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### COMMUNICATION

## Toward aceneporphyrinoids: synthesis and transformations of palladium(II) *meso*-anthriporphyrin†‡

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*meso*-Anthriporphyrin is a carbaporphyrinoid with an anthracene ring embedded in the tripyrrolic framework. The coordination of palladium(II) results in a specific intramacrocyclic metal(II)– $\eta^2$ -CC interaction which facilitates the cleavage to palladium(II) acyclic oligopyrrole with the appended anthracene moiety.

An emerging group of aceneporphyrinoids-hybrid compoundswhich combine properties of acenes and porphyrins, exemplified by 1,4-naphthiporphyrin,<sup>1,2</sup> 1,4-naphthi-24-thiaporphyrin<sup>1</sup> and 1,3-naphthiporphyrin,<sup>2</sup> creates potentially an unique macrocyclic environment toward coordination. Such porphyrinoids preserve the essential features of the [18]porphyrin(1.1.1.1) frame and are expected to coordinate metal ions using the  $(C_n, N, N, N)$   $(n \ge 1)$ coordination core. A reasonable anticipation is that an incorporated acene ring may be able to participate in various metal-arene bonding modes ranging from  $\eta^1$  to  $\eta^6$ . In more general terms the whole class of carbaporphyrinoids is suitable to explore organometallic chemistry confined to a peculiar macrocyclic environment as the close proximity of CH or CC bonds to the metal ion enforces an unusual coordination geometry and eventually unique reactivity.<sup>3,4</sup> Formally aceneporphyrinoids are derived from benziporphyrins applying a fusion concept of external benzene ring(s) and a built-in phenylene moiety. Consequently these molecules may conserve the fundamental motive of benziporphyrin and in such a sense benziporphyrins demonstrate some essential properties of proper aceneporphyrins.<sup>5–8</sup> Recently we have demonstrated that the palladium(II) p-benzi-

porphyrin altered the fundamental reactivity of the benzene unit allowing facile palladium( $\pi$ ) stimulated contraction of *p*-phenylene to cyclopentadiene.<sup>9</sup>

Herein we have found that due to geometrical constraints of the porphyrinoid macrocycle an intramolecular rearrangement of palladium( $\pi$ ) *meso*-anthriporphyrin yielded the palladium( $\pi$ ) coordinated to the acyclic ligand with the appended anthracene

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moiety, revealing the alternative route of reactivity achievable in the aceneporphyrinoid core.

*meso*-Anthriporphyrin **1** is obtained in a simple modification of the condensation described for benziporphyrins<sup>5,6</sup> using pyrrole, benzaldehyde and 9,10-bis(phenylhydroxymethyl)anthracene **5** (Scheme 1).

1 and its monoprotonated form  $[1-H]^+$  demonstrate the tilt of the anthracene moiety toward the center of the molecule (Fig. 1). The dihedral angles between the anthracene A ring and the four *meso* carbon atom (C<sub>meso</sub> plane) plane for 1 and  $[1-H]^+$  are 72.9° and 73.9°, respectively. The C(20)–C(1) and C(4)–C(5) distances (1, 1.480(3) and 1.470(3) Å;  $[1-H]^+$ , 1.483(4) and 1.469(4) Å) approach the single-bond limit for C(sp<sup>2</sup>)–C(sp<sup>2</sup>). Marked alternations of C<sub> $\alpha$ </sub>–C<sub>meso</sub> distances resemble those observed for 1,4-naphthiporphyrin.<sup>1</sup> These structural features and the high values of the dihedral angles between the anthracene ring and four *meso* carbon atoms plane confirm that the anthracene incorporated in the framework of 1 or  $[1-H]^+$  limits essentially the macrocyclic aromatic delocalization while retaining the strong conjugation of the tripyrrolic brace. The monocation coordinates the TFA anion through two hydrogen bonds.

As the extent of macrocyclic  $\pi$ -conjugation is limited (Fig. S1, ESI‡), the  $\beta$ -H and NH <sup>1</sup>H NMR chemical shifts (1:  $\beta$  7.59, 6.52, 6.19 ppm; NH 6.77 ppm) resemble those of carbaporphyrinoids at the borderline cases of porphyrinoid aromaticity<sup>3</sup> approaching *m*-benziporphyrin where the strongly



Scheme 1 Synthesis of 1: (a) PhCOCl, AlCl<sub>3</sub>, 1,2-dichloroethane, reflux, 7 days, 92%; (b) LiAlH<sub>4</sub>, THF, 293 K, 15 min, 99%; (c) pyrrole, PhCHO, DCM,  $Et_2O\cdot BF_3$ , 293 K, 2 h; (d) DDQ, 0.5%.

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**Fig. 1** Molecular structures of (a) **1** and (b) its monocation  $[1-H]^+$  (counterion—trifluoroacetate): (top) perspective view; (bottom) side view with aryl groups omitted for clarity. The thermal ellipsoids represent 50% probability.

aromatic structure of benzene completely blocks a  $\pi$ -delocalization pathway for the entire molecule.<sup>5</sup> Two terminal benzene rings produce the single set of resonances in the whole investigated temperature range (Fig. S2, ESI‡). Thus the molecule switches rapidly between two equivalent conformations, which differ by opposite tilting of anthracene.

Reaction of palladium(II) chloride with *meso*-anthriporphyrin **1** in acetonitrile results in the formation of the four-coordinate palladium(II) *meso*-anthriporphyrin **2** (Scheme 2).

The geometry of **2** as determined by X-ray crystallography reflects the balance among constraints of the macrocycle ligand, the size of the palladium(II) ion, and the predisposition of the palladium(II) for the square planar geometry, resembling eventually the structure of palladium(II) vacataporphyrin,10 palladium(II) p-benziporphyrin<sup>9</sup> and palladium(II) 1,4-naphthiporphyrin.<sup>1</sup> The anthracene flat conformational motif of **1** is fundamentally changed. The units adopt a butterfly shape folded along the C(1)–C(4) vector by a dihedral angle ca.  $46^{\circ}$  (C(1) and C(4) are displaced from the C(2)C(3)C(21)C(22) plane by 0.54 and 0.51 Å). The bond lengths C(20)-C(1) 1.352(3) and C(4)–C(5) 1.349(3) are consistent with typical CC double bond character. Thus the geometry corresponds to anthraquinodimethane type molecular structure.<sup>11,12</sup> Actually, the peculiar orientation of the anthracene (Fig. 3, the side-on projection) nicely reveals the macrocyclic cleft formation which is defined by anthracene and tripyrrolic arms. The bond distances within the tripyrrolic framework of 2-Cl indicate that the macrocycle reveals the pattern expected for non-aromatic carbaporphyrinoids.<sup>3</sup>



Scheme 2 Synthesis of 2–X: (a) PdCl<sub>2</sub>, MeCN, DCM, 48 h, 99%; (b) AgBF<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>; (c) NaBr, MeOH, 100%.

The anthracene moiety approaches palladium(II) at distances shorter (Pd···C(21) = 2.98 Å, Pd···C(22) = 2.96 Å) than the expected van der Waals contact (Pd $\cdot \cdot C = 3.3$  Å) but clearly above the 2.110(7)-2.476(5) Å limits of the typical values for palladium(II) $-\eta^2$ -alkene complexes.<sup>13,14</sup> Thus, the palladium(II) ion interacts weakly with the bridging carbon center of anthracene in a  $\eta^2$  fashion, engaging the C(21) and C(22) carbon atoms. The projection of the palladium(II) ion onto the C(2)C(3)C(21)C(22)plane (C<sub>4</sub> plane) lies close to the center of the C(21)–C(22) bond (Fig. 3). A similar weak interaction has been observed for metal(II) *p*-benziporphyrin and palladium(II) 1,4-naphthiporphyrin complexes.<sup>1,6,7,9</sup> The distinct feature of the structure is the very pronounced bending of the chloride ligand on the opposite to the anthracene side of the macrocycle as a consequence of strain induced by incorporation of a metal-chloride bond into a macrocyclic surrounding (N(24)-Pd-Cl 154.44(7)°).

The structural features are preserved in solution as determined by <sup>1</sup>H NMR (Fig. 2a). The coordination of palladium(II) freezes the see-saw conformation equilibrium which yields a spectrum with well-defined two sets of resonances of inner and outer phenylenes.

Palladium(II) *meso*-anthriporphyrin **2**–X dissolved in acetonitrile undergoes a ring-opening process after heterogeneous addition of potassium carbonate at 293 K over a period of 12 h converting eventually to the spectroscopically identified palladium(II) complex **3–**X of the acyclic ligand with the appended anthracene moiety (Scheme 3). The reaction leads to the cleavage of the macrocyclic ring at the C<sub>1</sub>–C<sub>meso</sub> bond which is accompanied by oxidation and introduces a benzoyl group at the  $\alpha$  pyrrole position. Significantly the halogen substituent at the central anthracene ring originates from the equatorially coordinated chloride or bromide of **3–**X. The control experiment proved that dioxygen is necessary for the **2–**X to **3–**X conversion.

The <sup>1</sup>H NMR spectrum of **3**–Cl (Fig. 2b) reveals practically doubling of resonances as compared to **2**–Cl. Complete assignments of **3**–Cl resonances have been made on the basis of relative intensities and through a combination of homonuclear (COSY, NOESY, ROESY) and heteronuclear (HMQC, HMBC) correlation techniques. The  $\beta$ -H region of **3**–Cl (**3**–Br) resembles the basic features of non-aromatic conjugated acyclic molecules formed by the porphyrinoid cleavage.

The structural model of 3-Cl, generated by DFT optimization (Fig. 4), reflects the structural constraints determined by



Fig. 2 <sup>1</sup>H NMR spectra of (a) 2–Cl (CDCl<sub>3</sub>, 300 K), (b) 3–Cl (CDCl<sub>3</sub>, 300 K) and (c) 3–Cl (CDCl<sub>3</sub>, 220 K).



Fig. 3 Molecular structure of 2-Cl: (top) perspective view; (middle) side view with phenyl groups omitted for clarity; (bottom) geometry of the interaction between palladium(II) and the anthracene moiety. The thermal ellipsoids represent 50% probability.



Scheme 3 Synthesis of 3-X: (a) K<sub>2</sub>CO<sub>3</sub>, MeCN, 12 h, 16% for 3-Cl.

NOE measurements. The palladium(II) cation acquires a typical square planar coordination geometry<sup>15,16</sup> whereas four donating atoms (three pyrrolic nitrogen atoms and one carbonyl oxygen atom) are provided by the acyclic oligopyrrole. The NOE correlations (Fig. S7, ESI<sup>‡</sup>), which result from the unique through-space interactions between appended anthracene and

Fig. 4 DFT-optimized structure of 3-Cl. C light gray, H white, N blue, O red, Pd orange.

adjacent meso aryls, allowed the specific identification of the meso aryl substituents distinguished remarkably also by a peculiar spread of 5-Ph and anthracene resonances.

<sup>1</sup>H NMR chemical shifts of **3**–Cl have been calculated using the GIAO-B3LYP method for the optimized (DFT-B3LYP with the LANL2D basis set for Pd and 6-31G\*\* for other atoms) geometry. This is a satisfactory qualitative agreement for the considered set of theoretical and experimental data readily demonstrated by linear correlation between the calculated and experimental chemical shifts values (Fig. S25, ESI<sup>‡</sup>).

In conclusion, meso-anthriporphyrin is the new porphyrinoid, which belongs to the group of aceneporphyrins. Potentially an anthracene ring may be able to participate in various metal-arene bonding modes. This study demonstrates considerable parallel in the coordination properties of meso-anthriporphyrin and its lower benzologues: p-benziporphyrin and 1,4-naphthiporphyrin toward palladium(II). In contrast to palladium(II) p-benziporphyrin and palladium(II) 1,4-naphthiporphyrin complexes, which undergo facile intramacrocyclic contractions in basic conditions,<sup>1,9</sup> the alternative mechanism is operating for palladium(II) meso-anthriporphyrin resulting in the C1-Cmeso cleavage.

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