



# Selective nitration and bromination of surprisingly ruffled phosphorus corroles



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## ABSTRACT

Phosphorus complexes of corrole have recently attracted increasing interest since these compounds can be easily prepared in good yields, are stable, and show unusual optical properties. For these reasons, phosphorus corroles represent a class of interesting compounds to be exploited in the field of material science or for biomedical investigations and the definition of synthetic pathways for their functionalization is an important step to optimize their properties for various applications. We report here the reactivity of the phosphorus complex of 5,10,15-tritolyrcorrole in the nitration or bromination reaction. Both these attempts were successful, allowing the preparation of substituted phosphorus corroles, which can be used as intermediates of more complex architectures endowed with useful properties. Furthermore, the crystallographic characterization of both complexes shows that they have an unusual ruffled geometry of the corrole core, a conformation that has not been considered possible for such a macrocycle.

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## 1. Introduction

Corrole chemistry has experienced impetuous growth in the last decade, during which a number of papers focused on corrole synthesis, functionalization and applications, using either the corrole free bases or metal complexes, have been published [1–3].

The intense interest in corrole chemistry is largely due to some unusual properties that make this contracted macrocycle different from the more common porphyrin system. For example the inner cavity of corrole is smaller than that of porphyrin, due to the replacement of a methine bridge with a direct pyrrole–pyrrole bond; the presence of three inner core protons also confers to corrole the capability to stabilize metal ions in formally high oxidation states. The preparation of many metallo–corrolates containing p-block elements of the periodic table has already been reported [3–10]. Some of these complexes show interesting photophysical properties: Al, Ga and P corrolates are endowed with luminescence features that can parallel those of Mg porphyrin derivatives [5–7,11–14]. Despite the recent expansion of the metallo–corrolate periodic table, functionalization of the corresponding complexes is not as well developed as is their synthetic methodology. A few papers have been published concerning halogenation reaction at the peripheral positions of Al and Ga corrolates [12,13] as well as the nitration of the Ga complex [15], while for the Ge corrolate the functionalization of  $\beta$ -pyrrole positions either by bromination [16] or by nitration [17] has been investigated. The halogenation reaction yielded

interesting results, providing the first example of a partially brominated corrole, thereby demonstrating how the metal ion affects the reactivity or the macrocycle. Moreover, the Ge derivative yields chloro, hydroxyl, and  $\mu$ -oxo dimer species [16], depending on the reaction work up.

Among the main group derivatives, phosphorus corrole complexes were among the first to be reported in the literature. We reported the first example of phosphorus(V) corrole complex by reaction of 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole [EMCorrH<sub>3</sub>] with POCl<sub>3</sub> in pyridine, to give [(EMCorr)P(OH)Cl] [18]. A few years later, Kadish and co-workers investigated complexes of 2,3,7,8,12,13,17,18-octaethylcorrole (OECorrH<sub>3</sub>) containing alkyl, aryl, oxo and hydrido axial ligands [19]. In the triarylcorrole series, Gross investigated phosphorus coordination to 5,10,15-tris-pentafluorophenylcorrole [20], while more recently the axial chemistry of P-triarylcorrolates has been studied in detail using <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, to characterize the equilibrium between five- and six-coordinated species [5]. These compounds react quantitatively with an excess of trifluoroacetic acid to give the five-coordinate P=O *meso*-triarylcorrole [6]. The products show interesting luminescence properties, endowed with a high fluorescence quantum yield; phosphorus corrole derivatives have also been recently investigated by Kobayashi and coworkers, with the aim to study their potential exploitation in bioimaging of cells [7].

These properties make interesting to study the functionalization of P-triarylcorroles, with the aim to pave the way for the development of more complex structures based on these macrocycles. From this point of view, –NO<sub>2</sub> and –Br moieties are very versatile functional groups, since they represent the starting point for further corrole modifications. For the preparation of these functionalized phosphorus corrole derivatives, two

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different approaches can be followed: firstly to functionalize the corrole free base and then insert the phosphorus ion, or else perform the reaction directly on the final complex [21]. Usually the facile oxidation of corrole makes the macrocycle quite sensitive to the reaction conditions, preventing the direct functionalization of the free base. For this reason we decided to investigate the direct functionalization of a P-corrole, which can allow one to explore for the first time the reactivity of such a species.

In this paper we report bromination and nitration reactions carried out on the P(V) complex of tritolyllcorrole, and the characterization of the reaction products.

## 2. Experimental

### 2.1. General

Silica gel 60 (70–230 mesh, Sigma Aldrich) or neutral alumina oxide (Grade III or IV, Merck) were used for column chromatography. Reagents and solvents (Aldrich, Merck or Fluka) were of the highest grade available and were used without further purification. UV–vis spectra were measured in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 9:1 on a Cary 50 spectrophotometer. <sup>1</sup>H NMR and <sup>31</sup>P spectra were recorded on a Bruker AV300 spectrometer operating at 300.13 MHz (<sup>1</sup>H) or at 121.48 MHz (<sup>31</sup>P), usually by addition of 10 μL of CD<sub>3</sub>OD to 600 μL of CDCl<sub>3</sub>. Chemical shifts are given in ppm relative to residual CHCl<sub>3</sub> (7.26 ppm) for <sup>1</sup>H and to a CDCl<sub>3</sub> solution of PPh<sub>3</sub> (−6.10 ppm) as external standard for <sup>31</sup>P. Mass spectra were recorded on a VGQuattro spectrometer in the positive-ion mode, using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix (FAB). 5,10,15-Tris-(4-methylphenyl)corrole (TTCorrH<sub>3</sub>) and (dimethoxy)phosphorus-[5,10,15-tris-(4-methylphenyl)corrolate] TTCorrP(OCH<sub>3</sub>)<sub>2</sub> were prepared according to literature methods [5,22].

### 2.2. X-ray crystallographic data

Diffraction data for [(3,17-(NO<sub>2</sub>)<sub>2</sub>-TTCorr)P(OH)(OCH<sub>3</sub>) and brominated [Br<sub>x</sub>TTCorr]P(OCH<sub>3</sub>)<sub>2</sub> were collected at low temperature on a Bruker Kappa Apex-II DUO diffractometer equipped with MoKα radiation (λ = 0.71073 Å) and a Triumph curved monochromator or CuKα radiation (λ = 1.54184 Å) from a IμS microfocus source. Absorption corrections were by the multiscan method, using SADABS [23]. Refinement was by full-matrix least squares using SHELXL-97 [24], with H atoms in idealized positions, guided by difference maps. In both cases, disordered solvent was removed by the SQUEEZE procedure [25]. The crystal of brominated [Br<sub>x</sub>TTCorr]P(OCH<sub>3</sub>)<sub>2</sub> contained substitutional disorder in which Br substituents are fully occupied at the 2, 3, 8, 12 and 17 positions, and also present with 55% occupancy at the 7 position and 7.5% at the 13 position. This disorder also causes the Br at the 18 position to occupy two different positions with occupancies 92.5 and 7.5%. The 7.5%-occupied Br lies 1.33 Å out of the plane of the C16–C19 pyrrole, thus the pyrrole must be tipped 7.5% of the time. However, the C atoms of this minor conformer, which would each amount to only 0.45 electrons, could not be located. Crystal data: For [(3,17-(NO<sub>2</sub>)<sub>2</sub>-TTCorr)P(OH)(OCH<sub>3</sub>): C<sub>41</sub>H<sub>31</sub>N<sub>6</sub>O<sub>6</sub>P<sub>2</sub>·3(CH<sub>3</sub>OH), monoclinic space group P2<sub>1</sub>/c, a = 14.4918(4), b = 7.8403(2), c = 33.8409(8) Å, β = 95.7730(10)°, Z = 4, T = 90 K, μ(CuKα) = 1.19 mm<sup>−1</sup>. A total of 26,988 data was collected at θ = 68.3°. R = 0.036 for 5998 data with I > 2σ(I) of 6986 unique data and 494 refined parameters, CCDC 1406402. For brominated [Br<sub>x</sub>TTCorr]P(OCH<sub>3</sub>)<sub>2</sub>: C<sub>42</sub>H<sub>28.4</sub>Br<sub>6.6</sub>N<sub>4</sub>O<sub>2</sub>P<sub>0.5</sub>(CH<sub>2</sub>Cl<sub>2</sub>), triclinic space group P-1, a = 9.7797(4), b = 13.6287(5), c = 16.5666(7) Å, α = 86.842(3), β = 88.822(3), γ = 73.037(3)°, Z = 2, T = 100 K, μ(MoKα) = 6.45 mm<sup>−1</sup>. A total of 23,288 data was collected to θ = 27.8°. R = 0.057 for 6422 data with I > 2σ(I) of 9779 unique data and 530 refined parameters, CCDC 1406403.

#### 2.2.1. Nitration of phosphorus corrole, method A

A solution of TTCorrP(OCH<sub>3</sub>)<sub>2</sub> (20 mg, 0.03 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (11 mL), was treated with 1 mL of a solution of LiNO<sub>3</sub> (80 mg,

1.16 mmol) in acetic acid (4 mL) and acetic anhydride (2.3 mL), and the mixture stirred to reflux. After 10 min the color of the solution changed from purple to green and TLC analysis (alumina/CH<sub>2</sub>Cl<sub>2</sub>) showed the absence of the starting material. The mixture was diluted with 10 mL of CH<sub>2</sub>Cl<sub>2</sub>, washed with water, aqueous NaHCO<sub>3</sub>, dried over Na<sub>2</sub>SO<sub>4</sub> and then the solvent was removed under vacuum. The residue was purified by column chromatography (alumina grade III, eluted with CH<sub>2</sub>Cl<sub>2</sub> then CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 2%). The first band eluted was identified as compound [(3-NO<sub>2</sub>)-TTCorr]P(OCH<sub>3</sub>)<sub>2</sub>, while the second fraction was collected and purified further by column chromatography (alumina grade IV, CH<sub>2</sub>Cl<sub>2</sub>) to yield compound [(3,17-(NO<sub>2</sub>)<sub>2</sub>-TTCorr)P(OH)(OCH<sub>3</sub>).

#### 2.2.2. Nitration of phosphorus corrole, method B

TTCorrP(OCH<sub>3</sub>)<sub>2</sub> (20 mg, 0.03 mmol) and NaNO<sub>3</sub> (6.5 mg, 0.075 mmol) were dissolved in acetic anhydride (5.3 mL) and stirred at 45 °C, before addition of acetic acid (1.2 mL). After 15 min the color of the solution changed from purple to green and TLC analysis (alumina/CH<sub>2</sub>Cl<sub>2</sub>) showed the absence of the starting material. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL), then washed with water, aqueous NaHCO<sub>3</sub>, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under vacuum. The residue was purified by column chromatography (alumina grade III, eluted with CH<sub>2</sub>Cl<sub>2</sub> then CHCl<sub>3</sub>). A first fraction was identified as [(3-NO<sub>2</sub>)-TTCorr]P(OCH<sub>3</sub>)<sub>2</sub>. The second fraction collected was purified further by column chromatography (alumina grade IV, CH<sub>2</sub>Cl<sub>2</sub>) and identified as [(3,17-(NO<sub>2</sub>)<sub>2</sub>-TTCorr)P(OH)(OCH<sub>3</sub>).

2.2.2.1. [(3-NO<sub>2</sub>)-TTCorr]P(OCH<sub>3</sub>)<sub>2</sub>. Crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yield: method A 28% (6 mg), method B 14% (3 mg). UV–vis (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 9:1): λ<sub>max</sub>, nm (log ε) 391 (sh), 428 (4.73), 447 (4.98), 590 (sh), 635 (4.61). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD): δ, ppm 9.56 (d, 1 H, <sup>4</sup>J<sub>P-H</sub> = 2.81 Hz, β-pyrrole C-2), 9.05 (dd, 2 H, <sup>3</sup>J<sub>H-H</sub> = 2.10 Hz, <sup>4</sup>J<sub>P-H</sub> = 1.92 Hz, β-pyrrole), 8.91 (dd, 2 H, <sup>3</sup>J<sub>H-H</sub> = 4.14 Hz, <sup>4</sup>J<sub>P-H</sub> = 3.32 Hz, β-pyrrole), 8.82 (m, 2 H, β-pyrrole), 8.61 (m, 2 H, β-pyrrole), 8.11 (d, 2 H, J = 7.68 Hz, meso-phenyl), 8.00–7.93 (m, 4 H, meso-phenyl), 7.61 (d, 2 H, J = 7.53 Hz, meso-phenyl), 7.54 (t, 4 H, J = 8.40 Hz, meso-phenyl), 2.70 (s, 3 H, p-CH<sub>3</sub>), 2.68 (s, 3 H, p-CH<sub>3</sub>), 2.66 (s, 3 H, p-CH<sub>3</sub>), −1.96 (d, 6 H, <sup>3</sup>J<sub>P-H</sub> = 24.3 Hz, axial −OCH<sub>3</sub>). <sup>31</sup>P NMR (121.48 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD): δ, ppm −173.8. MS (FAB): m/z (%) 672 [M-OCH<sub>3</sub>] (100), 704 [M] (80), 825 [M-OCH<sub>3</sub> + NBA] (20). C<sub>42</sub>H<sub>34</sub>N<sub>5</sub>O<sub>4</sub>P: calcd. C 71.68, H 4.87, N 9.95; found C 71.73, H 4.91, N 9.92.

2.2.2.2. [(3,17-(NO<sub>2</sub>)<sub>2</sub>-TTCorr)P(OH)(OCH<sub>3</sub>]. Crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane. Yield: method A 4% (1 mg), method B 18% (4) mg. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH 9:1): λ<sub>max</sub>, nm (log ε) 382 (sh), 434 (5.16), 462 (5.24), 602 (sh), 661 (5.15). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD): δ, ppm 9.42 (d, 1 H, <sup>4</sup>J<sub>P-H</sub> = 2.92 Hz, β-pyrrole), 8.82 (dd, 2 H, <sup>3</sup>J<sub>H-H</sub> = 2.55 Hz, <sup>4</sup>J<sub>P-H</sub> = 3.30 Hz, β-pyrrole), 8.56 (dd, 2 H, <sup>3</sup>J<sub>H-H</sub> = 2.71 Hz, <sup>4</sup>J<sub>P-H</sub> = 3.03 Hz, β-pyrrole), 7.94 (m, 6 H, meso-phenyl), 7.56 (t, 6 H, J = 7.14 Hz, meso-phenyl), 2.68 (s, 3 H, p-CH<sub>3</sub>), 2.66 (s, 6 H, p-CH<sub>3</sub>), −1.97 (d, 3 H, <sup>3</sup>J<sub>P-H</sub> = 25.5 Hz, axial −OCH<sub>3</sub>), −3.91 (br s, 1 H, axial −OH). <sup>31</sup>P NMR (121.48 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD): δ, ppm −185.3. MS (FAB): m/z (%) 717 [M-OH] (100). C<sub>41</sub>H<sub>31</sub>N<sub>6</sub>O<sub>6</sub>P: calcd. C 67.03, H 4.25, N 11.44; found C 67.09, H 4.19, N 11.51.

#### 2.2.3. Bromination of phosphorus corrole, method A

To a solution of TTCorrP(OCH<sub>3</sub>)<sub>2</sub> (20 mg, 0.03 mmol) in CHCl<sub>3</sub> (10 mL) was added dropwise a pre-prepared solution of Br<sub>2</sub> (55 μL, 1.08 mmol) and CHCl<sub>3</sub> (5 μL). The mixture was stirred at room temperature for 90 min, before pyridine (104 μL, 1.3 mmol) was added, the solvent was removed under vacuum and the residue purified by passage through a silica gel plug (silica gel, eluted with CHCl<sub>3</sub>) to remove the decomposition product; then further purification was accomplished by PLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/hexane 3:2). The second green fraction

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