Synthesis and Functionalization of *meso*-Aryl-Substituted Corroles

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The Rothemund condensation reaction of pyrrole and aldehydes is an extensively used route to *meso*-tetraarylporphyrins, but simple modifications of the reaction conditions allow the formation of different macrocycles other than the expected porphyrin. In the presence of an excess of pyrrole, this modified Rothemund approach leads to the synthesis of *meso*-triaryl-substituted corroles. This methodology allows the preparation of a wide range of substituted corroles starting from commercially available products. Higher yields have been obtained in the case of benzaldehydes bearing electron-withdrawing substituents, while the reaction fails in the presence of 2,6-disubstituted benzaldehydes. Although if not isolated, some experimental evidences indicate that the linear 5,10,15-triphenylbilane **4** is the precursor of the final corrole ring. Reaction of 5,10,15-triphenylcorrole **2** with an excess of NBS leads to the complete bromination of the macrocycle. Spectroscopic characterization seems to indicate the formation of the porphodimethene-like structure **5**, where the macrocyclic aromatic conjugation is interrupted at the 10 position. Metalation of this compound with cobalt acetate and PPh_3 affords the corresponding complex. The X-ray crystal structure of triphenylphosphine [2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(4-nitrophenyl)corrolato]-cobalt(III) **8** confirms the ability of corrole ring to retain an almost planar conformation when fully substituted at the peripheral positions.

Introduction

Synthetic porphyrins have been a useful tool to fully understand the complex reactions performed by these macrocycles in biological systems.[1] Furthermore, the attempt to mimic the peculiar chemistry operated by natural porphyrins opened the way to their possible exploitation in a wide range of practical applications.[2]

While β-octaalkylporphyrins represent the more direct counterpart to natural porphyrins, *meso*-tetraarylporphyrins, with *meso*-tetraphenylporphyrin (H_2TPP) as the prototypical example, have been the most often used macrocycles in these studies. The popularity of H_2TPP is probably due to the facile preparation from commercially available products and to the possibility to introduce a wide range of functional groups at the β-pyrrolic or at the *meso*-aryl positions.[3] For this reason, H_2TPP has been the ideal platform used to build more complex systems, providing a fruitful and significant contribution to porphyrin studies.

However, a similar possibility is rarely found with regards to porphyrin analogues, macrocycles having some modification in the molecular skeleton with respect to that of the parent porphyrin.[4] While the interest on these compounds has greatly increased because the structural modifications can induce new and interesting properties to the resulting macrocycles,[5] the synthetic pathways developed for these porphyrin analogues are generally related to β-alkyl substitution patterns.

This limitation has been true also for corrole, a porphyrin analogue that has recently undergone a significant renaissance in interest.[6] Corroles have demonstrated the ability to coordinate a wide range of metals and exhibits a coordinative behavior that is quite peculiar and different from that of porphyrins.[7]

We have been interested in the chemistry of this compound for a certain time and have studied the possibility to develop a synthetic route to *meso*-aryl-substituted corroles.[8] In 1994, we reported the first example of a *meso*-aryl-substituted corrole from a one-pot reaction,[9] however this reaction was of limited synthetic interest and in fact it afforded the fully substituted corrole as triphenylphosphino-Co(III) complex **1**. Both Cobalt and β-substituted pyrroles were necessary to drive the tetramerization of the starting pyrrole to the

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[†] Università di Roma Tor Vergata.

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(1) *The Porphyrins*; Dolphin, D. Ed.; Academic Press: New York, 1978; Vol. VII, Parts A and B.

(2) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 6.

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(8) Paolesse, R.; Licoccia, S.; Fanciullo, M.; Morgante, E.; Boschi, T. *Inorg. Chim. Acta* **1993**, *203*, 107.

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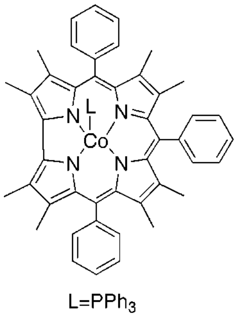
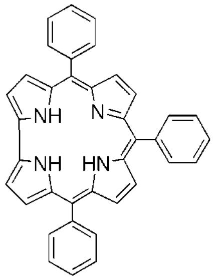
corrole. In the other cases, the expected porphyrin was the macrocycle obtained.



1

We did not attempt to direct the reaction between pyrrole and benzaldehyde to obtain **2** because the competitive formation of H_2TPP seemed to be an overwhelming obstacle to the formation of **2**. The seminal papers of Furuta[10] and Latos-Grazynsky[11] groups, about the formation of other macrocycles such as N-confused porphyrins and sapphyrins from the direct condensation of pyrrole and aromatic aldehydes, aroused the suspicion that also corrole can be obtained by this way. This hypothesis was correct and in 1999 we reported the synthesis of **2** from pyrrole and benzaldehyde by a modified Rothemund reaction.[12] That same year Gross and co-workers reported the synthesis of 5,10,15-tris(pentafluoro)phenylcorrole by reaction of pyrrole and pentafluorobenzaldehyde in the absence of solvent.[13] These approaches allow for a novel approach to the preparation of *meso*-aryl-substituted corroles and can also be of tremendous importance for the complete development of the chemistry of corrole, opening the way for its potential applications in different fields.



2

Herein we study the generality of the Rothemund synthesis of corroles by reaction between pyrrole and aldehydes as well as the functionalization of the resulting macrocycles via bromination. We report also the first X-ray characterization of a fully brominated triarylcorrole as a triphenylphosphinocobalt complex.

Results and Discussion

It is quite surprising that until now the formation of corrole from the Rothemund reaction between pyrrole and aromatic aldehydes has never been reported, taking into account the wide application of this reaction for the synthesis of *meso*-tetraarylporphyrins.[3] However, it should be noted that the formation of corrole is significantly influenced by the molar ratio between pyrrole and aldehydes and only in the presence of excess pyrrole is it possible to obtain corrole in appreciable yields.[12] In fact, we obtained the highest yields of corrole using a 3:1 pyrrole/benzaldehyde molar ratio in refluxing acetic acid. In these conditions the expected H_2TPP was obtained in comparable yields, while other chromophores, such as N-confused porphyrin and sapphyrin, were observed by TLC in very low amounts and were not separated.

Table 1. Comparison of Reaction Yields of Different *meso*-Triarylcorroles

aryl aldehyde	5,10,15-TAC yield (%)
benzaldehyde	6
4-NO_2 benzaldehyde	22
3-NO_2 benzaldehyde	15
2-NO_2 benzaldehyde	8
4-Br benzaldehyde	5
3-Br benzaldehyde	9
2-Cl benzaldehyde	9
4-CH_3 benzaldehyde	6
4-OCH_3 benzaldehyde	7
2,5-$(OCH_3)_2$ benzaldehyde	5
F_5-benzaldehyde	4
4-pyridinecarboxaldehyde	9
2-furalaldehyde	trace
mesitaldehyde	no
2,6-$(OCH_3)_2$ benzaldehyde	no
2,6-Cl_2 benzaldehyde	no

When the reaction was carried out in the presence of lower pyrrole/benzaldehyde molar ratios the formation of corrole significantly decreased and H_2TPP was the major product of the reaction. A higher excess of pyrrole led to a drastic drop in the formation of macrocyclic products and instead the formation of polypyrroles which made purification of the reaction mixtures very difficult.

We obtained highest yields of **2** with pyrrole concentration in the 0.25 M range and consequently benzaldehyde 0.08 M. Both higher and lower concentrations (up to 10^{-4} M) of reagents induced significant decreases of the reaction yields and from this point of view these results are quite similar to those observed in the case of the synthesis of H_2TPPs,[14] indicating that a similar mechanism is probably present in these reactions, as discussed below.

A critical step of this synthetic route is the chromatographic separation of **2** from H_2TPP. This separation can be performed either on silica gel (CH_2Cl_2 as eluent) or on neutral alumina (Brockman grade III, CH_2Cl_2/hexane 1:1 as eluent), but it is necessary to take particular care because the relative R_f values are quite similar. This problem limits also the possibility to carry out the reaction in larger scale.

An important point to clarify of the Rothemund synthesis of corroles should be its versatility to the preparation of various tri-arylcorroles. For this reason we studied the reaction of pyrrole with different aromatic aldehydes, using the reaction conditions giving the highest yields of **2**; the results obtained are reported in Table 1.

It is important to mention that the formation of corrole is general for monosubstituted aldehydes whatever be the

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[10] Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767.

[11] Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779.

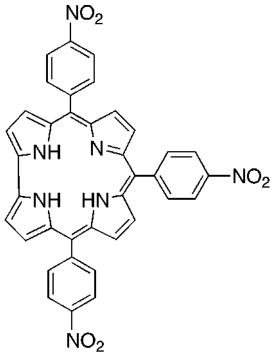
[12] Paolesse, R.; Jaquinod, L.; Nurco, D. J.; Mini, S.; Sagone, F.; Boschi, T.; Smith, K. M. *Chem. Commun.* **1999**, 1307.

[13] Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1427.

[14] Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1968**, *5*, 669.

substituent position on the aromatic aldehyde. This result is very important, demonstrating that the one pot reaction between pyrrole and aldehydes can allow the preparation of a wide range of substituted tri-arylcorroles.

Higher yields have been obtained in the case of aldehydes bearing electron-withdrawing groups. In the case of 4-NO_2 benzaldehyde we obtained a quite unexpected 22% yield of **3** without formation of the corresponding porphyrin. This is of particular importance because it allowed us to obtain the corresponding corrole in a gram scale along with a facile separation procedure. In fact the absence of porphyrin among reaction products avoid the problem of corrole-porphyrin separation, the most tedious purification step of this synthetic approach.



3

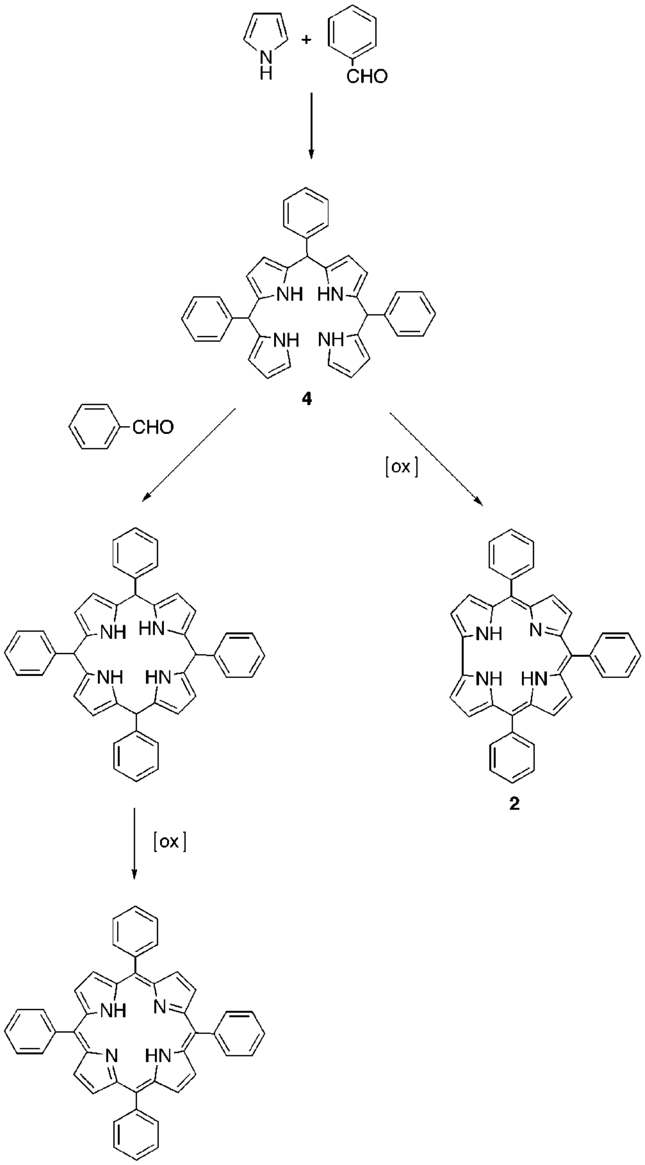
The higher yields obtained in the case of benzaldehydes bearing electron-withdrawing groups are not an obvious result. It is not possible to discuss in detail this point because we are in the presence of a multistep reaction and we have no experimental indications about the reaction mechanism. However, it is quite reasonable to hypothesise the linear tetrapyrrole **4** as the precursor of the final corrole ring (Scheme 1). This hypothesis is supported by the presence of **4** as one of the reaction products of the acidic condensation of pyrrole and benzaldehyde.[15]

The linear tetrapyrrole can lead to the porphyrinogen and then to the porphyrin, by attack of an aldehyde unit, or to the corrole ring by a cyclization due to a pyrrole-pyrrole link formation.

Our group has previously observed a similar pathway in the case of the acidic cyclization of *a*,*c*-biladienes,[16] and **4** has recently been converted to **2** by oxidative cyclization.[17] Furthermore when the reaction was carried out in the presence of an oxidant, such as chloranil, we observed a significant reduction of the reaction time with no substantial differences in the corrole yield; this result again supports the presence of **4** as reaction intermediate.[18]

In the case of electron-poor aldehydes, their higher reactivity induces their facile reaction with pyrrole and consequently their rapid disappearance from the reaction mixture. In this case, the linear tetrapyrrole cannot react with residual aldehyde units to form the porphyrinogen, explaining the absence of porphyrin as reaction product and the higher yields of corrole.

Scheme 1



Heteroaromatic aldehydes have also been tested. For example, 5,10,15-tris(4-pyridyl)corrole has been obtained in 9% yield, while in the case of furfural aldehyde only traces of corrole have been obtained.

The spectral characteristics of these corroles are in good agreement with those observed for the parent macrocycle **2**.[12] Their electronic spectra show a Soret-like band around 415−420 nm and broad Q-bands in the 515−650 nm region; due to the lower symmetry of the corrole ring in the ^1H NMR spectrum there is the spread of the β-pyrrolic protons resonances. In the case of 5,10,15-tris(4-methoxyphenyl)corrole and 5,10,15-tris(2,5-dimethoxyphenyl)corrole we experienced a significant line broadening, that prevented to obtain a resolved ^1H NMR spectrum. This feature is not unusual in the case of corrole free-bases[19] and can be avoided by obtaining diamagnetic metal complexes of these macrocycles.

On the other hand, the reaction failed in the case of 2,6-disubstituted benzaldehydes, such as 2,6-dichloro or 2,6-dimethoxybenzaldehyde. This result parallels the

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(15) Ka, J.-W.; Lee, C.-H. *Tetrahedron Lett.* **2000**, *41*, 4609.

(16) Licoccia, S.; Di Vona, M. L.; Paolesse, R. *J. Org. Chem.* **1998**, *63*, 3, 3190.

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(18) We gratefully acknowledge a referee for this helpful suggestion.

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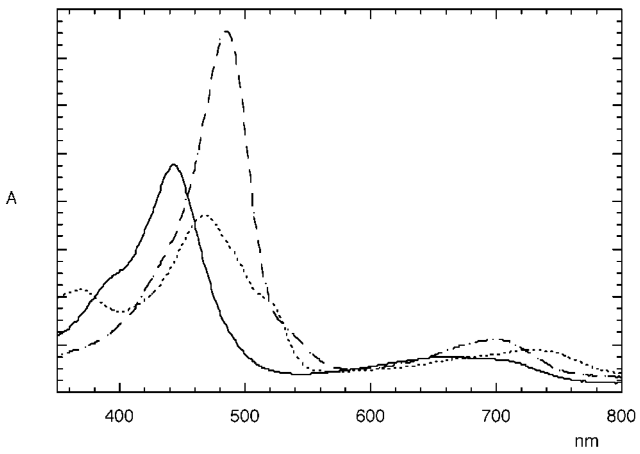


Figure 1. Visible spectra of **5** (solid line), **5** + TFA (dashed line), and **5** + NEt_3 (pointed line), in CH_2Cl_2.

lower efficiency of the Adler's method for the preparation of 2,6-disubstituted H_2TPPs to respect the classical Rothemund approach.[20] For this reason we attempted the reaction of pyrrole and 2,6-disubstituted aromatic aldehyde using collidine as solvent and copper acetate as templating agent, but the results obtained were discouraging. The reaction products were the corresponding copper porphyrin, in low yields, and only traces of the desired corroles as supported by the FAB-mass spectrum.

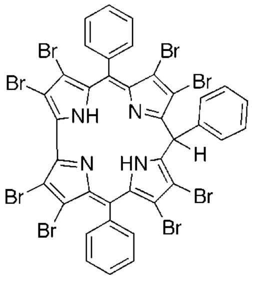
The failure of the reaction in the case of 2,6-disubstituted benzaldehydes can be ascribed to steric factors that prevent the formation of the linear tetrapyrrolic intermediate. In the case of 2,5-dimethoxybenzaldehyde, in fact, the reaction was successful and it was possible to obtain the corresponding corrole in reasonable yield.

The use of this modified Rothemund approach can open the way to the synthesis of a wide range of *meso*-substituted corroles, which can serve as an ideal platform to obtaining more complex systems based on these macrocycles. To explore this possibility we decided to study the bromination of **2**, because in the case of H_2TPP this reaction is one of the most widely used to obtain modified porphyrins.[21]

Due to the higher reactivity of corroles with respect to the corresponding porphyrins toward electrophilic reagents,[22] we reacted at room temperature **2** with an excess of NBS in $CHCl_3$.

The progress of the reaction was monitored by TLC until no further evidence of starting material was present. Upon work up a green product was obtained in good yields. FAB mass spectrum of this compound showed a molecular peak corresponding to the fully brominated corrole, confirming the peculiarity of corrole chemistry. In Fact, H_2TPP is tetrabrominated in these conditions at the antipodal positions.[23] The use of lower amounts of NBS gave a mixture of partially substituted corroles due to the lower symmetry of the corrole ring; the separation of this mixture by chromatography has not be attempted. Spectroscopic characterization of the reaction product yielded however unexpected data. The ^1H NMR spectrum showed no resonances for both the β-pyrrolic protons, confirming the complete substitution of these positions, and the internal NH protons; an unexpected downfield signal around 13 δ was instead present. Furthermore, in the visible spectrum in $CHCl_3$ (Figure 1), the typical corrole Soret-like band was substituted by a broad absorption around 440 nm. The signal at 13 δ in ^1H NMR spectrum disappeared by addition of a drop of NEt_3, whereas the visible spectrum showed the changes reported in Figure 1 upon addition of NEt_3 or TFA.

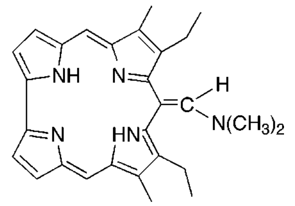
These results seem to indicate that the conjugation pathway of the corrole macro-ring has been interrupted and they are reasonably consistent with the formation of the species **5**, where a tautomeric shift of an internal proton causes the interruption of the macrocyclic aromatic pathway, with the formation of a porphodimethene-like structure.[24]



5

This structure can explicate the molecular peak obtained in the FAB mass spectrum and the signal around 13 δ present in the ^1H NMR spectrum, that can be in fact related to the downfield shifts of the inner NH protons observed in analogous porphodimethenes.[24] The attempt of the corrole ring to reduce the sterical strain induced by the NH protons and by the peripheral bromo substituents with the displacement of one inner proton can reasonably explicate the formation of **5**. TFA induced the protonation of the macrocycle, with the concomitant re-aromatization of the distorted macrocycle, as evidenced by the appearance in the visible spectrum of a red shifted Soret-like band at 480 nm (Scheme 2).

The peculiarity of corrole to accommodate a similar porphodimethene-like structure has been previously observed in the case of the Vilsmeier formylation of octa-alkylcorroles, with formation of the 10-dimethylaminomethene derivative **6**.[22]



6

When the bromination reaction was carried out on **3**, we obtained the corresponding fully brominated corrole, which showed similar spectroscopic results.

Unfortunately, we were unable to obtain crystals of **5** suitable for X-ray analysis. To gain further insights on its structure, we decided to react **5** with cobalt (II) acetate

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(20) Rothemund, P. *J. Am. Chem. Soc.* **1939**, *61*, 2912.

(21) Jaquinod, L.; Khoury, R. G.; Shea, K. M.; Smith, K. M. *Tetrahedron* **1999**, *55*, 13151.

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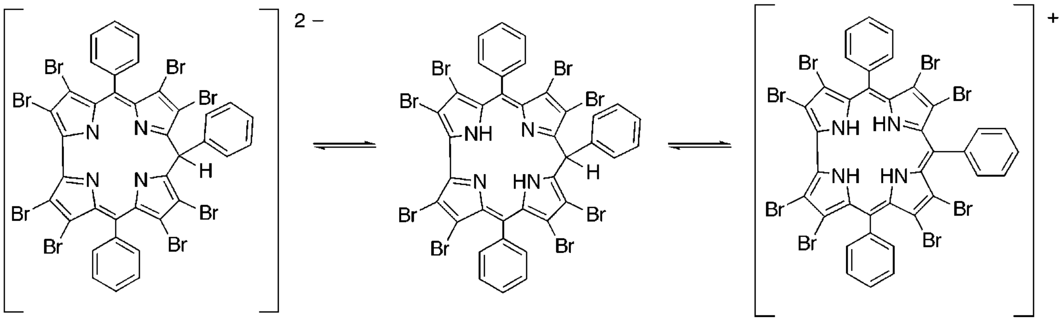
Scheme 2



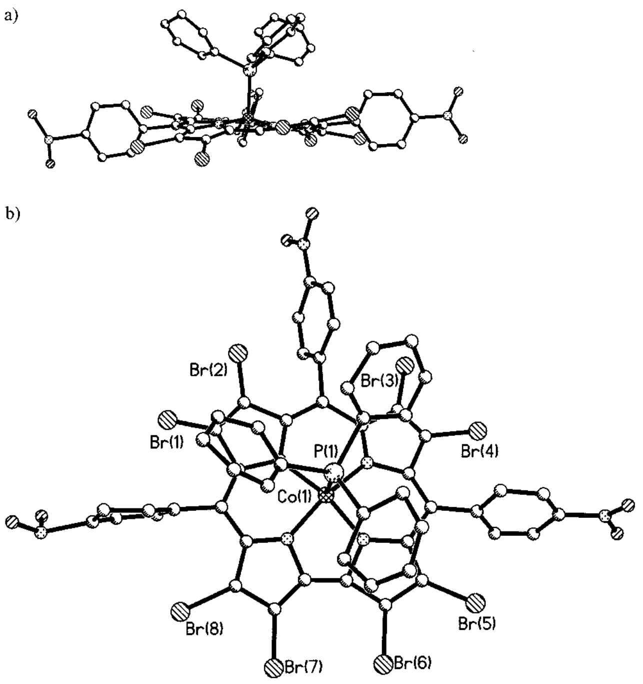
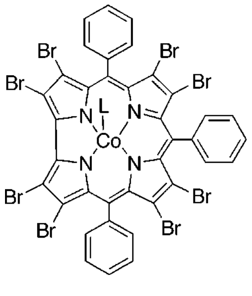


Figure 2. Molecular structure of **8**: (a) top view; (b) side view. Hydrogen atoms have been omitted for clarity.

and triphenylphosphine to obtain the corresponding complex. As observed in the case of **6**, the coordination of Co (III) ions induced the re-aromatization of the macrocycle, with the formation of the corresponding triphenylphosphino cobalt complex **7**.

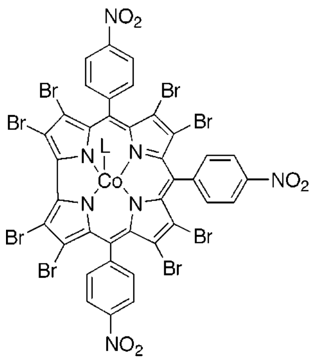


L=PPh$_3$

7

Spectral characterization of **7** gave features similar to that of a corresponding triphenylphosphino cobalt (III) corrole.[9] Quite surprisingly the visible spectrum showed a Soret band without significant red shift, indicating the absence in this case of deviations from the planarity. This feature was confirmed by the ^{1}H NMR spectrum, where the signals of the axial PPh$_3$ showed chemical shifts similar to that of the corresponding cobalt corrole complexes.[7] In this case, it seems that the corrole is able to retain a planar conformation as observed in the case of the fully substituted corrole **1**.[9]

We obtained in a similar way the complex **8**, which showed similar spectroscopic features. In this case X-ray characterization performed on a single-crystal allowed its unambiguous structural identification.[25] The molecular structure is shown in Figure 2.



L=PPh$_3$

8

The cobalt atom exhibits a pentacoordinated geometry and lies 0.37 Å out of the mean corrole plane. Based on the 23 core atoms the corrole is fairly planar with a mean plane deviation of 0.169 Å. This deviation is higher than that observed in the case of the corresponding Co-TPCPPh$_3$ complex,[12] but it is comparable with that observed in the case of **1**, confirming the ability of cobalt corroles to retain an almost planar conformation when fully substituted. This behavior is completely different from the corresponding porphyrin complexes, where severe deviations from the planarity has been observed.[26] The Co−N bond lengths average is 1.92 Å [Co−N(21) 1.93, Co−N(22) 1.92, Co−N(23) 1.88, Co−N(24) 1.94]. These bond lengths are slightly longer than those measured in the similar complex CoTPCPPh$_3$, where we obtained lengths in the range 1.86−1.89 Å.

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(25) The authors have deposited atomic coordinates and a full structure description for **8** with the Cambridge Crystallographic Data Centre. The structure can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(26) Senge, M. O. *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R. Eds.; Academic Press: New York, 2000; Vol. 1, p 239.

In conclusion we have accomplished, in reasonable yields, the synthesis of different tri-aryl corroles by a modified Rothemund reaction. The possibility to introduce substituents at the peripheral positions of the corrole has been demonstrated possible by the bromination reaction. Also, the behavior showed by corrole is quite different from that of the corresponding *meso*-tetraarylporphyrins, confirming that corrole chemistry is peculiar and somewhat unpredictable. Further studies are now in progress in this area and our results will be reported in due course.

Experimental Section

General conditions are as previously reported[16] with the exception that electronic absorption spectra were measured using a Cary 50 spectrophotometer in CH_2Cl_2 solutions.

5,10,15-Triphenylcorrole (2). Pyrrole (4.2 mL, 60.5 mmol) and benzaldehyde (2.0 mL, 20 mmol) were dissolved in 250 mL of acetic acid. The solution was refluxed under stirring and the course of the reaction was monitored by UV−vis spectroscopy; after 3 h, the reaction mixture was cooled at room temperature and 250 mL of distilled water were added. The precipitate (H_2TPP almost pure) was filtered off and NaCl was added to the filtrate. The resulting precipitate was filtered off and the crude solid was dissolved in CH_2Cl_2 and chromatographed on silica gel (CH_2Cl_2 eluent). The first red-brown band was H_2TPP, the second green fraction contained the desired product. This fraction was collected, the solvent evaporated under vacuum and the residue was crystallized from CH_2Cl_2/hexane to give green-violet microcrystals of 5,10,15-triphenylcorrole (0.21 g, 6% yield).UV−vis: λ_{max} 415 (ϵ 110 000), 567 (ϵ 16 000), 615 (ϵ 12 500), 648 (ϵ 10 500). ^1H NMR ($CDCl_3$) δ −2.91 (s, 3H), 7.72−7.82 (m, 9H), 8.16 (d, 2H, $J = 5$ Hz), 8.39 (d, 4H, $J = 7$ Hz), 8.53, 8.58, 8.86, 8.93 (each d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 527 (M^+). Anal. Calcd for $C_{37}H_{26}N_4$: C, 84.39; H, 4.98; N, 10.64. Found: C, 84.24; H, 4.92; N, 10.49.

5,10,15-Tris(4-nitrophenyl)corrole (3). This corrole was prepared, as described for **2**, starting from 4-nitrobenzaldehyde (3.05 g, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol), but in this case the formation of the corresponding porphyrin was not observed. For this reason the residue was chromatographed through a short column of silica gel eluting with CH_2Cl_2. The resulting corrole was crystallized from CH_2Cl_2/hexane (1:2) (0.98 g, 22% yield). UV−vis: λ_{max} 425 nm (ϵ 64 500), 595 nm (ϵ 12 600). ^1H NMR ($CDCl_3$) δ −2.82 (s, 3H), 8.40 (t, 3H, $J = 9$ Hz), 8.54 (d, 4H, $J = 8$ Hz), 8.58 (d, 2H, $J = 4$ Hz), 8.66 (m, 2 H), 8.71 (d, 4H, $J = 8$ Hz), 8.83 (s, 1H), 8.90 (d, 2H, $J = 4$ Hz), 9.11 (d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 662 (M^+). Anal. Calcd for $C_{37}H_{23}N_7O_6$: C, 67.17; H, 3.50; N, 14.82. Found: C, 67.34; H, 3.42; N, 14.49.

5,10,15-Tris(2-nitrophenyl)corrole. This corrole was prepared, as described for **2**, from 2-nitrobenzaldehyde (3.05 g, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol), (0.36 g, 8% yield). UV−vis: λ_{max} 421 nm (ϵ 135 000), 518 nm (ϵ 10 500), 575 nm (ϵ 15 300), 612 nm (ϵ 11 200), 648 nm (ϵ 7000). ^1H NMR ($CDCl_3$) δ −2.51 (br s, 3H), 7.90 (m, 2H), 7.96 (m, 4H), 8.35 (m, 6H), 8.63 (m, 4H), 8.95 (m, 4H). LRMS (FAB): *m/z* 622 (M^+). Anal. Calcd for $C_{37}H_{23}N_7O_6$: C, 67.17; H, 3.50; N, 14.82. Found: C, 67.02; H, 3.82; N, 14.99.

5,10,15-Tris(3-nitrophenyl)corrole. This corrole was prepared as described for **2**, from 3-nitrobenzaldehyde (3.04 g, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol), (0.67 g, 15% yield). UV−vis: λ_{max} 421 nm (ϵ 137 800), 515 nm (ϵ 9500), 578 nm (ϵ 22 200), 615 nm (ϵ 13 800), 645 nm (ϵ 9200). ^1H NMR ($CDCl_3$) δ −2.80 (s, 3H), 8.05 (m, 3H), 8.55 (m, 9H), 8.85 (d, 2H, $J = 4$ Hz), 9.08 (d, 4H, $J = 4$ Hz), 9.25 (d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 622 (M^+). Anal. Calcd for $C_{37}H_{23}N_7O_6$: C, 67.17; H, 3.50; N, 14.82. Found: C, 67.21; H, 3.42; N, 14.54.

5,10,15-Tris(4-bromophenyl)corrole. This corrole was prepared as described for **2**, starting from 4-bromobenzaldehyde (3.73 g, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol). Crystallization from CH_2Cl_2/ hexane(1:2) afforded the title compound in 5% yield (0.26 g). UV−vis: λ_{max} 418 (ϵ 140 000), 577 (ϵ 24 000), 617 (ϵ 20 400), 650 (ϵ 17 000) nm. ^1H NMR ($CDCl_3$) δ −2.78 (br s, 3H), 7.9−8.15 (m, 6H), 8.25 (d, 4H, $J = 4$ Hz), 8.6 (m, 4H), 8.85 (d, 4H, $J = 4$ Hz), 9.00 (d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 763 (M^+). Anal. Calcd for $C_{37}H_{23}$ Br_3N_4: C, 58.22; H, 3.04; N, 7.34. Found: C, 58.28; H, 3.11; N, 7.49.

5,10,15-Tris(3-bromophenyl)corrole. This corrole was prepared, as described for **2**, starting from 3-bromobenzaldehyde (3.73 g, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol) in 9% yield (0.46 g,). UV−vis: λ_{max} 419 nm (ϵ 125 800), 513 nm (ϵ 14 000), 575 (ϵ 16 800), 615 (ϵ 13 500), 648 (ϵ 12 300) nm. ^1H NMR ($CDCl_3$) δ −2.82 (s, 3H), 7.87 (m, 2H), 8.15 (m, 4H), 8.28 (d, 2H, $J = 8$ Hz), 8.35 (d, 2H, $J = 8$ Hz), 8.51 (s, 2H), 8.56, 8.62, 8.88, 9.04 (each d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 763 (M^+). Anal. Calcd for $C_{37}H_{23}$ Br_3N_4: C, 58.22; H, 3.04; N, 7.34. Found: C, 58.04; H, 2.96; N, 7.52.

5,10,15-Tris(2-chlorophenyl)corrole. This corrole was prepared, as described for **2**, from chlorobenzaldheyde (2.27 mL, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol), (0.38 g, 9% yield). UV−vis: λ_{max} 418 nm (ϵ 132 000), 562 (ϵ 12 700), 604 (ϵ 7600) nm. ^1H NMR ($CDCl_3$) δ −1.55 (s, 3H), 7.70 (m, 7H), 8.15 (m, 4H), 8.38 (d, 2H, $J = 4$ Hz), 8.42 (d, 2H, $J = 4$ Hz), 8.58 (d, 2H, $J = 4$ Hz), 8.78 (m, 1H), 8.95 (d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 630 (M^+). Anal. Calcd for $C_{37}H_{23}$ Cl_3N_4: C, 70.54; H, 3.68; N, 8.89. Found: C, 70.33; H, 3.76; N, 8.61.

5,10,15-Tris(4-methylphenyl)corrole. This corrole was prepared, as described for **2**, from *p*-tolualdehyde (2.38 mL, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol), (yield: 0.23 g, 6%). UV−vis: λ_{max} 418 (ϵ 135 800), 518 (ϵ 10 000), 566 (ϵ 21 100), 617 (ϵ 16 300), 648 (ϵ 12 500) nm. ^1H NMR ($CDCl_3$) δ −2.74 (br s, 3H), 2.72 (s, 6H), 2.74 (s, 3H), 7.55 (d, 2H, $J = 7.5$ Hz), 7.65 (d, 4H, $J = 7.5$ Hz), 8.09 (d, 2H, $J = 7.5$ Hz), 8.28 (d, 4H, $J = 7.5$ Hz), 8.58, 8.62, 8.88, 8.98 (each d, 2H, $J = 4$ Hz). LRMS (FAB): *m/z* 569 (M^+). Anal. Calcd for $C_{40}H_{32}N_4$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.19; H, 5.52; N, 9.58.

5,10,15-Tris(4-methoxyphenyl)corrole. This corrole was prepared, as described for **2**, from 4-methoxybenzaldheyde (2.47 mL, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol), (0.29 g, 7% yield). UV−vis: λ_{max} 418 (ϵ 121 000), 576 (ϵ 29 800), 618 (ϵ 26 400), 648 (ϵ 19 800) nm. LRMS (FAB): *m/z* 617 (M^+). Anal. Calcd for $C_{40}H_{32}N_4O_3$: C, 77.90; H, 5.23; N, 9.08. Found: C, 80.05; H, 5.38; N, 8.89.

5,10,15-Tris(2,5-dimethoxyphenyl)corrole. This corrole was prepared, as described for **2**, from 2,5-dimethoxybenzaldheyde (3.35 g, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol). In this case the chromatographic separation was carried out on neutral alumina (Brockmann, Grade III elution with CH_2Cl_2), to give 0.24 g of the title compound (5% yield) after crystallization from CH_2Cl_2/hexane. UV−vis: λ_{max} 421 (ϵ 122 500), 515 (ϵ 22 600), 575 (ϵ 22 300), 647 (ϵ 19 300) nm. LRMS (FAB): *m/z* 707 (M^+). Anal. Calcd for $C_{43}H_{38}N_4O_6$: C, 73.07; H, 5.42; N, 7.93. Found: C, 72.88; H, 5.61; N, 7.78.

5,10,15-Tris(4-pyridyl)corrole. This corrole was prepared, as described for **2**, from 2,5-dimethoxybenzaldheyde (1.93 mL, 20.2 mmol) and pyrrole (4.2 mL, 60.5 mmol). In this case the chromatographic separation was carried out on neutral alumina (Brockmann, Grade III elution with CH_2Cl_2), to give 0.32 g of the title compound (9% yield) after crystallization from CH_2Cl_2/hexane. UV−vis: λ_{max} 417 (ϵ 119 600), 576 (ϵ 23 000), 616 (ϵ 18 400), 651 (ϵ 17 300) nm. ^1H NMR ($CDCl_3$) δ −1.76 (br s, 3H), 8.16 (d, 2H, $J = 5$ Hz), 8.30 (d, 4H, $J = 5$ Hz), 8.63 (d, 2H, $J = 5$ Hz), 8.68 (d, 2H, $J = 5$ Hz), 8.95 (d, 2H, $J = 5$ Hz), 9.02 (d, 2H, $J = 5$ Hz), 9.06 (d, 4H, $J = 5$ Hz), 9.12 (d, 2H, $J = 5$ Hz). LRMS (FAB): *m/z* 530 (M^+). Anal. Calcd for $C_{34}H_{23}N_7$: C, 77.11; H, 4.38; N, 18.51. Found: C, 76.92; H, 4.52; N, 18.19.

5,10,15-Tris(pentafuorophenyl)corrole. This corrole was obtained following the procedure described above for **2**, starting from pyrrole (4.2 mL, 60.5 mmol) and pentafluorobenzaldehyde (3.96 g, 20.2 mmol) in 4% yield. Spectral properties were in accord with data previously reported[13] and with an authentic sample prepared according to the literature.[13]

2,3,7,8,12,13,17,18-Octabromo-5,10,15-triphenylcorrole (5). **2** (35 mg, 0.07 mmol) was dissolved in 50 mL of anhydrous $CHCl_3$ and NBS (189 mg, 1.06 mmol) was added to the solution. The mixture was stirred at room temperature, under nitrogen, for 12 h; it was then treated with a saturated aqueous solution of $NaHCO_3$, dried on anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue was chromatographed on neutral alumina (Brockmann, Grade III elution with CH_2Cl_2/hexane 1:1). The first green fraction was collected, the solvent evaporated under vacuum and the resulting residue was crystallized from CH_2Cl_2/hexane (1:2) to give the title compound (47 mg, 58% yield). UV−vis: λ_{max} 438 (ϵ 32 700), 665 (ϵ 6700) nm.^{1}H NMR ($CDCl_3$) 6.98 (d, 2H, J = 8 Hz), 7.38−7.52 (m, 14H), 13.12 (s, 2H). LRMS (FAB): m/z 1158 (M^+). Anal. Calcd for $C_{37}H_{18}Br_8N_4$: C, 38.38; H, 1.57; N, 4.84. Found: C, 38.24; H, 1.78; N, 4.52.

2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(4-nitrophenyl)corrole. 3 (122.3 mg, 0.19 mmol), was dissolved in anhydrous CHCl3 (100 mL) and treated with NBS (527 mg, 2.96 mmol); the solution was refluxed for 2 h under nitrogen. The mixture was washed with a saturated solution of NaHCO3, dried over anhydrous Na2SO4 and the solvent was evaporated under vacuum. The resulting residue was dissolved in CH_2Cl_2 and chromatographed on silica gel. The green fraction was collected, evaporated to dryness and crystallized from a CH_2Cl_2/hexane (1:2) to give the title product (44 mg, 18% yield). UV−vis: λ_{max} 422 (ϵ 33 900), 633 (ϵ 10 100) nm. ^{1}H NMR ($CDCl_3$) δ 5.95−6.12 (br m, 3H), 7.56−8.35 (m, 10H) 13.25 (s, 2H). LRMS (FAB): m/z 1293 (M^+). Anal. Calcd for $C_{37}H_{15}Br_8N_7O_6$: C, 34.38; H, 1.17; N, 7.58. Found: C, 34.24; H, 1.04; N, 7.49.

Triphenylphosphine [2,3,7,8,12,13,17,18-Octabromo-5,10,15-triphenylcorrolato]cobalt(III) (7). 5 (50 mg, 0.043 mmol) was dissolved in 50 mL of MeOH and treated with an excess of cobalt(II) acetate (50 mg, 0.20 mmol) and triphenylphosphine (50 mg, 0.19 mmol). The mixture was refluxed under stirring and the course of the reaction was monitored by UV−visible spectroscopy; after 1 h the solvent was evaporated under vacuum, and the resulting residue was chromatographed on silica gel (CH_2Cl_2 eluent).

The first red fraction was collected and crystallized from CH_2Cl_2/hexane (1:2) (53 mg, 83% yield). UV−vis: λ_{max} 390 (ϵ 29 000), 568 (ϵ 12 000) nm. ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 5H), 7.56 (m, 10H), 7.08 (m, 3 H), 6.72 (m, 6H), 4.81 (m, 6H). LRMS (FAB): m/z 1214 ($M^+ - PPh_3$). Anal. Calcd for $C_{55}H_{30}Br_8CoN_4P$: C, 44.76; H, 2.05; N, 3.80. Found: C, 44.74; H, 1.99; N, 3.73.

Triphenylphosphine [2,3,7,8,12,13,17,18-Octabromo-5,10,15-tris(4-nitrophenyl)corrolato]cobalt(III) (8). This compound was obtained, as described for **7**, from 2,3,7,8,12,13,17,18-octabromo-5,10,15-tris(4-nitro)phenylcorrole (50 mg, 0.04 mmol), (55 mg, 78% yield). UV−vis: λ_{max} 386 (ϵ 32 000), 566 (ϵ 13 900) nm. ^{1}H NMR ($CDCl_3$) δ 8.46 (d, 4H, J = 8 Hz), 8.41 (d, 2H, J = 8 Hz), 7.70 (br d, 2H), 7.60 (m, 4H), 7.16 (m, 3H), 6.95 (m, 6H), 4.76 (m, 6H). LRMS (FAB): m/z 1349 ($M^+ - PPh_3$). Anal. Calcd for $C_{55}H_{27}Br_8CoN_7O_6P$: C, 41.01; H, 1.69; N, 6.09. Found: C, 41.08; H, 1.75; N, 6.02.

Crystallographic Data. Single crystals of **8**, [$C_{55}H_{27}Br_8CoN_7O_6P \cdot 10(H_2O)$], were grown from CH_2Cl_2/hexane. Crystals were placed in oil and a single purple crystal of dimensions 0.15 × 0.12 × 0.12 mm was selected, mounted on a glass fiber, and placed in low-temperature N_2 stream. The unit cell was orthorhombic with a space group of Pna2(1). Cell dimensions: $a = 21.870(4)$ Å, $b = 15.120(3)$ Å, $c = 31.050(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 10267(4)$ Å^3 and $Z = 8$ (FW = 1770.19, $\rho = 2.29$ g·cm^{-3}). Reflections were collected from $1.85° \le \theta \le 25.88°$ for a total of 12 675 of which 5522 were unique ($R_{int} = 0.089$) having $I > 4\sigma(I)$; number of parameters = 1489. Final R factors were $R1 = 0.09$ (based on observed data, $wR2 = 0.213$ (based on all data), GOF = 1.39, maximal residual electron density = 0.944 eÅ^{-3}. X-ray diffraction data for 8 was collected on a Nonius KappaCCD diffractometer with a graphite monochromatized Mo Kα radiation ($\lambda = 0.710\,71$ Å). φ scans, at 173 K. The structure solution of 8 was determined using direct methods and refined (based on F^2 using all independent data) by full matrix least-squares methods (SHELXTL 97). Hydrogen atoms were included at calculated positions by using a riding model.

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Supporting Information Available: X-ray crystallographic data of **8** and ^{1}H NMR spectra of **2**, **3**, **5**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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