N-Fused Pentaphyrins and Their Rhodium Complexes: Oxidation-Induced Rhodium Rearrangement

Shigeki Mori,[a] Ji-Young Shin,[a] Soji Shimizu,[a] Fumiaki Ishikawa,[a] Hiroyuki Furuta,[b] and Atsuhiro Osuka*[a]

Abstract: *meso*-Aryl-substituted pentaphyrins were isolated in the modified Rothemund–Lindsey porphyrin synthesis as a 22-π-electron N-fused pentaphyrin ([22]NFP$_5$) and a 24-π-electron N-fused pentaphyrin ([24]NFP$_5$), which were reversibly interconvertible by means of two-electron reduction with NaBH$_4$ or two-electron oxidation with dichlorodicyanobenzoquinone (DDQ). Judging from ^{1}H NMR data, [22]NFP$_5$ is aromatic and possesses a diatropic ring current, while [24]NFP$_5$ exhibits partial anti-aromatic character. Metalation of [22]NFP$_5$ **1** with a rhodium(I) salt led to isolation of rhodium complexes **9** and **10**, whose structures were unambiguously characterized by X-ray diffraction analyses and were assigned as conjugated 24-π and 22-π electronic systems, respectively. In the rhodium(I) metalation of **1**, the complex **9** was a major product at 20 °C, but the complex **10** became preferential at 55 °C. Upon treatment with DDQ, compound **9** was converted to **10** with an unprecedented rearrangement of the rhodium atom.

Keywords: aromaticity · macrocyclic ligands · porphyrinoids · rearrangement · rhodium

Introduction

Expanded porphyrins with more than four pyrrolic units have emerged as a new class of functional macrocycles in light of their unique and interesting optical, electrochemical, and coordination properties.[1,2] As a result, a variety of expanded porphyrins have been prepared differing in ring size, ring connectivity, and hetero-atom replacement. However, the synthesis of *meso*-aryl-substituted expanded porphyrins, which can be regarded as real homologues of *meso*-aryl-substituted porphyrins in terms of the regular alternate arrangement of a pyrrole group and a *meso*-methine carbon atom, has still remained rather limited.[3] Recently we found that a series of *meso*-aryl-substituted expanded porphyrins were formed in the reaction of 2,6-disubstituted aryl aldehyde and pyrrole under the modified Rothemund–Lindsey conditions.[4,5]

Although there are extensive studies on pentapyrrolic macrocycles such as sapphyrins,[1b,6] core-modified sapphyrins,[7] and N-confused sapphyrins,[8] only little attention has been paid to pentaphyrins that have a regular alternate arrangement of five pyrrole groups and five methine carbon atoms. In 1983, Gossauer et al. first reported the synthesis of a β-alkyl-substituted pentaphyrin through an acid-catalyzed [2+3]MacDonald condensation.[9] The pentaphyrin was characterized as a 22-π electronic system on the basis of its ^{1}H NMR, ^{13}C NMR, and absorption spectra. Similar β-alkyl-substituted pentaphyrins were prepared in a better yield by Sessler et al. and a uranium complex was characterized by X-ray diffraction analysis.[10] *meso*-Diphenyltetra-β-alkyl-substituted pentaphyrin was prepared by Dolphin et al. in 1997.[3b] In contrast, *meso*-aryl-substituted pentaphyrin had not been prepared, to the best of our knowledge, before the synthesis based on the modified Rothemund–Lindsey protocol,[5] despite its unique position bridging *meso*-aryl-substituted expanded porphyrins and *meso*-aryl-substituted porphyrins.[11] In our synthesis of *meso*-aryl-substituted expanded porphyrins, *meso*-pentaaryl-substituted pentaphyrins were isolated, not in their intact form, but in an N-fused form containing a tripentacyclic ring. It has been shown that the N-fused pentaphyrin (which we have given the trivial name NFP$_5$[5]) can exist in two stable oxidation states with

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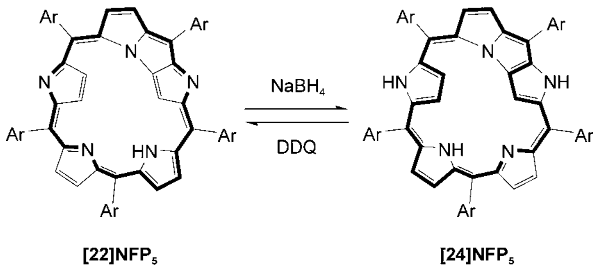
22-π and 24-π electronic systems (Scheme 1), [22]NFP$_5$ and [24]NFP$_5$, respectively.[5] These reversible two redox states also stand in contrast to other nonfused pentaphyrins that all exhibit a distinct diatropic ring current arising from the 22-π electronic system.[3b,9,10]

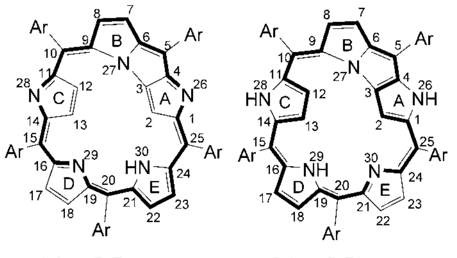


Scheme 1. Redox reaction between [22]NFP$_5$ and [24]NFP$_5$.

In this paper, we report the detailed chemistry of both [22]NFP$_5$ and [24]NFP$_5$, including their crystal structures, with a particular attention to the aromatic nature of these conjugated macrocycles. We also report the rhodium(I) metalation of [22]NFP$_5$ that provides two rhodium complexes **9** and **10**, which have been characterized by X-ray diffraction analysis. In the course of these studies, we found an unprecedented pivotlike rhodium rearrangement during the oxidation of **9** with dichlorodicyanobenzoquinone (DDQ).

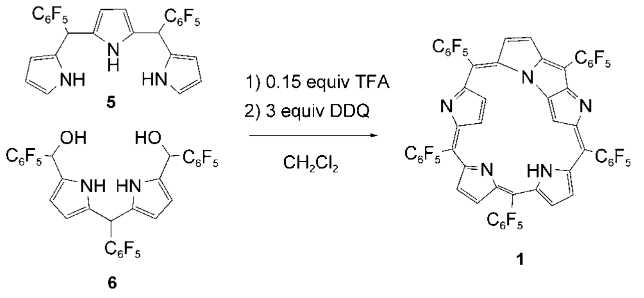
Results and Discussion

Synthesis of N-fused pentaphyrins: *meso*-Pentafluorophenyl-substituted N-fused pentaphyrins **1** and **2** were prepared from the reaction of pentafluorobenzaldehyde and pyrrole under the modified Rothemund–Lindsey conditions. Combined yield of **1** and **2** varied upon the concentration of the substrates; less than 1% at <20mM, 2% at 25mM, 10% at 50mM, 18% at 67mM, 11% at 100mM. Yields of other *meso*-aryl expanded porphyrins were roughly parallel with the yields of **1** and **2**. Relative amounts of **1** and **2** depended on the amount of DDQ used in the oxidation step. Thus, the oxidation with an excess amount of DDQ for a long reaction time (>15 h) provided **1** as a sole product in 18% isolated yield. Upon treatment with NaBH$_4$, **1** was quantitatively reduced to **2** (Scheme 1). In solution, the colors of **1** and **2** were red and yellowish red, respectively, but both were green in the solid states. In a similar manner, *meso*-2,6-dichlorophenyl-substituted N-fused pentaphyrin ([22]NFP$_5$ **3**) was prepared in 10% yield from the reaction of 2,6-dichlorobenzaldhyde and pyrrole and was converted to its reduced form [24]NFP$_5$ **4** by NaBH$_4$ reduction. Both **2** and **4** were quantitatively oxidized back to **1** and **3**, respectively, by DDQ oxidation. Alternatively, **1** was prepared in 28% yield by the acid-catalyzed [3+2] condensation of tripyrrane **5** and dipyrromethane dicarbinol **6** followed by oxidation with DDQ (Scheme 2).[11a] In this case, separation of **1** was much easier due to a smaller number of byproducts.



1 Ar = C_6F_5 **2** Ar = C_6F_5

3 Ar = 2,6-$Cl_2C_6H_3$ **4** Ar = 2,6-$Cl_2C_6H_3$



Scheme 2. Synthesis of **1** through [3+2] cyclization route from **5** and **6**.

Figure 1 shows the absorption spectra of **3** and **4**, which are similar to those of **1** and **2**.[5] The aromatic [22]NFP$_5$'s **1** and **3** exhibit absorption spectra with three peaks at 349.5, 460.5, and 553.5 nm and 348, 450, and 548 nm, respectively, while the anti-aromatic [24]NFP$_5$'s **2** and **4** exhibit absorption spectra with single peaks at 499 and 486 nm, respectively. Interestingly, the absorption tails of **1**–**4** all extend over 1000 nm, indicating substantial lowering of the singlet excited state energy in comparison to porphyrins.

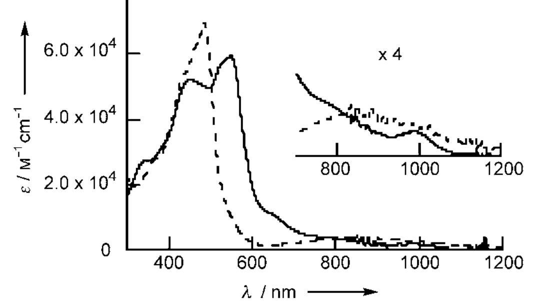


Figure 1. Absorption spectra of **3** (——) and **4** (-----) in CH_2Cl_2.

^{1}H NMR spectra of N-fused pentaphyrins: The ^{1}H NMR spectrum indicates that **1** possesses a distinct ring current, in that the inner protons appear at high field; the C(12) and C(13) protons at 2.19 and 1.70 ppm, the inner N(30) proton at 1.26 ppm, and the C(2) proton at −2.26 ppm, and the outer protons appear at low field in the range of 8.31–9.11 ppm (Figure 2). Lowering the temperature to 200 K led to enhancement of ring current, probably through rigidification of its conformation, indicated by the observed changes in the chemical shifts; the peak due to the inner proton at C(2) moved to −2.95 ppm, and the singlet resonance of the β-protons at 9.11 ppm shifted to two doublets at 9.36 and 9.40 ppm. These ^{1}H NMR data are consistent with its 22-π aromatic electron network. In contrast, the ^{1}H NMR spectrum of **2** exhibits chemical shifts that are entirely different from those of **1**. Namely, the C(2) proton appears at 7.84 ppm, the C(12) and C(13) protons appear as two doublets at 8.18 and 8.10 ppm with $J = 3.7$ Hz, and the N(29) proton appears at 13.73 ppm, all being considerably downfield shifted. The extremely low-field-shifted N(29)H signal could be partly attributed to possible strong N−H···N hydrogen bonding. However it is remarkable that the inner protons of the macrocycle appear in positions significantly shifted downfield and that the outer β-positions are all substantially upfield shifted in the range of 6.19–5.58 ppm. These chemical shifts could be much better interpreted as an indication of partial anti-aromatic character for **2**. Finally, it is worth noting that differences in the chemical shifts of the inner protons between **1** and **2** are as much as 10~12 ppm.

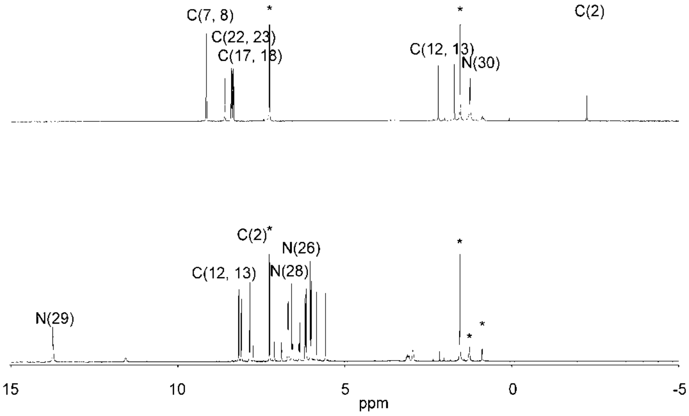


Figure 2. ^{1}H NMR spectra of **1** (top) and **2** (bottom) in $CDCl_3$. * indicates solvent and impurity.

Similarly, the ^{1}H NMR spectrum of the *meso*-2,6-dichlorophenyl-substituted [22]NFP$_5$ **3** indicates a diatropic ring current, while that of the *meso*-2,6-dichlorophenyl-substituted [24]NFP$_5$ **4** indicates anti-aromatic character. Characteristically, in the ^{1}H NMR spectrum of **3**, the C(2) proton appears at −1.78 ppm, the C(12) and C(13) protons appear at 1.88 and 2.30 ppm as a pair of doublets ($J = 4.6$ Hz), the inner N(30)H proton appears at 1.27 ppm, and the outer β-protons appear in the range of 8.05–8.83 ppm. In contrast, the ^{1}H NMR spectrum of **4** displays the inner N(29) proton at 16.98 ppm, the inner β-proton at C(2) at 12.01 ppm, and the inner β-protons at C(12) and C(13) at 9.69 and 9.62 ppm, but the outer NH protons at N(26) and N(28) at 5.43 and 7.01 ppm, and the outer β-protons in the range of 5.18–4.59 ppm. To support the above discussion on aromaticity and anti-aromaticity of NFP$_5$, we calculated nucleus-independent chemical shift (NICS) values of these compounds, which will be discussed in a later section.

X-ray structural characterization of N-fused pentaphyrins: Extensive efforts to obtain crystals of **1** suitable for X-ray analysis have been unsuccessful. Slow vapor diffusion of water into an acetonitrile solution of **1** gave crystals, which provided a preliminary structure (Supporting Information) in line with its ^{1}H NMR data.[12] The X-ray structure of **2** was reported previously,[5] and the important features are outlined here. The fused tripentacyclic ring with the inward- and outward-pointing nitrogen atoms is found in the pentapyrrolic core. The macrocycle consists of three planar parts, the fused tripentapyrrolic core (pyrroles A and B), the dipyrromethene unit (pyrroles D and E), and the pyrrole C. With respect to the most planar fused tripentacyclic moiety, the dipyrromethene unit is tilted at 44.2° and the pyrrole C is tilted at 79.5°, and accordingly the macrocycle is considerably distorted with the mean plane deviation of 4.27 Å. In addition, there are distinct bond-length alternations for the pyrrole bridging carbon–carbon bonds.

The solid-state structural information was fortunately obtained for both **3** and **4**. Diffraction grade crystals of **3** were grown by vapor diffusion of hexane into a solution of **3** in $CHCl_3$, and those of **4** were obtained by slow addition of water into a solution of **4** in methanol. Both solid-state structures contain a fused tripentacyclic ring and an inverted pyrrole in the core (Figure 3). The NH groups are positioned at N(30) in **3**, and at N(26), N(28), and N(29) in **4**.

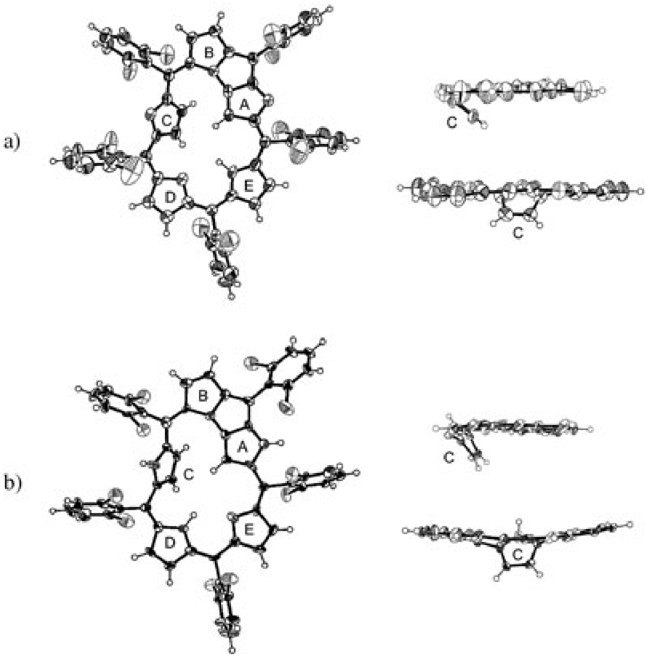


Figure 3. X-ray structure of a) **3** and b) **4**; top views (left) and side views (right). *meso*-Aryl substitutents for side views are omitted for clarity.

With respect to the planar tripentacyclic ring (pyrroles A and B), the dipyrromethene unit (pyrroles D and E) is tilted at 4.2° and the pyrrole C is tilted at 41.4° in **3**, and the dipyrromethene unit (pyrroles D and E) is tilted at 11.6° and the pyrrole C is tilted at 54.0° in **4**. The overall mean plane deviations are 1.85 Å and 2.53 Å for **3** and **4**, respectively (Figure 4). The pentapyrrolic skeleton of **3** is mostly flat except for the pyrrole C, probably reflecting its strong aromaticity, while **4** shows a more nonplanar macrocyclic structure. The bond-length alternation of the conjugated system is evident for **4**, whereas that for **3** is rather small (Figure 5).

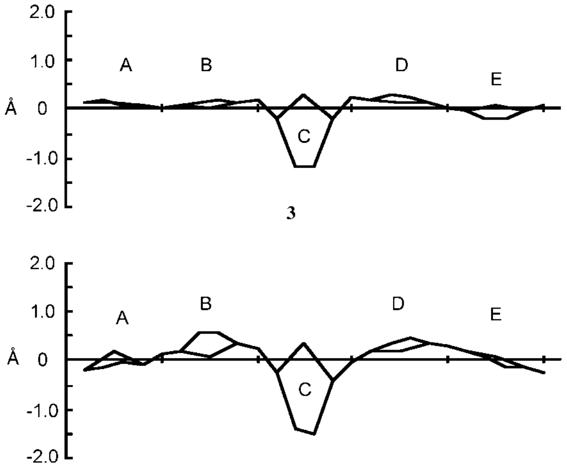


Figure 4. Views of the skeletal deviations of the macrocycle atoms from the 30 atoms plane for **3** and **4**.

We calculated nucleus-independent chemical shift (NICS) values[13] for parent [22]NFP$_5$ **7** and [24]NFP$_5$ **8**, in which all *meso*-aryl groups were replaced by protons. The optimization was carried out at the B3LYP/6–311+G** level.[14,15] Figure 6 depicts the optimized structures of **7** and **8**, both of which adopt rather flat conformations. The bond-length alternation for both optimized structures is in fair agreement with those for both crystal structures. The NICS values were similarly calculated at the B3LYP/6–311+G** level with GIAO method at the ring centers (nonweighted means of the carbon and nitrogen coordinates on the conjugate pathways). The large negative NICS of [22]NFP$_5$ ($\delta = -29.3$) confirms its strong aromatic character, whereas the anti-aromatic nature of [24]NFP$_5$ is predicted by a positive NICS value ($\delta = +7.2$).

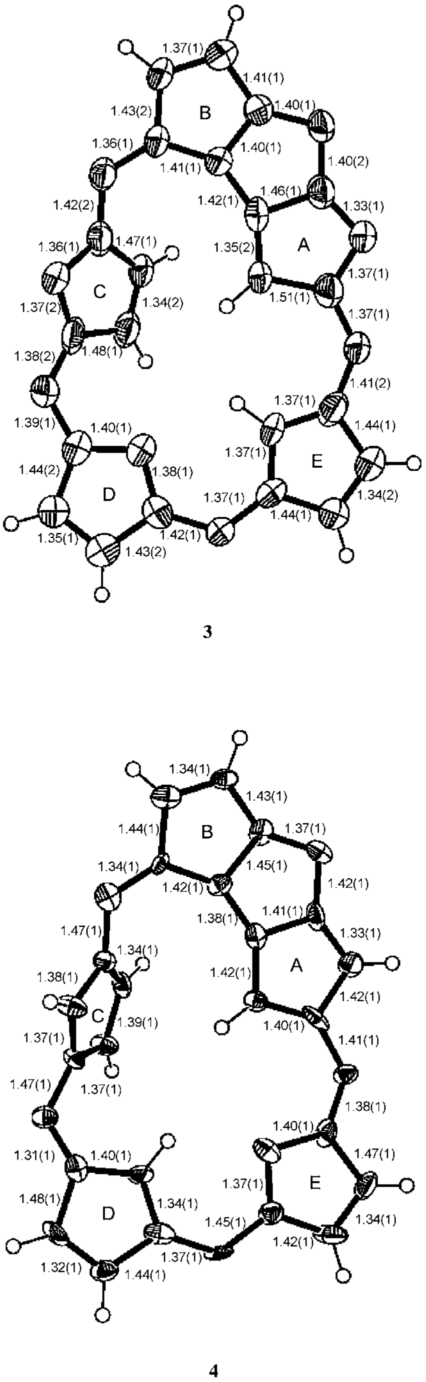


Figure 5. Bond lengths [Å] of **3** and **4**.

Rhodium(I) complexation of N-fused pentaphyrin 1: To explore a potential use of NFP$_5$ as a metal-coordinating ligand, we have attempted Rh^{I} complexation, since η^2-type coordination of Rh^{I} ion is known for porphyrins and expanded porphyrins that bear a dipyrromethene unit.[16,17] Here we report the metalation behavior of **1** with $[RhCl(CO)_2]_2$.

The [22]NFP$_5$ **1** was treated with $[RhCl(CO)_2]_2$ in CH_2Cl_2 in the presence of sodium acetate. Two rhodium complexes **9** and **10** were isolated as bluish violet and reddish purple stable solids, respectively, with yields that depended on the reaction time and temperature (Table 1). The metalation did not proceed at 0 °C, but proceeded slowly at 20 °C. Product ratio of **9** to **10** increased for longer reaction time and under refluxing conditions the yield of **10** (42 %) was distinctly higher than that of **9** (18 %). These results indicated the conversion of **9** to **10** at high reaction temperature. From the reaction of **2** with $[RhCl(CO)_2]_2$, the complex **9** was better

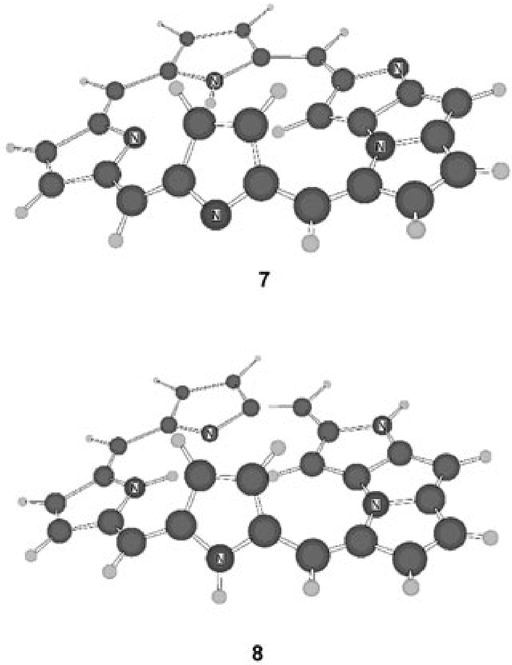
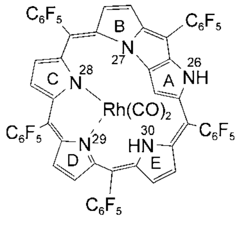


Figure 6. Optimized structures of [22]NFP$_5$ **7** (NICS = −29.3) and [24]NFP$_5$ **8** (NICS = +7.2).



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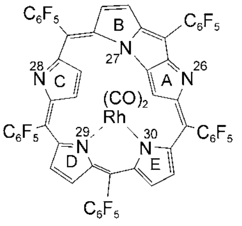

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Table 1. Reaction of **1** with [RhCl(CO)$_2$]$_2$.

Run	[RhCl(CO)$_2$]$_2$[a]	T [°C]	t [h]	**9** [%]	**10** [%]
1	2	20	1	4	0
2	2	20	2	19	1.8
3	2	20	4	23	2.4
4	2	20	12	26	7.6
5	2	55	1	18	42

[a] Number of equivalents with respect to compound **1**.

prepared in 60% yield at room temperature for 1 h, in which the formation of **10** was not detected even under refluxing conditions.

Structural characterizations of 9 and 10: The parent ion peaks of **9** and **10** were measured by high resolution FAB mass spectroscopy, which gave $m/z = 1374.9541$ for **9** (calcd for $C_{57}H_{11}F_{25}N_5O_2Rh$: 1374.9569) and $m/z = 1373.9213$ for **10** [M+H$^+$] (calcd for $C_{57}H_9F_{25}N_5O_2Rh$: 1373.9410). Single crystals suitable for an X-ray study for **9** were grown from vapor diffusion of hexane into a solution of **9** in CHCl$_3$. X-ray diffraction analysis revealed that the complex **9** preserves a basic NFP$_5$ structure with a tripentacyclic fused ring system. The rhodium atom in **9** is bound to the N(28) and N(29) atoms of the pyrroles C and D with N(28)−Rh = 2.083(5) Å and N(29)−Rh = 2.112(4) Å in a η^2 fashion as shown in Figure 7a. Curiously, the pyrrole C is inverted, from the nitrogen-pointing-outward conformation in the free base [22]NFP$_5$ into the nitrogen-pointing-inward conformation so as to participate in the coordination to the rhodium atom. Despite the fully conjugated electronic system, the complex **9** exhibits a largely distorted bent conformation (Figure 8). In particular, the pyrrole C is canted almost perpendicularly toward the tripentacyclic ring (pyrroles A and B) with a dihedral angle of 80.9°. The dipyrromethene unit consisting of pyrroles D and E is relatively planar and is canted with respect to the tripentacyclic ring with an angle of 37.8°. The ^{1}H NMR spectrum of **9** displays resonances due to the outer NH and inner NH protons at 9.44 and 0.68 ppm, a resonance due to the inner β-CH proton at 0.10 ppm, and four pairs of mutually coupled resonances due to the outer β-CH protons at 8.33 and 7.36, 7.96 and 7.88, 7.86 and 7.74, and 6.66 and 5.05 ppm. The doublet of doublets at 7.96 and 7.88 ppm were changed to simple doublets upon treatment with D$_2$O, thus indicating that these signals are due to the outer β-CH protons on the pyrrole E. The doublets at 6.66 and 5.05 ppm have been assigned to the outer β-CH protons on the pyrrole B, while the remaining double doublets have been assigned to the outer β-CH protons on the pyrroles C and D, because of the coupling

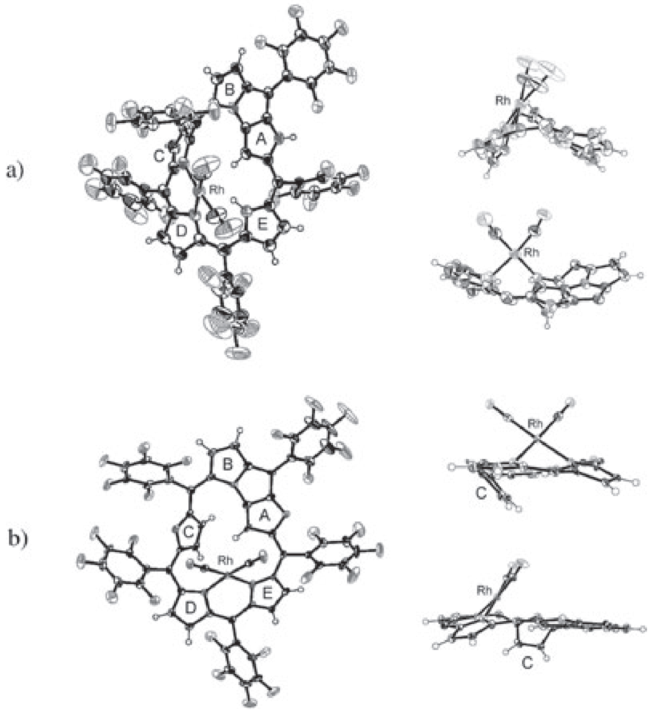


Figure 7. X-ray structure of a) **9** and b) **10**; top views (left) and side views (right). *meso*-Aryl substituents for side views are omitted for clarity.

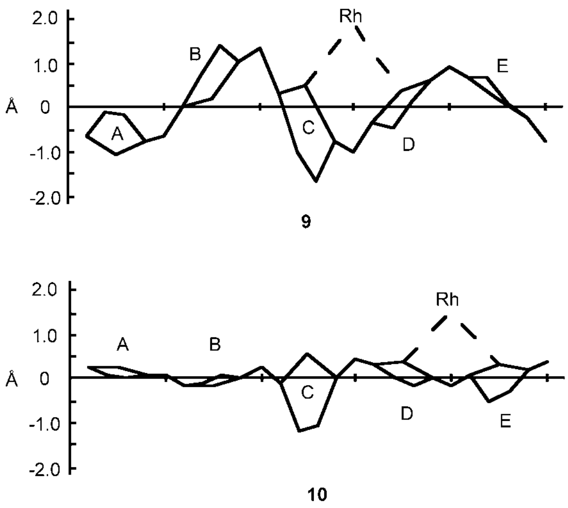


Figure 8. Views of the skeletal deviations of the macrocycle atoms from the 30 atoms plane for **9** and **10**.

with the rhodium atom. These ^{1}H NMR data indicate a substantial diatropic ring current for **9**, despite its 24-π electrons along the conjugated network. The IR spectrum indicates the C≡O stretching vibrations at 2078 and 2008 cm^{-1}.

Diffraction-grade crystals of **10** were obtained from vapor diffusion of heptane into a solution of **10** in CH_2Cl_2. Its X-ray structure indicated the preservation of a basic [22]NFP$_5$ framework with a planar tripentacyclic unit and the rhodium atom coordinated in a η^2-fashion by N(29) and N(30) atoms in the pyrroles D and E, respectively (Figure 7b). The structure of **10** reveals a conjugated 22-π-electron network spread over a relatively planar macrocycle, which stands in marked contrast to that of **9**. In accord with this, the ^{1}H NMR spectrum of **10** reveals a stronger ring current, exhibiting the inner C(2) proton as a singlet at 0.05 ppm, the inner β-pyrrolic protons as a pair of doublets at 1.62 and 1.16 ppm with $J = 4.5$ Hz, the outer β-pyrrolic protons as three pairs of mutually coupled doublets at 9.23 and 9.21 ppm with $J = 4.6$ Hz, at 8.61 and 8.29 ppm with $J = 4.6$ Hz, and at 8.21 and 8.13 ppm with $J = 4.2$ Hz, which are assigned to the outer β-CH protons at the pyrroles B, D, and E, respectively. The IR spectrum indicates the C≡O stretching vibrations at 2081 and 2020 cm^{-1}.

Since the complex **10** became the major product at high temperature, we examined the heating of **9** in CH_2Cl_2, which did not cause the conversion of **9** to **10**. The number of π electrons along the conjugated network is 24 for **9** and 22 for **10**, which suggests a possible interconversion between these complexes upon two-electron oxidation or reduction. With this in mind, the oxidation of **9** with DDQ was examined. Upon treatment with DDQ even at room temperature, complex **9** was rapidly and quantitatively changed to **10** with a pivot rearrangement of the rhodium atom from the coordination by the pyrroles C and D to that by the pyrroles D and E. This oxidation process from **9** to **10** with DDQ was monitored by ^{1}H NMR spectroscopy (Figure 9), in which an

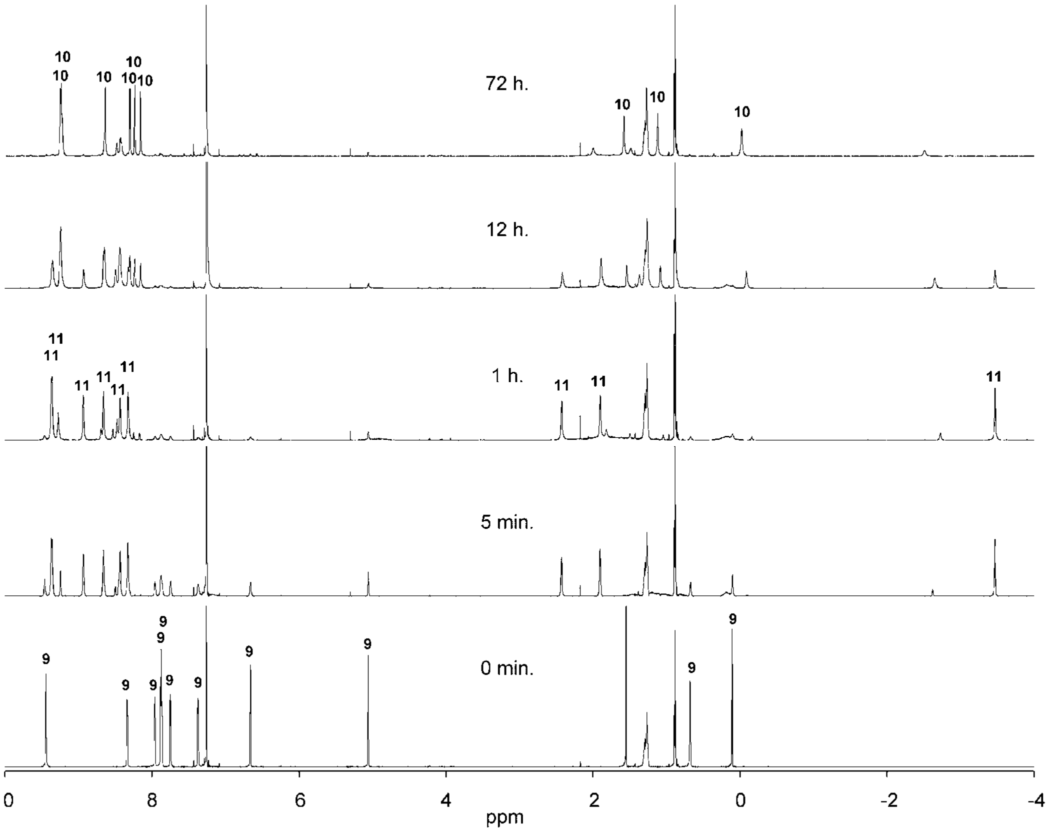
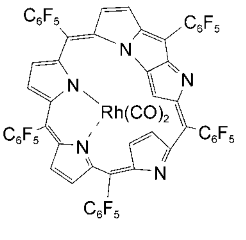


Figure 9. ^{1}H NMR spectral changes during the conversion of **9** to **10** at room temperature in $CDCl_3$.

intermediate was clearly detected before the final formation of **10**. Typically, the ^{1}H NMR spectrum at 1 h indicated the formation of an intermediate, whose ^{1}H NMR spectrum is different from both **9** and **10**. This intermediate could not be isolated at this stage, but was tentatively assigned as **11**, an oxidized form of **9**. The structure of **11** predicts a 22-π electronic conjugated macrocycle, which should exhibit a diatropic ring current. The singlet peak at −3.47 ppm could be assigned to the C(2) proton and two mutually coupled doublets peaks at 1.90 and 2.43 ppm are assigned to C(22) and C(23) protons at the pyrrole E that may be inverted in **11**. Intermediate **11** smoothly converts into **10** following the migration of the Rh atom. Severe distortion of **9** may drive this rhodium rearrangement. In contrast, the reduction of **10** with $NaBH_4$ afforded **2** without production of **9**.



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In summary, *meso*-pentaaryl-substituted pentaphyrins were isolated as [22]NFP_5 and [24]NFP_5 forms, both of which were interconvertible through two-electron oxidation with DDQ and two-electron reduction with $NaBH_4$. [22]NFP_5 possesses a diatropic ring current, while [24]NFP_5 shows a ^{1}H NMR spectrum that suggests anti-aromatic character. Two Rh^I complexes **9** and **10** were obtained from the reaction of **1** with $[RhCl(CO)_2]_2$. The oxidation of **9** with DDQ proceeded smoothly to give **10** with a pivotlike rhodium rearrangement, via an intermediate.

Experimental Section

General: All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by distilling over CaH_2. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (^{1}H NMR: $\delta=7.260$, ^{13}C NMR: $\delta=77.0$). The spectroscopic grade CH_2Cl_2 was used as solvent for all spectroscopic studies. UV-visible absorption spectra were recorded on a Shimadzu UV-3100 spectrometer. Mass spectra were recorded on a JEOL HX-110 spectrometer, using positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix, or on a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using positive-MALDI ionization method with/without CA matrix. Preparative separations were performed by silica gel flash column chromatography (Merck Kieselgel 60H Art. 7736), and silica gel gravity column chromatography (Wako gel C-400).

***meso*-Pentafluorophenyl-substituted N-fused pentaphyrins 1 and 2**: Pentaphyrin **1** was obtained from the reaction of 2,3,4,5,6-pentafluorobenzaldehyde with pyrrole under the modified Rothemund–Lindsey conditions. A solution of $BF_3 \cdot OEt_2$ in CH_2Cl_2 (2.5 M, 100 µl) was added to a solution of pentafluorobenzaldehyde (494 µl, 4 mmol) and pyrrole (278 µl, 4 mmol) in CH_2Cl_2 (60 mL), and the resulting mixture was stirred for 2 h under nitrogen. After adding DDQ (2.27 g, 10 mmol), the solution was stirred for 10 h, then passed through a short alumina column to remove the tar. The reaction mixture was then separated by column chromatography on silica gel with a 1:4 mixture of CH_2Cl_2 and hexane. A red fraction containing **1** that eluted after a purple fraction of *meso*-pentafluorophenyl-substituted [26]hexaphyrin was collected. After the solvent was evaporated, the residue was recrystallized from hexane to give pure **1** (146 mg, 15%). $NaBH_4$ (22.7 mg, 0.6 mmol) was added to a solution of **1** (50 mg, 0.04 mmol) in CH_3OH (10 mL) and the resulting solution was stirred for 10 min under nitrogen. After removing the solvent, the residues were dissolved in CH_2Cl_2, and filtered through a short alumina column. After evaporation, the residue was recrystallized from hexane to give **2** (50 mg, quant.).

Data for compound 1: M.p. >300 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=9.14$ (m, 2H), 8.60 (d, $J=4.0$ Hz, 1H), 8.40 (d, $J=5.0$ Hz, 1H), 8.38 (d, $J=4.5$ Hz, 1H), 8.34 (d, $J=4.5$ Hz, 1H), 2.20 (d, $J=5.0$ Hz, 1H), 1.71 (d, $J=4.0$ Hz, 1H), 1.24 (br s, 1H; NH), −2.25 ppm (s, 1H; C(2)H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=161.0$, 160.9, 160.4, 159.7, 153.4, 152.2, 150.9, 148.1, 146.9, 136.6, 133.8, 133.3, 132.8, 132.4, 132.3, 131.5, 131.3, 129.3, 123.2, 122.4, 120.5, 112.7, 109.6, 100.7, 99.1 (C(2)), 99.0 ppm. It should be noted that pentafluorophenyl signals could not be assigned because of the multiple coupling of ^{13}C–^{19}F; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=349.5$ (40600), 460.5 (59500), 553.5 (62600), 991.5 nm (2100 $M^{-1}cm^{-1}$); FAB-MS: m/z calcd for $C_{55}H_{10}F_{25}N_5$ [M^+]: 1215.0537; found: 1215.0522 (100%).

Data for compound 2: M.p. >300 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=13.73$ (br s, 1H; N(29)H), 8.18 (dd, $J=3.7$ Hz, $J=2.3$ Hz, 1H), 8.10 (d, $J=3.7$ Hz, $J=2.3$ Hz, 1H), 7.84 (d, $J=1.9$ Hz, 1H; C(2)H), 6.69 (br s, 1H; N(28)H), 6.59 (br s, 1H; N(26)H), 6.19 (d, $J=5.5$ Hz, 1H), 6.16 (d, $J=5.5$ Hz, 1H), 6.03 (d, $J=5.5$ Hz, 1H), 6.00 (d, $J=5.0$ Hz, 1H), 5.85 (d, $J=4.5$ Hz, 1H), 5.58 ppm (d, $J=5.5$ Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta=165.1$, 154.3, 150.8, 150.6, 150.2, 142.3, 136.9, 136.3, 133.7, 133.4, 133.3, 132.1, 129.5, 128.4, 126.9, 125.9, 125.0, 112.8, 110.6, 108.5, 106.9, 104.9 (C(2)), 102.0, 101.5, 93.9, 90.3 ppm. It should be noted that pentafluorophenyl signals could not be assigned because of the multiple coupling of ^{13}C–^{19}F.; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=443.0$ (51100), 499.0 (63100), 771.0 nm (7200 $M^{-1}cm^{-1}$); FAB-MS: m/z calcd for $C_{55}H_{12}F_{25}N_5$ [M^+]: 1217.0693; found: 1217.0652 (100%).

***meso*-2,6-Dichlorophenyl-substituted N-fused pentaphyrins 3 and 4**: Pentaphyrins **3** and **4** were prepared from the reaction of 2,6-dichlorobenzaldehyde and pyrrole. A solution of $BF_3 \cdot OEt_2$ in CH_2Cl_2 (2.5 M, 250 µl) was added to a solution of 2,6-dichlorobenzaldehyde (1.75 g, 10 mmol) and pyrrole (750 µl, 10 mmol) in CH_2Cl_2 (150 mL). The resulting solution was stirred for 2 h under nitrogen. After DDQ (6.81 g, 30 mmol) was added to the reaction mixture, the solution was stirred for 10 h, then passed through a short alumina column to remove the tar. The reaction mixture was then separated by column chromatography on silica gel with a 98:2 mixture of CH_2Cl_2/EtOAc. A red fraction containing **3** eluted after a purple fraction of *meso*-2,6-dichlorophenyl-substituted [26]hexaphyrin. After the solvent was evaporated, the residue was recrystallized from CH_2Cl_2/hexane to give pure **3** (218 mg, 9.8%). $NaBH_4$ (22.7 mg, 15 equiv) was added to a solution of **3** (44 mg, 0.04 mmol) in CH_3OH (10 mL), and the resulting solution was stirred for 10 min under nitrogen. After the solvent was evaporated, the residues were dissolved in CH_2Cl_2. This solution was passed through a short alumina column. After the solvent was evaporated, the residue was recrystallized from CH_2Cl_2/hexane to give **4** (44 mg, quant.).

Data for compound 3: M.p. >300 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta=8.84$ (d, $J=5.2$ Hz 1H), 8.71 (d, $J=4.6$ Hz, 1H), 8.26 (d, $J=4.0$ Hz, 1H), 8.13 (d, $J=4.6$ Hz, 1H), 8.06 (d, $J=4.6$ Hz, 1H), 8.03 (d, $J=4.6$ Hz, 1H), 7.83–7.28 (m, 15H; Ar-H), 2.30 (d, $J=4.6$ Hz, 1H), 1.88 (d, $J=4.6$ Hz, 1H), 1.27 (br s, 1H; N(30)H), −1.78 ppm (s, 1H; C(2)H); UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=348$ (27100), 450 (51900), 548 (59400), 993 nm (1900 $M^{-1}cm^{-1}$); FAB-MS: m/z calcd for $C_{55}H_{25}Cl_{10}N_5$ [M^++H]: 1105.9073; found: 1105.9017 (100%).

Data for compound 4: M.p. >300 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta=16.98$ (br, 1H; N(29)H), 12.01 (br, 1H; C(2)H), 9.69 (br, 1H), 9.62 (br, 1H), 7.37–6.96 (m, 15H; Ar-H), 7.02 (br, 1H; N(28)H), 5.43 (br, 1H; N(26)H), 5.18 (br, 1H), 5.13 (br, 2H), 5.06 (d, $J=5.5$ Hz, 1H), 4.93 (br, 1H), and 4.59 ppm (br, 1H); UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon)=363$ (sh, 27000), 434 (sh, 53000), 486 (69200), 848 nm (3700 $M^{-1}cm^{-1}$); FAB-MS m/z calcd for $C_{55}H_{25}Cl_{10}N_5$ [M^++H]: 1107.9230; found: 1107.9243 (100%).

Preparation of 1 through [3+2] cyclization: Trifluoroacetic acid (1 M, 30 µl, 0.15 equiv) was added under N_2 atmosphere to a solution of tripyrrane **5** (110 mg, 200 μmol) and dipyrromethane dicarbinol **6**[11b] (140 mg, 200 μmol) in CH_2Cl_2 (20 mL) at 0 °C, and the resulting solution was stirred for 2 h in the dark. DDQ (136 mg, 3 equiv) was then added, after which the solution was stirred at room temperature for 10 h. After removal of the solvent, the residue was passed through a short basic alumina column and separated by silica gel column chromatography with a 1:1 mixture of CH_2Cl_2/hexane as an eluent. Light green first fraction was *meso*-pentafluorophenyl decaphyrin (7 mg, 3 %, dark green solids) as judged from its MALDI-TOF mass spectrum ($m/z = 2441.1$), and red second fraction was **1** (68 mg, 28 %).

Rhodium(I) complexes of N-fused pentaphyrin 9 and 10: In a 100 mL round-bottomed flask, **1** (96.4 mg, 79 μmol) was dissolved in distilled CH_2Cl_2 (20 mL) under a nitrogen atmosphere. NaOAc (32 mg, 400 μmol) and then $[RhCl(CO)_2]_2$ (32.3 mg, 83 μmol) were added to this solution. The resulting mixture was refluxed for 1 h, and the solvent was removed under reduced pressure. After evaporation of the solvent, the residue was separated by silica gel column chromatography with a mixture of dichloromethane/hexane (1:4). The first bluish violet fraction was **9** (20.1 mg, 18 % yield) and the second reddish purple fraction was **10** (45.6 mg, 42 % yield). Diffraction-grade crystals of **9** were grown by the vapor diffusion of hexane into a solution of **9** in $CHCl_3$, and those of **10** were grown by the vapor diffusion of heptane into a solution of **10** in CH_2Cl_2.

Oxidative conversion of 9 to 10: DDQ (114 mg, 5 equiv) was added to a solution of **9** (137 mg, 100 μmol) in CH_2Cl_2, and the resulting solution was stirred for 15 min at room temperature. The reaction mixture was passed through a short basic alumina column and then was purified by a short silica gel column to give **10** (127 mg, 93 %).

Data for complex 9: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 9.44$ (s, 1 H; N-H), 8.33 (t, $J =$ Hz, 1 H), 7.96 (dd, $J = 4.8$ Hz, $J_{\text{N-H}} = 1.5$ Hz, 1 H), 7.88 (d, $J = 4.6$ Hz, 1 H), 7.86 (dd, $J = 4.6$ Hz, $J = 2.3$ Hz, 1 H), 7.74 (dd, $J = 4.8$ Hz, $J = 2.5$ Hz, 1 H), 7.36 (dd, $J = 4.8$ Hz, $J = 3.4$ Hz, 1 H), 6.66 (d, $J = 4.1$ Hz, 1 H), 5.05 (d, $J = 4.6$ Hz, 1 H), 0.68 (s, 1 H; N-H), 0.10 ppm (d, $J_{\text{N-H}} = 1.4$ Hz, 1 H; inner β-H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 179.3$ (d, $J_{\text{Rh-C}} = 65.5$ Hz, *C*O), 177.5 (d, $J_{\text{Rh-C}} = 69.8$ Hz, *C*O), 165.1, 149.4, 147.1, 146.5, 146.0, 138.9, 138.7, 133.0, 132.5, 131.8, 131.7 (β-carbon), 130.5 (β-carbon), 130.4 (β-carbon), 127.3 (β-carbon), 127.0 (β-carbon), 124.0 (β-carbon), 123.3 (β-carbon), 123.1 (β-carbon), 114.9, 112.5 (β-carbon), 108.2, 97.1 (inner β-carbon), 96.6, 93.1, 87.4 ppm; UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (ε) = 410 (37 800), 572 (83 700), 626 (42 900), 847 (12 000), 922 nm (10 100 $M^{-1}cm^{-1}$); FT-IR (KBr): $\tilde{\nu} = 2920$, 2852, 2078, 2008, 1520, 1497, 990, 668 cm^{-1}; FAB-MS: *m*/*z* calcd for $C_{57}H_{11}F_{25}N_5O_2Rh$ [M^+]: 1374.9569; found: 1374.9541 (35 %); *m*/*z* calcd for [$M^+ - 2CO$]: 1318.9670; found: 1318.9823 (100 %)

Data for compound 10: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 9.22$ (m, 2 H), 8.61 (d, $J = 4.6$ Hz, 1 H), 8.29 (d, $J = 4.1$ Hz, 1 H), 8.21 (d, $J = 4.6$ Hz, 1 H), 8.13 (d, $J = 4.6$ Hz, 1 H), 1.62 (d, $J = 4.1$ Hz, 1 H; inverted β-H), 1.16 (d, $J = 4.6$ Hz, 1H inverted β-H), 0.05 ppm (s, 1 H; inner C-H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 178.5$ (d, $J_{\text{Rh-C}} = 69.7$ Hz, *C*O), 178.1 (d, $J_{\text{Rh-C}} = 68.5$ Hz, *C*O), 163.9, 163.7, 161.0, 159.7, 158.5, 154.7, 147.8, 146.1, 144.3, 136.4, 136.0 (invert β-carbon), 134.7 (β-carbon), 133.7 (invert β-carbon), 130.4, 129.9 (β-carbon), 129.2 (β-carbon), 128.4 (β-carbon), 128.4 (β-carbon), 124.8, 124.6, 123.5 (β-carbon), 119.3, 109.9, 101.8 (inner β-carbon), 100.4 ppm; UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (ε) = 360 (35 300), 435 (36 500), 501 (51 400), 579 (60 800), 792 nm (5100 $M^{-1}cm^{-1}$); FT-IR (KBr): $\tilde{\nu} = 3445$, 3071, 2920, 2856, 2081, 2020, 1651, 1520, 1498, 992, 752 cm^{-1}; FAB-MS: *m*/*z* calcd for $C_{57}H_9F_{25}N_5O_2Rh$ [M^++H]: calcd: 1373.9410; found: 1373.9213 (5 %); *m*/*z* calcd for [$M^+ - 2CO$]: 1316.9514; found: 1316.9502 (100 %).

Computational methods: All calculations were carried out with the Gaussian 03 program.[14] All structures were optimized with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3 LYP),[15] employing the 6–311 + G** basis set for all atoms. The NICS values were obtained with the GIAO method at the B3 LYP/6–311 + G** level. The ring centers were designated at the nonweighted means of the carbon and nitrogen coordinates on the conjugate pathways.

X-ray crystallography: Details of the X-ray meansurements are given in Table 2. CCDC-255770 (**3**), CCDC-255771 (**4**), CCDC-255772 (**9**), and CCDC-255773 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement of **3**, **4**, **9**, and **10**.

	3	**4**	**9**	**10**
formula	$C_{55}H_{25}N_5Cl_{10}O_2$	$C_{56}H_{29}N_5Cl_{12}$	$C_{120}H_{36}N_{10}F_{50}O_4Rh_2$	$C_{121}H_{18}N_{10}F_{50}O_5Rh_2$
M_r	1142.36	1197.31	2837.40	2847.27
T [K]	123	123	123	123
crystal system	monoclinic	monoclinic	triclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$Pbca$
a [Å]	16.585(2)	18.43(1)	15.3541(1)	22.8893(16)
b [Å]	22.865(3)	14.65(1)	16.0710(1)	28.468(2)
c [Å]	16.986(3)	20.89(1)	26.1560(5)	33.970(3)
α [°]	90	90	72.8972(9)	90
β [°]	118.113(4)	113.37(3)	84.6971(9)	90
γ [°]	90	90	62.1349(7)	90
V [Å]	5681(1)	5177(6)	5445.7(1)	22 136(3)
Z	4	4	2	8
ρ_{calcd} [g cm^3]	1.335	1.536	1.730	1.709
μ [cm^{-1}]	5.337	6.86	4.503	4.45
F (000)	2368.00	2416.00	2796.00	11 152
crystal size [mm^3]	0.30 × 0.20 × 0.10	0.25 × 0.15 × 0.10	0.80 × 0.60 × 0.40	0.55 × 0.20 × 0.10
$2\theta_{\max}$ [°]	55.0	55.0	55.0	50.0
observed reflns	4293	5540	15 648	19 488
total reflns	23 948	21 362	41 886	112 647
parameters	672	687	1681	1653
absorpn correction				empirical
R_1 [$I > 3\sigma(I)$]	0.075	0.053	0.046	0.0837 ([$I > 2\sigma(I)$])
wR_2 [$I > 3\sigma(I)$]	0.091	0.058	0.052	0.1151 (all data)
GOF	1.050	0.86	0.613	1.149

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