

Unprecedented Formation of a Rhodium Cluster Triggered by Rhodium-Fastened N-Confused Gable Porphyrin

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Thermal reaction of N-confused porphyrin (NCP) with $[\text{RhCl}(\text{CO})_2]_2$ caused unprecedented formation of tetranuclear rhodium complex $\text{Rh}_4(\text{NCP})_2(\text{CO})_4$ having a gable-porphyrin-type structure, where two porphyrin π systems were electronically connected by the rhodium cluster.

In recent years, construction of porphyrin dimers or oligomers has become an extremely important field of investigation.¹ In addition to the biomimetic approach that aims at developing functional models of enzyme active sites, a current goal consists of building well-defined porphyrin assemblies for use in energy conversion, catalysis, or optoelectronics. While several covalent or noncovalent strategies have been developed to make porphyrin assemblies,¹ no methods utilized coordination to metal clusters. Yet, this strategy would generate unique $d-\pi$ -conjugated systems similar to ferrocene, which has been widely exploited in every field because of its stability and electronic flexibility. Here, we have succeeded, for the first time, in constructing a rhodium cluster with the aid of an N-confused gable porphyrin. The rhodium complex² thus obtained displays an unprecedented large $d-\pi$ -conjugated system spreading over the whole molecule. Though self-assemblies of N-confused porphyrins³ through metal coordination were often observed, no system includes a direct metal–metal bond or such a large $d-\pi$ -conjugated system.⁴

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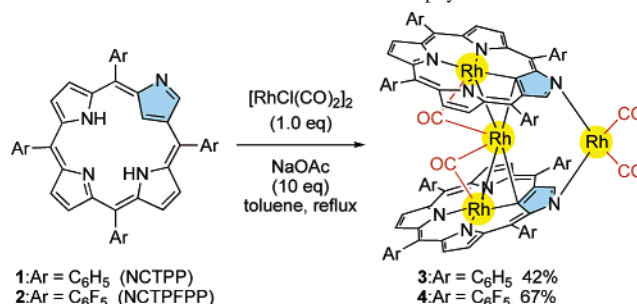
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- (1) (a) Blanc, M.-J.; Jiménez, M. C.; Chambron, J.-C.; Heitz, V.; Linke, M.; Sauvage, J.-P. *Chem. Soc. Rev.* **1999**, 28, 143. (b) Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, 101, 2751. (c) Scandola, F.; Chiorboli, C.; Prodi, A.; Iengo, E.; Alessio, E. *Coord. Chem. Rev.* **2006**, 250, 1471.
- (2) (a) Srinivasan, A.; Furuta, H.; Osuka, A. *Chem. Commun.* **2001**, 1666. (b) Srinivasan, A.; Toganoh, M.; Niino, T.; Osuka, A.; Furuta, H. *Inorg. Chem.* **2006**, submitted for publication.

Scheme 1. Two Features of N-Confused Porphyrin



Synthetic procedures for the construction of a rhodium cluster are extremely simple. Upon heating of N-confused tetraphenylporphyrin (NCTPP, **1**) with $[\text{RhCl}(\text{CO})_2]_2$ in toluene at 110 °C under basic conditions, the N-confused gable porphyrin bearing the trinuclear rhodium cluster, $\text{Rh}_4(\text{NCTPP})_2(\text{CO})_4$ (**3**), was obtained in 42% isolated yield (Scheme 1). Generalization of this method was illustrated by the reaction of $[\text{RhCl}(\text{CO})_2]_2$ with N-confused tetrakis-(pentafluorophenyl)porphyrin (NCTPFPP, **2**)⁵ under similar reaction conditions, which afforded $\text{Rh}_4(\text{NCTPFPP})_2(\text{CO})_4$ (**4**) in 67% yield. Because the rhodium complexes **3** and **4** were stable in air and in acidic media (ca. $\text{CF}_3\text{CO}_2\text{H}$) at ambient temperature, they could be purified easily by classical silica gel column chromatography. The N-confused gable porphyrin **3** showed IR (2074 and 2006 cm^{-1} for external CO's and 1848 and 1819 cm^{-1} for bridging CO's), mass (FAB, $[\text{M} + \text{H}]^+ = 1747$), and NMR spectra consistent with those of the structure shown in Scheme 1. For example,

- (3) (a) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, 116, 767. (b) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Głowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 779.
- (4) (a) Hung, C.-H.; Chen, W.-C.; Lee, G.-H.; Peng, S.-M. *Chem. Commun.* **2002**, 1516. (b) Harvey, J. D.; Ziegler, C. J. *Chem. Commun.* **2002**, 1942. (c) Furuta, H.; Ishizuka, T.; Osuka, A. *J. Am. Chem. Soc.* **2002**, 124, 5622. (d) Chmielewski, P. J.; Schmidt, I. *Inorg. Chem.* **2004**, 43, 1885. (e) Toganoh, M.; Naoyuki, H.; Morimoto, T.; Furuta, H. *Chem.—Eur. J.* **2006**, in press.
- (5) Maeda, H.; Osuka, A.; Ishikawa, Y.; Aritome, I.; Hisaeda, Y.; Furuta, H. *Org. Lett.* **2003**, 5, 1293.

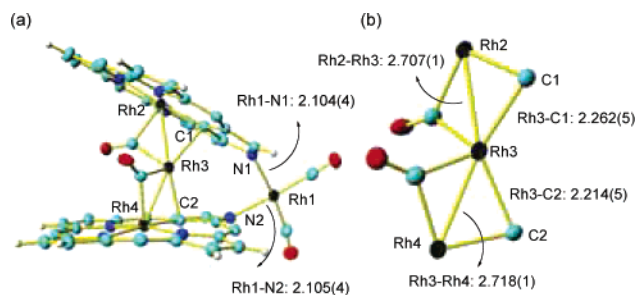


Figure 1. Molecular structure of the N-confused gable porphyrin **3**: (a) side view; (b) zoom view around the rhodium cluster. The solvent molecule and the *meso*-phenyl groups were omitted for clarity. The ellipsoids are drawn at the 30% probability level. Selected bond lengths in angstroms are also displayed.

the resonance corresponding to α -CH of the confused pyrrole was observed at 9.22 ppm in the ^1H NMR spectrum. In accordance with the C_2 -symmetrical structure, only one set of signals due to the porphyrin substructures was observed in both the ^1H and ^{13}C NMR spectra. Similar results were obtained for **4**.

Unambiguous structural assignment of **3** was achieved by X-ray crystallographic analysis (Figure 1).⁶ The outer rhodium metal (Rh1) fastens the two N-confused porphyrin planes through coordination to the peripheral nitrogen atoms (N1 and N2), where the porphyrin planes have fairly flat structures. The dihedral angle between the two porphyrin planes is 51.7° , confirming the gable arrangement. The Rh1–N1 and Rh1–N2 bond lengths are 2.104(4) and 2.105(4) Å, respectively. These values are typical for Rh(I)–N(sp^2) bond lengths,⁷ suggesting a facile formation of the gable architecture. While many covalently linked gable porphyrins have been reported,⁸ this is essentially the first example of the metal-assisted formation of gable porphyrins. The inner rhodium metal (Rh3) is sandwiched between the two center metals (Rh2 and Rh4) of the macrocycles. The Rh2–Rh3 distance is 2.707(1) Å, and the Rh3–Rh4 distance is 2.718(1) Å.⁹ The resulting trinuclear substructure is anchored by the two bridging carbonyl ligands. The coordination sphere of Rh3 is completed by two η^1 coordinations from the π orbitals of the two inner carbon atoms (C1 and C2). The Rh3–C1 bond length [2.262(5) Å] and the Rh3–C2 bond length [2.214(5) Å] are sufficiently short for making Rh–C(sp^2) bonds.¹⁰ This time only the trans isomers were

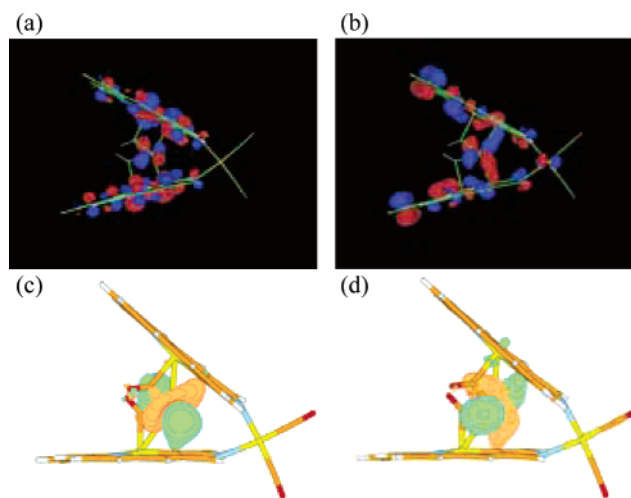


Figure 2. Molecular orbitals of N-confused gable porphyrin: (a) HOMO; (b) HOMO-19; (c and d) one of the occupied LMOs.

obtained as the N-confused gable porphyrins, while two isomers (cis and trans about the relative position of the peripheral nitrogen atoms) are possible.¹¹

Formation of the d– π -conjugated system was evidenced as follows. First, the existence of unique η^1 coordinations to the rhodium metal by the inner sp^2 carbon atoms was demonstrated by density functional theory (DFT) studies.¹² In highest occupied molecular orbital (HOMO) (Figure 2a) and HOMO–19 (Figure 2b), the bondings between the central rhodium atom and the inner sp^2 carbon atoms were implied. More straightforward support of the η^1 coordinations was obtained by the localized molecular orbital (LMO) analysis. The interactions between the π orbitals of the inner carbon atoms and the $4d_{z^2}$ orbital of the central rhodium are clearly observed in Figure 2c. The corresponding interactions of the $4d_{xz}$ orbitals are also revealed in Figure 2d (see the Supporting Information about the detailed orbital figures). These interactions would be helpful for stabilizing the trinuclear rhodium clusters. Consequently, the two porphyrin π systems are connected through d– π interactions to form the interesting conjugated system totaling as much as 74 electrons. Establishment of such a system was supported by the molecular orbital spreading over the whole molecule (e.g., Figure 2a,b) and also by the highly deformed absorption spectrum of **3** (vide infra). Further support was given by the electrochemical analysis of **3** in a 0.1 M $\text{Bu}_4\text{NPF}_6 \cdot \text{CH}_2\text{Cl}_2$ solution; the reversible two-electron-oxidation wave was observed at the fairly low oxidation potential (-0.06 V vs Fc/Fc^+).

Absorption spectra of **1** and **3** are shown in Figure 3. While the absorption spectrum of **1** shows the typical profile of porphyrin derivatives, that of **3** has completely lost such

(6) Crystal data: **3**· CH_2Cl_2 , purple prism, $\text{C}_{93}\text{H}_{56}\text{Cl}_2\text{N}_8\text{O}_4\text{Rh}_4$, M_w 1832.00, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.374(6)$ Å, $b = 24.425(10)$ Å, $c = 22.097(10)$ Å, $\beta = 102.66(4)^\circ$, $V = 7569(6)$ Å³, $Z = 4$, $T = 123$ K, $R = 0.0540$ [$I > 2\sigma(I)$], $R_w = 0.1462$ (all data), GOF on $F^2 = 1.035$ (all data), CCDC reference number 612136.

(7) (a) Simkhovich, L.; Rosenberg, S.; Gross, Z. *Tetrahedron Lett.* **2001**, *42*, 4929. (b) Sridevi, B.; Narayanan, S. J.; Rao, R.; Chandrashekar, T. K.; Englich, U.; Ruhlandt-Senge, K. *Inorg. Chem.* **2000**, *39*, 3669. (c) Sessler, J. L.; Gebauer, A.; Guba, A.; Scherer, M.; Lynch, V. *Inorg. Chem.* **1998**, *37*, 2073. (d) Burrell, A. K.; Sessler, J. L.; Cyr, M. J.; McGhee, E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 91.

(8) (a) Tabushi, I.; Sasaki, T. *Tetrahedron Lett.* **1982**, *23*, 1913. (b) Sessler, J. L.; Hugdahl, J.; Johnson, M. R. *J. Org. Chem.* **1986**, *51*, 2838. (c) Meier, H.; Kobuke, Y.; Kugimiya, S. *J. Chem. Soc., Chem. Commun.* **1989**, 923. (d) Takahashi, R.; Kobuke, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2372.

(9) The common Rh–Rh bond lengths in Rh cluster complexes are ca. 2.75 Å. For instance, see: Farrar, D. H.; Grachova, E. V.; Lough, A.; Patrana, C.; Poë, A. J.; Tunik, S. P. *J. Chem. Soc., Dalton Trans.* **2001**, 2015.

(10) Kakkar, A. K.; Jones, S. F.; Taylor, N. J.; Collins, S.; Marder, T. B. *Chem. Commun.* **1989**, 1454.

(11) The trans conformation of **4** was also confirmed by the X-ray analysis.

(12) The DFT calculations were performed on a model compound, where all the *meso* substituents were replaced by hydrogen atoms. The model compound was optimized at B3LYP/LANL2DZ for Rh and at 3-21.G* for the rest, and the natural population analysis was achieved at the same level. For orbital analysis, the single-point calculation at B3LYP/LANL2DZ for Rh and at 6-31.G** for the rest was adopted.

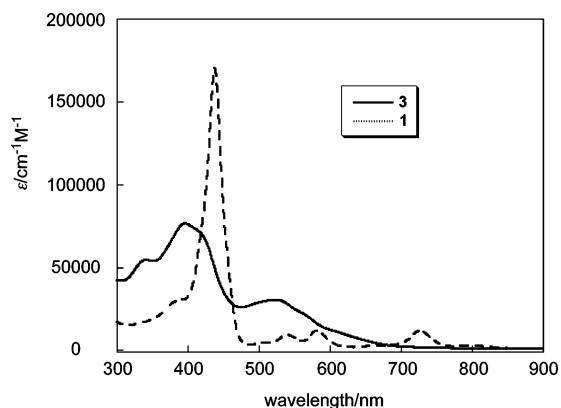


Figure 3. Absorption spectra of **1** and **3** in CH_2Cl_2 .

features possibly because of electronic connectivity between the two porphyrin π systems through the trinuclear rhodium cluster. Note that simple rhodium coordination did not cause significant deformation of the spectrum profile.²

At present, the exact electronic states of the rhodium cluster are not certain. Because no counteranion was observed and each N-confused porphyrin took the trianionic form in **3** and **4**,¹³ the overall formal charge of the four rhodium atoms is 6+. The surrounding geometry (square planar) and the charge of the outer metal obtained by natural population analysis (Rh3, 0.063+) are similar to those of the rhodium-(I) dicarbonyl complexes bearing the porphyrinoid ligands⁷ and, hence, the oxidation state of Rh3 was determined to be 1+. Consequently, the charge of the remaining trinuclear rhodium cluster is 5+. Thus, the assignment of the formal oxidation states for Rh2, Rh3, and Rh4 in the metal trimer is either [2+, 1+, 2+] or [1+, 3+, 1+] for symmetry reasons. However, it is more likely that the mixed-valence-delocalized oxidation states are produced in the actual metal trimer system.¹⁴ In solution, an antiferromagnetic coupling between the rhodium cations could explain the diamagnetic

(13) Furuta, H.; Ishizuka, T.; Osuka, A.; Dejima, A.; Nakagawa, H.; Ishikawa, Y. *J. Am. Chem. Soc.* **2001**, *123*, 6207.

NMR signals and the silent electron spin resonance spectra. Supplemental support of the antiferromagnetic coupling was obtained by X-ray photoelectron spectroscopy analysis on **3**. The significantly broadened signals due to the binding energy of Rh(3d_{5/2}) and Rh(3d_{3/2}) were detected at around 309.5 and 314 eV, respectively.

In conclusion, the first rhodium-fastened N-confused gable porphyrins were prepared, where unprecedented formation of the trinuclear rhodium clusters bearing a unique coordination mode was observed. Generation of a fascinating d- π -conjugated system in these molecules was also illustrated. The elegant strategy developed here should be applicable to a wide range of metals, and in combination with the rich coordination chemistry of a *confused* porphyrin family,^{2,15–17} it will generate a series of molecules having unprecedented d- π -conjugated electronic structures. Work is underway to explore these possibilities.

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Supporting Information Available: Crystallographic data of **3** (CIF), experimental details for the preparation of **3** and **4**, and Cartesian coordinate and orbital figures for the calculated N-confused gable porphyrin. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Cotton, F. A.; Murillo, C. A.; Walton, R. A., Eds. *Multiple Bonds between Metal Atoms*, 3rd ed.; Springer Science and Business Media, Inc.: New York, 2005.
- (15) Niino, T.; Toganoh, M.; Andrioletti, B.; Furuta, H. *Chem. Commun.* **2006**, 4335–4337.
- (16) Toganoh, M.; Konagawa, J.; Furuta, H. *Inorg. Chem.* **2006**, *45*, 3852.
- (17) (a) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795. (b) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134. (c) Ghosh, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1918. (d) Chmielewski, P. J.; Latos-Grażyński, L. *Coord. Chem. Rev.* **2005**, *249*, 2510. (e) Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10. (f) Harvey, J. D.; Ziegler, C. J. *J. Inorg. Biochem.* **2006**, *100*, 869.