Metathesis-like Splitting Reactions of Metallated [36]Octaphyrins(1.1.1.1.1.1): Experimental and Computational Investigations

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meso-Octakis(pentafluoro-Abstract: phenyl)-substituted [36]octaphyrin(1.1.1.1.1.1.1) (1) is a figure-of-eight nonaromatic macrocycle that serves as a unique platform to induce a metathesis-like splitting reaction upon bis-Cu^{II} metalation. To get a better understanding of this splitting reaction, we examined the metalation of 1 with several metal ions. In contrast with the smooth and quantitative splitting reaction of bis-Cu^{Π} complex **1**–CuCu, free-base **1**, mono-Cu^{II} complex 1-Cu, and bis-Zn^{II} complex 1-ZnZn do not undergo the splitting reaction. Mono-Co^{II} complex 1-Co was selectively produced from metalation with the Co^{II} ion, from which hybrid complex 1-CoCu was synthesized. The hybrid complex 1-CoCu undergoes the splitting reaction to give 2-Co and 2-Cu quantitatively.

Activation parameters of the splitting reactions were determined: $E_a =$ 104 kJ mol^{-1} , $\Delta H^{\pm} = 101 \text{ kJ mol}^{-1}$, $\Delta S^{\pm} = -25.0 \text{ J mol}^{-1} \text{K}^{-1}$, and $\Delta V^{\pm} =$ $18 \text{ cm}^3 \text{mol}^{-1}$ for **1**-CuCu and $E_a =$ $105 \text{ kJ mol}^{-1}, \Delta H^{\pm} = 102 \text{ kJ mol}^{-1}, \text{ and}$ $\Delta S^{\pm} = -29.9 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$ for **1**–CoCu. A marked difference between the splitting reaction reactivity of 1-CuCu and 1-ZnZn has been examined by DFT calculations at the B3LYP/631SDD// B3LYP/LANL2DZ level, which revealed that the reaction proceeds through a stepwise route involving initial C1-C20 bond formation to give INT1 as the rate-determining step and

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subsequent C21-C40 bond formation to give a spirocyclobutane intermediate (INT2), followed by a radical reverse cycloaddition reaction to give two metalloporphyrins. Inherent instability of 1-CuCu, which may arise from its strongly distorted structure, was indicated to be a main factor in the smooth splitting reaction. Finally, a new bis-Pd^{II} complex (5-PdPd) was isolated in the metalation of 1 with $Pd(OAc)_2$ in a 9:1 mixture of 2,2,2-trifluoroethanol and methanol as a manifestation of the transannular electronic interaction in metalated octaphyrin complexes. Collectively, these results underscore the importance of the transannular electronic interactions that are enhanced by metalation, depending upon the coordinated metal ions.

Introduction

In recent years, increasing attention has been focused on expanded porphyrins^[1] that are pyrrolic conjugated macrocycles larger than porphyrin because of their large conjugated π systems,^[2] multiple oxidation states,^[3] conformational flexibilities,^[4] anion-binding abilities,^[5] and novel aromatic characters.^[3,6,7] Aside from these intriguing properties, the metalation of expanded porphyrins is quite effective for producing unique metal complexes of novel structures and properties, as illustrated by the interesting examples, such as the bis-Cu^{II} complex of amethyrin,^[8] the bis-Au^{III} complexes of [26]hexaphyrin(1.1.1.1.1.1),^[3b,d] the heterometallic complexes of [40]nonaphyrin(1.1.1.1.1.1),^[9] and Möbius aromatic-metal complexes.^[10]

With increasing molecular size, expanded porphyrins tend to take distorted structures, such as figure-of-eight conformations or helical structures as a consequence of a fully conjugated and cyclic structure.^[2,9] In some cases, such distorted molecular systems lead to unique irreversible chemical reactions aided by the transannular interactions. Vogel et al. found that the metalation of 5,24-dioxo-octaphyrin(1.1.1.0.1.1.1.0) with Ni^{II} ions caused an unexpected rear-

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rangement to a bis-Ni^{II} complex of spirodicorrole through the extrusion of two carbon dioxide molecules.^[11] They also reported that the Pd^{II} metalation of [34]octaphyrin(1.1.1.0.1.1.1.0) caused the formation of a bis-Pd^{II} complex of a quite unprecedented bis-spirodiporphyrin skeleton, again through the transannular interaction.^[11]

We have previously reported the synthesis of a series of meso-pentafluorophenyl-substituted expanded porphyrins under the modified Rothemund-Lindsey protocol for porphyrin synthesis.^[12] This synthetic method allowed us to explore the new chemistry of these expanded porphyrins. For instance, we found unexpected cross-bridging reactions of 5,20-bis-ethynyl-substituted [26]hexaphyrins to provide vinylene-bridged hexaphyrins^[13a] and the [3+2] annulation re-</sup> action of 5-aryl-20-ethynyl-substituited [26]hexaphyrins to provide 1,3-indenylene-bridged hexaphyrins.^[13b] These two reactions are apparently triggered by the transannular interactions, which are enforced during dynamic conformational changes.^[13] As a more surprising reaction, we found the clean splitting reaction of the bis-Cu^{II} complex of meso-pentafluorophenyl-substituted [36]octaphyrin(1.1.1.1.1.1.1) (1-CuCu) that quantitatively produced two molecules of Cu^{II}porphyrins 2-Cu.^[14] This reaction mode is quite unprecedented because it requires the rupture and formation of two carbon-carbon double bonds similar to a metathesis reaction. Another interesting example is the extrusion of mesopentafluorophenyl-substituted B^{III}-subporphyrin from the corresponding [32]heptaphyrin(1.1.1.1.1.1) upon treatment of its mono-Cu^{II} complex with the B^{III} ion.^[15] These two reactions are also initiated by the transannular electronic interactions in distorted expanded porphyrins.

a)

Herein, we examine the thermal splitting reactions of metal complexes of 1. Among these, only bis-Cu^{II} complex 1-CuCu and hybrid complex 1-CoCu undergo the splitting reaction. To determine the reaction profile, the activation parameters $(E_{\rm a}, \Delta H^{\pm}, \Delta S^{\pm}, \text{ and } \Delta V^{\pm})$ of the splitting reactions were determined and discussed. Theoretical calculations were also performed for the splitting reactions of 1-CuCu and 1-ZnZn at the B3LYP/631SDD//B3LYP/ LANL2DZ level. Finally, in the metalation with $Pd(OAc)_2$, we isolated an interesting complex, 5-PdPd, which has C1-C20 and C2-N5 (pyrrole E) bonds as evidence for the effective transannular interactions. Collectively, these results provide valuable insight into the molecular mechanism of the splitting reaction.

Results and Discussion

Free-base octaphyrin: The solid-state structure of octaphyrin **1** exhibits a figure-ofeight conformation with C_2 symmetry (Figure 1a).^[16] The two hemi-porphyrin-like segments are roughly planar and arranged in a roughly parallel manner with an interplanar distance of 3.4 Å. Accordingly, the Figure 1. Crystal structures of a) **1**, b) **1**–CuCu, c) **1**–ZnZn, and d) **1**–Co; top views (left) and side views (right). The thermal ellipsoids are scaled to the 50% probability level. *meso*-Aryl substituents are omitted for clarity.

distances from C1 to C20 and from C19 to C40, which are considered to form bonds during the metathesis-like splitting reaction, are 4.127 and 4.176 Å. The free-base **1** does not undergo the splitting reaction, even under harsh conditions.

Cu^{II} complexes: To obtain 1–Cu and 1–CuCu, the metalation should be conducted at 0°C to avoid the thermal splitting reaction of 1–CuCu. A solution of 1 in a mixture of dichloromethane and methanol was stirred in the presence of Cu(OAc)₂ (3 equiv) and NaOAc (3 equiv) for 1 h to provide 1–Cu (77%) and 1–CuCu (9%) (see Scheme 1). The complex 1–CuCu was selectively prepared by stirring 1 in the presence of Cu(OAc)₂ (10 equiv) and NaOAc (5 equiv) for 7 h to give 81% yield. Similarly to 1, the mono-Cu^{II} complex 1–Cu is not split upon prolonged heating, highlighting the crucial importance of the two coordinated Cu^{II} ions for the



Scheme 1. Metalation of 1 with $Cu(OAc)_2$ and subsequent thermal splitting reaction of 1-CuCu.

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splitting reaction. The splitting reaction of 1-CuCu was conducted by stirring a solution of 1-CuCu in toluene at 50°C. The progress of the reaction was monitored by UV/Vis absorption spectroscopy. More simply, almost the same absorption spectral changes were observed by stirring a solution of 1 in toluene in the presence Cu- $(OAc)_2$ (10 equiv) and NaOAc (5 equiv) at 50 °C. Absorption bands at 410 and 643 nm due to **1** changed to the absorption bands at 412 and 668 nm due to 1-Cu after 2 h and then to the absorption bands at 351 and 522 nm due to 1-CuCu (Figure 2a) after 4 h. These spectral assignments were based on referring to the respective authentic absorption spectra (see the Supporting Information). Surprisingly, the absorption spectrum of this reaction mixture changed dramatically upon prolonged heating, and finally reached the absorption spectrum with a sharp absorption band at 408 nm and two small absorption bands at 535 and 570 nm after 2 weeks. The final absorption spectrum of the reaction mixture clearly indicated the exclusive formation of 2-Cu, which was actually isolated in 67% yield from this reaction mixture. Elevating the reaction temperature to 111 °C completed the splitting reaction within 2 h, to provide 2-Cu in a better yield of 91%. Single-crystal Xray diffraction analysis of 1-CuCu indicated a distorted structure of C_2 symmetry, in which the two Cu atoms are bound to the four pyrrolic nitrogen atoms but the coordination features are far from those of usual square-planar complexes.^[14a] As shown in Figure 1b, pyrrole rings C, B, and D and F, G, N, and H constitute relatively planar segments, but pyrrole



Figure 2. Absorption spectra of a) 1–CuCu, b) 1–ZnZn, c) 1–Co, d) 1–CoZn, and e) 1–CoCu in CH_2Cl_2 (left) and in acetonitrile (right).

rings A and H are significantly tilted from these segments. This severely distorted structure of 1-CuCu suggests that a

relief of the strain in **1**–CuCu may be a main driving force for this splitting reaction.

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The rates of the splitting reaction were determined by monitoring the increasing absorbance of 2-Cu at 410 nm at various temperature to be $5.1 \times 10^{-5} \text{ s}^{-1}$ at 60 °C, $7.8 \times 10^{-5} \text{ s}^{-1}$ at 65°C, $1.4 \times 10^{-4} \text{ s}^{-1}$ at 70°C, $2.5 \times 10^{-4} \text{ s}^{-1}$ at 75°C, and $4.1 \times 10^{-4} \,\mathrm{s}^{-1}$ at 80 °C. By using these results, the activation parameters of the splitting reaction have been determined as the following: activation energy, $E_a = 104 \text{ kJ mol}^{-1}$; activation enthalpy, $\Delta H^{\pm} = 101 \text{ kJ mol}^{-1}$; and activation entropy, $\Delta S^{\pm} = -24.4 \ J \, mol^{-1} \, K^{-1}$ (see the Supporting Information). The reaction rates and activation parameters were also measured in the more polar acetonitrile solution: $4.3 \times 10^{-5} \text{ s}^{-1}$ at 60 °C, $7.7 \times 10^{-5} \text{ s}^{-1}$ at 65 °C, $1.4 \times 10^{-4} \text{ s}^{-1}$ at 70 °C, $2.4 \times 10^{-4} \text{ s}^{-1}$ $10^{-4} \,\mathrm{s}^{-1}$ at 75 °C, and $3.5 \times 10^{-4} \,\mathrm{s}^{-1}$ at 80 °C, and $E_a =$ 104 kJ mol^{-1} , $\Delta H^{\pm} = 101 \text{ kJ mol}^{-1}$, $\Delta S^{+} =$ and -25.0 J mol⁻¹K⁻¹, which indicates no significant solvent-polarity effects for the splitting reaction. In spite of the dissociative nature of the splitting reaction, the observed negative activation entropy is notable, since it suggests an increased ordering in the transition state from the initial state. We also determined an activation volume (ΔV^{\dagger}) of the splitting reaction by measuring the reaction rate at high pressure at 75°C.^[17] With increasing pressure, the reaction was decelerated $(2.7 \times 10^{-4} \text{ s}^{-1} \text{ at } 1 \text{ bar}, 1.9 \times 10^{-4} \text{ s}^{-1} \text{ at } 500 \text{ bar}, \text{ and } 1.1 \times 10^{-4} \text{ s}^{-1} \text{ at } 500 \text{ bar}$ $10^{-4} \,\mathrm{s}^{-1}$ at 1000 bar), which led to an evaluation of $\Delta V^{\dagger} =$ 18 cm³mol⁻¹. The positive value of the activation volume indicated an increased volume in the transition state from the initial state. Taking these results into consideration, one possible mechanism of the splitting reaction is [2+2] cycloaddition to give a spirocyclobutane intermediate, which is split into two molecules of 2-Cu through a reverse cycloaddition reaction (Scheme 2), since the proposed spirocyclobutane structure is more ordered and larger in volume than the initial state. In accordance with this consideration, the distance between C1 and C20, which will be connected during the reaction, is 3.728 Å in 1-CuCu, which is distinctly shorter than that of **1** (4.127 Å).

Zn^{II} complex: Zinc(II) metalation of **1** was conducted by heating a solution of **1** in methanol at reflux in the presence of excess amounts of Zn(OAc)₂ and Na(OAc) for 2 h, which gave **1**–ZnZn almost quantitatively (Scheme 3). High-resolution electrospray ionization time-of-flight (HR ESI-TOF) mass analysis of **1**–ZnZn showed the parent ion peak at m/z 2110.9160 ([M+Cl]⁻, calcd for C₈₈H₁₆F₄₀N₈Zn₂Cl= 2110.9117). The ¹H NMR spectrum exhibited eight signals in the range from 6.1 to 7.5 ppm, suggesting its C₂ symmetric structure and nonaromatic character (see the Supporting In-

a)

C20 AI

1-ZnZn





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heat

no reaction



Scheme 3. A possible mechanism of the thermal splitting reaction of 1– CuCu to 2–Cu. *meso*-Pentafluorophenyl substituents were omitted for clarity. Newly formed bonds are indicated as red lines.

formation). The UV/Vis absorption spectrum of 1-ZnZn changes depending on the solvent (Figure 2b), and the solution color also changes; red in CH₂Cl₂ and green in acetonitrile probably due to the coordination of acetonitrile molecules to the Zn^{II} ions. The structure of **1**–ZnZn has been revealed to be a severely distorted figure-of-eight conformation, in which the two Zn^{II} ions are each bound to the porphyrin-like four nitrogen atoms in a similar manner to that of 1-CuCu (Figure 1b). The Zn-N bond lengths are 2.08, 2.01, 2.02, and 2.03 Å, and the Zn-Zn distance is 5.21 Å. Pyrrole rings B, C, and D constitute a relatively flat tripyrrolic segment with the mean plane deviation of 0.22 Å, to which pyrrole A is held with a large tilting angle of 62°. Despite the distorted structure comparable to that of 1-CuCu, complex 1-ZnZn is thermally robust and does not undergo splitting reactions even by prolonged heating at reflux. Importantly, the distance between C1 and C20 in 1-ZnZn is 3.859 Å, which is slightly, but distinctly longer than that of **1**–CuCu (3.728 Å).

Co^{II} complexes: A solution of **1** in dichloromethane was heated at reflux in the presence of $Co(OAc)_2$ (10 equiv), NaOAc (10 equiv), and a small amount of methanol for 2 h to give mono-Co^{II} complex **1**–Co almost quantitatively. Interestingly, under these forcing conditions, the formation of **1**–CoCo was not detected. The HR ESI-TOF mass spectrum of **1**–Co shows the parent ion peak at m/z 2005.0354 ($[M-H]^-$, calcd for C₈₈H₁₇F₄₀N₈Co₁=2005.0307). The structure of **1**–Co was determined by single-crystal X-ray diffraction analysis to be a distorted figure-of-eight conformation

(Figure 1 d), which is similar to those of **1**, **1**–CuCu, and **1**– ZnZn. In this complex, the Co^{II} ion is bound to the four nitrogen atoms of the pyrroles A, B, C and D with distances of 2.149, 2.024, 2.115, and 2.116 Å and to the nitrogen atom of the crystallizing solvent acetonitrile with a distance of 2.222 Å. The

spin state of Co^{II} ion is considered to be the high-spin state from its temperature-dependent magnetic susceptibility (see the Supporting Information). The complex **1**–Co is thermally quite robust and does not undergo the splitting reaction.

Because 1–Co holds a vacant hemi-porphyrin-like tetrapyrrolic cavity, further metalation was attempted to synthesize hetero-metal complexes of [36]octaphyrin. First, hetero bis-metal complex 1–CoZn was prepared by the metalation of 1–Co with $Zn(OAc)_2$ (Scheme 4). Although some deme-



Scheme 4. Metalation of 1 with $Co(OAc)_2$ and the synthesis and thermal splitting reaction of 1–CoCu.

talation of the Zn^{II} ion occurred during work up, pure 1-CoZn was obtained in 77% yield along with recovery of 1-Co (22%). The parent ion peak of 1-CoZn was observed at m/z 2103.9173 ([M+Cl]⁻, calcd for C₈₈H₁₆F₄₀N₈CoZnCl= 2103.9179) in the HR ESI-TOF mass spectrum. The absorption spectrum of 1-CoZn was revealed to be solvent dependent. In dichloromethane, the spectrum is ill-defined feature with broad bands at 346, 516, 689, and 817 nm (Figure 2d), whereas that in acetonitrile exhibits rather similar features to that of 1-ZnZn, in which there is a relatively intense band at 700 nm along with weaker bands at 357, 434, and 1025 nm. Measurement of the magnetic susceptibility of 1-CoZn suggested that the Co^{II} ion is in the high-spin state. The ¹H NMR spectrum in CDCl₃ shows β -pyrrolic proton signals at 95.42, 90.63, 83.21, 76.00, 62.15, 55.67, 54.07, 24.67, 12.58, 6.89, 6.31, 3.39, 0.09, -2.77, -2.96, and -25.55 ppm, suggesting the effect of a paramagnetic shift by Co^{II}. The splitting reaction of 1-CoZn was attempted by heating solutions in toluene or acetonitrile, which, however, led to facile liberation of the Zn^{II} ion and thus further examinations were abandoned. In the next step, hetero bis-metal complex 1-CoCu was efficiently prepared by treatment of 1-Co with $Cu(OAc)_2$ under similar conditions. The complex 1–CoCu was also synthesized by the metalation of 1-Cu with Co-(OAc)₂. The hetero bis-metal composition was confirmed by the parent ion peak at m/z 2065.9507 ($[M]^-$, calcd for $C_{88}H_{16}F_{40}N_8CoCu = 2065.9493$) in the HR ESI-TOF mass spectrum. The spin state of the Co^{II} ion was again revealed to be high spin from its magnetic susceptibility (see the Supporting Information). The absorption spectrum of 1-CoCu in dichloromethane is similar to that of **1**-CuCu, showing broad bands at 347 and 522 nm and weaker bands at 688, 821, and 984 nm (Figure 2e). The complex **1**-CoCu is red in color in dichloromethane.

The thermal splitting reaction of 1-CoCu was examined. While heating 1-CoCu in toluene led to its decomposition, the clean splitting reaction of 1-CoCu was observed in acetonitrile, which gave an equal mixture of 2-Co and 2-Cu as indicated by UV/Vis absorption and ¹⁹F NMR spectroscopies (see the Supporting Information). We indeed isolated both 2-Co and 2-Cu in more than 90% yields from the thermolysis of 1-CoCu by heating at reflux in acetonitrile for 24 h. This contrasting solvent effect on the thermal reactivity of 1-CoCu is difficult to explain at this stage. The red color of 1-CoCu in dichloromethane changes to green in acetonitrile. In fact, the absorption spectrum of 1-CoCu shows a relatively intense band at 697 nm along with smaller bands at 440, 909, and 1030 nm in acetonitrile (Figure 2e). These spectral changes may be ascribed to additional coordination of an acetonitrile molecule on the CoII ion, as in the crystal structure of 1-Co (Figure 1d). The rates of the splitting reaction were measured by monitoring the UV/Vis absorbance of a mixture of 2-Co and 2-Cu at variable temperatures. The reaction rates thus determined were $2.1 \times 10^{-5} \, \text{s}^{-1}$ at 60 °C, $3.2 \times 10^{-5} \text{ s}^{-1}$ at 65 °C, $6.3 \times 10^{-4} \text{ s}^{-1}$ at 70 °C, $1.1 \times 10^{-6} \text{ s}^{-1}$ 10^{-4} s^{-1} at 75 °C, and $3.5 \times 10^{-4} \text{ s}^{-1}$ at 80 °C. The splitting reaction rates of 1-CoCu were slower than those of 1-CuCu at the same temperature. By analyzing these data with Arrhenius and Eyring plots, an activation energy $(E_a =$ 105 kJ mol⁻¹) and activation parameters ($\Delta H^{\pm} = 102$ kJ mol⁻¹ and $\Delta S^{+} = -29.9 \text{ Jmol}^{-1} \text{K}^{-1}$) were estimated. Importantly E_a and ΔH^{\dagger} values of the splitting reaction of **1**-CoCu are almost the same as those in 1-CuCu, but the ΔS^{\dagger} value of 1-CoCu was more negative by $4.9 \,\text{Jmol}^{-1}\text{K}^{-1}$ than that of 1-CuCu. Thus, the slow splitting reaction of 1-CoCu can be ascribed mainly to the entropy term. The splitting reaction of 1-CoCu is probably more ordered and includes the coordinated acetonitrile molecule in the transition state.

Computational investigations: At this stage, we investigated the reaction mechanism by computational methods with the hope of understanding the marked difference in the splitting reactivity between 1-CuCu and 1-ZnZn. All calculations were carried out by using the Gaussian 03 program. DFT calculations were performed starting from the model systems of 1-CuCu and 1-ZnZn. Initial geometries were obtained from the crystal structures of 1-CuCu and 1-ZnZn. To reduce the calculation time, we replaced two pentafluorophenyl groups at the 20-, and 40-positions with 2,6-difluorophenyl groups, which seem to have significant influence on the reaction path, and other six pentafluorophenyl groups, which are probably not critical, were replaced by hydrogen atoms. The structures of the intermediates and transition states were obtained by estimates. The spin states were designated as triplet for all bis-copper complexes because the triplet ground state ($S=1/2\times 2$) for **1**-CuCu was elucidated by the magnetic susceptibility measurement, in which no

magnetic interaction was observed between two isolated spins (see the Supporting Information). The structures were fully optimized with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP), employing LANL2DZ basis set for all atoms. Zero-point and thermal energy corrections were conducted for all optimized structures. The obtained transition states gave single imaginary frequencies and intrinsic reaction coordinate (IRC) calculations supported the transition structures. At the optimized geometries, energies were further calculated by the B3LYP method with SDD basis set for copper and zinc and 6-31G* for the rest of atoms (denoted as 631SDD).

The optimized structure of the model compound 1–CuCu is in good agreement with the X-ray crystal structure (Figure 3). It is noteworthy that the distance between C1



Figure 3. Optimized structures of intermediates and transition states for the splitting reaction of **1**–CuCu to **2**–Cu at the B3LYP/LANL2DZ level. Hydrogen atoms were omitted for clarity.

and C20 is only 3.519 Å, indicating very close proximity between α - and *meso*-carbon atoms in the crossing point of the figure-of-eight structure. This is important for the reaction mechanism because bond formation between α - and *meso*carbon atoms is required for the formation of porphyrin from octaphyrin. By reducing the distance between C1 and C20 gradually, we found the transition state **TS1**, which then changes to the singly bridged intermediate **INT1** (Figure 3 and Scheme 2). The activation energy of this initial process was calculated to be $E_a = 41.7 \text{ kcal mol}^{-1}$ at the B3LYP/ 631SDD//B3LYP/LANL2DZ level (Figure 4a). Then we lo-



Figure 4. Calculated reaction coordinates for the splitting reaction of a) **1**–CuCu to **2**–Cu and b) **1**–ZnZn to **2**–Zn. Energies were calculated at the B3LYP/631SDD//B3LYP/LANL2DZ level.

cated the transition state **TS2** with very small activation energy ($E_a = 2.0 \text{ kcal mol}^{-1}$) for the second C–C bond formation between C21 and C40 from **INT1** to a spirocyclobutane intermediate **INT2**.

A reverse cycloaddition reaction of the cyclobutane in INT2 would provide two porphyrins, but the concerted mechanism is thermally prohibited for retro [2+2] cycloaddition. Consequently, a stepwise pathway involving two sequential homolytic cleavages of two C-C bonds is reasonably expected. In fact, transition-state TS3 with an activation energy of 11.8 kcalmol⁻¹ was obtained for the initial C1-C40 bond scission of the spirocyclobutane intermediate. Transition-state TS3 exhibits a significant radical character with $\langle S^2 \rangle = 2.372$ (B3LYP/631SDD//B3LYP/LANL2DZ), whereas all other bis-Cu^{II} species have very small spin density on the macrocycle ($< S^2 > = 2.006 - 2.008$, see the Supporting Information), which only resulted from the spin on Cu^{II} . Here, $\langle S^2 \rangle$ denotes the expectation value of the total spin angular momentum. In INT2, C1 and C20 have Mulliken spin densities of 0.00242 and 0.00084, while the spin densities at those carbon atoms in TS3 are 0.136 and -0.271, respectively (see the Supporting Information). This implies a partial singlet biradical character of the C-C bond cleavage process in TS3. All Cu^{II} species including 2-Cu posses Mulliken spin densities on copper centers ranging from 0.614 to 0.635, thus indicating no significant change of the valence state of copper during the splitting reaction. No further intermediates could be found from **TS3** to **2**–Cu, and the IRC calculation confirmed that the second C–C bond cleavage between C1 and C20 occurs successively from **TS3** without any intermediate. Probably such an intermediate species with a strong singlet biradical nature is too unstable to be optimized and provides two porphyrins directly.

These DFT calculations indicate that the initial C–C bond formation from 1–CuCu to **INT1** is the rate-determining step. On the basis of the frequency calculation, the activation entropy for this process is estimated to be $\Delta S^{\pm} = -24.2 \text{ Jmol}^{-1}\text{K}^{-1}$, which is matched well with the experimental value $-24.4 \text{ Jmol}^{-1}\text{K}^{-1}$ in toluene.

To investigate the origin of the different reactivity between 1–CuCu and 1–ZnZn, we also calculated the reaction pathway for the similar splitting of 1–ZnZn to 2–Zn. Similar intermediates and transition states (1–ZnZn, **TS1**, **INT1**, **TS2**, **INT2**, **TS3**, and 2–Zn) were obtained (Figure 4b). In the case of Zn^{II} complexes, the activation energy (E_a = 53.0 kcalmol⁻¹) for the initial step from 1–ZnZn to **TS1** is significantly higher than that of 1–CuCu (E_a =41.7 kcal mol⁻¹). Again, **TS3** also has significant biradical character with $\langle S^2 \rangle = 0.464$ (B3LYP/631SDD//B3LYP/LANL2DZ)



Figure 5. Calculated structures of 1–CuCu and 1–ZnZn at the B3LYP/ LANL2DZ level. Several metal–N and C1–C20 bond lengths are also indicated in Å.

and the Mulliken spin densities of C21 and C40 are 0.150 and -0.336, respectively.

Then, the question remains as to the reason for such a high activation energy for the initial step. Since the structural factors are similar between 2-Cu and 2-Zn, it is meaningful to compare relative energies of intermediates and transition states on the basis of the energies of 2-Cu and 2-Zn (Figure 3). This clearly highlights the relative instability of 1-CuCu in comparison with 1-ZnZn. This inherent instability of 1-CuCu may be a main reason for its smooth splitting reaction. The instability of 1-CuCu largely arises from the ring strain. Characteristically, the calculated C1-C20 distance in 1-CuCu is 3.519 Å, which is distinctly shorter that that (3.797 Å) in 1–ZnZn (Figure 5). Such a short C1–C20 distance forces a larger distortion for the ring system of 1-CuCu. In addition, a shorter N-metal bond length causes shrinkage of the octaphyrin macrocycle to decrease the distance between α - and *meso*-carbon atoms and thus induce more strain. In fact, the calculated Cu-N bond lengths are in the range of 2.013-2.096 Å in 1-CuCu, whereas Zn-N bond lengths are 2.092-2.162 Å in 1-ZnZn. These tendencies are confirmed in the crystal structures of the real systems 1-CuCu and 1-ZnZn: the C1-C20 distance is 3.728 Å and Cu-N bond lengths are 1.974-2.059 Å in 1-CuCu, whereas the C1-C20 distance is 3.859 Å and Zn-N bond lengths are 2.007–2.079 Å in 1–ZnZn. In this context, it is interesting to note that the C1-C20 distances of the monometal complexes are calculated to be 3.889 Å for 1-Cu and 4.048 Å for 1–Co.

Pd^{II} complexes: Recently, we reported the formation of bis-Pd^{II} complexes **3**–PdPd and **4**–PdPd in yields of 51 and 20%, respectively, in the metalation of **1** with $Pd(OAc)_2$ (Scheme 5). These two products have been identified as a twisted Hückel antiaromatic molecule and a twisted Möbius aromatic molecule, respectively.^[10a] The complex **4**–PdPd is one of the first Möbius aromatic molecules with distinct aromaticity.^[7,18,19] We also found that a new complex, **5**–PdPd, was formed in 21% yield along with **3**–PdPd (28%) and **4**–PdPd (trace), when the metalation of **1** with Pd(OAc)₂ was conducted in a 9:1 mixture of 2,2,2-trifluoroethanol and



Scheme 5. Metalation of 1 with Pd(OAc)₂. A part of 5-PdPd is highlighted, where newly generated bonds are indicated in grey.

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methanol. The HR ESI-TOF mass analysis of **5**–PdPd showed the parent ion peak at m/z 2157.8976 ($[M]^-$, calcd for C₈₈H₁₆N₈F₄₀Pd₂, 2157.8967), which is the same as those of **3**–PdPd and **4**–PdPd. The structure of **5**–PdPd was revealed by X-ray analysis, as shown in Figure 6.^[20] The com-

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Figure 6. Crystal structure of **5**–PdPd; top view (left) and side view (right). Newly generated bonds are indicated in red. The thermal ellipsoids are scaled to the 50% probability level. *meso*-Aryl substituents are omitted for clarity.

plex 5–PdPd takes a unique structure, in which the Pd1 atom is bound to the four nitrogen atoms of pyrrole rings A, B, C, and D with distances of 1.994, 1.974, 1.950, and 2.000 Å, and the Pd2 atom is bound to the three nitrogen atoms of pyrrole rings F, G, and H with distances of 2.078, 2.032, and 1.993 Å and the β -carbon atom of pyrrole ring A with a distance of 1.956 Å. In addition, the *meso*-carbon (C20) and the α -carbon of pyrrole ring A (C1) are directly connected and the β -carbon of pyrrole ring A (C3) has two

hydrogen atoms. In agreement with this structure, the ¹H NMR spectrum of **5**–PdPd showed fourteen doublet signals due to the β -pyrrolic protons and two singlet signals at δ =2.87 ppm due to the saturated β -pyrrolic protons. The structure was also confirmed by measuring the absorption spectrum, which is shown in Figure 7.



Figure 7. Absorption spectrum of 5-PdPd in CH₂Cl₂.

The three complexes 3-PdPd, 4-PdPd, and 5-PdPd are each thermally stable and no interconversions were observed, even when heated at reflux in toluene. A plausible reaction pathway to 5-PdPd is shown in Scheme 6, in which complex 6-PdPd is postulated as a precursor for 5-PdPd. Probably due to the intrinsic C-H activation ability of Pd^{II} ion when coordinated in expanded porphyrins, the NNNN metalation as observed for 1-CuCu and 1-ZnZn is impossible for Pd^{II} metalation. As a result, symmetric NNNC metalation led to the formation of 3-PdPd and non-symmetric NNNC and NNNN metalation provided 6-PdPd. In 3-PdPd, the distances between the *meso*-carbon and the pyrrolic α carbon are relatively long (4.835 and 4.824 Å),^[10a] which may explain the lack of transannular reactivity. On the other hand, the transannular interaction is enhanced in 6-PdPd, which causes the C1-C20 bond formation reaction to give 7-PdPd and subsequent C2-N5 (pyrrole ring E) bond formation with concurrent hydrogen transfer from pyrrole ring



Scheme 6. A possible metalation pathway to 5-PdPd and comparison with splitting reaction pathway of 1-CuCu. Newly generated bonds are indicated in red.

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E to the β -carbon of pyrrole ring A affords **5**–PdPd. It is noteworthy that the reaction sequence from **6**–PdPd to **7**– PdPd is similar to that from **1**–CuCu to **INT1** and the structure of **5**–PdPd is the manifestation of the transannular electronic interaction.

Conclusions

Metalation of 1 with Cu^{II}, Zn^{II}, Co^{II}, and Pd^{II} ions was examined. Cu^{II}, Zn^{II}, and Co^{II} ions favor NNNN coordination to form figure-of-eight complexes 1-Cu, 1-CuCu, 1-ZnZn, and 1-Co, whereas Pd^{II} prefers NNNC and NNNN coordination. Among these, 1-CuCu and 1-CoCu undergo the splitting reaction to two porphyrins upon heating, but the reaction rate was faster for 1-CuCu. The large negative reaction entropies observed for the splitting reactions of 1-CuCu and 1-CoCu and DFT calculations suggested a stepwise route via intermediates INT1 and INT2 (spirocyclobutane) followed by a radical reverse cycloaddition reaction. Bis-Pd^{II} complex 5-PdPd was newly isolated as the manifestation of the transannular electronic interactions in the metalated octaphyrins. Collectively, these results indicate that octaphyrin 1 is a unique scaffold to effect the topological splitting reactions through the transannular electronic interactions that are enhanced upon metalation.

Experimental Section

General: ¹H and ¹⁹F NMR spectra were recorded on a JEOL ECA-600 spectrometer (600 MHz for ¹H and 565 MHz for ¹⁹F). Chemical shifts were reported on the delta scale in ppm relative to the residual solvent as the internal reference for ¹H (δ = 7.260 ppm), and hexafluorobenzene was used as external reference for ¹⁹F ($\delta = -162.9$ ppm). NMR signals were assigned from the 1H-1H COSY spectra, and from comparison with the spectra in the presence of D₂O (signals assigned for NH protons disappear in the presence of D₂O) and the simulated spectra. UV/Vis spectra were recorded on a Shimadzu UV-3100PC spectrometer. MALDI-TOF mass spectra were recorded on a Shimadzu KRATOS KOMPACT MALDI4 spectrometer by using the positive or negative MALDI method. High-resolution FAB mass spectra were recorded on a JEOL HX110 spectrometer by using the fast atom bombardment method in the positive ion mode with a 3-nitrobenzylalcohol matrix. High-resolution ESI-TOF mass spectra of samples in acetonitrile were recorded on a BRUKER microTOF instrument in the positive or negative ion mode. X-ray data were recorded on a Rigaku-Raxis imaging plate system, or on a BRUKER-APEX X-Ray diffractometer equipped with a large area CCD detector. The magnetic susceptibility was measured for the powder samples with the temperature range from 2 to 300 K at 0.1 T magnetic field by using Quantum Design MPMS-5. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Silica gel column chromatography was performed on Wakogel C-300 and C-400. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F₂₅₄ (Merck 5554).

Bis-zinc(II) complex of [36]octaphyrin (1–ZnZn): $Zn(OAc)_2$ (18.9 mg, 0.10 mmol; 10 equiv) and NaOAc (8.7 mg, 0.10 mmol; 10 equiv) were added to a solution of **1** (19.5 mg, 0.01 mmol; 1.0 mM in MeOH) and the resulting mixture was heated at reflux for 2 h under a nitrogen atmosphere in the dark. After removing the solvent, the residues were dissolved in CH₂Cl₂, washed with water, dried over Na₂SO₄, and the solvent was removed under reduced pressure. Purification by column chromatog-

raphy on silica gel gave 1-ZnZn (20.0 mg, 96%). ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 7.50$ (t, J = 4.14 Hz, 2H), 6.60 (d, J = 4.14 Hz, 2H), 6.58 (brs, 2H), 6.48 (brs, 2H), 6.38 (d, J=4.14 Hz, 2H), 6.31 (d, J= 4.14 Hz, 2H), 6.26 (d, J=4.8 Hz, 2H), 6.12 ppm (d, J=4.8 Hz, 2H); ¹⁹F NMR (564.73 MHz, CDCl₃, 298 K): $\delta = -131.87$ (d, J = 22.02 Hz, 2F; o-F), -132.90 (d, J=23.4 Hz, 2F; o-F), -136.63 (d, J=23.46 Hz, 2F; o-F), -137.05 (d, J=19.02 Hz, 2F; o-F), -138.34 (t, J=24.9 Hz, 4F; o-F), -140.37 (d, J=22.02 Hz, 2F; o-F), -141.54 (brs, 2F; o-F), -151.37 (t, J=19.02 Hz, 2F; p-F), -153.10 (t, J=21.96 Hz, 2F; p-F), -153.30 (t, J= 21.96 Hz, 2F; p-F), -153.37 (t, J = 22.02 Hz, 2F; p-F), -160.13 (dt, $J_1 =$ 5.88 Hz, $J_2 = 20.52$ Hz, 2F; m-F), -160.73 (d, J = 19.08 Hz, 2F; m-F), -161.39 (m, 8F; *p*-F), -161.71 ppm (m, 4F; *p*-F); UV/Vis (CH₂Cl₂): λ_{max} $(\varepsilon) = 350$ (59200), 517 (71300), 678 (30200), 807 (17500), 958 nm $(10000 \text{ m}^{-1} \text{ cm}^{-1})$; UV/Vis (CH₃CN): λ_{max} (ε)=359 (44400), 435 (71000), 693 (135000), 787 (sh, 24500), 1030 nm (6200 м⁻¹ сm⁻¹); HR ESI-TOF-MS (negative mode): m/z calcd for $C_{88}H_{16}F_{40}N_8Zn_2Cl$ [M+Cl]⁻: 2110.9117; found: 2110.9160 (100).

CCDC-716724 contains 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.

Mono-cobalt(II) complex of [36]octaphyrin (1–Co): A solution of Co-(OAc)₂ (55.9 mg, 10 equiv) and NaOAc (26.4 mg, 10 equiv) in methanol (10 mL) was added to a solution of **1** (58.6 mg, 0.03 mmol) in CH₂Cl₂ (30 mL) and the resulting mixture was heated at reflux for 2 h. The residues were washed with water, dried over Na₂SO₄, and the solvent was removed. Purification by chromatography on silica gel gave **1**–Co (55.2 mg, 92%). UV/Vis (CH₂Cl₂): λ_{max} (ε)=411 (75500), 682 nm (102000 m⁻¹ cm⁻¹); UV/Vis (CH₃CN): λ_{max} (ε)=411 (73600), 678 nm (99000 m⁻¹ cm⁻¹); HR ESI-TOF-MS (negative mode): *m/z* calcd for C₈₈H₁₇F₄₀N₈Co₁ [*M*–H]⁻: 2005.0307; found: 2005.0354.

CCDC-716725 contains 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.

Cobalt(II)-zinc(II) hetero complex of [36]octaphyrin (1-CoZn): A solution of Zn(OAc)₂ (18.3 mg, 10 equiv) and NaOAc (8.2 mg, 10 equiv) in methanol (10 mL) was added to a solution of 1-Co (20.4 mg, 0.01 mmol) in CH₂Cl₂ (10 mL), and the resulting mixture was stirred for 1 h. The residues were washed with water, dried over Na2SO4, and the solvent was removed. Purification by chromatography on silica gel gave 1-CoZn (16.0 mg, 77%) and demetalated 1–Co (4.4 mg, 22%). $^{1}HNMR$ (600 MHz, CDCl₃, 298 K): $\delta = 95.42$ (s, 1 H), 90.63 (s, 1 H), 83.21 (s, 1 H), 76.00 (s, 1H), 62.15 (s, 1H), 55.67 (s, 1H), 54.07 (s, 1H), 24.67 (s, 1H), 12.58 (s, 1H), 6.89 (s, 1H), 6.31 (s, 1H), 3.39 (s, 1H), 0.09 (s, 1H), -2.77 (s, 1H), -2.96 (s, 1H), -25.55 ppm (s, 1H); ¹⁹F NMR (564.73 MHz, $CDCl_3$, 298 K): $\delta = -75.70$ (s, 1F), -107.34 (s, 1F), -108.87 (s, 1F), -119.99 (s, 1F), -134.18 (d, J = 22.02 Hz, 1F), -136.47 (d, J = 22.02 Hz, 1F), -137.71 (s, 2F), -139.15 (s, 1F), -140.33 (t, J=29.34 Hz, 2F), -140.77 (s, 2F), -140.94 (s, 2F), -141.12 (s, 2F), -146.68 (s, 1F), -148.06 (s, 2F), -150.25 (s, 1F), -150.50 (s, 1F), -151.13 (s, 1F), -152.66 (t, J=22.02 Hz, 1F), -153.44 (t, J=21.96 Hz, 1F), -154.73 (s, 1F), -155.80 (s, 1F), -155.95 (s, 1F), -160.41 (t, J = 22.02 Hz, 1F), -161.10 (t, J = 22.02 Hz, 1F), -161.23 (t, J = 22.02 Hz, 1F), -161.43 (t, J=22.02 Hz, 1F), -162.33 (t, J=29.40 Hz, 1F), -162.38 (s, 1F), -165.76 (s, 1F), -168.56 (s, 1F), -176.64 (s, 1F), -195.97 (s, 1F), -201.57 ppm (s, 1F); UV/Vis (CH₂Cl₂): λ_{max} (ε) = 346 (53000), 416 (39700), 516 (47400), 689 (41400), 817 nm (16400 M^{-1} cm⁻¹); UV/Vis (CH₃CN): λ_{max} (ϵ)=357 (42000), 434 (58000), 700 (125000), 1025 nm (5700 M⁻¹ cm⁻¹); HR ESI-TOF-MS (negative mode): m/z calcd for $C_{88}H_{16}ClCoF_{40}N_8Zn [M+Cl]^-$: 2103.9179: found: 2103.9173.

Cobalt(II)-copper(II) hetero complex of [36]octaphyrin (1–CoCu): A solution of Cu(OAc)₂ (55.9 mg, 10 equiv) and NaOAc (26.4 mg, 10 equiv) in methanol (10 mL) was added to a solution of **1**–Co (20.2 mg, 0.01 mmol) in CH₂Cl₂ (30 mL), and the resulting mixture was stirred for 1 h. The residues were washed with water, dried over Na₂SO₄, and the solvent was removed. Purification by chromatography on silica gel gave **1**–CoCu (19.0 mg, 92%). UV/Vis (CH₂Cl₂): λ_{max} (ε)=349 (60300), 521 (63900), 688 (16600), 834 (15200), 993 nm (10200 m⁻¹cm⁻¹); UV/Vis (CH₃CN): λ_{max} (ε)=350 (54700), 439 (58000), 524 (32000), 697 nm

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 $(98400 \text{ m}^{-1} \text{ cm}^{-1})$; HR ESI-TOF-MS (negative mode): m/z calcd for $C_{88}H_{16}F_{40}N_8Co^{63}Cu [M]^-$: 2065.9493; found: 2065.9507.

Bis-palladium(II) complex of [36]octaphyrin (5–PdPd): $Pd(OAc)_2$ (24.0 mg, 10 equiv) and NaOAc (9.2 mg, 10 equiv) was added to a solution of 1 (19.6 mg, 0.01 mmol) in a 9:1 mixture of CF_3CH_2OH (9 mL) and MeOH (1 mL), and the resulting mixture was heated at reflux for 2 h. After removal of the solvent under reduced pressure, the residues were dissolved in AcOEt, washed with water, dried over Na₂SO₄, and the solvent was again removed. Purification by chromatography on silica gel gave 3–PdPd (6.1 mg, 28%) and 5–PdPd (4.5 mg, 21%) along with a trace of 4–PdPd.

5–PdPd: ¹H NMR (600 MHz, CDCl₃, 298 K): $\delta = 6.98$ (t, J = 5.9 Hz, 2H), 6.95 (d, J=5.0 Hz, 1 H), 6.84 (d, J=5.5 Hz, 1 H), 6.78 (d, J=5.0 Hz, 1 H), 6.66 (t, J=5.0 Hz, 1 H), 6.64 (d, J=4.6 Hz, 1 H), 6.61 (d, J=5.0 Hz, 1 H), 6.43 (d, J=4.1 Hz, 1 H), 6.37 (d, J=5.0 Hz, 1 H), 6.16 (d, J=5.0 Hz, 1 H), 6.14 (d, J=4.1 Hz, 1 H), 6.12 (d, J=4.6 Hz, 1 H), 2.87 ppm (s, sp³-H, 2 H); ¹⁹F NMR (564.73 MHz, CDCl₃, 298 K): $\delta = -121.45$ (dd, $J_1 = 26$ Hz, $J_2 =$ 266 Hz, 1F; o-F), -127.90 (dd, J₁=24 Hz, J₂=265 Hz, 1F; o-F), -135.67 (dd, $J_1 = 26.4$ Hz, $J_2 = 65.9$ Hz, 1F; o-F), -136.28 (dd, $J_1 = 25.3$ Hz, $J_2 =$ 66.5 Hz, 1F; o-F), -136.62 (dd, $J_1=24.2$ Hz, $J_2=64.9$ Hz, 1F; o-F), -136.96 (dd, $J_1 = 8.8$ Hz, $J_2 = 26.4$ Hz, 1F; o-F), -137.30 (dd, $J_1 = 6.6$ Hz, $J_2 = 28.6$ Hz, 1F; o-F), -137.84 (dd, $J_1 = 5.5$ Hz, $J_2 = 24.2$ Hz, 1F; o-F), -138.57 (dd, $J_1 = 6.6$ Hz, $J_2 = 23.0$ Hz, 1F; o-F), -138.94 (d, J = 22.0 Hz, 1F; o-F), -139.13 (dd, $J_1 = 19.8$ Hz, $J_2 = 67.1$ Hz, 1F; o-F), -139.43 (d, $J = 23.1 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.61 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{ (d}, J = 27.5 \text{ Hz}, 1\text{ F}; o-\text{F}), -139.82 \text{$ 19.7 Hz, 1F; o-F), -140.1 (dd, $J_1 = 22.0$ Hz, $J_2 = 63.7$ Hz, 1F; o-F), -140.63 (dd, $J_1 = 24.2$ Hz, $J_2 = 63.8$ Hz, 1F; o-F), -151.08 (t, J = 23.0 Hz, 1F; p-F), -151.77 (m, 1F; p-F), -152.39 (t, J=22.0 Hz, 1F; p-F), -152.52 (t, J=22.0 Hz, 1F; p-F), -153.07 (t, J=22.0 Hz, 1F; p-F), -153.27 (t, J = 22.0 Hz, 1F; p-F), -153.41 (m, 1F; p-F), -153.92 (t, J =23.0 Hz, 1F; p-F), -160.97 (dt, $J_1=8.8$ Hz, $J_2=23.6$ Hz, 1F; m-F), -161.25 (dt, $J_1 = 8.8$ Hz, $J_2 = 22.5$ Hz, 1F; m-F), -161.49 (m, 5F; m-F), -161.69 (m, 4F; *m*-F), -161.85 (dt, $J_1 = 7.7$ Hz, $J_2 = 23.6$ Hz, 1F; *m*-F), -161.98 (dt, $J_1 = 7.7$ Hz, $J_2 = 23.1$ Hz, 1F; m-F), -162.59 (m, 2F; m-F), -162.83 (t, J=22.0 Hz, 1F; m-F), -163.73 (t, J=22.0 Hz, 1F; m-F), -165.19 ppm (t, J = 22.0 Hz, 1F; *m*-F); UV/Vis (CH₂Cl₂): λ_{max} (ϵ) = 306 (43200), 347 (37000), 415 (53800), 494 (56700), 749 (19400), 831 nm $(27600 \text{ m}^{-1} \text{ cm}^{-1})$; HR ESI-TOF-MS (negative mode): m/z calcd for C₈₈H₁₆N₈F₄₀Pd₂ [*M*]⁻: 2157.8967; found: 2157.8976.

CCDC-716726 contains 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.

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- a) B. Franck, A. Nonn, Angew. Chem. 1995, 107, 1941–1957; Angew. Chem. Int. Ed. Engl. 1995, 34, 1795–1811; b) A. Jasat, D. Dolphin, Chem. Rev. 1997, 97, 2267–2340; c) J. L. Sessler, D. Seidel, Angew. Chem. 2003, 115, 5292–5333; Angew. Chem. Int. Ed. 2003, 42, 5134– 5175; d) H. Furuta, H. Maeda, A. Osuka, Chem. Commun. 2002, 1795–1804; e) T. K. Chandrashekar, S. Venkatraman, Acc. Chem. Res. 2003, 36, 676–691; f) S. Shimizu, A. Osuka, Eur. J. Inorg. Chem. 2006, 1319–1335; g) R. Misra, T. K. Chandrashekar, Acc. Chem. Res. 2008, 41, 265–279.
- [2] a) J. L. Sessler, S. J. Weghorn, V. Lynch, M. R. Johnson, Angew. Chem. 1994, 106, 1572–1575; Angew. Chem. Int. Ed. Engl. 1994, 33, 1509–1512; b) J. L. Sessler, S. J. Weghorn, Y. Hisaeda, V. Lynch, Chem. Eur. J. 1995, 1, 56–67; c) E. Vogel, M. Bröring, J. Fink, D. Rosen, H. Schmickler, J. Lex, K. W. K. Chan, Y.-D. Wu, D. A. Plattner, M. Nendel, K. N. Houk, Angew. Chem. 1995, 107, 2705–2709; Angew. Chem. Int. Ed. Engl. 1995, 34, 2511–2514; d) M. Bröring, J.

Jendrny, L. Zander, H. Schmickler, J. Lex, Y.-D. Wu, M. Nendel, J. Chen, D. A. Plattner, K. N. Houk, E. Vogel, Angew. Chem. 1995, 107, 2709–2711; Angew. Chem. Int. Ed. Engl. 1995, 34, 2515–2517;
e) J. Setsune, Y. Katakami, N. Iizuna, J. Am. Chem. Soc. 1999, 121, 8957–8958;
f) J. Setsune, S. Maeda, J. Am. Chem. Soc. 2000, 122, 12405–12406;
g) V. G. Anand, S. K. Pushpan, S. Venkatraman, A. Dey, T. K. Chadrashekar, B. S. Joshi, R. Roy, W. Teng, K. R. Senge, J. Am. Chem. Soc. 2001, 123, 8620–8621;
h) S. Shimizu, N. Aratani, A. Osuka, Chem. Eur. J. 2006, 12, 4909–4918;
i) Y. Tanaka, J.-Y. Shin, A. Osuka, Eur. J. Org. Chem. 2008, 1341–1349.

- [3] a) M. G. P. M. S. Neves, R. M. Martins, A. C. Tomé, A. J. D. Silvestre, A. M. S. Silva, V. Félix, M. G. B. Drew, J. A. S. Cavaleiro, *Chem. Commun.* 1999, 385–386; b) S. Mori, A. Osuka, *J. Am. Chem. Soc.* 2005, *127*, 8030–8031; c) S. Mori, J.-Y. Shin, S. Shimizu, F. Ishikawa, H. Furuta, A. Osuka, *Chem. Eur. J.* 2005, *11*, 2417–2425; d) S. Mori, K. S. Kim, Z. S. Yoon, S. B. Noh, D. Kim, A. Osuka, *J. Am. Chem. Soc.* 2007, *129*, 11344–11345.
- [4] a) M. Suzuki, A. Osuka, *Chem. Commun.* 2005, 3685–3687; b) S.
 Shimizu, W.-S. Cho, J. L. Sessler, H. Shinokubo, A. Osuka, *Chem. Eur. J.* 2008, 14, 2668–2678; c) J. Setsune, M. Mori, T. Okawa, S.
 Maeda, J. M. Lintuluoto, *J. Organomet. Chem.* 2007, 692, 166–174.
- [5] a) J. L. Sessler, M. J. Cyr, V. Lynch, E. McGhee, J. A. Ibers, J. Am. Chem. Soc. 1990, 112, 2810–2813; b) J. L. Sessler, T. Morishima, V. Lynch, Angew. Chem. 1991, 103, 1018–1020; Angew. Chem. Int. Ed. Engl. 1991, 30, 977–980; c) S. Shimizu, R. Taniguchi, A. Osuka, Angew. Chem. 2005, 117, 2265–2269; Angew. Chem. Int. Ed. 2005, 44, 2225–2229.
- [6] a) D. Seidel, V. Lynch, J. L. Sessler, Angew. Chem. 2002, 114, 1480–1483; Angew. Chem. Int. Ed. 2002, 41, 1422–1425; b) T. Köhler, D. Seidel, V. Lynch, F. O. Arp, Z. Ou, K. M. Kadish, J. L. Sessler, J. Am. Chem. Soc. 2003, 125, 6872–6873.
- [7] a) M. Stępień, L. Latos-Grayński, N. Sprutta, P. Chwalisz, L. Szterenberg, Angew. Chem. 2007, 119, 8015–8019; Angew. Chem. Int. Ed. 2007, 46, 7869–7873; b) N. Jux, Angew. Chem. 2008, 120, 2577– 2581; Angew. Chem. Int. Ed. 2008, 47, 2543–2546.
- [8] S. J. Weghorn, J. L. Sessler, V. Lynch, T. F. Baumann, J. W. Sibert, *Inorg. Chem.* **1996**, *35*, 1089–1090.
- [9] Y. Kamimura, S. Shimizu, A. Osuka, Chem. Eur. J. 2007, 13, 1620– 1628.
- [10] a) Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, A. Osuka, *Angew. Chem.* **2008**, *120*, 693–696; *Angew. Chem. Int. Ed.* **2008**, *47*, 681–684; b) J. K. Park, Z. S. Yoon, M.-C. Yoon, K. S. Kim, S. Mori, J.-Y. Shin, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2008**, *130*, 438–489; c) S. Mori, S. Shimizu, R. Taniguchi, A. Osuka, *Inorg. Chem.* **2005**, *44*, 4127–4129.
- [11] E. Vogel, M. Michels, L. Zander, J. Lex, N. S. Tuzun, K. N. Houk, Angew. Chem. 2003, 115, 2964–2969; Angew. Chem. Int. Ed. 2003, 42, 2857–2862.
- [12] J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, J. Am. Chem. Soc. 2001, 123, 7190–7191.
- [13] a) M. Suzuki, A. Osuka, J. Am. Chem. Soc. 2007, 129, 464–465;
 b) M. Suzuki, A. Osuka, Angew. Chem. 2007, 119, 5263–5266;
 Angew. Chem. Int. Ed. 2007, 46, 5171–5174.
- [14] a) Y. Tanaka, W. Hoshino, S. Shimizu, K. Youfu, N. Aratani, N. Maruyama, S. Fujita, A. Osuka, J. Am. Chem. Soc. 2004, 126, 3046– 3047; b) L. Latos-Gráyński, Angew. Chem. 2004, 116, 5234–5238; Angew. Chem. Int. Ed. 2004, 43, 5124–5128.
- [15] S. Saito, K. S. Kim, Z. S. Yoon, D. Kim, A. Osuka, Angew. Chem. 2007, 119, 5687–5689; Angew. Chem. Int. Ed. 2007, 46, 5591–5593.
- [16] Re-analysis of the crystal structure of 1 gave better crystal data than that reported in ref. [12], thus new crystal data is indicated.
- [17] The activation volume ΔV^{+} can be defined by the following equation: $\Delta V^{+} = -RT(\delta \ln k/\delta p)T$; thus, $\ln k_{p} = \ln k_{0} \Delta V^{+} p/RT$.
- [18] a) E. Heilbronner, *Tetrahedron Lett.* 1964, *5*, 1923–1928; b) H. E.
 Zimmerman, *J. Am. Chem. Soc.* 1966, *88*, 1564–1567; c) H. S.
 Rzepa, *Chem. Rev.* 2005, *105*, 3697–3715; d) R. Herges, *Chem. Rev.* 2006, *106*, 4820–4842.

5684 -

- [19] a) D. Ajami, O. Oeckler, A. Simon, R. Herges, *Nature* 2003, 426, 819–821; b) D. Ajami, K. Hess, F. Köhler, C. Näther, O. Oeckler, A. Simon, C. Yamamoto, Y. Okamoto, R. Herges, *Chem. Eur. J.* 2006, 12, 5434–5445.
- [20] In the crystal of **5**–PdPd two *n*-heptane molecules were severely disordered. Thus, electron density due to the disordered *n*-heptane was removed by the use of the utility SQUEEZE in PLATON software package, giving the following better crystal data: $C_{88}H_{16}F_{40}N_8Pd_2\cdot C_7H_8$; $M_w = 2250.02$; triclinic; \bar{P} (No. 2); a = 13.03(3), b = 17.31(4), c = 21.91(5) Å; a = 67.23(10), $\beta = 84.84(9)$, $\gamma = 88.24(8)^\circ$; V = 4540 (18) Å³; Z = 2; $\rho_{calcd} = 1.646$ g cm⁻³; $R_1 = 0.0975$ ($I > 2.0\sigma(I)$); $wR_2 = 0.2633$ (all data); GOF = 0.848 ($I > 2.0\sigma(I)$). CCDC-716727

contains 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. PLATON/SQUEEZE is an effective tool for taking the contribution of disordered solvent into account in crystal structure refinement; see: a) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, **2005**; b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. A* **1990**, *46*, 194–201.

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