

Bis[iridium(I)] Complex of Inverted N-Confused Porphyrin

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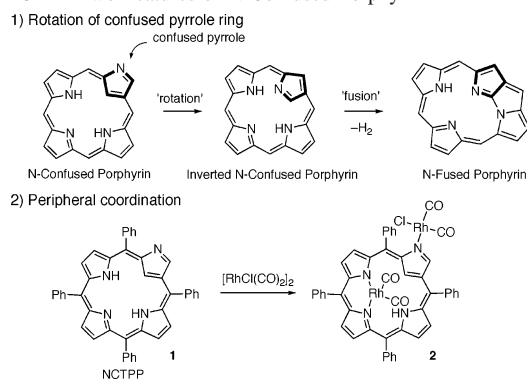
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The reaction of N-confused tetraphenylporphyrin with $\text{IrCl}(\text{CO})_2$ -(*p*-toluidine) gave a novel bis[iridium(I)] complex, wherein the confused pyrrole ring took an inverted conformation.

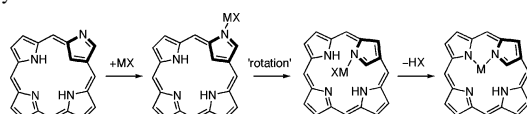
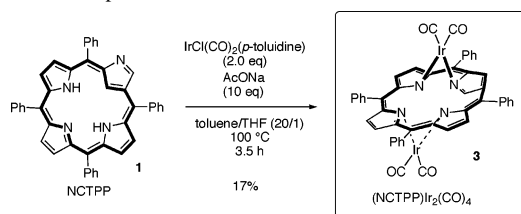
N-confused porphyrin is a unique isomer of porphyrin, where one of the four pyrrole rings is *confused*, that is, connected at not α and α' positions but α and β' positions.¹ Owing to the existence of the confused pyrrole ring, N-confused porphyrin intrinsically has two features (Scheme 1).² The first feature is rotation of the pyrrole ring. During conversion from N-confused porphyrins to N-fused porphyrins, rotation of the confused pyrrole ring was indispensable.^{3,4} Direct observation of an inverted conformation on the N-confused pyrrole ring was also achieved by introduction of a fairly bulky group to the inner C atom.⁵ While rotation of pentacyclic rings was commonly observed in expanded porphyrins,⁶ it became quite rare in the case of tetrapyrrolic porphyrins having rigid [18]porphyrin(1.1.1.1) frameworks.⁷ The second feature is peripheral coordination to metal atoms. For example, the reaction of N-confused tetraphenylporphyrin (NCTPP, **1**) with $[\text{RhCl}(\text{CO})_2]_2$ afforded a bis[rhodium(I)] complex **2**, in which one of the Rh atoms was placed at the peripheral position.⁸

This time we have successfully applied cooperation of the above two functions to prepare the first transition-metal

Scheme 1. Two Features of N-Confused Porphyrin



Scheme 2. Cooperation of the Two Functions of N-Confused Porphyrin

Scheme 3. Preparation of **3**

complex of [18]porphyrin(1.1.1.1) taking an inverted conformation (Scheme 2). Thus, treatment of **1** with $\text{IrCl}(\text{CO})_2$ -(*p*-toluidine) gave a bis[iridium(I)] complex of inverted **1** $[(\text{NCTPP})\text{Ir}_2(\text{CO})_4]$, **3** through delivery of the Ir atom from the outside to the inside of the porphyrin ring with the aid of rotation of the confused pyrrole moiety. To the best of our knowledge, such a dynamic metal-capturing system has not been reported with standard porphyrins.

When **1** was treated with 2.0 equiv of $\text{IrCl}(\text{CO})_2$ -(*p*-toluidine) and 10 equiv of NaOAc in toluene/THF = 20/1 (v/v) at 100 °C for 3.5 h, **3** was obtained in 17% yield (Scheme 3). Basic conditions were essential for the production of **3**. The reactions were significantly accelerated in the presence of THF as the cosolvent. Despite the distorted

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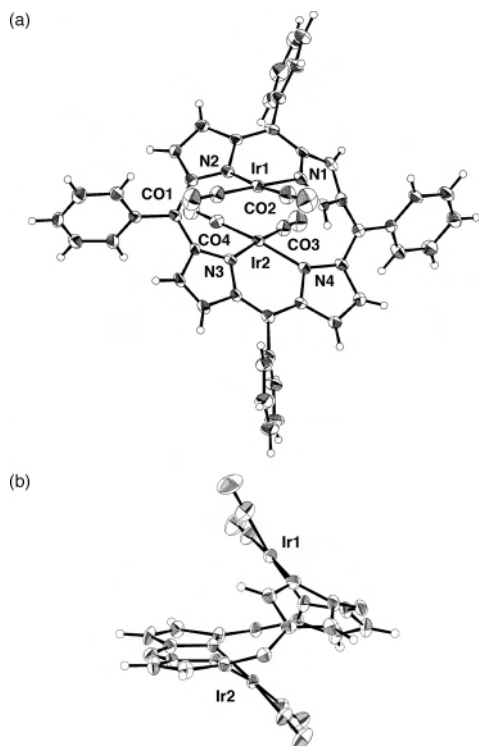


Figure 1. ORTEP drawing of **3** at the 30% level of ellipsoids: (a) top view; (b) side view. Phenyl groups are omitted for clarity in the side view. Selected bond lengths (in Å): Ir1–N1 2.039(7), Ir1–N2 2.051(7), Ir2–N3 2.089(7), Ir2–N4 2.078(7), Ir1–CO1 1.835(12), Ir1–CO2 1.841(10), Ir2–CO3 1.828(9), Ir2–CO4 1.859(10).

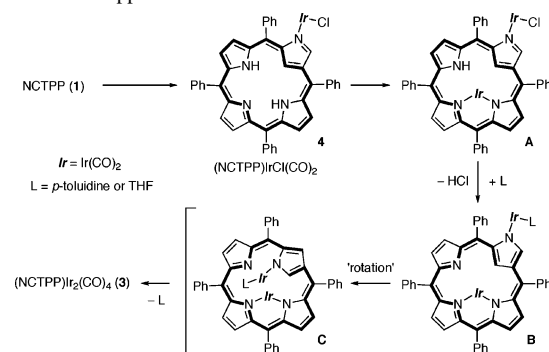
structure, **3** showed remarkable stability as porphyrinoid complexes. It could be handled in air without special care.⁹ No decomposition was observed by heating in 1,2-Cl₂C₆H₄ at 160 °C for 1 h. Surprisingly, no demetalation proceeded by the addition of an excess amount of CF₃COOH. The molecular formula of **3** was assigned from spectroscopic analysis, and details on its structure were elucidated by X-ray study. The strong absorptions at 2057, 2047, 1985, and 1974 cm⁻¹ were observed in the IR spectrum of **3**, suggesting the existence of carbonyl ligands coordinating to the metal centers. In the MALDI-TOF mass spectrum, the molecular ion peaks corresponding to M⁺ were reasonably observed at *m/z* 1106. The ¹H NMR spectrum as well as the ¹³C NMR spectrum was well consistent with the described structure (vide infra).

The molecular structure of **3** was unambiguously determined by X-ray crystallographic analysis.¹⁰ The ORTEP drawings of **3** are shown in Figure 1. The confused pyrrole ring of **3** is certainly inverted and locked with the neighboring pyrrole ring by κ^2 -iridium coordination. Another Ir atom is placed on the opposite side of the porphyrin plane and is coordinated by the other two pyrrole rings. The Ir1–N bond

(9) In the case of similar iridium(I) carbonyl complexes bearing normal porphyrinato ligands, gradual photodecomposition was observed. (a) Ogoshi, H.; Setune, J.; Yoshida, J. *J. Organomet. Chem.* **1978**, *159*, 317. (b) Kadish, K. M.; Deng, Y. J.; Yao, C.-L.; Anderson, J. E. *Organometallics* **1988**, *7*, 1979.

(10) Crystal data: **3**, dark-red prism, C₄₈H₂₈Ir₂N₄O₄, *M_w* 1109.14, triclinic, space group *P* $\bar{1}$ (No. 2), *a* = 11.305(2) Å, *b* = 12.171(2) Å, *c* = 16.957(3) Å, α = 105.996(3)°, β = 96.263(3)°, γ = 115.318(3)°, *V* = 1957.0(6) Å³, *Z* = 2, *T* = 223 K, *R* = 0.0485 [*I* > 2 σ (*I*)], *R_w* = 0.1291 (all data), GOF on *F*² = 0.935 (all data), CCDC reference number 293083.

Scheme 4. Supposed Mechanism for the Production of **3**



lengths (ave 2.05 Å) are slightly shorter than the Ir2–N bond lengths (ave 2.08 Å), which are similar to those of the porphyrinoid iridium(I) bis(carbonyl) complexes taking an uninverted conformation (~2.08 Å),¹¹ possibly because of the shorter atom distance of N1–N2 (2.66 Å) than of N3–N4 (2.85 Å). Summations of the angles around the Ir centers are both nearly 360° (Ir1, 360.2°; Ir2, 359.6°), indicating that no significant strain is charged on the inverted [18]-porphyrin(1.1.1.1) framework by Ir metal coordination. The atom distance between Ir1 and Ir2 is quite long (4.11 Å), and thus no interaction between the two metals is expected.

A supposed mechanism for the production of **3** is shown in Scheme 4. First, coordination of the peripheral N atom to an Ir metal afforded (NCTPP)IrCl(CO)₂ (**4**), which could be isolated in 90% yield by treatment of **1** with an equivalent amount of IrCl(CO)₂(*p*-toluidine). Second, coordination to another Ir metal gave an uninverted bis(iridium) complex (**A**). As shown in Scheme 1, a structure similar to that of **A** was observed in the case of Rh complexes. While isolation in a pure form has so far been difficult, the existence of **A** was implied by ¹H NMR and UV spectroscopic analysis.¹² Then, loss of an HCl molecule as well as coordination of a supplementary ligand (L) occurred to give **B**, and subsequent rotation of the confused pyrrole ring caused production of **C**. The rotation process would benefit from the loss of the HCl molecule because it caused breaking of the [18]-annulenic substructure. Finally, ligand exchange from L to the rest of the pyrrole ring afforded the inverted complex **3**, where the [18]annulenic substructure was reconstructed.

The ¹H NMR chemical shifts of the confused pyrrole moieties illustrated strong aromatic character of **4** and even **3**, both of which have the [18]annulenic substructures. Experimental as well as calculated ¹H NMR chemical shifts of **1**,

(11) Because no X-ray structures for iridium dicarbonyl complexes bearing tetrapyrrolic ligands were reported yet, comparison was achieved with some sapphyrin derivatives. (a) Burrell, A. K.; Sessler, J. L.; Cyr, M. J.; McGhee, E.; Ibers, J. A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 91. (b) Lisowski, J.; Sessler, J. L.; Lynch, V. *Inorg. Chem.* **1995**, *34*, 3567.

(12) After alumina column separation of the crude product, a mixture of polar compounds was obtained in addition to **3**. The ¹H NMR analysis indicated that the mixture was mainly composed of two NCTPP derivatives in a ratio of 3:1. The characteristic ¹H NMR signals were similar to those of **2**, and the absorption spectrum of the mixture closely resembled that of **2**. Hence, the mixture consisted of **A** and its isomer with different coordination sites of the inner Ir atom.

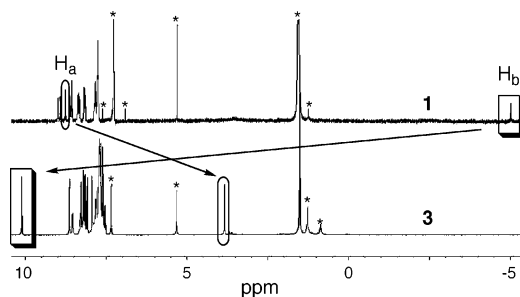


Figure 2. ^1H NMR spectra of **1** and **3** in CDCl_3 .

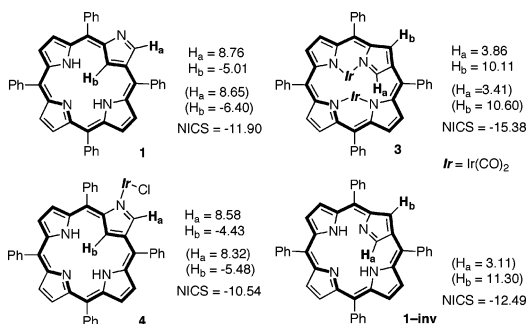


Figure 3. Experimental (in CDCl_3) chemical shift values of ^1H NMR spectra in ppm. The calculated shift values (in parentheses) and NICS values are also shown.

3, and **4** are summarized in Figures 2 and 3.¹³ The H_a proton of **4** was placed at the peripheral position and showed a significant low-field shift (δ 8.58 ppm) due to the strong deshielding effect. On the other hand, the H_b proton of **4** was placed within the macrocyclic ring, and the signal appeared at δ -4.43 ppm because of the strong shielding effect. The corresponding values of **1** were similar to those of **4**, indicating that peripheral coordination did not disturb the aromatic character of porphyrin macrocycles. The situation was reversed by transformation to **3**. Thus, H_a of **3** was placed inside of the macrocyclic ring, and H_b was placed at the peripheral position. H_a received the strong shielding effect (δ 3.86 ppm), and H_b received the strong deshielding effect (δ 10.11 ppm). The same trend was also observed in an inverted conformer of **1** (**1-inv**), while the chemical shifts were obtained only theoretically. This result indicated that **3** still keeps strong aromatic character despite its highly twisted [18]annulenic skeleton, which was further supported by the largely negative nucleus-independent chemical shift (NICS) value (-15.38 ppm).¹⁴

The absorption spectrum of **3** was remarkably different from that of **4** and implied a unique electronic structure of

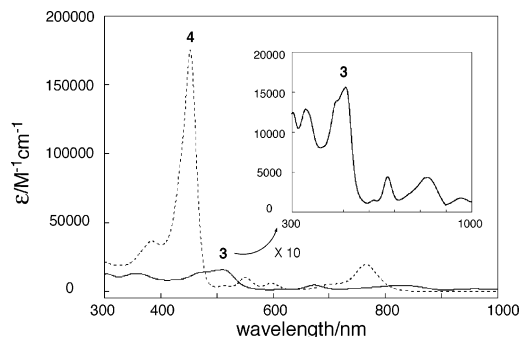


Figure 4. Absorption spectra of **3** and **4** in CH_2Cl_2 .

metal complexes bearing inverted porphyrinoid ligands (Figure 4). While the Soret-like band was clearly observed at 453 nm in the UV/vis spectrum of **4**, no distinct strong absorption was found in the case of **3**. Absorption coefficients for **3** were generally small, and the whole shape was quite unique among absorption spectra of [18]porphyrin(1.1.1.1) derivatives.

In conclusion, the bis[iridium(I)] complex of N-confused tetraphenylporphyrin **3** was synthesized for the first time, where the [18]porphyrin(1.1.1.1) framework took an inverted conformation. The synergy of *confusion* and metal coordination enabled the delivery of the Ir metal from the outside to the inside of the macrocyclic ring during conversion from **1** to **3**. The Ir complexes bearing porphyrinoid ligands often showed unique reactivity, and hence further study on the Ir chemistry of N-confused porphyrin would be promising.¹⁵ Application of pyrrole rotation to atom delivery is also worth considering and awaits further studies. Meanwhile, the strategy developed here would be effective for the production of twisted annulenic skeletons, which have offered new insight into the aromaticity of twisted π -conjugated systems.¹⁶ Twisted annulene skeletons are frequently observed in the expanded porphyrins and have exhibited unique properties such as Möbius aromaticity.¹⁷ Investigation of the twisted annulene system by using the confused porphyrin family is now underway.

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Supporting Information Available: Crystallographic data of **3** (CIF) and experimental details for the preparation of **3** and **4**. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) All of the calculations were performed by a B3LYP method with a *Gaussian03* program package. For structural optimizations, the LANL2DZ basis set was used for Ir and the 6-31G** basis sets were used for the other atoms. The NMR calculations were achieved with GIAO method, where the LANL2DZ basis set was used for Ir and the 6-311++G** basis sets were used for the other atoms.
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