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N-Heterocyclic Carbene Embedded in an N-Confused Porphyrin Framework

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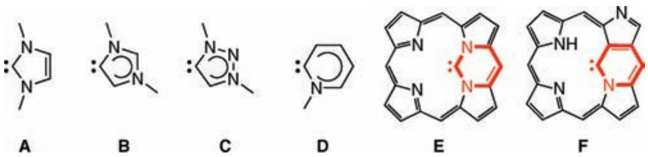
A rhenium(I) complex of an N-heterocyclic carbene ligand embedded in an N-confused porphyrin core was serendipitously synthesized by the reaction of an inner-methylated N-confused porphyrin with $Re_2(CO)_{10}$.

N-Heterocyclic carbenes (NHCs) and their metal complexes play a crucial role in organic and organometallic chemistry.[1] Although recent studies on NHC ligands have mainly targeted application to catalysis, the development of a new class of NHC ligands also continues to attract considerable attention.[2] In addition to the conventional NHC ligands like 2-imidazolylidenes (**A**), the unconventional NHC ligands such as 4-imidazolylidene (**B**),[3] 4-triazolylidene (**C**),[4] and 2-pyridylidene (**D**)[5] were already reported (Chart 1). The porphyrin derivatives possessing the NHC moiety at the periphery were also reported.[6]

We have recently been interested in the interior functionalization of porphyrins and related macrocycles, which would produce novel π systems with unique photophysical properties.[7−9] Along the line of these studies, we have designed a unique molecule, NHC embedded in porphyrin core (Chart 1, **E**). In the early stage of this study, we attempted the synthesis of a metal complex bearing a ligand **E** in vain, possibly because of the high rigidity of regular porphyrin frameworks.[10] Then, considering the flexibility of N-confused porphyrin (NCP),[11,12] a target molecule was shifted to **F** (a kind of **D**) in the meantime. A C(1) unit was introduced inside the core of NCP, and intramolecular oxidative cyclization reactions were examined using low-valent metal reagents. Fortunately, a rhenium(I) complex bearing an NHC ligand embedded in NCP (**1** and **1′**) was successfully obtained by the thermal reaction of inner-methylated NCPs with $Re_2(CO)_{10}$. It should be noted that rhenium metal often shows a versatile ability to stabilize carbene complexes.[13] This oxidative cyclization protocol would be applicable to a variety of porphyrins and related macrocycles. In this paper, the synthesis, structure, and properties of **1** are reported.

Chart 1. Structures of NHCs



The NHC complex **1** was prepared from inner-methylated NCPs.[14] When 22-MeNCP (**2**) was heated with 2 equiv of $Re_2(CO)_{10}$ in 1,2-dichlorobenzene at 140 °C for 16 h, the Re^{I}NHC complex (**1**) was obtained in 25% conversion yield together with the N-fused porphyrin rhenium(I) complex (**5**)[15] in 37% conversion yield (Scheme 1). On the other hand, the thermal reaction of 24-MeNCP (**3**) with $Re_2(CO)_{10}$ did

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[14] Details on the inner N-alkylation reactions will be reported elsewhere.

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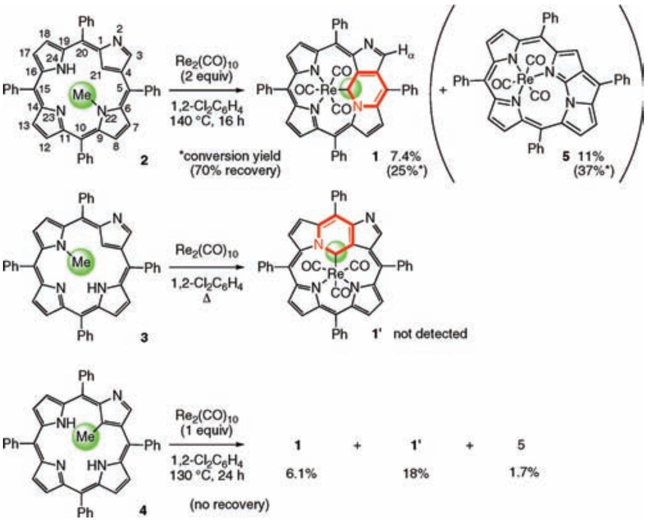
Scheme 1. Reactions of Inner-Methylated NCPs with $Re_2(CO)_{10}$



not afford **1**′, or an isomer of **1**, so far. Alternatively, the reaction of 21-MeNCP (**4**)[16] under the similar reaction conditions gave **1**′ in 18% yield together with **1** in 6.1% yield. In the formation of **1** from **2**, a loss of four hydrogen atoms is required, and it might be due to C−H bond activation by rhenium atoms. Nevertheless, a reaction mechanism is not fully known yet and further study is essential for a better understanding. Because **1** and **1**′ showed rather similar properties, the discussion below is based on **1** (see the Supporting Information for **1**′).

The structure of **1** was supported by spectroscopic data. In the ^1H NMR spectrum of **1** in $CDCl_3$, a signal due to the α-pyrrolic proton of the confused pyrrole ring (H_α) appeared at 10.13 ppm and the rest of the signals (26H for *β*-pyrrolic and phenyl protons) were observed in the aromatic region of 7.7−9.0 ppm. This means that the porphyrin macrocycle keeps its aromaticity in **1**. No other ^1H NMR signals due to **1** were detected in the region from −90 to +90 ppm. The characteristic signal assignable to the carbene carbon atom was observed at 196.44 ppm in the ^{13}C NMR spectrum, which was comparative to those of the reported Re^INHC complexes (192−194 ppm).[17]

Further evidence for the structure of **1** was obtained by X-ray crystallographic analysis (Figure 1).[18] Single crystals suitable for X-ray analysis were obtained by recrystallization from benzene. The rhenium metal is coordinated by the three CO ligands as well as one carbon and two nitrogen atoms of the macrocycle. The coordination geometry around the rhenium atom is distorted tetragonal-bipyramidal. The bond lengths around the metal center are similar to those of the reported Re^INHC complexes. For example, the Re−C(1) bond length of **1** [2.140(5) Å] is within the range of the reported Re^I−NHC bond lengths (2.14−2.20 Å).[17]

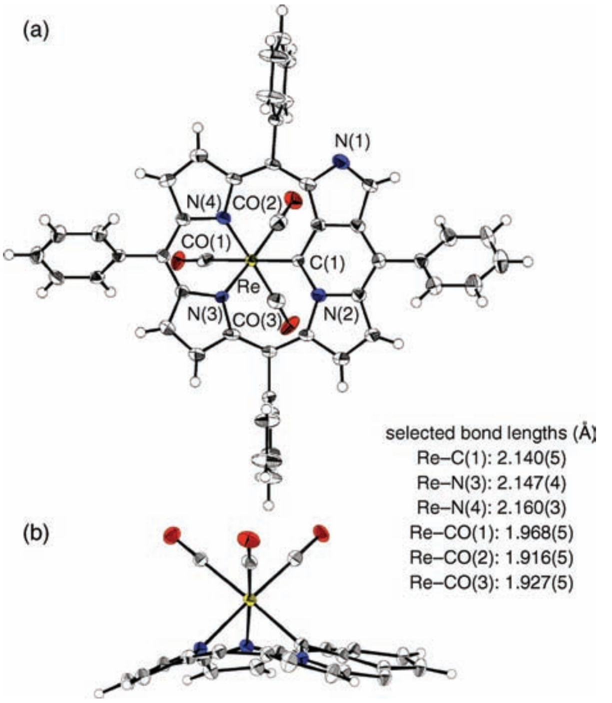


Figure 1. X-ray structures of $1\cdot C_6H_6$: (a) top view; (b) side view. The solvent molecule is omitted, and the *meso*-phenyl groups are removed in part b for clarity. The thermal ellipsoids are shown at the 30% probability level. The bond lengths around the metal center are shown.

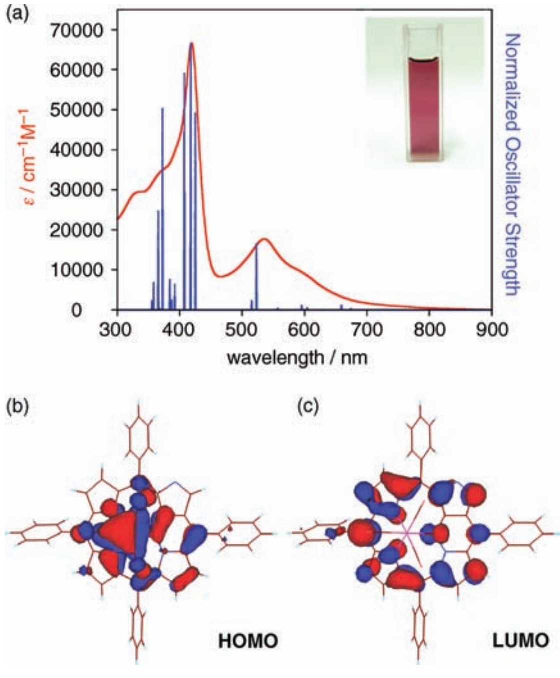


Figure 2. (a) Absorption spectrum of **1** in CH_2Cl_2 together with normalized oscillator strengths obtained by TD-DFT calculations at the B3LYP/6311LAN//B3LYP/631LAN level. A solution color of **1** in CH_2Cl_2 is shown in the inset. (b) HOMO of **1**. (c) LUMO of **1**.

The absorption spectrum of **1** in CH_2Cl_2 is shown in Figure 2a together with the theoretical oscillator strengths.[19] While the Soret-like band was observed at 419 nm, no distinct Q-type bands were observed. Only one broad peak appeared

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[18] Crystal data: $1\cdot C_6H_6$, violet prism, $C_{54}H_{33}N_4O_3Re$, M_W = 972.04, orthorhombic, space group *Pbca* (No. 61), a = 14.572(5) Å, b = 27.174(9) Å, c = 20.160(7) Å, V = 7983(5) Å^3, Z = 8, T = 123(2) K, R = 0.0421 [I > 2σ(*I*)], R_W = 0.1022 (all data), GOF = 1.181, CCDC 763256.

[19] See the Supporting Information for calculation details.

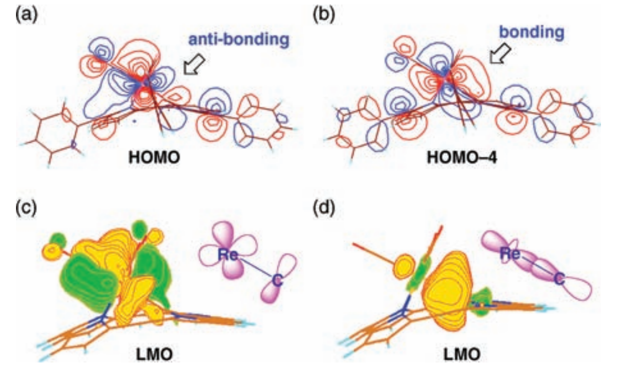

Figure 3. Orbital analyses around the Re−C(1) bond at the B3LYP/631LAN level: (a) cross section of HOMO; (b) cross section of HOMO−4; (c) LMO for π interaction; (d) LMO for σ interaction.

at 536 nm. Such spectral features are well simulated by the time-dependent density functional theory (TD-DFT) calculations. Signal broadening in the Q-type band region might be explained by metal-to-ligand charge-transfer character. While significant contribution of the metal d orbital was observed in the highest occupied molecular orbital (HOMO) of **1**, essentially no contribution was observed in the lowest unoccupied molecular orbital (LUMO; Figure 2b,c).

The experimental as well as theoretical results showed some signs of carbene character in **1**. As mentioned above, the ^{13}C NMR signal at 196.44 ppm and the short Re−C(1) bond length of 2.14 Å are appropriate for the carbene complex. The clear evidence of the d−π interaction in the Re−C(1) bond was derived from orbital analyses. In the HOMO of **1** (Figure 3a), antibonding d−π interaction was observed and the corresponding bonding d−π interaction appeared in HOMO−4 (Figure 3b). Furthermore, localized molecular orbital (LMO) analysis by the Boys method[20] afforded π (Figure 3c) as well as σ interactions (Figure 3d), separately. Meanwhile, natural bond orbital analysis on **1** gave a Wiberg bond index of 0.4956, which would be reasonable as carbene complexes (Figure 4).[19,21] For example, this value is almost the same as that of the model NHC complex **6** (0.4963) and larger than that of the noncarbene complex **7** (0.4696). The NHC complex with a conventional 2-imidazolylidene ligand (**8**) gave a Wiberg bond index of 0.4783. The calculated Re−C(1) bond length of **1** (2.159 Å) was also in good agreement with the carbene complexes **6** and **8**.

In the NHC ligand developed here (**NHC-NCP−**), carbenic forms as well as noncarbenic forms can be described as resonance structures (Scheme 2). Besides this, extension of the π systems of NHC ligands might cause a loss of their distinct carbenic character. Nevertheless, in the case of **1**, the carbenic character was clearly observed and then considerable contribution of the carbenic forms among the resonance structures could be expected.

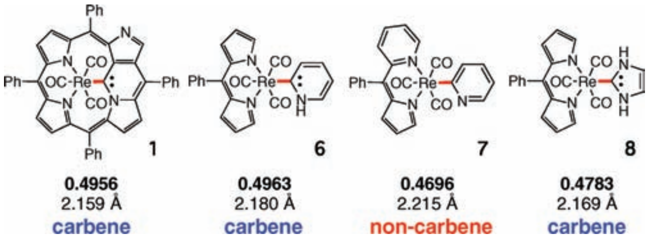

Figure 4. Wiberg bond indexes (bold) and the Re−C bond lengths of the rhenium(I) complexes calculated at the B3LYP/631LAN level.

Scheme 2. Resonance Structures of **NHC−NCP^{-}**

Finally, considerable stability of **1** was mentioned. The NHC complex **1** could be purified with standard silica gel column chromatography in which no special technique was required. The addition of an acid such as CF_3COOH only caused protonation at the peripheral nitrogen atom, and no decomposition or demetalation was observed (Figure S12 in the Supporting Information). The NHC complex **1** was also stable against electrochemical oxidation and reduction (Figure S11 in the Supporting Information). Cyclic voltammetry measurements in a CH_2Cl_2 solution with 0.1 M $Bu_4N^+PF_6^-$ gave a reversible one-electron-oxidation wave at 0.62 V and two reversible one-electron-reduction waves at −1.11 and −1.65 V (vs Fc/Fc$^+$).

In conclusion, the oxidative cyclization protocol to produce the NHC metal complexes embedded in the porphyrin framework was developed and their fundamental properties were investigated. The Re^{I}NHC complex **1** showed considerable stability despite its distinct carbenic character. The oxidative cyclization protocol developed here would be applicable to versatile porphyrin and calixphyrin systems, which would open up a new category of NHC ligands. Further studies on the properties of π-extended NHC metal complexes are now underway.

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Supporting Information Available: Synthetic procedures and spectroscopic data of **1** and **1′**, details on the theoretical studies, ^{1}H and ^{13}C NMR spectra, and crystallographic data of **1** and **1′** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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