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Synthesis and characterization of cobalt(III) complexes of *meso*-phenyl-substituted corroles

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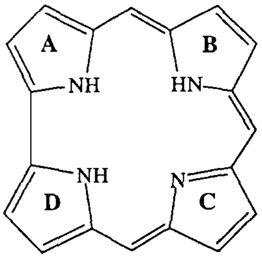
Abstract

The synthesis and characterization of two new cobalt(III) complexes of corrole: [triphenylphosphine-(2,3,7,8,12,13,17,18-octamethyl-10-phenylcorrolato)cobalt(III)] and [triphenylphosphine(2,3,7,8,12,13,17,18-octamethyl-5,10,15-triphenylcorrolato)cobalt(III) are reported. Such complexes represent the first examples of *meso*-substituted corrolates reported in the literature. The insertion of one or three phenyl groups at the *meso*-positions of the macrocyclic ligand has been achieved by designing different synthetic strategies. The spectroscopic characterization of the complexes shows the peculiarity of the corrole ligand which maintains a planar structure despite the steric hindrance of the peripheral substituents.

Introduction

Tetrapyrrolic macrocycles other than porphyrins have been widely studied because of their occurrence in natural systems [1] and their applications in catalysis and photocatalysis [2, 3].

In the last few years our attention has been focused on corrole (structure outlined below), a macrocycle that was synthesized for the first time by Johnson and Kay [4] twenty five years ago and that exhibits intriguing molecular structure and electronic properties.



Corrole can be considered as an intermediate between corrin and porphyrin: it has a direct link between pyrroles A and D, which makes its structure similar to that of a corrin, and retains an 18 π-electron aromatic system, analogous to that of a porphyrin. Another peculiarity of corrole is that, among tetradentate N_4 ligands, it completes the series corrin, porphyrin, corrole where one, two or three amino-like nitrogens are present in the chelating system.

We have recently reported different synthetic procedures leading to metallocorrolates [5–7]; several metal ions, including main group elements, can be coordinated by proper tuning of the experimental conditions. We have thus demonstrated the unexpected excellent chelating properties of corrole and set the foundations to build a periodic table of metallocorrolates similar to that of metalloporphyrinates.

An ^{1}H NMR study performed on a paramagnetic Fe(III) derivative [8] proved that the ligand field effect of corrole is very different from that of other tetrapyrrolic macrocycles which led us to further explore the chemistry of this macrocycle.

Very little has been published about the electronic structure of corrole [9–11] and a detailed MO description of metallocorrolates has not been reported in the literature so that a theoretical interpretation of the coordination chemistry of this macrocycle is not yet possible.

On the basis of our synthetic experience we have approached the problem of gaining further information on the electronic structure of corrole by modifying the ring by means of peripheral substitution. It is well known [12] that in the casc of porphyrins different substitution patterns induce relevant electronic variations: the energy level of the two HOMOs of the porphyrin π system (a_{1u} and a_{2u}) are in fact reversed in going from a *meso*-substituted porphyrin, such as tetraphenylporphyrin, to a β-substituted one, such as octaethylporphyrin.

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Electronic variations may also derive from conformational changes: recently Smith and coworkers have reported hybrid compounds [13] substituted both at *meso* and β positions, (2,3,7,8,12,13,17,18-octaethyl-) and (2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphinato)zinc(II). These complexes have a nonplanar conformation caused by the steric interactions of the substituents. Theoretical calculations indicate that such conformational changes cause a differential shift in the energies of the HOMO and LUMO and so modulate the electronic structure of the macrocycles [14, 15].

We now report the synthesis and characterization of two new cobalt(III) complexes of corrole; [triphenylphosphine(2,3,7,8,12,13,17,18-octamethyl-10-phenylcorrolato)cobalt(III)], [Co(OMMPC)PPh$_3$] and [triphenylphosphine(2,3,7,8,12,13,17,18-octamethyl-5,10,15-triphenylcorrolato)cobalt(III)], [Co(OMTPC)-PPh$_3$] where one or three phenyl groups have been introduced at the *meso* position of the macrocycle and studied the influence of such substitution on the properties of the complexes.

Experimental

Electronic spectra were recorded on a Philips PU8700 spectrophotometer as diethyl ether solutions. Fast atom bombardment (FAB) and electronic impact (EI) spectra were recorded on a VG Quattro spectrometer; 3-nitrobenzyl-alcohol was used as matrix for the FAB spectra. A Bruker AM 400 spectrometer was used to obtain ^{1}H NMR spectra as C^{2}HCl$_3$ solutions. All chemical shifts are given in ppm from tetramethylsilane (TMS).

All solvents (Farmitalia) were reagent grade and were used without further purification.

Synthesis of 3,4-dimethyl-2-hydroxybenzylpyrrole-5-carboxylic acid

3,4-Dimethyl-2-benzoylpyrrole-5-carboxylic acid [16] (**1**) (5 g) was suspended in methanol (200 ml) under argon and sodium borohydride (1.5 g) was carefully added. The resulting yellow solution was stirred for 1 h, then poured into a saturated ammonium chloride solution. The precipitate was filtered off, washed with water, then dried and the title pyrrole (**2**) was obtained as a pale pink powder (yield 82%).

Synthesis of [Co(OMMPC)PPh$_3$]

1,19-Dideoxy-2,3,7,8,12,13,17,18-octamethyl-10-phenylbiladiene-*a*,*c*-dihydrobromide (MPBD) was synthesized according to literature methods [4] from 3,3′,4,4′-tetramethyl-*meso*-phenyl-dipyrromethane-5,5′-dicarboxylic acid [16] (**3**) and 3,4-dimethyl-2-formylpyrrole [17].

[Co(OMMPC)PPh$_3$] was prepared following a procedure analogous to that previously reported for the *meso*-unsubstituted complex [18] and purified by recrystallization from methanol obtaining purple crystals (yield 40%).

Synthesis of [Co(OMTPC)PPh$_3$]

Route A

3 (0.5 g) and **1** (0.66 g) were heated together in phosphorus oxychloride (20 ml) for 30 min. The dark red solution was cooled and then poured into methanol; diluted sodium hydroxide was added and the solution was basified. Cobalt(II) acetate (0.5 g) and triphenylphosphine (0.5 g) were added and the solution was refluxed for 2 h. The solvent was vacuum evaporated and the residue was extracted with diethyl ether, then chromatographed on basic alumina (Merck, type T), using diethyl ether as eluent. The first red band contained [Co(OMTPC)PPh$_3$] which was recrystallized from methanol as red–violet crystals (yield 2%).

Route B

3 (0.5 g) and **2** (0.66 g) were dissolved in hot absolute ethanol; trifluoroacetic acid (1 ml) was then added and the dark red solution was refluxed for 15 min. An excess of sodium acetate was then added and the color of the solution turned to brown–green. Cobalt(II) acetate (0.5 g) and triphenylphosphine (0.5 g) were added and the solution was refluxed for 24 h. The reaction was followed by monitoring the UV–Vis spectrum of the mixture: the increase of a band at 370 nm revealed the formation of the complex. The solvent was then vacuum evaporated and the residue was purified as described in Route A. A second chromatographic separation was necessary to obtain a pure product. Crystallization from methanol afforded the complex as red–violet crystals (yield 20%).

Route C

3 (0.5 g) was dissolved in trifluoroacetic acid and stirred until no gas evolved from the mixture. Dichloromethane (100 ml) was then added to dilute the solution. Benzaldehyde (0.07 g) in dichloromethane (200 ml) was then added dropwise and the resulting purple solution was stirred for 30 min. Methanol (300 ml) was added and the solution was refluxed until the dichloromethane distilled off. Treatment with triethylamine buffered the solution and then small portions of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were carefully added until the band at 500 nm in the optical spectrum of the mixture completely disappeared. Usual purification procedure afforded [Co(OMTPC)-PPh$_3$] (yield 18%).

Elemental analyses and spectral properties of the complexes are reported in Tables 1 and 2.

TABLE 1. Elemental analyses for cobalt corrolates

Complex	C (%)		H (%)		N (%)	
	calc.	found	calc.	found	calc.	found
[Co(OMMPC)PPh$_3$]	76.10	76.25	5.75	5.90	6.95	6.85
[Co(OMTPC)PPh$_3$]	79.05	78.95	5.70	5.80	5.85	5.95

TABLE 2. Spectral properties of cobalt corrolates

Complex	Optical	^{1}H NMR[b]	
	λ_{max} (nm)[a] [$\epsilon \times 10^{-4}$]	δ (ppm)	Assignment
[Co(OMC)PPh$_3$]	366 [4.47]	9.42 (1H)	10-*meso*-H
	531 [0.70]	9.03 (2H)	5.15-*meso*-H
	573 [1.11]	7.00 (3H)	*o*-PPh$_3$
		6.66 (6H)	*m*-PPh$_3$
		4.70 (6H)	*p*-PPh$_3$
		3.23 (18H)	3,7,8,12,13,17-CH$_3$
		3.15 (6H)	2,18-CH$_3$
[Co(OMMPC)PPh$_3$]	367 [5.95]	9.03 (2H)	5,15-*meso*-H
	513 [1.07]	7.85 (1H, d)	*o*-10 Ph
	573 [1.22]	7.62 (1H, t)	*m*-10 Ph
		7.57 (1H, t)	*p*-10 Ph
		7.45 (1H, t)	*m*'-10 Ph[c]
		7.13 (1H, d)	*o*'-10 Ph[c]
		7.03 (3H)	*o*-PPh$_3$
		6.69 (6H)	*m*-PPh$_3$
		4.79 (3H)	*p*-PPh$_3$
		3.25 (6H)–3.15 (6H)	3,7,13,17-CH$_3$
		3.04 (6H)	2,18-CH$_3$
		2.15 (6H)	8,12-CH$_3$
		7.93–6.91 (15H, m)	*meso*-Ph
[Co(OMTPC)PPh$_3$]	378 [6.03]	7.07 (3H)	*o*-PPh$_3$
	574 [0.97]	6.75 (6H)	*m*-PPh$_3$
		5.00 (6H)	*p*-PPh$_3$
		3.03 (6H)	2,18-CH$_3$
		2.05 (12H)	3,7,17,18-CH$_3$
		2.00 (6H)	8,12-CH$_3$

[a] Diethyl ether solutions. [b] Deuterated chloroform solutions. [c] The prime indicates the *meso*-phenyl protons located on the same side of the axial ligand with respect to the macrocycle plane (see text).

Results and discussion

Synthetic strategies

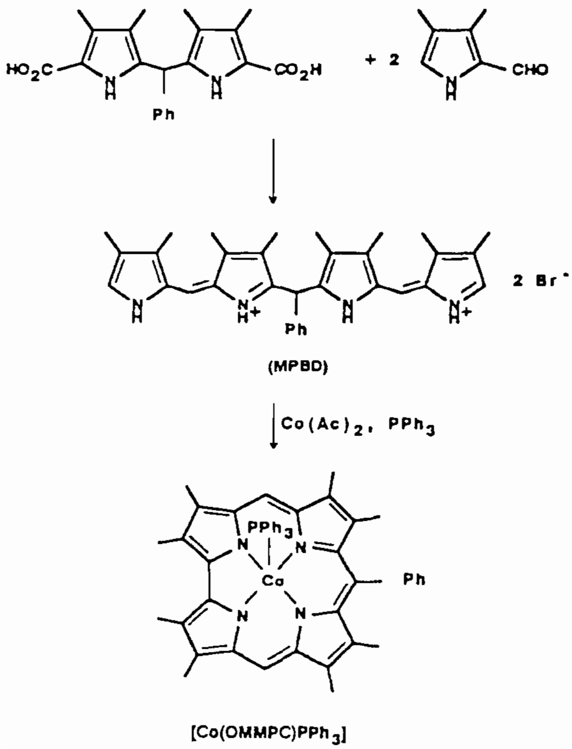
Both the number and the position of the phenyl groups are the key factors in determining the synthetic procedure to design in order to prepare *meso*-substituted corrolates.

The lower symmetry of corrole with respect to porphyrin does not allow the same synthetic approach to be followed for the two macrocycles. Thus the condensation of an aromatic aldehyde with a dialkylpyrrole or a dipyrromethane [19] is not a suitable route to prepare a *meso*-phenyl-substituted corrole.

A standard procedure for the synthesis of a *meso*-unsubstituted complex, [triphenylphosphine(2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III)], [Co(OMC)-PPh$_3$], is the base catalyzed, oxidative cyclization of the linear tetrapyrrolic precursor, 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethylbiladiene-*a*,*c*-dihydrobromide [18] (BD).

We have now extended such procedure to prepare the 10-phenyl-substituted complex [Co(OMMPC)PPh$_3$].

The proper precursor, 1,19-dideoxy-2,3,7,8,12,13,17,18-octamethyl-10-phenylbiladiene-*a*,*c*-dihydrobromide (MPBD) has been synthesized by condensation of 3,3',4,4'-tetramethyl-*meso*-phenyl-dipyrromethane-5,5'-dicarboxylic acid with two equivalents of 3,4-dimethyl-



Scheme 1.

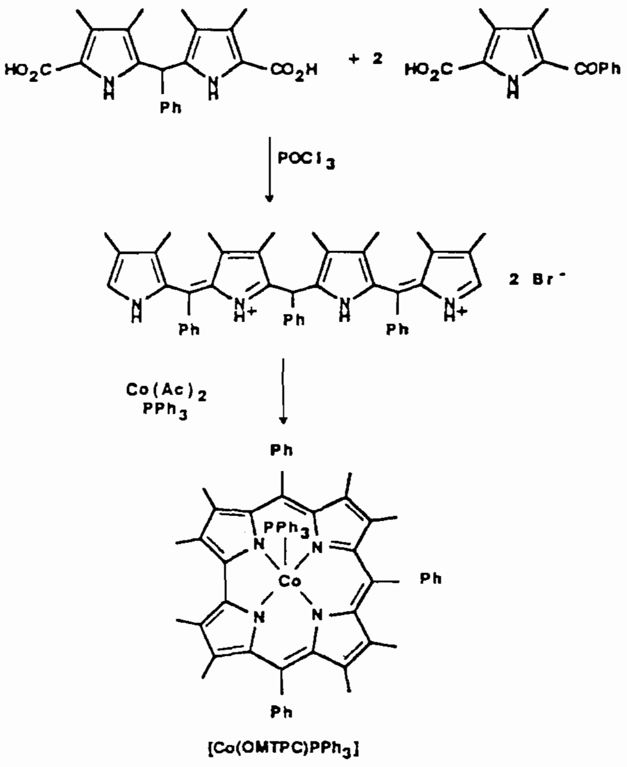
2-formylpyrrole in methanol. Subsequent cyclization in the presence of cobalt acetate and triphenylphosphine in buffered methanolic solution led to the desired complex in good yield (40%) (Scheme 1).

As in the case of the *meso*-unsubstituted complex, the presence of triphenylphosphine is essential for the isolation of the product. The stabilizing effect of an axial ligand in the synthesis of cobalt corrolates has been used in the preparation of the complex where no peripheral β substituents are present on the macrocycle which has been reported to decompose when attempts have been made to isolate it in the absence of triphenylphosphine [2].

A more complicated synthetic problem has been the insertion of three phenyl groups at the *meso* positions.

In a first attempt we tried to apply a procedure similar to that described above for the synthesis of MPBD. The reaction of the appropriate dipyrromethane with 3,4-dimethyl-2-benzoylpyrrole-5-carboxylic acid was carried out. Since the reactivity of a keto group is lower than that of a formyl group in a condensation reaction we used $POCl_3$ as condensating agent. However it was not possible to isolate the triphenyl biladiene salt and we attempted the subsequent cyclization reaction *in situ*.

Although the formation of the desired complexes occurred, the method gave overall discouraging results: we obtained [Co(OMTPC)PPh_3] with yields lower than 2% (Scheme 2).



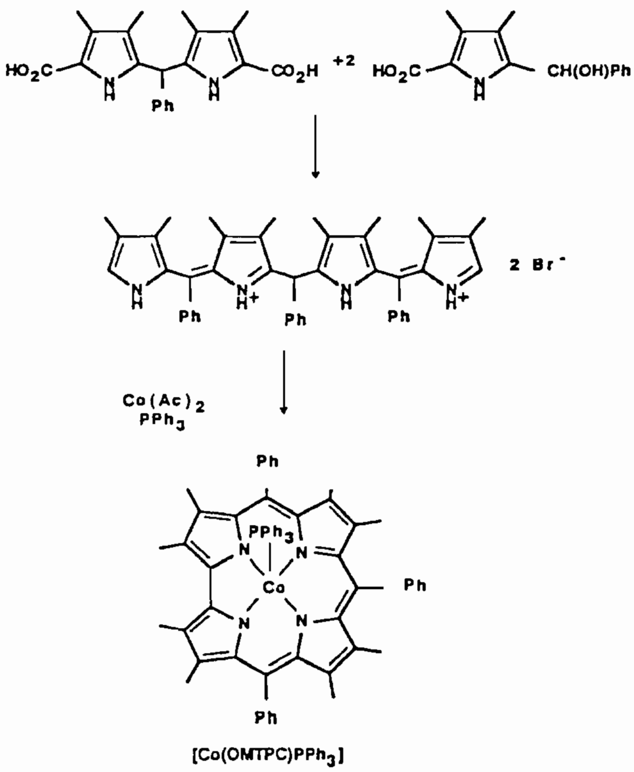
Scheme 2.

The main problem associated with the synthetic procedure described above is the low reactivity of benzoylpyrrole with respect to the condensation reaction with dipyrromethane: the drastic conditions required for the reaction caused a dramatic decrease of the yields. However the formation of the proper linear tetrapyrrolic precursor appeared to be a prerequisite step for the synthesis of triphenyl-substituted corrolates.

We then decided to approach the synthesis using as a starting product a pyrrole still bearing a phenyl substituent but with a functional group more reactive than an acyl towards the condensation reaction.

Studies reported in the literature on the mechanism of the synthesis of *meso*-tetraphenylporphyrin (TPP) [19] demonstrate that the reaction occurs via a carbinol intermediate, which self-condenses to give dipyrromethane or dipyrromethene and then the porphyrin. Furthermore TPP and other *meso*-substituted porphyrins have been synthesized by cyclization of acyl pyrroles reduced with $LiAlH_4$ [20].

The observation of such reasonably good reactivity towards condensation of an alcoholic group led us to react 3,3′,4,4′-tetramethyl-*meso*-phenyl-dipyrromethane-5,5′-dicarboxylic acid with 3,4-dimethyl-2-hydroxybenzylpyrrole-5-carboxylic acid in acidic ethanolic solution. The formation of a linear tetrapyrrole was evidentiated by monitoring by the visible spectrum of the reaction mixture ($\lambda_{max} = 500$ nm), but its isolation



Scheme 3.

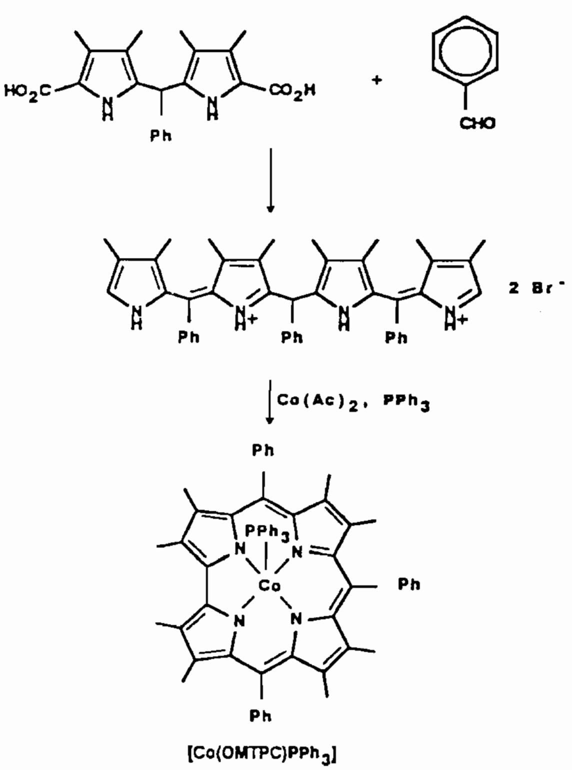
was impossible. The mixture was buffered by addition of sodium acetate and the cyclization reaction was again carried out *in situ* in the presence of cobalt acetate and triphenylphosphine.

The increase of the absorption at 375 nm in the optical spectrum of the reaction mixture and the concomitant decrease of the absorption at 500 nm revealed the formation of the product. Subsequent chromatographic purification afforded [Co(OMTPC)PPh$_3$] in 20% yield (Scheme 3).

In order to avoid the tedious purification procedures necessary to isolate [Co(OMTPC)PPh$_3$] we have developed a fourth synthetic method which is illustrated in Scheme 4.

The acidic condensation of benzaldehyde with two equivalents of 3,3′,4,4′-tetramethyl-*meso*-phenyl-dipyrromethane-5,5′-dicarboxylic acid in dichloromethane was carried out. The reaction mixture was then basified by the addition of triethylamine and reacted with cobalt acetate in the presence of triphenylphosphine and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) which allowed the requisite oxidative step. The reaction was monitored again by electronic spectroscopy and the product purified by column chromatography.

Although this procedure did not improve the reaction yield it is preferred because the starting products are either commercially available or can be easily synthesized.



Scheme 4.

All complexes gave satisfactory elemental analyses and have been characterized by electronic, NMR and mass spectra.

Mass spectra

Mass spectra were obtained by electron impact ionization and show similar characteristics for both complexes. The parent peak corresponds to $[M\text{-PPh}_3]^+$, with loss of the axial ligand. In addition, another peak, corresponding to $[M\text{-PPh}_3]^{2+}$, is present in the spectra and the fragmentation pattern shows the loss of the *meso*-phenyl groups.

The lack of the molecular peaks led us to measure the mass spectra by fast atom bombardment (FAB) technique, using *p*-nitrobenzyl alcohol as support matrix. With such procedure we were able to obtain the molecular peak for *meso*-phenyl corrolato Co(III) complexes.

Electronic spectra

The main features of the electronic spectra of metallocorrolates are two intense absorptions centered at 540–580 nm and 370–390 nm due to transitions within the π system of the ring which nature is similar to that of the Q and Soret bands of metalloporphyrinates [11]. The spectra of *meso*-phenyl-substituted cobalt corrolates are shown in Fig. 1 together with that of [Co(OMC)PPh$_3$] and relative data are reported in Table 2.

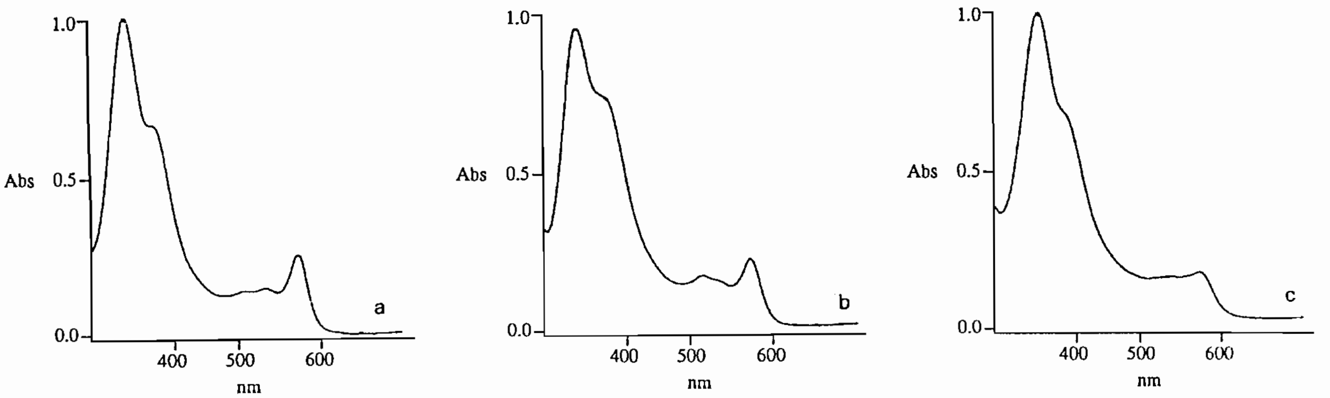


Fig. 1. Electronic spectra of cobalt corrolates in diethyl ether: (a) [Co(OMC)PPh_3], (b) [Co(OMMPC)PPh_3], (c) [Co(OMTPC)PPh_3].

All complexes exist in diethyl ether as pentacoordinated species [21] but a sixth ligand can be added to the coordination sphere of cobalt if a strongly binding solvent [22] such as pyridine is used (not shown).

The similarity between the spectra is evident. The small red shift observed by going from [Co(OMMPC)PPh_3] to [Co(OMTPC)PPh_3] seems to indicate that the corrole moiety is much less sensitive to substitution than the porphyrin and that the substantial planarity observed in the case of [Co(OMC)PPh_3] [23] is maintained in the case of the *meso*-phenyl-substituted complexes.

NMR spectra

The 400 MHz ^1H NMR spectra of [Co(OMMPC)PPh_3] and [Co(OMTPC)PPh_3] are shown in Fig. 2 together with that of [Co(OMC)PPh_3]. Chemical shifts and assignments are reported in Table 2.

All spectra are characterized by a strong upfield shift caused by the macrocycle ring current [24]. Such spectra confirm that the presence of the *meso*-phenyl substituents does not cause the loss of aromaticity. The *meso*-protons of [Co(OMMPC)PPh_3] resonate at the same chemical shifts value observed for [Co(OMC)PPh_3].

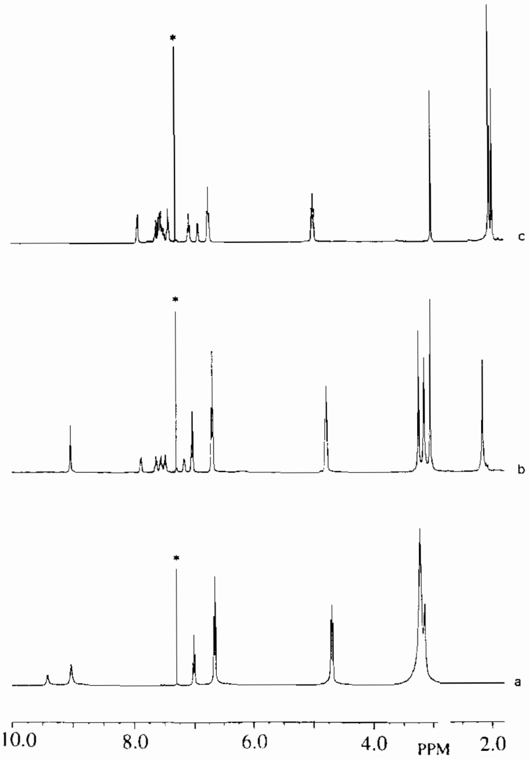


Fig. 2. 400 MHz ^1H NMR spectra of cobalt corrolates in C^2HCl_3: (a) [Co(OMC)PPh_3], (b) [Co(OMMPC)PPh_3], (c) [Co(OMTPC)PPh_3]. An asterisk marks the solvent residual signal.

The resonances due to the protons of the axial triphenylphosphine also demonstrate the shielding effect of the aromatic macrocycle. Such an effect decreases on going from [Co(OMMPC)PPh_3] to [Co(OMTPC)PPh_3] indicating that in the latter compound the axial ligand is at a larger distance from the macrocycle plane probably because of steric constraints introduced by the presence of the three phenyl substituents. The different patterns shown by the resonances due to the peripheral methyl groups depend on the number of *meso*-phenyl substituents. In the spectrum of [Co(OMMPC)PPh_3] the eight peripheral methyl groups give rise to four signals. Symmetry considerations and the shielding effect of the 10-phenyl group led us to assign the resonance at 2.15 ppm to the 8,12-CH_3 and the one at 3.05 ppm to the 2,18-CH_3. In the spectrum of [Co(OMTPC)PPh_3] the methyl groups appear as three signals at $\delta = 3.03$, 2.05, 2.00 ppm of relative intensity 6:12:6; again on the basis of symmetry considerations we can assign such signals to the 2,18-CH_3, 3,7,17,18-CH_3 and to the 8,12-CH_3 substituents, respectively. In the case of [Co(OMC)PPh_3] two signals are present in the high field region of the spectrum ($\delta = 3.23$, 3.15 ppm). Their relative intensity (18:6) and the comparison with the spectra of the *meso*-substituted complexes allows us to assign the signal at 3.15 ppm to the 2,18-methyl groups.

Five resonances, each one corresponding to a single hydrogen, are present in the aromatic region of the spectrum of [Co(OMMPC)PPh_3]. They can be attributed to the protons of the 10-phenyl substituent which is expected to be orthogonal to the macrocycle plane. Such geometry places two of the phenyl protons on the same side of the axial triphenylphosphine ligand with respect to the corrole plane. Since these protons will be shielded by the ring current of the axial ligand, we can assign the resonance at 7.13 ppm and that at 7.45 ppm to the *ortho*- and *meta*-protons there located and those at 7.85 and 7.62 ppm to *ortho*- and *meta*-protons situated on the opposite side of the PPh_3 moiety.

Conclusions

Synthetic strategies have been designed and applied to the preparation of *meso*-phenyl-substituted cobalt corrolates. Cobalt has been chosen because of the stability of the resulting compounds and because its complexes with *meso*-unsubstituted corroles are those for which more information has appeared in the literature [4, 11, 18, 22, 23, 25–27]. Furthermore the diamagnetism of this metal atom allows the study of its complexes by means of NMR spectroscopy.

The formation of the tetrapyrrolic linear precursor is the key problem of the syntheses which appeared to have the greatest efficiency if carried out in a two plus one (dipyrromethane plus pyrrole) scheme.

A general feature of *meso*-phenyl-substituted Co(III) corrolates is that the planarity of the macrocyclic ligand is maintained in solution.

This is demonstrated by several observations: the first evidence is the close similarity of the electronic spectra of these novel complexes with respect to that of [Co(OMC)PPh_3], which has been demonstrated to be essentially planar by crystallographic analysis [23].

This is an unexpected result that reveals the peculiarity of the corrole moiety with respect to other macrocycles: similarly substituted porphyrins have very different properties. In fact recent structural data [14] reported for (2,3,7,8,12,13,17,18-octamethyl-) and (2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrinato)-zinc(II) demonstrated that both molecules deviate severely from planarity and assume saddle shapes. Such conformational distortions are maintained in solution and significantly influence the optical properties of the complexes. So the Soret band is very red-shifted relative to either (tetraphenylporphyrinato)Zn(II) or (octaethylporphyrinato)Zn(II).

The distortions destabilize the π system of the macrocycle and principally raise the energy of the HOMO with a smaller perturbation of the LUMO. The result is a smaller energy gap between the HOMO and LUMO with a concomitant red shift of the first absorption band.

This is not observed in the case of *meso*-phenyl-substituted corrolates. However it is known that the electronic spectra of Co(III) corrolates are influenced by molecular distortions [22]. Hexacoordinated species show a red shift of the Soret band that has been attributed to steric constraints generated by the in plane position of the cobalt atom in this coordination environment.

The retention of the macrocyclic planarity is confirmed by the ^1H NMR spectra: the pattern shown by the resonances due to the peripheral methyl groups in fact are indicative of the existence of a C_2 symmetry axis secating the direct pyrrole–pyrrole bond typical of a planar corrole skeleton, confirmed also by the signals due to the *meso*-protons, when present.

Despite the presence of a direct pyrrole–pyrrole link then, corrole seems to be less sensitive to steric constraints than porphyrin. Such a direct bond between pyrroles A and D makes the two rings closer than in porphyrins and produces an expansion of the *meso*-positions [23, 28], minimizing steric interactions between the *meso*-phenyl and β-methyl groups allowing a planar conformation for these novel complexes.

Structural studies are in progress in order to confirm this analysis.

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