# Heterobismetal Complexes of [26]Hexaphyrin(1.1.1.1.1.1)

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Au$^{III}$Cu$^{III}$ and Au$^{III}$Rh$^I$ heterobismetal complexes of *meso*-aryl-substituted [26]hexaphyrin were rationally prepared from a monometal Au$^{III}$ complex. The Au$^{III}$Cu$^{III}$ complex is an aromatic molecule with a rectangular shape, while Au$^{III}$Rh$^I$ complexes are out-of-plane macrocycles, being either aromatic or antiaromatic depending upon the number of conjugated $\pi$ electrons. The 26$\pi$ Au$^{III}$Rh$^I$ complex was converted into an aromatic and planar 26$\pi$ Au$^{III}$Rh$^{III}$ complex via double C–H bond activation upon refluxing in pyridine.

Considerable attention has been paid to expanded porphyrins consisting of more than five pyrrolic units because of their attractive optical, electrochemical, and coordination properties.[1] Expanded porphyrins are particularly promising in metal coordination chemistry in light of their large and flexible macrocycles, versatile oxidation states, and multiple coordinating sites.[2] Our serendipitous finding of the facile one-pot synthesis of *meso*-aryl-substituted expanded porphyrins[3] triggered our studies on their metalation behaviors.[4,5] In these studies, *meso*-hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (**1**), first reported by Cavaleiro et al.,[6] possesses an important position because of its versatile metalation abilities, providing various metal complexes including homobismetal complexes.[5] However,

**Chart 1**
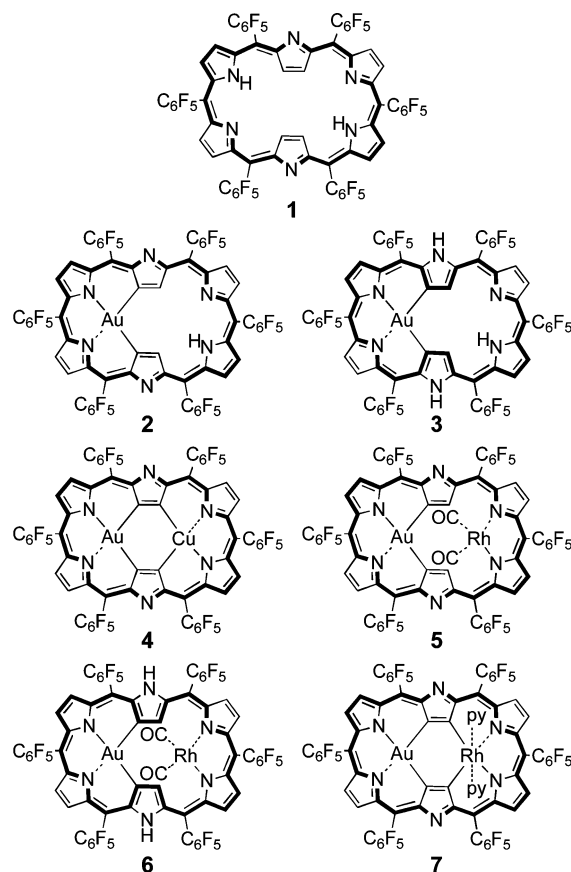


there has been no rational synthetic route to the heterobismetal complex so far. In this respect, monometal Au$^{III}$ complex **2** prepared by Au$^{III}$ metalation of **1** (Chart 1) is promising in terms of its preorganized vacant NNCC cavity,

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which would be used for coordination of a different metal ion. Analogous metalation behaviors involving C−H bond activation have been extensively explored for N-confused porphyrins,[7] carbaporphyrinoids,[8] and benziporphyrins.[9] The framework of mono- and bismetal $Au^{III}$ is also a useful platform for studies on aromatic−antiaromatic switching owing to their robust structures and facile redox reactivities via uptake and release of a pair of NH hydrogen atoms.[5d,e]

So far, only Au and Ag ions have been shown to be coordinated to the hexaphyrin NNCC cavity via double C−H bond activation.[5d] To extend this chemistry, we examined the metalation of **2** with $Mn^{III}$, $Fe^{II}$, $Fe^{III}$, $Ru^{II}$, $Ni^{II}$, $Pd^{II}$, and $Pt^{II}$ ions, but all of these attempts were unsuccessful. To our delight, however, we found that $Cu^{II}$ and $Rh^{I}$ ions are effectively coordinated into the NNCC cavity of **2**.

The reaction of **2** with $Cu(OAc)_2$ in a 4:1 mixture of $CH_2Cl_2$ and methanol in the presence of NaOAc for 10 h afforded $Au^{III}Cu^{III}$ complex **4** quantitatively after purification over a short silica gel column. The high-resolution electro-spray-ionization time-of-flight (HR-ESI-TOF) mass spectrum of **4** indicated the parent ion peak. Found: $m/z$ 1714.9386 ($[M + H]^+$). Calcd for $C_{66}H_9N_6F_{30}AuCu$: $m/z$ 1714.9366 (Supporting Information). The X-ray crystal analysis revealed a planar and rectangular framework for **4**, in which the Au atom is located within the NNCC pocket and the Cu atom is also bound to the other NNCC pocket in a square-planar fashion (Figure 1).[10] The bond lengths of Au−C are in the range of 1.940(9)−1.981(7) Å, those of Au−N are in the range of 2.013(8)−2.068(6) Å, those of Cu−C are in the range of 1.951(11)−2.010(20) Å, and those of Cu−N are in the range of 2.004(10)−2.040(20) Å (the two metal atoms are disordered). The $^1H$ NMR spectrum of **4** displayed four sharp doublets at 9.38, 9.33, 9.30, and 9.16 ppm due to the outer $\beta$ protons, indicating its diamagnetic nature and $Cu^{III}$ oxidation state. Interestingly, this result is in contrast to the metalation of **1** with a $Cu^{II}$ salt, which gave gable-shaped paramagnetic bismetal $Cu^{II}$ complexes with unique metal−metal interactions.[5a] The absorption spectrum of **4** features an intense Soret-like band at 670 nm and Q-like bands at 824, 937, 1036, and 1158 nm, which are similar to those of bismetal $Au^{III}$ complex,[5d] again indicating the aromaticity of **4**. An attempted reduction of **4** with $NaBH_4$ to provide its $28\pi$ hexaphyrin congener failed, merely giving demetalated monometal $28\pi$ $Au^{III}$ hexaphyrin complex **3**.
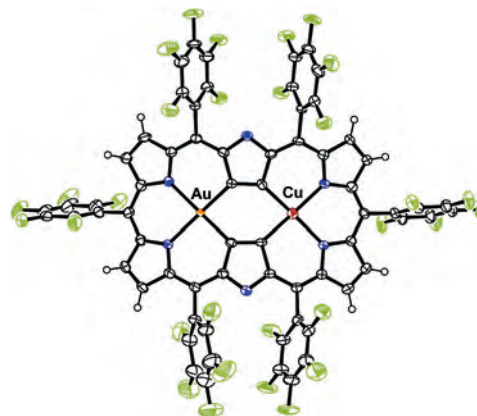


**Figure 1.** X-ray crystal structure of **4**. Thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

In next step, $Rh^{I}$ complexation of **2** was examined because $\eta^2$-type coordination of a dicarbonylrhodium(I) unit has been known for various porphyrinoids bearing a dipyrromethene moiety.[11,12] Metalation of **2** was conducted by treatment with $[RhCl(CO)_2]_2$ in the presence of NaOAc in $CH_2Cl_2$ to provide $Rh^{I}$ metal complexes depending upon the reaction conditions. Stirring the reaction mixture at 40 °C for 12 h gave $26\pi$ $Au^{III}Rh^{I}$ hexaphyrin complex **5** in 90% yield. Under mild conditions (at room temperature, 2 h), $28\pi$ $Au^{III}Rh^{I}$ hexaphyrin **6** became a major product (91%) along with **5** (2%).[13] HR-ESI-TOF mass analysis displayed the parent peaks $m/z$ 1812.9189 for **5** (calcd for $C_{68}H_{11}N_6F_{30}O_2AuRh$: $m/z$ 1812.9180 $[M + H]^+$) and $m/z$ 1813.9237 for **6** (calcd for $C_{68}H_{12}N_6F_{30}O_2AuRh$: $m/z$ 1813.9258 $[M]^+$). The solid-state structure of **5** determined by X-ray diffraction analysis revealed its out-of-plane structure (Figure 2).[14] The $Rh^{I}$ ion is bound in a square-planar coordination manner by the two N atoms of the dipyrromethene unit and the two carbonyl ligands, and the Rh−N lengths are 2.068(4) and 2.090(5) Å. In the $^1H$ NMR spectra, the outer $\beta$-proton signals appeared in the range of 9.76−8.79 ppm for **5** and 3.31−2.82 ppm for **6** and and the inner $\beta$-proton signals were observed at −2.96 ppm for **5** and at 29.17 ppm for **6**. The outer NH proton resonated at 1.17 ppm for **6**, which disappeared upon treatment with $D_2O$. These results clearly represent a diatropic ring current for **5** and a paratropic ring current for **6**. The UV/vis absorption spectra exhibited split Soret-like bands at 605 and 641 nm and Q-like bands at 779, 902, and 1014 nm for **5** and two absorption peaks at 518 and 625

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(10) Crystallographic data of **4**: $C_{66}H_8N_6F_{30}AuCu \cdot 0.83C_7H_8$, $M_w$ = 1791.78, monoclinic, $P2_1/c$ (No. 14), $a = 28.665(5)$ Å, $b = 7.5735(19)$ Å, $c = 32.376(6)$ Å, $\beta = 114.843(6)°$, $V = 6378(2)$ Å$^3$, $D_c = 1.866$ g/cm$^3$, $Z = 4$, R1 = 0.0670 [$I > 2.0\sigma(I)$], wR2 = 0.1682 (all data), GOF = 1.099 [$I > 2.0\sigma(I)$]. Only one of two structures is drawn in the figure, although both metal atoms are disordered.

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(13) Although the mechanism of the high yield formation of **6** is not clear, the $Rh^{I}$ salt is likely to act as a reductant to **2**.

(14) Crystallographic data of **5**: $C_{68}H_{10}N_6F_{30}AuRh \cdot 2C_2H_3N$, $M_w$ = 1894.80, triclinic, $P\bar{1}$ (No. 2), $a = 15.110(4)$ Å, $b = 15.121(5)$ Å, $c = 15.498(5)$ Å, $\alpha = 88.653(13)°$, $\beta = 64.428(10)°$, $\gamma = 77.577(13)°$, $V = 3109.4(17)$ Å$^3$, $D_c = 2.024$ g/cm$^3$, $Z = 2$, R1 = 0.0464 [$I > 2.0\sigma(I)$], wR2 = 0.1196 (all data), GOF = 1.045 [$I > 2.0\sigma(I)$].
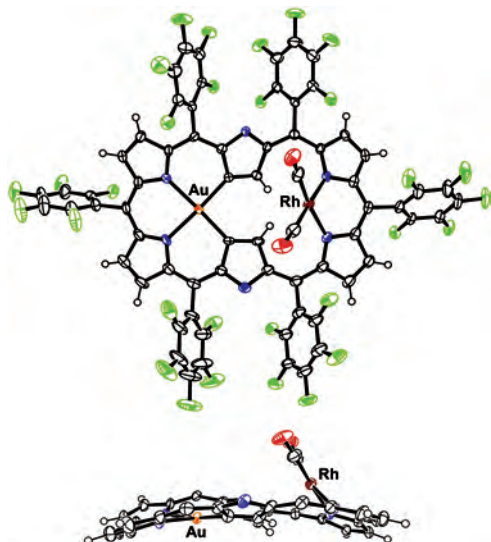
**Figure 2.** X-ray crystal structure of **5**. The thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

nm, and no absorption in the longer wavelength range was observed for **6** (Supporting Information), which is in line with the observations in the mono- and bismetal Au[III] complexes.[5d,f] The IR spectra indicated the stretching vibrations of C≡O at 2084 and 2023 cm$^{-1}$ for **5** and at 2080 and 2021 cm$^{-1}$ for **6**, which are comparable with those of dicarbonylrhodium(I) complexes of other porphyrinoids. Importantly, oxidation of **6** to **5**, an antiaromatic-to-aromatic conversion, proceeded smoothly and quantitatively with DDQ, but the reverse reduction failed despite many attempts. $NaBH_4$ reduction of **5** merely gave **3**.

Upon refluxing in pyridine, the Au[III]Rh[I] complex **5** was converted into Au[III]Rh[III] complex **7** in 25% yield along with the formation of **3**. The parent ion peak of **7** was detected by HR-ESI-TOF mass spectroscopy at *m/z* 1912.9921 ([M + H]$^{+}$) (calcd for $C_{76}H_{19}N_8F_{30}AuRh$: *m/z* 1912.9969). The $^1H$ NMR spectrum of **7** exhibited four doublets due to the outer $\beta$ protons in the range of 9.71−9.30 ppm and signals at 0.62, 4.17, and 5.34 ppm due to the ortho, meta, and para protons of the coordinated pyridine, respectively, hence indicating its strong diatropic ring current. The crystal structure of **7** was determined by X-ray diffraction analysis (Figure 3).[15] The coordination structural features around the Au[III] ion are similar to those of bis- and monometal Au[III] complexes of hexaphyrin. The Au−C bond lengths are 1.996(5) and 1.984(5) Å, and the Au−N bond lengths are 2.073(5) and 2.083(4) Å. The Rh[III] atom is coordinated in an octahedral geometry within the NNCC pocket and with the two coordinated pyridines located in the axial direction. The Rh−C bond lengths are 1.986(5) and 1.981(5) Å, the Rh−$N_{eq}$ bond lengths are 2.122(5) and 2.110(4) Å, and
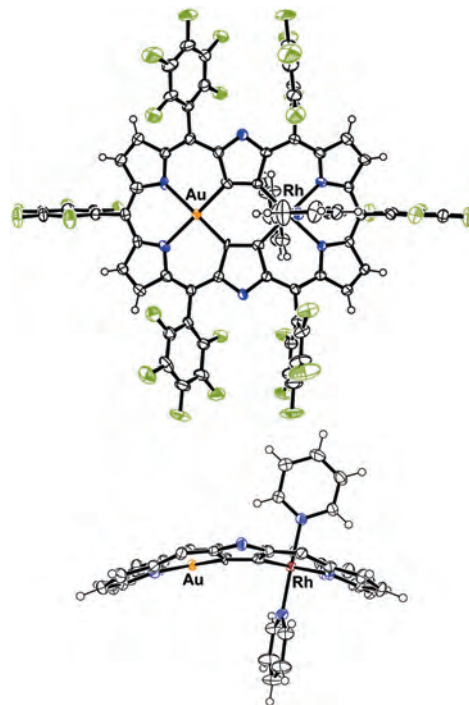


**Figure 3.** X-ray crystal structure of **7**. The thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

the Rh−$N_{ax}$ bond lengths are 2.044(5) and 2.054(5) Å. The absorption spectrum of **7** exhibited Soret-like bands at 520, 549, and 708 nm with a shoulder peak at 655 nm and several Q-like bands at 823, 915, and 1005 nm, in line with its aromaticity. To explore the antiaromatic Au[III]Rh[III] complex, the reduction of **7** was attempted with $NaBH_4$. Reduction of **7** actually proceeded to provide its reduction product, as revealed by thin-layer chromatography and $^1H$ NMR analysis, which however was found to be very unstable and readily oxidized back to **7** during workup.

In summary, the metalation of monometal Au[III] complex **2** with a Cu[II] salt led to the quantitative formation of the planar and rectangular Au[III]Cu[III] complex **4**, whereas the metalation with the dicarbonylrhodium(I) salt provided the out-of-plane $26\pi$ and $28\pi$ complexes **5** and **6**. Upon refluxing in pyridine, the complex **5** was converted into in-plane $26\pi$ Au[III]Rh[III] complex **7** via double C−H bond activation.

**Supporting Information Available:** Synthetic procedures, absorption spectra, HR-ESI-TOF mass spectra, and $^1H$, $^{13}C$, $^{19}F$, and $^{13}C-^1H$ COSY NMR spectra for **4**−**7**, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystallographic data of **7**: $C_{76}H_{18}N_8F_{30}AuRh \cdot 1.64C_6H_{14} \cdot 1.86CHCl_3$, $M_w = 2295.32$, triclinic, $P\bar{1}$ (No. 2), $a = 17.223(4)$ Å, $b = 17.784(7)$ Å, $c = 18.132(6)$ Å, $\alpha = 105.845(13)°$, $\beta = 107.214(10)°$, $\gamma = 111.214(10)°$, $V = 4457(2)$ Å$^3$, $D_c = 1.724$ g/cm$^3$, $Z = 2$, R1 = 0.0549 [$I > 2.0\sigma(I)$], wR2 = 0.1572 (all data), GOF = 1.063 [$I > 2.0\sigma(I)$].