallographic analysis (Figure 1).[16] The presence of 0.5 $CHCl_3$ molecule per carbaporphyrin within the crystal lattice is consistent with the combustion analysis data. The silver ion fits into the macrocyclic cavity extremely well as illustrated by the complex's strikingly planar geometry that displays only a minor tilting of 5.09° for the indene unit relative to the mean macrocyclic plane. The metal is centered between the donor

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(16) Crystal data for **10b**: $C_{43}H_{34}AgN_3 \cdot 0.5CHCl_3$, $M = 760.3$, triclinic space group $P\bar{1}$ (No. 2), $D_c = 1.486$ g cm^{-3}, $Z = 4$, $a = 8.8529(5)$ Å, $b = 12.3329(8)$ Å, $c = 16.8933(10)$ Å, $\alpha = 100.043(1)°$, $\beta = 101.405(1)°$, $\gamma = 104.638(1)°$, $V = 1699.7(2)$ Å^3, $T = 193$ K, μ(Mo Kα) = 0.748 mm^{-1}, 10051 reflections measured, 6839 unique, final R1 = 0.046, wR2(F^2) = 0.109 for 451 parameters and 5453 data with $F_o^2 > 2\sigma(F_o^2)$.

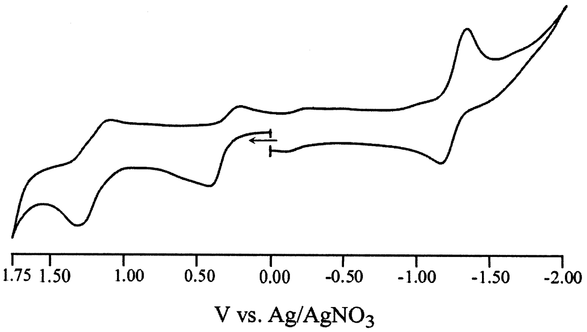

Figure 2. Cyclic voltammogram of silver complex **6b** in anhydrous CH_2Cl_2 solution, under Ar, 200 mV s^{-1} scan rate, Bu_4NBF_4 (0.2 M) supporting electrolyte, Pt working electrode, $Ag/AgNO_3$ (0.01 M) reference electrode.

ligands with equivalent *trans*-Ag−N, 2.038(4) and 2.046(4) Å bond lengths, and a slightly distended *cis*-Ag(1)−N(23) bond length of 2.084(4) Å. The latter may be explained by the *trans* effect of the more Lewis basic alkenyl, C(21), donor. The shorter Ag(1)−C(21) bond length of 2.015(4) Å is consistent with the smaller covalent bonding radius of the carbon compared to nitrogen and compares favorably with the carbon−silver bond length, 2.04(2) Å, reported by Furuta for **5**.[10]

In order to provide further evidence for the assignment of **6** as silver(III) complexes, electrochemical studies were also performed. The cyclic voltammogram (Figure 2) of complex **6b** shows one quasi-reductive couple at $E_{1/2} = -1.24$ V. This wave displays some features (much smaller waves on either side of the main peak) that indicate that it is not a simple redox couple. However, it is similar to the reductive couple observed for complex **5** by Furuta et al.[10] which also has some complicating features. Silver(III) doubly confused porphyrin,[15] silver(III) complex **5**, and Ag^{III}OEP all display a reductive couple at a potential between the first reductive wave and the first oxidative wave of the free base porphyrin, whereas Ag(II) porphyrin complexes display a reversible oxidative couple in this same region.[17] In the cyclic voltammogram of **6b**, we observe a quasi-reversible *reductive* wave ($E_{1/2} = -1.24$ V), assigned to the Ag(III/II) couple, between the first reductive wave ($E_{1/2} = -1.58$ V) and the first oxidative wave ($E_{p,a} = 0.52$ V) of the free base carbaporphyrin. The presence of this reductive wave suggests that the silver ion is in the Ag^{3+} oxidation state.

The mechanism by which the silver(I) cation inserts into the macrocycle and oxidizes to the silver(III) level is not known. An excess of AgOAc was generally used in these experiments, but the same results were obtained irrespective of whether the reaction was carried out open to atmospheric oxygen or under an inert nitrogen atmosphere. We speculate that the electrophilic Ag^+ cation is initially incorporated and subsequent reductive elimination of hydrogen occurs to give the Ag(III) derivative. The small scales used for these reactions will most likely not allow the detection of H_2, and further studies will be required to provide evidence for this proposal.

Carbaporphyrins and azuliporphyrins have complementary coordination chemistry that together is comparable to the two main coordination motifs exhibited by the N-confused porphyrins. Hence, the organometallic chemistry of the carbaporphyrinoid systems appears to have an exciting future.

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Supporting Information Available: Experimental details; UV−vis, NMR, and EI mass spectra of **6a**,**b**; a structure report for **6b**; and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Complete X-ray structural data will be deposited at the Cambridge Crystallographic Data Center CCDC No. 179075. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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