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Selective Mono- and Bis-Au(III) Metalations of 5,10,15,20,25,30-Hexaaryl-[26]hexaphyrins(1.1.1.1.1.1)

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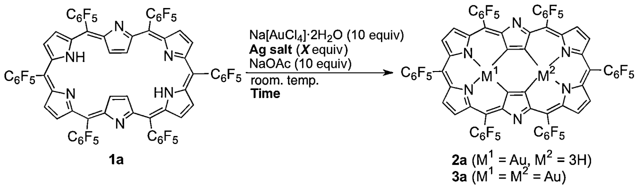
Selective mono- and bis-Au(III) metalations of [26]hexaphyrins(1.1.1.1.1.1) were achieved in a 4:1 mixture of CH_2Cl_2 and methanol by using $Na[AuCl_4]$ as a Au(III) ion source and Ag_3PO_4 and Ag_2CO_3 as Au(III)-activating reagents.



Scheme 1. Au(III) metalation of hexaphyrin **1a**.

Table 1. Effect of Ag salts on the metalation of hexaphyrin **1a**

Entry	Ag salt (*X*)	Time/h	Yield[a]/%		
			1a	**2a**	**3a**
1	none	72	15[b]	16[b]	14[b]
2	AgOTf (40)	1	15[b]	9[b]	39[b]
3	AgOTf (40)	24	—	—	35
4	$AgBF_4$ (40)	>72	—	—	22
5	$AgSbF_6$ (40)	72	—	—	15
6	$AgClO_4$ (40)	24	—	—	26
7	AgOAc (40)	24	77	—	—
8	Ag_2SO_4 (20)	72	—	—	7
9	Ag_2O (100)	72	6	—	—
10	Ag_3PO_4 (13.3)	24	3	34	6
11	Ag_2CO_3 (20)	24	32	trace	42

[a] ^1H NMR yields except for Entries 1 and 2. [b] Isolated yields.

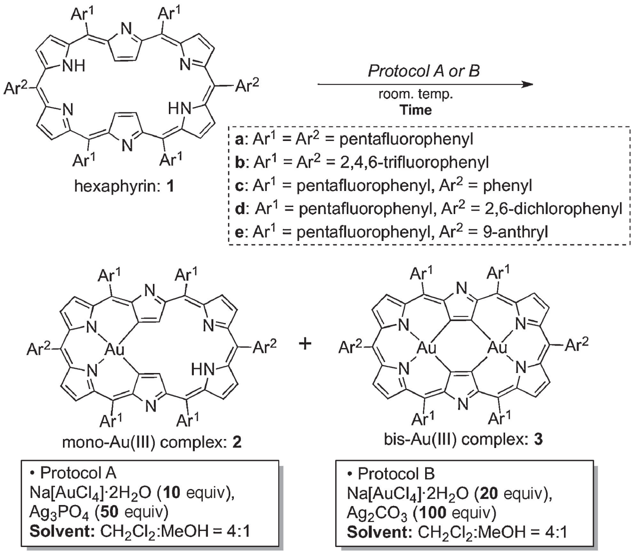
In recent years, the chemistry of expanded porphyrins has witnessed a considerable upsurge,[1] displaying their attractive properties such as multi-metal coordination,[2,3] anion sensing,[4] unprecedented skeletal rearrangements,[2b,2c,5] large nonlinear optical properties,[6] and versatile oxidation states including stable radical species.[7] Moreover, expanded porphyrins can serve as an effective platform for the realization of Möbius aromatic and antiaromatic systems.[8–10] Among many metal complexes of expanded porphyrins,[3] mono- and bis-Au(III) complexes of hexaphyrins are useful molecules since they are held in rigidly rectangular shapes, and become aromatic and antiaromatic depending upon the number of π electrons in the conjugated circuits.[11] Mono-Au(III) complexes can be used for the preparation of hetero-bis-metal complexes such as Au(III)–Ag(III), Au(III)–Cu(III), Au(III)–Rh(I), and Au(III)–Rh(III) complexes.[11,12] Intriguingly, antiaromatic Au(III) complexes of [28]hexaphyrins are stable enough to allow their full characterization, including the evaluation of the aromatic versus antiaromatic influence on their optical and electrochemical properties.[11] By taking advantage of these properties, researchers have revealed the two-photon absorption cross sections of aromatic [26]hexaphyrin complexes to be approximately 4–5 times larger than those of the corresponding antiaromatic [28]hexaphyrin complexes.[11b]

We previously reported that the mono- and bis-Au(III) complexes **2a** and **3a** were prepared in 16% and 14% yields, respectively, through the reaction of **1a** with $Na[AuCl_4]$ in the presence of NaOAc using a 4:1 mixture of CH_2Cl_2 and methanol as a solvent for 3 days (Scheme 1 and Table 1, Entry 1).[11a] This mixed solvent was used to assure certain solubilities of **1a** and $Na[AuCl_4]$. Later, we found that the addition of AgOTf accelerated the Au(III) metalation significantly to yield **2a** and **3a** in 9% and 39% yields after only 1 h (Table 1, Entry 2).[11b] The silver salt added was considered to activate the Au(III) cation by capturing chloride anions. This method allowed rapid metalation but at the same time tended to cause the oxidative decompositions of **1a**–**3a**, probably owing to the highly activated Au(III) cation, which was suggested by the result with a longer reaction time (Table 1, Entry 3). It was envisioned that the efficiency and/or selectivity of Au(III) metalations of [26]hexaphyrins might be improved by the addition of other silver salts.

With this idea in mind, we examined the effect of various Ag salts in the Au(III) metalation of hexaphyrin **1a** (Scheme 1). While notable improvements were not observed for additions of $AgBF_4$, $AgSbF_6$, $AgClO_4$, AgOAc, Ag_2SO_4, and Ag_2O (Table 1, Entries 4–9), we found that the addition of Ag_3PO_4 led to the selective formation of the mono-Au(III) complex **2a** as a rare case (Table 1, Entry 10), and the addition of Ag_2CO_3 gave an improved yield of the bis-Au(III) complex **3a** with better material balance (Entry 11). After extensive optimization experiments, we employed 10 equiv of $Na[AuCl_4]$ and 50 equiv of Ag_3PO_4 for mono-Au(III) metalation (protocol A) and 20 equiv of $Na[AuCl_4]$ and 100 equiv of Ag_2CO_3 for bis-Au(III) metalation (protocol B) for better results.

In the course of this study, solvent effects on the Au(III) metalation of hexaphyrin **1a** were also examined. Almost no Au(III) metalation was observed in acetone, ethyl acetate, THF, nitromethane, DMF, or DMSO. In acetonitrile, the metalation with 20 equiv of $Na[AuCl_4]$ and 100 equiv of Ag_2CO_3 produced **3a** in 58% yield. However, the metalation with 20 equiv of $Na[AuCl_4]$ and 50 equiv of Ag_3PO_4 resulted in the nonselective formation of **2a** and **3a** in 11% and 33% yields, respectively, and [26]hexaphyrins are usually only poorly soluble in acetonitrile.

Then, we applied the selective Au(III) metalation methods (protocols A and B) to the hexaphyrins **1b**–**1e** (Scheme 2). In all the hexaphyrin substrates examined, protocol A afforded the mono-Au(III) complexes **2b**–**2e** and protocol B provided the

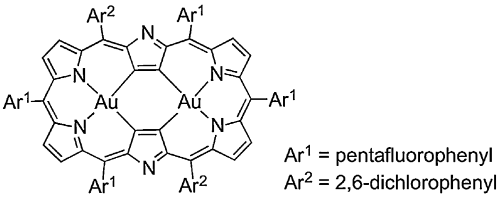


Scheme 2. Au(III) metalation of hexaphyrins.

Table 2. Au(III) metalation of hexaphyrins

Entry	Hexaphyrin	Protocol	Time/h	Yield[a]/%
1	**1a**	A	18	**2a**; 50
2	**1b**	A	7	**2b**; 33
3	**1c**	A	3	**2c**; 19
4	**1d**	A	24	**2d**; 37
5	**1e**	A	24	**2e**; 68
6	**1a**	B	24	**3a**; 51
7	**1b**	B	10	**3b**; 36
8	**1c**	B	10	**3c**; 5
9	**1d**	B	9	**3d**; 37[b]
10	**1e**	B	17	**3e**; 47

[a]Isolated yield. [b]1:2 mixture of **3d** and **3d′**.



3d'

Scheme 3. The structure of **3d′**.

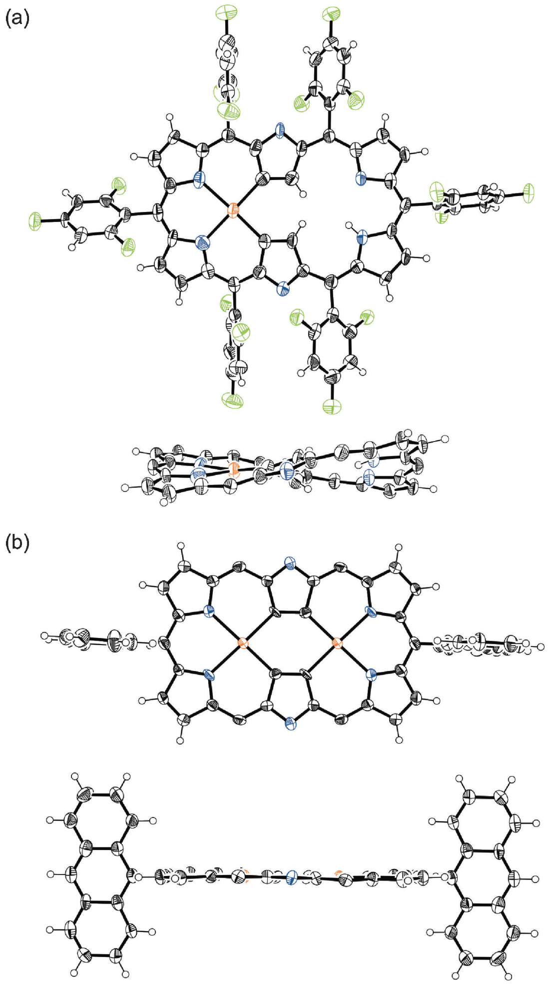


Figure 1. X-ray crystal structures of (a) **2b** and (b) **3e**. Top: top view. Bottom: side view. The thermal ellipsoids are scaled to 50% probability. Solvent molecules, 2,4,6-trifluorophenyl groups (bottom in (a)), and pentafluorophenyl groups are omitted for clarity.

bis-Au(III) complexes **3b**–**3e** selectively, without significant contamination with undesired complexes (Table 2). The observed selective formation of either mono- or bis-Au(III) complexes was advantageous, making the separation steps quite easy. The roles of the anions in the Ag salts are not clear at present but may tune the reactivity of the Au(III) species through complexation. With Na[AuCl$_4$]/AgOTf, the reactivity of the Au(III) cation is high, accelerating the complexation but causing serious oxidative damage. Since the PO_4^{3-} and CO_3^{2-} anions are more basic than the TfO^- anion, the reactivities of the Au(III) species from Na[AuCl$_4$]/Ag$_3$PO$_4$ and Na[AuCl$_4$]/Ag$_2$CO$_3$ may be attenuated through the interactions with the anions. PO_4^{3-} is more basic than CO_3^{2-}, which may lead to a suitable reactivity of mono-Au(III) metalation for PO_4^{3-} and of bis-Au(III) metalation for CO_3^{2-}.

As shown in Table 2, there is a tendency that the yields of the Au(III) complexes **2** and **3** are better for hexaphyrin substrates bearing more electron-withdrawing *meso*-aryl substituents. This tendency may indicate that electron-withdrawing *meso*-aryl substituents suppress the undesired oxidative decompositions. High yields of **2e** and **3e** (Table 2, Entries 9 and 10) may reflect the effective steric protection of bulky 9-anthryl groups against oxidation at the *meso*-positions. In the bis-Au(III) metalation of **1d**, two isomers of **3d** and **3d′** (Scheme 3) were obtained in a 1:2 ratio, which implies the occurrence of a caterpillar-motion-like macrocyclic ring rotation[13] during the bis-Au(III) metalation, while such isomerization was not observed for the corresponding mono-Au(III) metalation.

The structures of **2b**, **2c**, **2d**, **3b**, **3c**, **3d**, **3d′**, and **3e** were confirmed by X-ray crystallographic analyses performed on their single crystals (SI).[14,15] Of these compounds, the structures of **2b** and **3e** are shown in Figure 1. Complex **2b** exhibits a twisted

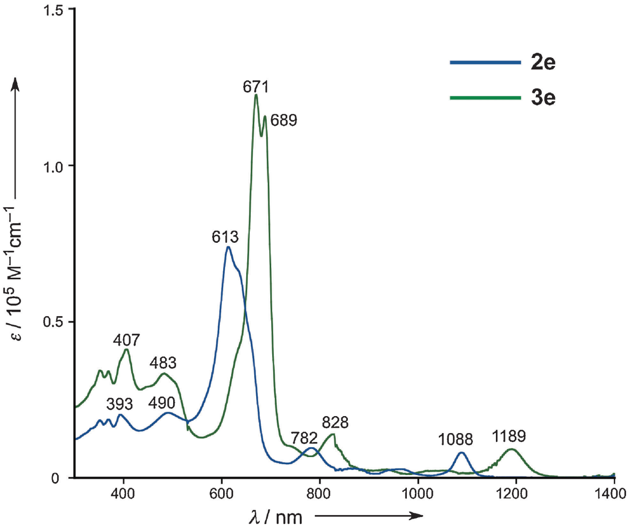


Figure 2. Absorption spectra of **2e** and **3e** in CH_2Cl_2.

structure, in which the metalated half is planar but the other free-base half is distorted owing to repulsion between the inner pyrrolic β-protons. On the other hand, X-ray analysis of **3e** reveals a remarkably planar structure with two anthryl groups at the shorter side, in accordance with the ^{1}H NMR data. It also displays a crystal-packing structure with an infinite molecular network aided by the C–H and π interactions of the anthryl groups with the π surfaces of the hexaphyrins (SI).[15] Other Au(III) metal complexes also show similar crystal structures (SI).[15]

Figure 2 shows the absorption spectra of **2e** and **3e** in CH_2Cl_2. Other Au(III) metal complexes also show similar absorption spectra (SI).[15] The mono-Au(III) hexaphyrin **2e** exhibits a Soret-like band at 613 nm, and Q-like bands at 782 and 1088 nm, and the bis-Au(III) hexaphyrin **3e** displays split and intensified Soret-like bands at 671 and 689 nm, and Q-like bands at 828 and 1189 nm, both of which are red-shifted compared to those of **2e**.

In summary, we have developed simple protocols allowing the selective preparations of mono- and bis-Au(III) hexaphyrin complexes by using Ag_3PO_4 and Ag_2CO_3, respectively. Further applications of these Au(III) complexes are currently under investigation in our laboratory and will be reported elsewhere.

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14 CCDC 905507 (**2b**), 905508 (**3b**), 905504 (**2c**), 905511 (**3c**), 905505 (**2d**), 905510 (**3d**), 905509 (**3d′**), and 905506 (**3e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.