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Aromatic and Antiaromatic Gold(III) Hexaphyrins with Multiple Gold−Carbon Bonds

Shigeki Mori and Atsuhiro Osuka*

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Received March 15, 2005; E-mail: osuka@kuchem.kyoto-u.ac.jp

Porphyrin with an 18π-electronic aromatic network is an ubiquitous active component of many naturally occurring pigments that has been extensively studied for more than a century. In recent years, expanded porphyrins that are homologues of porphyrin have emerged as a new class of conjugated pyrrolic macrocycles because of their intriguing optical, electrochemical, and coordination properties that are difficult to find in porphyrins.[1] Expanded porphyrins are also interesting from the viewpoint of the annulene chemistry, since the number of π electrons in the conjugated circuit usually determines the aromaticity of the macrocycles. Among these, *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) **1**[2] is an attractive aromatic molecule in light of its planar and rectangular shape and strong aromaticity with a 26π conjugated circuit. In addition, two inverted pyrroles in **1** are particularly intriguing in view of C−H bond activation, as judged from the recent reports on the formation of organometallic species during the metalations of N-confused porphyrins (NCP),[3] carbaporphyrinoids,[4] and benziporphyrins.[5] A square planar arrangement of the internal two pyrrolic nitrogens and two β-carbons of the inverted pyrroles encourages its potential as an effective ligand with twin CCNN cores such as doubly N-confused porphyrins (N_2CP).[6] Such metalation of **1** is quite attractive but, to the best of our knowledge, has not been achieved thus far.[7]

In this communication, we report Au(III) metalation of [26]-hexaphyrin **1**. A solution of **1** and 10 equiv of $NaAuCl_4$ in a 4:1 mixture of CH_2Cl_2 and methanol was stirred in the presence of sodium acetate at room temperature for 3 days. Separation over a silica gel column provided mono-Au(III) complex **2** and bis-Au(III) complex **3** in 16 and 14% yields, respectively, along with recovery of **1** (15%). Au(III) metalation proceeded slowly, but either longer reaction time or higher reaction temperature decreased yields of **2** and **3** with concomitant increase of byproducts. Positive-mode high-resolution electrospray ionization mass spectroscopy (HR-ESI-TOF-MS) revealed the molecular weights of **2** and **3** at m/z = 1655.0290 and 1848.9744; calcd for $C_{66}H_{12}F_{30}N_6Au$, 1655.0304 ($[M + H]^+$), and for $C_{66}H_9F_{30}N_6Au_2$, 1848.9735 ($[M + H]^+$), respectively. Structures of **2** and **3** have been revealed by single-crystal X-ray diffraction analysis (Figure 1).[8,9] Curiously, in both cases, the inner β-protons are activated to form Au−C bonds, and Au(III) ions are coordinated similarly with two pyrrolic nitrogen atoms and two pyrrolic β-carbon atoms within a flat [26]hexaphyrin macrocycle. Au−N bond lengths are 2.081(6) and 2.085(6) Å and Au−C bond lengths are 1.976(8) and 2.012(8) Å in **2** and Au−N bond lengths are 2.099(6), 2.100(5), 2.105(6), and 2.113(6) Å, and Au−C bond lengths are 2.011(6), 2.018(7), 2.025(7), and 2.037(6) Å in **3**. The mono-Au(III) complex **2** exhibits a planar but twisted structure with a large mean plane deviation of 0.520 Å. Deviation from planarity is larger in the free base part compared with the Au(III) complexed part, which is attributable to the steric congestion between the inner pyrrolic β-protons. Thus, the complex **3** takes a more planar but overall bent structure, since bis Au(III) metalation eliminates such steric congestion.

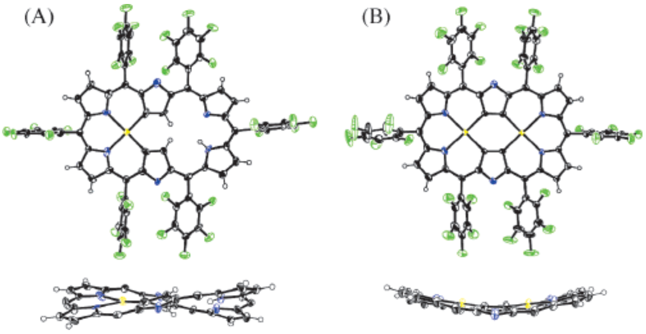
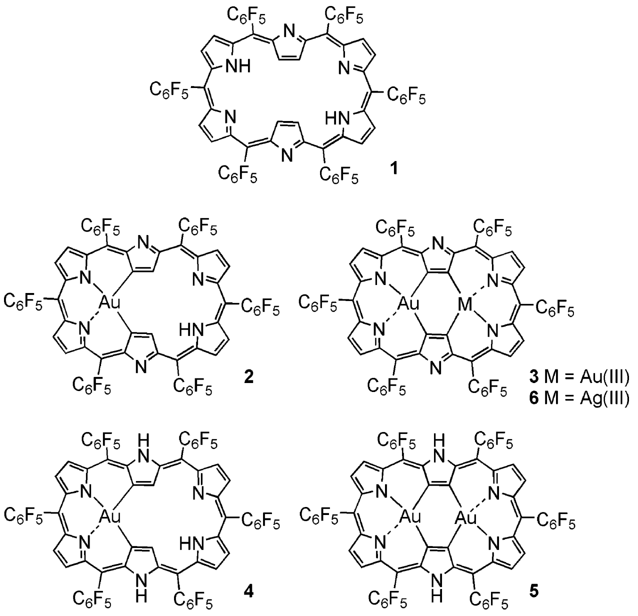


Figure 1. X-ray crystal structures of **2** (A) and **3** (B). The thermal ellipsoids are scaled to the 50% probability level. In side views, *meso*-pentafluorophenyl substituents are omitted for clarity.

Chart 1. Structures of Hexaphyrins Studied in This Contribution



Diatropic ring currents of the [26]hexaphyrins **2** and **3** are evident from their ^1H NMR spectra, in which the outer β-protons appear in a downfield region at 9.51, 9.36, 9.35, and 9.03 ppm, and the inner β-protons and inner NH protons appear in an upfield region at −2.93 and −2.08 ppm in **2**, and the outer β-protons appear at 9.66 and 9.51 ppm in **3**. These data indicate that **2** and **3** retain strong aromaticity like that of **1**. The absorption spectra of **2** and **3** both show strong Soret-like bands and small Q-band-like bands, indicating their aromatic nature. Both the Soret-like bands and Q-band-like (0,0) bands are red-shifted in order of **1** < **2** < **3** (Figure 2).

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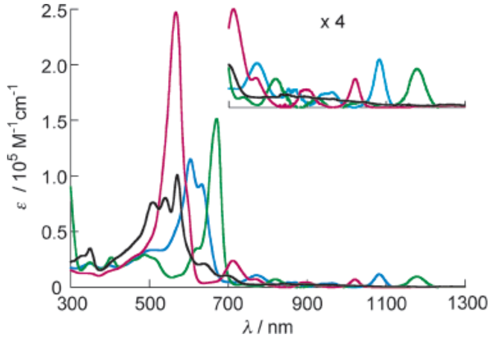

Figure 2. Absorption spectra of **1** (red), **2** (blue), **3** (green), and **5** (black) in CH_2Cl_2.

In the next step, **2** and **3** were reduced with $NaBH_4$ to give complexes **4** and **5** both in quantitative yields without demetalation, indicating inertness of the Au−C bonds and coordinated Au(III) ion under the reduction conditions. The complexes **4** and **5** show respectively the parent ion peaks at $m/z = 1655.0322$, calcd for $C_{66}H_{12}F_{30}N_6Au$ ($[M - H]^-$), 1655.0315; and at $m/z = 1848.9763$, calcd for $C_{66}H_9F_{30}N_6Au_2$ ($[M - H]^-$), 1848.9746. Both **4** and **5** exhibit the absorption spectra consisting of ill-defined Soret-like bands without Q-band-like bands, indicating nonaromaticity (Figure 2 and Supporting Information, SI). Consistent with the Hückel's rule, the ^1H NMR spectrum of the [28]hexaphyrin **4** reveals a paratropic ring current, exhibiting the inner β-protons and NH proton at 19.39 and 24.57 ppm, while exhibiting the outer β-protons as four doublets at 5.02, 4.92, 4.32, and 4.07 ppm and the outer NH protons at 4.10 ppm. Similarly, the ^1H NMR spectrum of **5** exhibits the outer β-protons as a pair of doublets at 3.16 and 3.10 ppm and the outer NH protons as a broad singlet at 1.81 ppm, respectively. These data clearly indicate the antiaromatic nature for **4** and **5**. Of particular interest is a large change in the chemical shift of the inner β-proton of **4** upon aromatic-to-antiaromatic switch, which reaches a large $\Delta\delta$ value of 22.32 ppm. As such, the realization of a stable antiaromatic conjugated system underscores an important difference between porphyrin and expanded porphyrins, since stable antiaromatic porphyrin has been unknown so far. Even for expanded porphyrins, only a few stable antiaromatic examples were reported in the literature.[10] In the present case, the enforced planarity caused by the Au(III)-metalation plays an important role for strong antiaromaticity of **4** and **5**.

The complex **2** still possesses a rigid N_2CP-type vacant cavity that may be used for metalation of a different metal ion. This possibility was tested by treating a solution of **2** in CH_2Cl_2 with 10 equiv of CF_3COOAg in the presence of sodium acetate at room temperature for 12 h, which gave Au(III)−Ag(III) mixed metalated complex **6** in 58% yield. The complex **6** exhibits the parent ion peak at $m/z = 1760.9174$, calcd for $C_{66}H_9F_{30}N_6AuAg$ ($[M + H]^+$), 1760.9132. The absorption spectrum of **6** is similar to those of **2** and **3** (SI), except for split Soret-like bands at 654 and 672 nm. The ^1H NMR spectrum of the diamagnetic complex **6** exhibits four sharp doublets at 9.76, 9.63, 9.60, and 9.51 ppm due to the outer β-protons, showing that the complex **6** is an aromatic Ag(III) organometallic derivative, as have been reported for modified porphyrinoid macrocycles including NCP, carbaporphyrinoids, and benziporphyrins.[3−6] Thus, it is concluded that the CCNN core in **2** serves as a trianionic ligand also for Ag ion.

The electrochemical properties were studied by cyclic voltammetry in CH_2Cl_2 versus Fc/Fc ion using tetrabutylammonium tetrafluoroborate as an electrolyte. The [26]hexaphyrin **1** undergoes two reversible one-electron reductions at −0.52 and −0.85 V, and the complexes **2** and **3** undergo two one-electron reductions at −0.41 and −0.80 V, and −0.33 and −0.71 V, respectively. These data indicate that the Au(III) metalation lowers the energy level of the LUMO orbital of hexaphyrin. The mixed complex **6** exhibits reduction waves at −0.35 and −0.72 V, which are similar to those of **3**. On the other hand, the [28]hexaphyrins **4** and **5** undergo oxidations at −0.05 and 0.30 V and at −0.03 and 0.35 V, respectively.

In summary, Au(III) metalation of **1** led to the formation of all-in-plane Au(III) complexes **2** and **3** via the C−H bond activation of the inner β-protons. Two-electron reduction of the aromatic complexes **2** and **3** provided the antiaromatic complexes **4** and **5** that exhibit distinct paratropic ring currents. The complex **2** serves as a nice platform for construction of a mixed bis-metal complex. Our efforts are directed toward this possibility using a variety of transition metals.

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Supporting Information Available: Synthetic procedures and spectral data of complexes **2**−**6** including absorption spectra, high-resolution ESI-TOF mass spectra, and ^1H NMR spectra. CIF files for the X-ray structural analysis for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystallographic data of **2**: $C_{66}H_{11}N_6F_{30}Au$, $M_w = 1654.77$, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.427(6)$ Å, $b = 24.541(15)$ Å, $c = 19.626(11)$ Å, $\beta = 90.29(2)°$, $V = 5504(5)$ Å^3, $D_c = 1.997$ g/cm^3, $Z = 4$, $R = 0.0526$, wR$_2$ (all data) $= 0.0976$, GOF $= 0.784$ ($I > 2.0\sigma(I)$).

(9) Crystallographic data of **3**: $C_{74}H_8N_6F_{30}Au_2Cl_2$, $M_w = 2015.70$, orthorhombic, space group *Pbca* (No. 61), $a = 17.983(7)$ Å, $b = 26.930(10)$ Å, $c = 28.196(10)$ Å, $V = 13654(9)$ Å^3, $D_c = 1.961$ g/cm^3, $Z = 8$, $R = 0.0507$, wR$_2$ (all data) $= 0.1451$, GOF $= 1.081$ ($I > 2.0\sigma(I)$).

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