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Communication

Group 10 Metal Complexes of *meso*-Aryl-Substituted [26]Hexaphyrins with a Metal–Carbon Bond

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Nickel(II), palladium(II), and platinum(II) complexes of *meso*-aryl-substituted [26]hexaphyrin have been prepared and structurally characterized. In mono-metalated complexes, the metal ion is commonly bound with three pyrrolic nitrogen atoms and one pyrrolic β-carbon, whereas a bis-Pd(II) complex exhibits a unique structure involving a Pd–C_α bond. These results reveal novel coordination abilities of the hexaphyrin that lead to a metal–carbon bond at either pyrrolic C_β or C_α position.

In recent years, increasing attention has been focused on the study of so-called expanded porphyrins that consist of five or more conjugated pyrrolic subunits.[1] Our own activity in this area has been triggered by our unexpected finding that a series of *meso*-aryl-substituted expanded porphyrins can be prepared in a simple one-pot reaction of a 2,6-substituted aryl aldehyde with pyrrole under modified Rothemund−Lindsey conditions.[2] Among these expanded porphyrins, [26]hexaphyrin, **1**, is a particularly attractive molecule in light of its strong aromaticity and planar and rectangular structure with two inverted pyrroles,[2,3] which are analogous to the characteristics of porphyrins. Moreover the hexaphyrin **1** can be easily reduced to its 28π state by $NaBH_4$ reduction.[3] In view of the rich chemistry of metalloporphyrins, the metalation of [26]hexaphyrin is also intriguing. In particular, the inverted pyrrole rings in **1** are quite attractive in light of C−H bond activation, as they might offer an opportunity to form a metal−carbon bond. Such C−H activations have been demonstrated in several modified porphyrinoids involving N-confused porphyrins (NCPs),[1c,4] carbaporphyrinoids,[5] and benziporphyrins[6] that share the same CNNN internal core. These reactivities allowed for the creation of novel organometallic species of unusual valence states. Despite this promise, metalation of **1** has been only poorly studied so far.[7−9] Cu(II) metalation of **1** did not lead to the formation of a metal complex with a carbon−metal bond but provided gable bis-Cu(II) complexes, in which the two Cu(II) ions are each bound to three pyrrolic nitrogen atoms and an oxygen atom attached at the meso position.[7]

In this Communication, we report metalations of **1** with group 10 metals such as Ni(II), Pd(II), and Pt(II). When a

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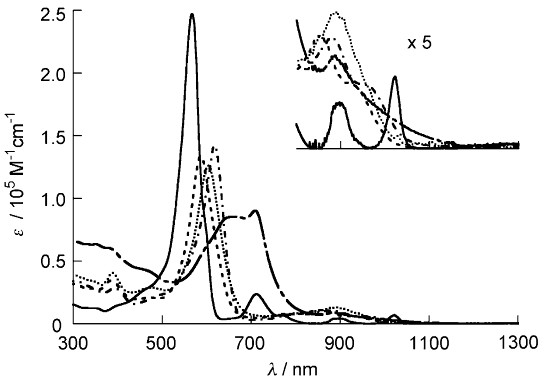


Figure 1. Absorption spectra of **1** (—), **3** (···), **5** (- · - · -), **6** (— · —), and **7** (- - -) in CH_2Cl_2.

toluene solution of **1** and 10 equiv of $Ni(acac)_2$ is refluxed for 1 h in the presence of sodium acetate under anaerobic conditions, nickel(II) hexaphyrin complex **3** was isolated in 50% yield after separation over a silica gel column. By high-resolution ESI-TOF mass spectroscopy, the molecular weight of **3** was determined to be $m/z = 1517.0091$ ($[M - H]^-$); calcd for $C_{66}N_6F_{30}H_{13}Ni$ 1517.0082. The absorption spectrum (Figure 1) shows a Soret-like band at 604 nm and a Q-band-like band at 892 nm. The ^1H NMR spectrum of the diamagnetic complex **3** exhibits signals for three NH protons at 9.02, 5.33, and 2.30 ppm; 10 resonances due to the pyrrolic β-protons in the range of 7.60−5.71 ppm; and one doublet coupled ($J = 2$ Hz) with a pyrrolic NH proton appearing at exceptionally higher field, 1.70 ppm. Because **3** was unstable under aerobic conditions in solution, crystals of **3** suitable for X-ray crystallography were grown by vapor diffusion of heptane into a CH_2Cl_2 solution of **3** in a glovebox. The structure of **3** was solved by single-crystal X-ray diffraction analysis (Figure 2).[10] The pyrroles F, A, B, and E constitute an NCP-like hemimacrocycle, in which the nickel atom is bound with three pyrrolic nitrogen atoms (the pyrroles F, A, and B) and the β-carbon atom of the inverted pyrrole E with bond distances of $Ni-N_F$, 1.891(2) Å; $Ni-N_A$, 1.904(2) Å; $Ni-N_B$, 1.878(2) Å; and Ni−C, 1.898(3) Å. The pyrroles C, D, and E are indicated to bear a NH hydrogen, thus leading to assignment of **3** as a [28]hexaphyrin. Three Ni−N bonds and the Ni−C bond in **3** are all slightly shorter than those in $Ni^{II}NCP$.[4b,c] The pyrroles F, A, B, and inverted E are helically arranged with a large mean plane deviation of 0.55 Å defined by the constituent 23 atoms. The tilting angles of pyrroles F, A, B, and E to this mean plane are 14.5°, 22.1°, 44.5°, and 21.6°, respectively. Curiously, one meso-substituted pentafluorophenyl group (marked Ar* in Chart 1) is located quite near the Ni(II) atom, which is displaced by 0.18 Å toward Ar* from the mean plane. On the basis of the X-ray crystal structure, the doublet at 1.70 ppm was assigned to the β-proton (H^a) of the pyrrole E because of its location just over the pyrrole B ring.

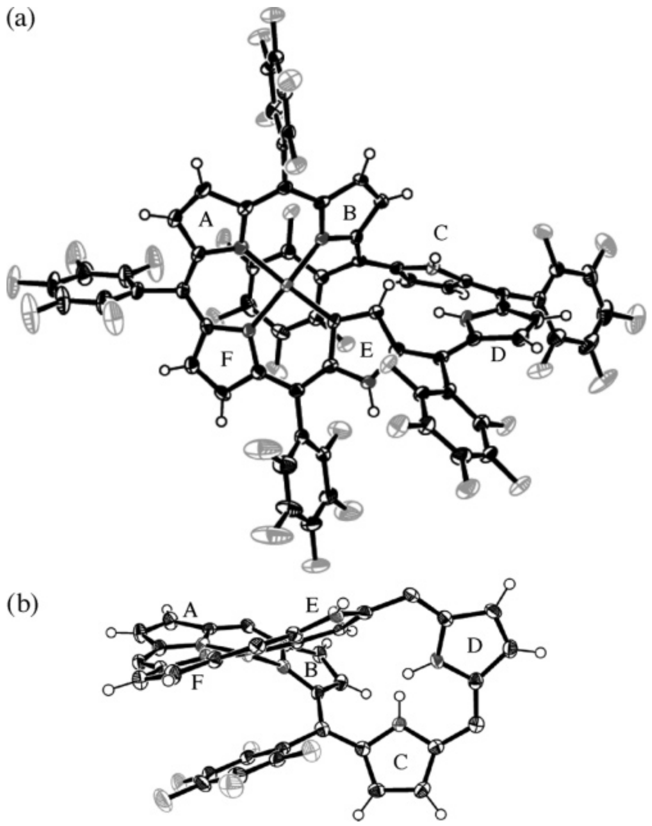
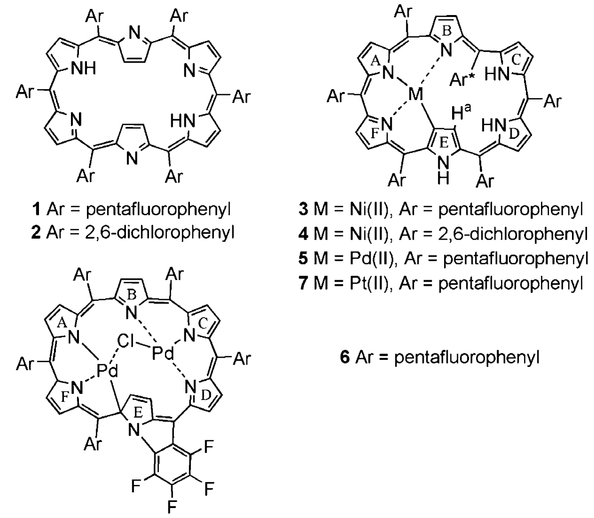


Figure 2. Crystal structure of **3**: (a) top view and (b) side view. The thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are partially omitted for clarity.

Chart 1



1 Ar = pentafluorophenyl
2 Ar = 2,6-dichlorophenyl

3 M = Ni(II), Ar = pentafluorophenyl
4 M = Ni(II), Ar = 2,6-dichlorophenyl
5 M = Pd(II), Ar = pentafluorophenyl
7 M = Pt(II), Ar = pentafluorophenyl

6 Ar = pentafluorophenyl

When *meso*-hexakis(2,6-dichlorophenyl)hexaphyrin **2** was used instead of **1**, nickel(II) hexaphyrin complex **4** was obtained in 66% yield. Complex **4** exhibits the parent ion peak at $m/z = 1390.8153$ ($[M - H]^-$) (calcd for $C_{66}N_6Cl_{12}H_{31}Ni$, 1390.8157), and its absorption spectrum shows bands at 604 and 892 nm that are quite similar to those of **3**. The preliminary X-ray crystal structure of **4** (Supporting Information) is practically the same as that of **3**. In the ^1H NMR spectrum of **4**, it is interesting to note that a set of signals is observed in a rather high-field region at 5.97 (meta), 5.70 (para), and 5.14 ppm (meta), which has

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(10) Crystallographic data for **3**: $C_{73}H_{30}N_6F_{30}Ni$, $M_w = 1619.73$, monoclinic, space group $P2/n$ (No. 14), $a = 15.063(2)$ Å, $b = 15.694(2)$ Å, $c = 28.468(4)$ Å, $\beta = 102.352(2)°$, $V = 6573.7(16)$ Å^3, $D_c = 1.636$ g/cm^3, $Z = 4$, $R = 0.056$, R_w [$I > 3.0\ \sigma(I)$] = 0.070, GOF = 1.443 [$I > 3.0\ \sigma(I)$].

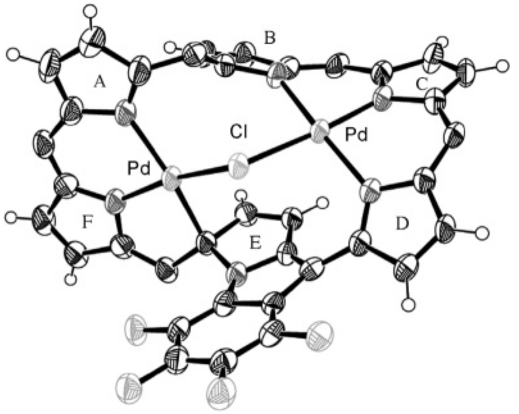

Figure 3. Crystal structure of **6**. The thermal ellipsoids are scaled to the 50% probability level. *meso*-Pentafluorophenyl substituents are partially omitted for clarity.

been assigned to the 2,6-dichlorophenyl group (denoted as Ar* in Chart 1) that is placed just below the Ni(II) center.

Pd(II) metalation was performed by refluxing a CH_2Cl_2 solution of **1** and 10 equiv of $PdCl_2$ for 12 h in the presence of sodium acetate. Separation over a silica gel column gave mono-Pd(II) complex **5** and bis-Pd(II) complex **6** in 50% and 9% yields, respectively. Complex **5** exhibits the parent ion peak at $m/z = 1564.9831$ ($[M - H]^-$) (calcd for $C_{66}N_6F_{30}H_{13}Pd$, 1564.9784). The absorption spectrum of **5** shows bands at 618 and 876 nm, which is quite similar to the spectra of **3** and **4**. The ^1H NMR spectrum of **5** is also quite similar to those of **3** and **4**, featuring three signals due to the NH protons and 10 signals due to the pyrrolic β-protons in the normal region, as well as one doublet due to the β-protons of the pyrrole E at 0.80 ppm (Supporting Information). X-ray crystallographic analysis revealed that **5** has a structure similar to those of **3** and **4** with bond distances of $Pd-N_F$, 2.007(6) Å; $Pd-N_A$, 2.034(6) Å; $Pd-N_B$, 2.011(5) Å; and Pd−C, 1.993(7) Å.[11] Unlike the Ni complex **3**, the Pd complex **5** is rather stable in solution in the presence of air.

The absorption spectrum of **6** exhibits a broad band between 651 and 709 nm and a small band at 888 nm, which are quite different from those of **3**−**5**. The ^1H NMR spectrum of **6** shows no NH signal and 12 signals due to the pyrrolic β-protons in the range of 7.36−6.31 ppm, in addition to two mutually coupled doublets at 8.82 and 5.61 ppm. The structure of **6** was determined by single-crystal X-ray diffraction method as shown in Figure 3.[12] Of two Pd(II) ions that are bridged by a chloride atom, one Pd(II) ion is bound to three pyrrolic nitrogen atoms with bond distances of 2.031(7), 1.984(8), and 2.046(7) Å, and the other is bound to two pyrrolic nitrogen atoms with bond distances of 2.080(8) and 1.952(7) Å, and a pyrrolic α-carbon, at which pyrrole a N-fusion reaction takes place to form a planar tricyclic ring.[13] The $Pd-C_\alpha$ bond distance is 2.106(9) Å, and the Pd−Cl bond distances are 2.372(2) and 2.439(3) Å. The two Pd atoms are coordinated in a square-planar manner with mean plane deviations of 0.18 and 0.05 Å. The fused tricyclic moiety is tilted against the Pd-coordinating square planes with 87.3° and 34.8°. Formation of the $Pd-C_\alpha$ bond causes disruption of a conjugated π-network of hexaphyrin, which leads to attenuation of the absorption coefficient of **6** compared to those of **1**. Because the pyrrole E has a different environment from the rest of the pyrroles, the pairs of doublets at 8.82 and 5.61 ppm that are differentiated from the other signals are tentatively assigned to the β-protons of the pyrrole E.

Finally, Pt(II) metalation of **1** was performed by refluxing a solution of **1** and sodium acetate in CH_2Cl_2 in the presence of 10 equiv of $PtCl_2$ under argon atmosphere. Monitoring of the reaction mixture revealed that the metalation was quite slow in comparison to Ni(II) and Pd(II) metalations but the amount of a mono-Pt(II) hexaphyrin complex gradually increased without any indication of further metalated product. After 5 days of refluxing, the usual workup provided platinum(II) hexaphyrin complex **7** in 56% yield. Complex **7** exhibits the parent ion peak at $m/z = 1654.0301$ ($[M - H]^-$) (calcd for $C_{66}H_{13}F_{30}N_6Pt$, 1654.0380) and the absorption spectrum characterized by bands at 586 and 844 nm. The ^1H NMR spectrum is quite similar to those of the mono-metalated complexes **3**−**5**. Therefore, we assigned **7** again as the mono-Pt(II) complex, whose structure is similar to those of **3**−**5**. A preliminary X-ray crystal structure of **7** also supports the assigned structure. Finally, the stability of **7** is comparable to that of **5**.

In summary, the metalations of **1** with Ni(II), Pd(II), and Pt(II) metal ions led to the formation of the mono-metalated complexes **3**, **5**, and **7**, in which the internal β-pyrrolic C−H bond is activated to form a metal−carbon bond. The bis-Pd(II) complex **6** was also isolated and structurally characterized to contain a $Pd-C_\alpha$ bond. These results reveal novel coordination abilities of [26]hexaphyrins.

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Supporting Information Available: Synthetic procedures, absorption spectra of **2** and **4**, ^1H NMR and ^{19}F NMR spectra of **3**−**7**, and preliminary X-ray structures of **4** and **7**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystallographic data for **5**: $C_{68}H_{14}N_6F_{30}PdCl_6$, $M_w = 1803.97$, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.4793(8)$ Å, $b = 17.2353(18)$ Å, $c = 25.250(3)$ Å, $\alpha = 77.918(2)°$, $\beta = 86.328(2)°$, $\gamma = 86.770(2)°$, $V = 3173.2(6)$ Å^3, $D_c = 1.888$ g/cm^3, $Z = 2$, $R = 0.0944$, R_w (all data) = 0.1134, GOF = 1.047 [$I > 2.0\ \sigma(I)$].

(12) Crystallographic data for **6**: $C_{76}H_{12}N_6F_{29}Pd_2Cl_6$, $M_w = 1985.42$, triclinic, space group $P\bar{1}$ (No. 2), $a = 13.838(7)$ Å, $b = 14.394(8)$ Å, $c = 18.255(10)$ Å, $\alpha = 99.10(5)°$, $\beta = 90.36(4)°$, $\gamma = 104.40(5)°$, $V = 3473(3)$ Å^3, $D_c = 1.898$ g/cm^3, $Z = 2$, $R = 0.0988$, R_w (all data) = 0.2846, GOF = 1.028 [$I > 2.0\ \sigma(I)$].

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