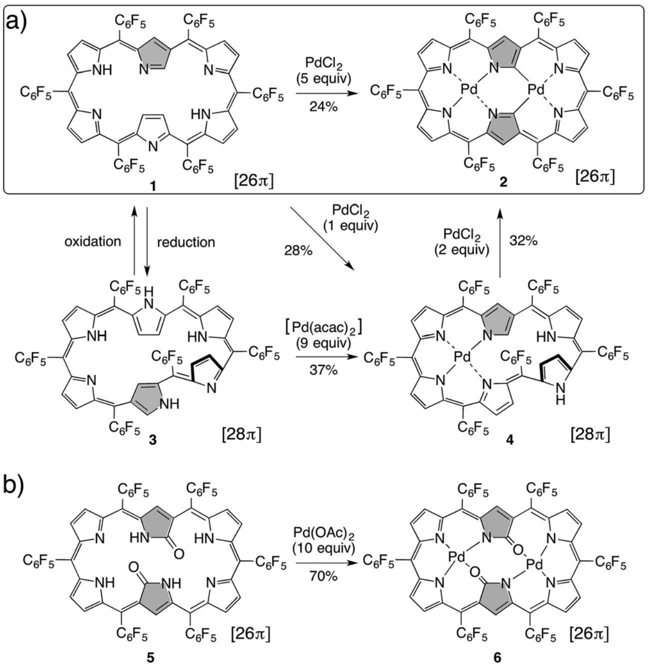
Expanded Porphyrins

DOI: 10.1002/anie.201302955

# Palladium-Induced Pyrrolic Rearrangement of a Singly to a Doubly N-Confused [26]Hexaphyrin**

*Sabapathi Gokulnath, Keiichi Nishimura, Motoki Toganoh, Shigeki Mori, and Hiroyuki Furuta**

Macrocyclic compounds generally possess flexible skeletons, which results in them having a variety of conformations or molecular shapes. In the case of macrocycles with $\pi$ systems, the conformation governs their electronic states, as well as their reactivity. As a result of the recent developments in the synthesis of expanded porphyrins,[1] many studies of the relationships between their conformations and electronic properties have been reported.[2] Peripheral modification of expanded porphyrins to construct rigid frameworks have also been investigated.[3] Importantly, expanded porphyrins purely composed of regular pyrroles (connected to the *meso*-carbon atoms at the $\alpha,\alpha'$-positions) are often less stable or in a metastable state, and undergo skeletal transformation induced by external stimuli. In particular, metal coordination can trigger unique skeletal transformations. For example, heptaphyrins and octaphyrins were split in two upon metal coordination.[4,5] A notable example of such a skeletal transformation is a "confusion reaction", for example, the conversion of a regular hexaphyrin into doubly N-confused dioxohexaphyrin through oxidative copper metalation.[6] The results of this particular reaction suggest that N-confused pyrroles (connected to the *meso*-carbon atoms at the $\alpha,\beta'$-positions) would stabilize the skeleton of expanded porphyrins. Herein, we describe a palladium-induced unique skeletal rearrangement from a singly N-confused hexaphyrin to a doubly N-confused hexaphyrin, to give a bis(Pd$^{II}$) complex of doubly N-confused [26]hexaphyrin **2** with a markedly decreased HOMO–LUMO band gap of less than 1 eV. This is the first example of organometallic doubly N-confused hexaphyrin complexes and of a *cis*-configured doubly N-confused hexaphyrin.



***Scheme 1.*** Preparation of a) doubly N-confused hexaphyrin Pd$^{II}$ complexes and b) doubly N-confused dioxohexaphyrin Pd$^{II}$ complex.

The palladium-induced skeletal rearrangement reaction was discovered during a study on palladium coordination chemistry of the singly N-confused [26]hexaphyrin **1** (Scheme 1a).[7] A solution of **1** and 5 equivalents of PdCl$_2$ in acetonitrile was heated at reflux for 30 min and, after the usual workup and chromatographic separation, the bis(Pd$^{II}$) complex of doubly N-confused [26]hexaphyrin **2** was isolated in 24% yield. Complex **2** was stable both as a solid and in solution under ambient conditions. The laser desorption/ionization mass spectrum of **2** displayed the parent ion signal around $m/z = 1670$, thus indicating that it could be the bis(Pd) complex. The $^1$H NMR and $^{19}$F NMR spectra of **2** in CDCl$_3$ at room temperature suggest a $C_s$ symmetric structure. A singlet signal assignable to the $\beta$-CH of N-confused pyrrole rings was observed at $\delta = 8.80$ ppm (2H). In the $^1$H NMR spectrum, a pair of doublet signals corresponding to two regular pyrrole rings appeared at 8.34 and 8.25 ppm (both 2H, $J = 4.9$ Hz) and a singlet signal corresponding to the remaining two regular pyrrole rings appeared at 8.50 ppm (4H). Signals for six *meso*-C$_6$F$_5$ groups are observed in a 2:2:1:1 ratio, thus supporting the $C_s$ symmetric structure.[8] When the reaction of **1** was performed with 1 equivalent of PdCl$_2$, a mono(Pd$^{II}$) complex of singly N-confused [28]hexaphyrin **4** was obtained in 28% yield; this compound could also be prepared by the treatment of singly N-confused [28]hexaphyrin **3** with [Pd(acac)$_2$].[7a] Increasing the amount of the palladium reagent

---

[*] Dr. S. Gokulnath, K. Nishimura, Dr. M. Toganoh, Prof. Dr. H. Furuta
Department of Chemistry and Biochemistry
Graduate School of Engineering, Kyushu University
Fukuoka 819-0395 (Japan)
E-mail: hfuruta@cstf.kyushu-u.ac.jp

Prof. Dr. H. Furuta
International Research Center for Molecular Systems
Kyushu University, Fukuoka 819-0395 (Japan)

Dr. S. Mori
Department of Molecular Science, Integrated Center for Science
Ehime University, Matsuyama 790-8577 (Japan)

[**] The present work was supported by a Grant-in-Aid for Scientific Research (22350020 and 23108715) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201302955.

led to the formation of both **2** and **4** in a comparable combined yield. For example, 18% yield of **2** and 11% yield of **4** were obtained when 3 equivalents of $PdCl_2$ were used. Although the reaction of **4** with excess amounts of [Pd(acac)$_2$] did not afford **2**, it was successfully obtained in 32% yield from the reaction of **4** with 2 equivalents of $PdCl_2$. Palladium metalation of doubly N-confused dioxo-[26]hexaphyrin **5** proceeded smoothly to give the corresponding bis(Pd$^{II}$) complex **6** in 70% yield (Scheme 1b). Notably, palladium metalation of regular hexaphyrins never gave any N-confused products.[9]

Explicit proof of the molecular structure of **2** came from X-ray crystallographic analysis (Figure 1). Owing to the skeletal rearrangement, **2** adopts a $C_s$ symmetric structure, which is in agreement with its NMR spectra. The solid-state structure shows that the compound contains an NNNN cavity and an NNCC cavity. In each cavity there a Pd ion is bound with a square planar geometry. The Pd–Pd distance is 3.94 Å, which is longer than twice its van der Waals radius. Upon incorporation of the Pd ions into the planar macrocycle of **1**, a bent framework is formed to accommodate the Pd ions bound in each of the NNNN and NNCC cavities. A study of the bond lengths would provide little insight into the structure, owing to the disorder in the crystal. However, the coordination bond lengths are similar to those of the carbaporphyrin Pd$^{II}$ complexes.[10]

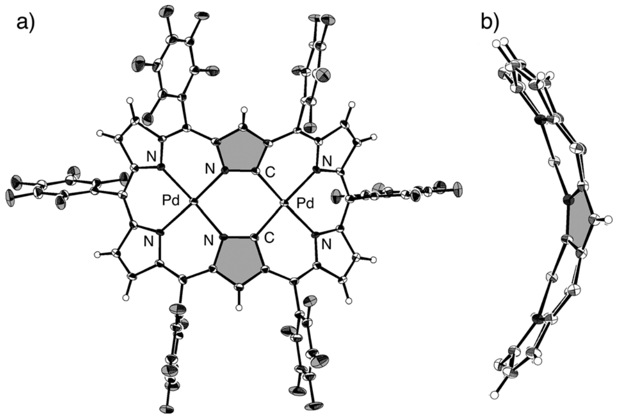


*Figure 1.* X-ray crystal structure of **2**: a) top view, b) side view. Pentafluorophenyl groups are omitted for clarity in the side view. The thermal ellipsoids are scaled to the 50% probability level.[15]

The palladium complex **2** exhibits a noteworthy electronic structure as exemplified by its photoabsorption spectrum. The absorption spectra of **1**, **2**, and **6** in $CH_2Cl_2$ are shown in Figure 2. The complex **2** exhibits split Soret-type bands in the region of 640–730 nm, thus reflecting its bent-shaped framework. Interestingly, the Q-type bands of **2** reach deep into the near-IR region of 1600 nm, which is significantly longer than those of **1** (ca. 1100 nm) and **6** (ca. 1300 nm).

The electrochemical properties of **2** and **6** were studied by cyclic voltammetry in $CH_2Cl_2$ versus ferrocene/ferrocenium ion with tetrabutylammonium hexafluorophosphate as electrolyte (Figure 3). Complex **2** is robust against electrochemical oxidation and reduction, and thus undergoes only one reversible oxidation at 0.49 V and three reversible reductions at −0.45, −0.88, and −1.91 V. The second oxidation at 0.85 V would be quasi-reversible. The electrochemical properties of **6** are similar to those of **2**; it exhibits two reversible oxidations at 0.53 and 0.77 V, and three reversible reductions at −0.57, −0.98, and −1.81 V. The electrochemical HOMO–LUMO gap for **2** was estimated to be small (0.94 V), compared to that of **6** (1.10 V); this finding is consistent with their absorption spectra.

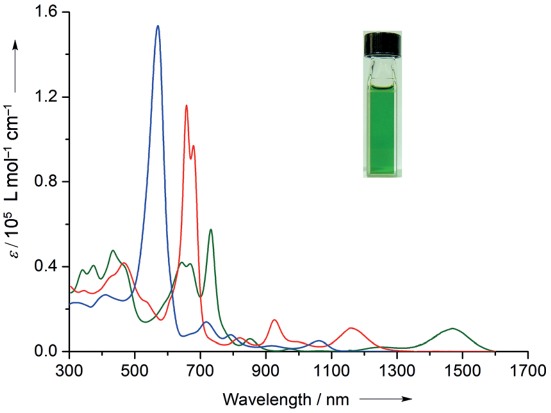


*Figure 2.* Photoabsorption spectra of **1** (blue), **2** (green), and **6** (red) in $CH_2Cl_2$. The inset shows a solution **2** in $CH_2Cl_2$.

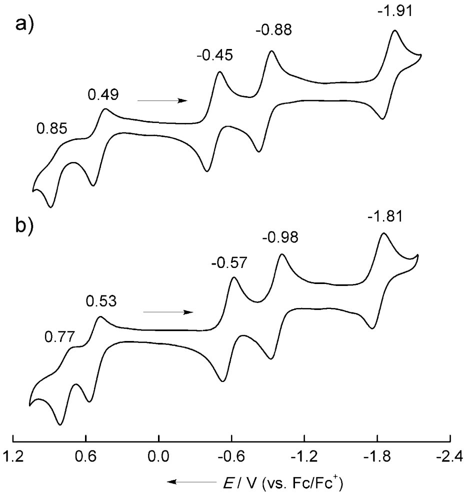


*Figure 3.* Cyclic voltammogram of solutions of a) **2** and b) **6** containing $Bu_4NPF_6$ (0.1 M) in $CH_2Cl_2$ with a 0.1 V s$^{-1}$ scan rate. The arrows indicate the direction of the cyclic voltammetry measurements.

Both photoabsorption and electrochemical properties suggest that **2** has an unusually narrow HOMO–LUMO band gap, which would stem from a loss of orbital degeneracy. The bis(Pd$^{II}$) complexes of an unsubstituted regular hexaphyrin (**7**), a singly N-confused hexaphyrin (**8**), doubly N-confused hexaphyrins (*cis*-**9** and *trans*-**9**), and doubly N-confused dioxohexaphyrin (*trans*-**10**) were subjected to DFT calculations.[11] **8** has not yet been synthesized, whereas the synthesis of **7** was reported recently.[12] Orbital energies for this series of hexaphyrin palladium complexes are summarized in Figure 4. ΔHOMO (HOMO-HOMO-1) and ΔLUMO (LUMO + 1-LUMO) become larger with increased confu-

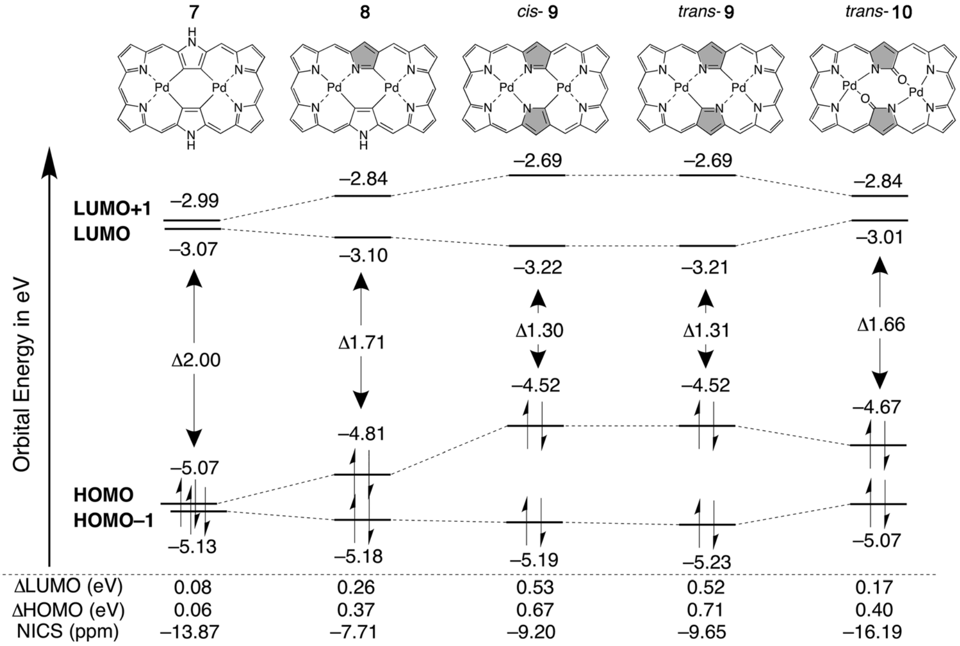
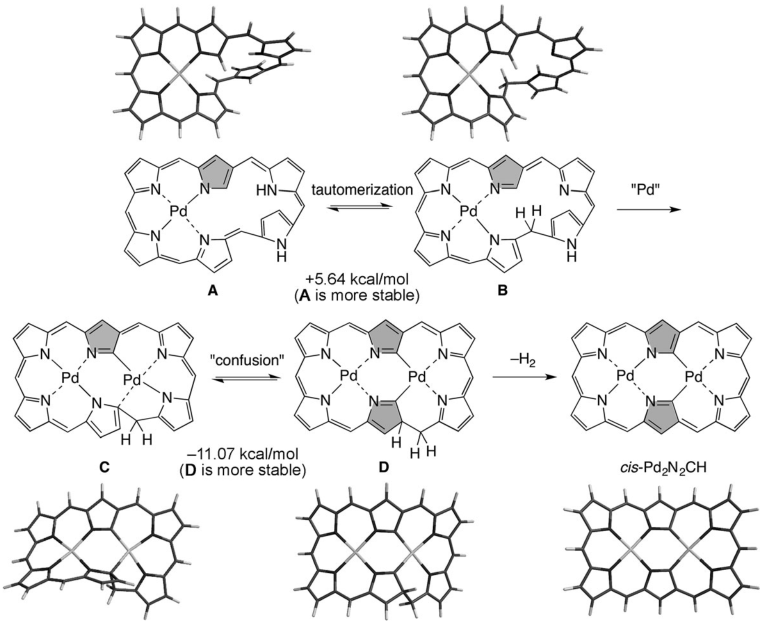


***Figure 4.*** Orbital energies for a series of hexaphyrin bis(Pd$^{II}$) complexes.

sion, reaching 0.53 and 0.67 eV, respectively, for *cis*-**9**. Only a negligible difference was observed in the HOMO–LUMO band gap for *cis*-**9** and *trans*-**9**. The Pd–C bonds seem to have a significant influence, as ΔHOMO (0.40 eV) and ΔLUMO (0.17 eV) of *trans*-**10** are much smaller. Accordingly, *cis*-**9** has a very narrow HOMO–LUMO band gap of 1.30 eV.

A notable feature of **9** is its high thermodynamic stability as well as its aromatic nature despite having non-degenerate HOMOs and LUMOs. *cis*-**9** is theoretically more stable than **8** and **7** by 10.6 and 25.2 kcal mol$^{-1}$, respectively. Such stabilization is unique in confused porphyrinoids. The aromatic nature of doubly N-confused hexaphyrins, such as *cis*-**9,** was demonstrated by the $^{1}$H NMR spectra of **2**, which contained signals in the typical aromatic region (8.25–8.80 ppm). The strongly negative nucleus-independent chemical shift (NICS) value obtained for *cis*-**9** (−9.20 ppm) at the center of the macrocyclic framework also supports distinct aromaticity (Figure 4, bottom). The curved structure is not a critical factor for the loss of orbital degeneracy, as the same trend is also observed in planar free-base doubly N-confused hexaphyrins.[2a] Therefore, *cis*-**9** constitutes a rare example of an isolated aromatic compound with non-degenerate HOMOs and LUMOs.

Mechanistically, reduction from 26π system to a 28π system would be one of the key factors in the reaction, since the molecular skeleton of [28]hexaphyrin is considered to be more flexible than that of [26]hexaphyrin, which is beneficial for skeletal rearrangement.[2c] Actually, palladium metalation of singly N-confused [28]hexaphyrin mono(Pd$^{II}$) complex **4** afforded doubly N-confused [26]hexaphyrin bis(Pd$^{II}$) complex **2** as described above. As the formation of **4** from **1** can be explained simply by reduction and metalation, only the transformation from **4** to **2** is discussed below. Importantly, **4** was thermally stable at least up to 110 °C in a toluene solution and the skeletal rearrangement reaction proceeded below 70 °C. Thus, coordination of the second palladium atom should trigger pyrrolic rearrangement. In addition, we have postulated the generation of an sp$^{3}$-hybridized carbon atom at the *meso* position provides flexibility in the macrocycle. Pyrrolic rearrangement directly from the fully π-conjugated macrocycle or an sp$^{2}$-hybridized carbon atom would be unfavorable with regard to the activation energy. A plausible mechanism is shown in Scheme 2. First, tautomerization of the starting complex **A** gives **B**. Then, the right vacant site would be available to coordinate a second metal atom to form the bis(palladium) complex **C**. Coordination of a palladium atom by the pyrrolic α-carbon atom was previously observed in the regular hexaphyrin Pd$^{II}$ complex.[9a] This metalation step would proceed though C–H bond activation by palladium metal. The significant advantage of $PdCl_2$ over [Pd(acac)$_2$] might be due to the chloride ion facilitating the C–H bond activation during the second metal insertion.[13] Next, pyrrolic rearrangement of **C** proceeds to



***Scheme 2.*** A plausible mechanism for the pyrrolic rearrangement to *cis*-**9**.

give **D**. Finally, aromatization of **D** through a loss of an hydrogen molecule gives *cis*-**9**.

The DFT calculations provide some support for the proposed mechanism (Scheme 2). The mono(palladium) complexes **A** and **B** are tautomers and could exist under equilibrium, where **A** is more stable. The energy difference between **A** and **B** is only 5.6 kcal mol$^{-1}$. This small energy difference provides support for their existence because the energy differences between hexaphyrin isomers tend to be smaller in *meso*-aryl derivatives than in *meso*-free derivatives.[2a] More importantly, the transformation of **C** to give **D** is exothermic by 11.1 kcal mol$^{-1}$, thus suggesting that the N-confused system could be a thermodynamically favorable resting state for hexaphyrin frameworks. Also, the transformation to *trans*-**9** was also examined and was shown to be energetically less favorable (Scheme S1).

In summary, we have found an unprecedented pyrrolic rearrangement reaction of a singly N-confused hexaphyrin mediated by $PdCl_2$, to afford the doubly N-confused hexaphyrin bis(Pd$^{II}$) complex. Mechanistic consideration on the pyrrolic rearrangement revealed that the reduction from [26]hexaphyrin to [28]hexaphyrin as well as formation of the sp$^3$-hybridized carbon atom at the *meso* position play important roles in this reaction. Palladium-induced skeletal rearrangement proceeded under relatively mild conditions and is expected to be applicable for the other N-confused expanded porphyrinoids. The bis(Pd$^{II}$) complex thus formed shows a very narrow HOMO–LUMO band gap owing to the loss of orbital degeneracy. Nevertheless, it retains aromaticity and is more stable than the regular and singly N-confused derivatives. Further studies into the synthesis and coordination chemistry of multiply N-confused expanded porphyrins, and skeletal rearrangement imposed by Pd metal[14] are now underway.

Received: April 9, 2013

**Keywords:** aromaticity · expanded porphyrins · hexaphyrins · macrocycles · palladium

---

[1] a) S. Saito, A. Osuka, *Angew. Chem.* **2011**, *123*, 4432 – 4464; *Angew. Chem. Int. Ed.* **2011**, *50*, 4342 – 4373; b) M. Stépień, N. Sprutta, L. Latos-Grażyński, *Angew. Chem.* **2011**, *123*, 4376 – 4430; *Angew. Chem. Int. Ed.* **2011**, *50*, 4288 – 4340; c) J. L. Sessler, D. Seidel, *Angew. Chem.* **2003**, *115*, 5292 – 5333; *Angew. Chem. Int. Ed.* **2003**, *42*, 5134 – 5175; d) M. Toganoh, H. Furuta, *Chem. Commun.* **2012**, *48*, 937 – 954.

[2] a) M. Toganoh, H. Furuta, *J. Org. Chem.* **2010**, *75*, 8213 – 8223; b) J. M. Lim, J. S. Lee, H. W. Chung, H. W. Bahng, K. Yamaguchi, M. Toganoh, H. Furuta, D. Kim, *Chem. Commun.* **2010**, *46*, 4357 – 4359; c) J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568 – 13579; d) Y.-S. Xie, K. Yamaguchi, M. Toganoh, H. Uno, M. Suzuki, S. Mori, S. Saito, A. Osuka, H. Furuta, *Angew. Chem.* **2009**, *121*, 5604 – 5607; *Angew. Chem. Int. Ed.* **2009**, *48*, 5496 – 5499.

[3] a) M. Ishida, S.-J. Kim, C. Preihs, K. Ohkubo, J. M. Lim, B. S. Lee, J. S. Park, V. M. Lynch, V. V. Roznyatovskiy, T. Sarma, P. K. Panda, C.-H. Lee, S. Fukuzumi, D. Kim, J. L. Sessler, *Nat. Chem.* **2013**, *5*, 15 – 20; b) K. Naoda, H. Mori, N. Aratani, B. S. Lee, D. Kim, A. Osuka, *Angew. Chem.* **2012**, *124*, 9994 – 9997; *Angew. Chem. Int. Ed.* **2012**, *51*, 9856 – 9859; c) T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim, A. Osuka, *Chem. Sci.* **2011**, *2*, 1414 – 1418.

[4] a) 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; b) T. Yoneda, S. Saito, H. Yorimitsu, A. Osuka, *Angew. Chem.* **2011**, *123*, 3537 – 3540; *Angew. Chem. Int. Ed.* **2011**, *50*, 3475 – 3478.

[5] a) 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; b) Y. Tanaka, H. Shinokubo, Y. Yoshimura, A. Osuka, *Chem. Eur. J.* **2009**, *15*, 5674 – 5685.

[6] a) M. Suzuki, M.-C. Yoon, D. Y. Kim, J. H. Kwon, H. Furuta, D. Kim, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 1754 – 1759; b) A. Srinivasan, T. Ishizuka, A. Osuka, H. Furuta, *J. Am. Chem. Soc.* **2003**, *125*, 878 – 879.

[7] a) S. Gokulnath, M. Toganoh, K. Yamaguchi, S. Mori, H. Uno, H. Furuta, *Dalton Trans.* **2012**, *41*, 6283 – 6290; b) S. Gokulnath, K. Yamaguchi, M. Toganoh, S. Mori, H. Uno, H. Furuta, *Angew. Chem.* **2011**, *123*, 2350 – 2354; *Angew. Chem. Int. Ed.* **2011**, *50*, 2302 – 2306.

[8] The *cis* isomer is $C_s$ symmetric, whereas the *trans* isomer is $C_2$ symmetric. For the *trans* isomer, $^{19}$F NMR signals should be observed in a 1:1:1 ratio. The formation of *trans* isomer was not observed under the reaction conditions used.

[9] a) S. Mori, S. Shimizu, R. Taniguchi, A. Osuka, *Inorg. Chem.* **2005**, *44*, 4127 – 4129; b) H. Rath, S. Tokuji, N. Aratani, K. Furukawa, J. M. Lim, D. Kim, H. Shinokubo, A. Osuka, *Angew. Chem.* **2010**, *122*, 1531 – 1533; *Angew. Chem. Int. Ed.* **2010**, *49*, 1489 – 1491; c) M. Inoue, A. Osuka, *Angew. Chem.* **2010**, *122*, 9678 – 9681; *Angew. Chem. Int. Ed.* **2010**, *49*, 9488 – 9491; d) T. Tanaka, A. Osuka, *Chem. Eur. J.* **2012**, *18*, 7036 – 7040.

[10] a) H. Furuta, N. Kubo, H. Maeda, T. Ishizuka, A. Osuka, H. Nanami, T. Ogawa, *Inorg. Chem.* **2000**, *39*, 5424 – 5425; b) Z. Zhang, G. M. Ferrence, T. D. Lash, *Org. Lett.* **2009**, *11*, 101 – 104; c) H. Furuta, H. Maeda, A. Osuka, M. Yasutake, T. Shinmyozu, Y. Ishikawa, *Chem. Commun.* **2000**, 1143 – 1144.

[11] All the calculations were achieved with a Spartan'10 or Gaussian 09 program package at the B3LYP/LACVP level. See the Supporting Information for calculation details.

[12] T. Yoneda, S. Mori, A. Osuka, The *93rd Annual Meeting of Chemical Society of Japan* **2013**, March, Kusatsu. Abstract 3M1-09.

[13] Z. Ke, T. R. Cundari, *Organometallics* **2010**, *29*, 821 – 834.

[14] a) T. D. Lash, *Org. Lett.* **2011**, *13*, 4632 – 4635; b) B. Szyszko, L. Latos-Grażyński, L. Szterenberg, *Angew. Chem.* **2011**, *123*, 6717 – 6721; *Angew. Chem. Int. Ed.* **2011**, *50*, 6587 – 6591.

[15] CCDC 908362 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.