First Direct Synthesis of a Corrole Ring from a Monopyrrolic Precursor. Crystal and Molecular Structure of (Triphenylphosphine)-(5,10,15-triphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III)–Dichloromethane

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The first synthesis of the corrole ring by self-condensation of a monopyrrolic unit is reported. The reaction occurs only in the presence of cobalt ions; it leads to the formation of (triphenylphosphine)(5,10,15-triphenyl-2,3,7,8,-12,13,17,18-octamethylcorrolato)cobalt(III), [Co(OMTPC)PPh₃] and represents the first example of interconversion between a porphyrinoid and a corrole structure. Crystals of [Co(OMTPC)PPh₃]·CH₂Cl₂ have been obtained by slow diffusion of methanol into a dichloromethane solution of the complex and have been characterized by single-crystal X-ray analysis. They crystallize in the triclinic system, space group $P\bar{1}$, with $a = 10.628(2)$ Å, $b = 11.585(2)$ Å, $c = 22.352(4)$ Å, $\alpha = 84.93(2)°$, $\beta = 78.56(2)°$, $\gamma = 72.93(2)°$, and $Z = 2$. The structure was solved by heavy-atom methods and refined by least-square techniques to $R = 0.051$ for 6377 unique data $[F_o > 4 \sigma(F_o)]$. The analysis reveals the substantial planarity of the macrocyclic ring. In the 23-atom core of the corrole moiety each atom shows an average displacement from the plane of best fit of 0.14 Å, with the largest deviations being +0.33 and –0.33 Å for C(2) and C(12), respectively. The synthesis of diphenyl derivatives of corrole: (triphenylphosphine)-(5,10-diphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III), [Co(5,10-OMDPC)PPh₃], and (triphenylphosphine)(5,15-diphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III), [Co(5,15-OMDPC)PPh₃], is also reported. Plausible reaction pathways leading to the formation of the two isomers are discussed together with the spectral properties of the complexes.

Introduction

Metal complexes of tetrapyrrolic macrocycles play a central role in Earth's life because of their implications in a variety of enzymatic systems.[1] Their ability to carry out reactions rather unusual in organic chemistry has been the object of intensive investigations aiming to utilize them as model compounds for biological systems and as catalysts.[2]

Porphyrins are the most representative example of this class of compounds, but a large spread of macrocycles, with modifications in the molecular skeleton, are present in nature and the reason for such variations is still matter of debate. A possible interpretation is that the macrocycle strongly influences the chemical reactivity of the chelated metal ions by modifying its electronic structure through steric and conformational changes.[3] Thus a corrin nucleus is necessary in vitamin B₁₂ to enable the cobalt atom to carry out reactions, such as methylations or isomerizations, impossible for an analogous cobalt porphyrinate.[4]

During our investigations on the chemistry of tetrapyrroles, our attention has been focused on corrole (Figure 1), an intriguing macrocycle that may be considered as an intermediate between porphyrin and corrin. In fact it has a molecular structure similar to that of corrin with a direct link between the A and D pyrrole rings, but retains an 18-electron aromatic π system which has a close relationship to that of porphyrin.
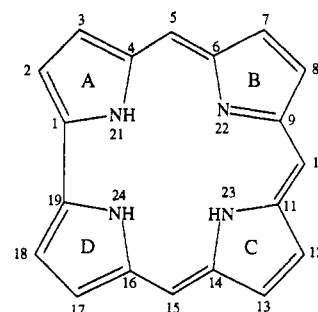

Figure 1. Structural formula of corrole with the atom numbering and ring labeling schemes.

Despite the postulated steric constraint of the corrole ring, whose chelating cavity is much smaller than that of porphyrins, this macrocycle has demonstrated to be a very versatile ligand capable of coordination of several transition or main group metals, and in the last few years, we have established different synthetic methods leading to metallocorrolates.[5–7]

The ligand field effect of corrole is quite different from that of other macrocycles as evidenced by an NMR study carried out on paramagnetic iron(III) derivatives,[8] and different spin states are possible for the metal depending on its axial coordination environment.

The use of cobalt corroles as models for the natural systems is supported by several evidences: a variety of oxidation states is indeed accessible to the cobalt ion, and the redox processes also influence the axial ligand binding equilibria.[9] Furthermore the

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average Co–N distance in cobalt corrole is 1.87 Å,[10] *i.e.* very close to the corresponding distance in cobalt derivatives of corrins,[11] but much shorter than those reported[12] for cobalt(III) porphyrinates, which range between 1.95 and 1.98 Å.

The flexibility of the corrin ring has been considered to be one of the reasons why nature uses a contracted macrocyclic ligand specifically in coenzyme B_{12} rather than a porphyrin.[13] Such flexibility can be imposed on a ligand by the introduction of peripheral substituents which are known to induce severe distortions from planarity,[14] thus modifying the coordinative properties of the macrocycle.

In order to examine the influence of peripheral crowding on the chemistry of corrole we have recently synthesized and characterzied (triphenylphosphine)(10-phenyl-2,3,7,8,12,13,17,-18-octamethylcorrolato)cobalt(III), [Co(OMMPC)PPh₃], and (triphenylphosphine)(5,10,15-triphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III), [Co(OMTPC)PPh₃],[15] the first examples of *meso*-substituted corrolates reported in the literature.

At variance with what happens with other macrocyclic systems, spectroscopic evidences indicated that, despite the steric hindrance of the β-methyl and *meso*-phenyl substituents, no ruffling of the macrocycle occurs and [Co(OMTPC)PPh₃] retains in solution a planar conformation, similar to that of the corresponding *meso*-unsubstituted cobalt complex.

This paper reports the first synthesis of a corrole ring from a monopyrrolic precursor, which may be considered as an analog of the vitamin B_{12} biosynthesis and represents the first example of interconversion between a porphyrin and a corrole structure.

The X-ray crystal structure of [Co(OMTPC)PPh₃]·CH₂Cl₂ confirms the substantially planar conformation of the complex in the solid state and the peculiarity of the corrole ligand.

To achieve a better understanding of such intriguing feature and modulate the influence of the peripheral substitution, we have also prepared diphenyl derivatives of corrole. With the synthetic procedure followed different pathways are possible and the reaction affords two isomers: (triphenylphosphine)(5,10-diphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III)], [Co(5,10-OMDPC)PPh₃], and (triphenylphosphine)(5,15-diphenyl-2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III), [Co-(5,15-OMDPC)PPh₃].

Experimental Section

Electronic spectra were recorded on a Philips PU8700 spectrophotometer as diethyl ether solutions.

Fast atom bombardment (FAB) and electronic impact (EI) mass spectra were recorded on a VG Quattro spectrometer; 3-nitrobenzyl alcohol was used as a matrix for the FAB spectra.

A Bruker AM 400 spectrometer was used to obtain ¹H NMR spectra as $C_6{}^2H_6$ solutions. All chemical shifts are given in ppm from tetramethylsilane (TMS).

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

3,4-Dimethyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid and 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid were prepared by literature methods.[15,16]

Synthesis of [Co(OMTPC)PPh₃]. 3,4-Dimethyl-2-(α-hydroxybenzyl)-pyrrole-5-carboxylic acid (0.5 g, 2.04 mmol) was dissolved in hot absolute

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Table 1. Spectral Properties of Cobalt *meso*-Phenylcorrolates[a]

complex	λ_{max} (nm)[b]	ϵ (10^4 cm⁻¹ M⁻¹)	δ (ppm)	assignment
			¹H NMR[c]	
[Co(5,10-OMDPC)PPh₃]	375	5.60	9.40 (s, 1H)	15-*meso*-H
	572	0.75	7.86–7.20 (m, 10H)	*meso*-Ph
			6.83 (t, 3H)	*p*-PPh₃
			6.63 (t, 6H)	*m*-PPh₃
			5.26 (t, 6H)	*o*-PPh₃
			3.25 (s, 3H)	18-Me
			3.20 (s, 3H)	2-Me
			3.14 (s, 3H)	17-Me
			3.11 (s, 3H)	13-Me
			2.43 (s, 3H)	3-Me
			2.40 (s, 3H)	12-Me
			2.39 (s, 6H)	7,8-Me
[Co(5,15-OMDPC)PPh₃]	375	5.60	9.80 (s, 1H)	10-*meso*-H
	572	0.75	7.87–7.42 (m, 10H)	*meso*-Ph
			6.78 (t, 3H)	*p*-PPh₃
			6.56 (t, 6H)	*m*-PPh₃
			5.18 (t, 6H)	*o*-PPh₃
			3.15 (s, 12H)	2,8,12,18-Me
			2.48 (s, 12H)	3,7,13,17-Me
[Co(OMTPC)PPh₃]	378	6.03	7.91–7.43 (m, 15H)	*meso*-Ph
	574	0.97	6.83 (t, 3H)	*p*-PPh₃
			6.64 (t, 6H)	*m*-PPh₃
			5.36 (t, 6H)	*o*-PPh₃
			3.14 (s, 6H)	2,18-Me
			2.37 (s, 12H)	3,7,17,18-Me
			2.33 (s, 6H)	8,12-Me

[a] Data relative to the electronic spectrum of [Co(OMTPC)PPh₃] are taken from ref 15. [b] Diethyl ether solutions. [c] $C_6{}^2H_6$ solutions.

Table 2. Crystallographic Data for [Co(OMTPC)PPh₃]·CH₂Cl₂

chem formula $C_{64}H_{56}Cl_2CoN_4P$	fw = 1041.9
a = 10.628(2) Å	space group $P\bar{1}$
b = 11.585(2) Å	T = 23 °C
c = 22.352 (4) Å	λ = 0.710 73 Å
α = 84.93(2)°	ρ_{calcd} = 1.343 gcm⁻³
β = 78.56(2)°	μ = 5.1 cm⁻¹
γ = 72.93(2)°	$R(F_o)^a$ = 5.1
V = 2577.2(8)Å³	$R_w(F_o)^b$ = 6.4
Z = 2	

[a] $R(F_o) = \sum|F_o - |F_c||/\sum F_o$. [b] $R_w(F_o) = [\sum w(F_o - |F_c|)^2/\sum w(F_o{}^2)]^{1/2}$.

ethanol (200 mL); trifluoroacetic acid (1 mL) was then added, and the dark red solution was refluxed for 15 min. An excess of sodium acetate (2 g, 24.4 mmol) was then added and the color of the solution turned to brown-green. Cobalt(II) acetate (0.5 g, 1.91 mmol) and triphenylphosphine (0.5 g, 2.00 mmol) were added, and the solution was refluxed for 24 h. The solvent was vacuum evaporated and the residue extracted with diethyl ether and then chromatographed on basic alumina (Merck, type T), using diethyl ether as eluent. The first red band eluted contained [Co(OMTPC)PPh₃], which was recrystallized from CH₂Cl₂/CH₃OH 1:3 (125 mg, yield 25%).

Anal. Calcd for $C_{63}H_{54}N_4PCo$: C, 79.05; H, 5.70; N, 5.85. Found: C, 78.95; H, 5.80; N, 5.95.

A crystal suitable for X-ray analysis was obtained by slow diffusion of methanol in a dichloromethane solution of the purified complex.

Synthesis of [Co(5,10-OMDPC)PPh₃] and [(Co(5,15-OMDPC)PPh₃]. 3,3′,4,4′-Tetramethyldipyrromethane-5,5′-dicarboxylic acid (0.6 g, 2.07 mmol) was dissolved in hot absolute ethanol (200 mL); trifluoroacetate acid (1 mL) was added, and then a diluted solution of 3,4-dimethyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid (0.5 g, 2.04 mmol) in absolute ethanol (100 mL) was added dropwise. The resulting dark red solution was treated as above. Chromatography afforded a mixture of the two isomers, [Co(5,10-OMDPC)PPh₃] and [Co(5,15-OMDPC)PPh₃], in a 1:2 ratio (90 mg, total yield 20% based on (α-hydroxybenzyl)pyrrole).

The mixture of the two isomers was dissolved in *n*-pentane and recrystallized at –30 °C: [Co(5,10-OMDPC)PPh₃] was obtained as red needles. An analytical pure sample of the 5,15-isomer was obtained from the solution after several crystallizations.

Table 3. Atomic coordinates($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$)

	x	y	z	U^a (Å^2)		x	y	z	U^a (Å^2)
Co	788(1)	1589(1)	2636(1)	32(1)	C(31)	−4424(6)	1278(5)	5479(2)	75(3)
P	−512(1)	1360(1)	2026(1)	33(1)	C(32)	−3132(7)	1108(5)	5551(2)	74(3)
N(1)	−560(3)	2704(3)	3143(2)	38(1)	C(33)	−2147(5)	1165(4)	5049(2)	57(2)
N(2)	586(3)	323(3)	3215(1)	36(1)	C(34)	3252(4)	−2578(4)	2722(2)	45(2)
N(3)	2500(3)	727(3)	2223(1)	34(1)	C(35)	4115(5)	−3121(4)	3119(2)	58(2)
N(4)	1098(3)	3036(3)	2283(2)	36(1)	C(36)	4716(6)	−4363(5)	3128(3)	74(2)
C(1)	−721(4)	3914(3)	3006(2)	41(2)	C(37)	4430(6)	−5055(5)	2730(4)	89(3)
C(2)	−1721(4)	4601(4)	3469(2)	46(2)	C(38)	3601(7)	−4540(6)	2339(3)	91(3)
C(3)	−2180(4)	3793(4)	3880(2)	46(2)	C(39)	3005(5)	−3293(5)	2324(3)	67(2)
C(4)	−1429(4)	2588(4)	3667(2)	41(2)	C(40)	3807(4)	2640(4)	902(2)	45(2)
C(5)	−1434(4)	1442(4)	3921(2)	41(2)	C(41)	3595(5)	2376(5)	346(2)	60(2)
C(6)	−480(4)	365(3)	3695(2)	38(1)	C(42)	4340(7)	2678(6)	−191(3)	80(3)
C(7)	−426(5)	−858(4)	3918(2)	46(2)	C(43)	5288(7)	3251(6)	−179(3)	92(3)
C(8)	685(4)	−1615(4)	3593(2)	46(2)	C(44)	5533(6)	3506(5)	361(4)	83(3)
C(9)	1341(4)	−885(3)	3150(2)	38(1)	C(45)	4787(5)	3211(4)	908(3)	63(2)
C(10)	2536(4)	−1254(3)	2736(2)	40(1)	C(46)	−1049(4)	2738(3)	1563(2)	39(2)
C(11)	3123(4)	−494(3)	2314(2)	37(1)	C(47)	−499(5)	2805(4)	946(2)	55(2)
C(12)	4385(4)	−815(4)	1897(2)	41(2)	C(48)	−853(6)	3859(5)	605(3)	72(3)
C(13)	4486(4)	177(4)	1534(2)	42(2)	C(49)	−1777(7)	4844(5)	870(3)	83(3)
C(14)	3298(4)	1150(4)	1735(2)	37(1)	C(50)	−2338(6)	4818(4)	1476(3)	73(3)
C(15)	2965(4)	2343(4)	1484(2)	39(1)	C(51)	−1960(5)	3768(4)	1834(2)	53(2)
C(16)	1889(4)	3263(3)	1746(2)	38(1)	C(52)	130(4)	201(3)	1440(2)	38(1)
C(17)	1399(4)	4546(4)	1590(2)	44(2)	C(53)	1444(5)	−106(4)	1155(2)	55(2)
C(18)	372(4)	5056(4)	2049(2)	45(2)	C(54)	1888(5)	−874(5)	662(2)	68(2)
C(19)	185(4)	4097(3)	2480(2)	39(1)	C(55)	1011(6)	−1353(5)	471(2)	64(2)
C(20)	−2153(6)	5944(4)	3504(3)	69(2)	C(56)	−281(6)	−1076(5)	757(3)	72(2)
C(21)	−3187(6)	4124(4)	4453(2)	67(2)	C(57)	−718(5)	−316(5)	1244(2)	61(2)
C(22)	−1418(6)	−1283(4)	4393(2)	69(2)	C(58)	−2038(4)	988(3)	2405(2)	38(1)
C(23)	1098(6)	−2973(4)	3717(3)	69(2)	C(59)	−3317(4)	1683(4)	2371(2)	46(2)
C(24)	5486(5)	−1989(4)	1880(2)	61(2)	C(60)	−4420(5)	1291(5)	2641(2)	58(2)
C(25)	5666(4)	223(4)	1052(2)	59(2)	C(61)	−4240(5)	197(5)	2947(5)	60(2)
C(26)	1863(5)	5221(4)	1022(2)	66(2)	C(62)	−2962(5)	−523(5)	2980(2)	59(2)
C(27)	−423(5)	6354(4)	2089(3)	66(2)	C(63)	−1880(5)	−139(4)	2721(2)	47(2)
C(28)	−2472(4)	1377(4)	4466(2)	45(2)	Cl(1)	2523(3)	2047(3)	3853(1)	186(2)
C(30)	4749(6)	1493(5)	4906(3)	71(2)	C(64)	1608(11)	3517(9)	3924(5)	173(6)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Anal. Calcd for $\text{C}_{57}\text{H}_{50}\text{N}_4\text{PCo}$: C, 77.70; H, 5.70; N, 6.35. Found for the 5,15-isomer: C, 77.15; H, 5.45; N, 6.25. Found for the 5,10-isomer: C, 77.55; H, 5.60; N, 6.25.

Spectral properties of the complexes are reported in Table 1.

Crystal Structure Determination. Crystallographic data for [Co-(OMTPC)PPh$_3$]·CH$_2$Cl$_2$ are summarized in Table 2, while other numbers related to data collection and refinement procedure have been deposited as supplementary material.

Cell parameters were determined from 50 high-angle data ($2\theta > 24°$). No decrease in the intensity of two periodically remeasured reflections was noted. For the calculation of the structure factors, corrections of the Lorentz–polarization effects and absorption, using an empirical method based on ψ-scans of six reflections at $\chi \approx 90°$, were made ($I(\text{max})/I(\text{min})$ was 1.0/0.65).

The structure was solved by using standard heavy-atom methods to locate Co and P atoms with subsequent difference Fourier maps yielding the positions of the remaining non-hydrogen atoms. The hydrogens were included in calculated positions, and for them only a common, isotropic thermal parameter was refined.

The dichloromethane molecule is disordered as shown by the high thermal parameters and by the relevant maxima in its vicinity detectable from the final ΔF map. Attempt to refine the disordered solvent, including in the least-squares procedure site occupation factors as additional variables, was unsuccessful. In the final difference Fourier synthesis the largest peaks were 0.9 e Å^{-3} (1.3 Å from Cl(2)) and 0.8 e Å^{-3} (1.2 Å from Cl(1)).

Complex atom scattering factors were employed and corrections for anomalous dispersion were included for all non-hydrogen atoms.[17] The SHELXTL-PLUS package[18] of computer programs was used for the solution and refinement of the structure. Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 3, while selected bond distances and angles are listed in Table 4.

(17) *International Table for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.
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Table 4. Selected Bond Lengths (Å) and Bond Angles (deg)

Co–N(1)	1.879(3)	C(6)–N(2)	1.391(5)
Co–N(2)	1.900(3)	N(2)–C(9)	1.397(5)
Co–N(3)	1.894(3)	C(9)–C(10)	1.391(5)
Co–N(4)	1.878(3)	C(10)–C(11)	1.413(6)
Co–P	2.205(1)	C(11)–N(3)	1.390(5)
P–C(46)	1.831(4)	N(3)–C(14)	1.390(5)
P–C(52)	1.844(4)	C(14)–C(15)	1.416(6)
P–C(58)	1.827(4)	C(15)–C(16)	1.385(5)
C(1)–N(1)	1.376(5)	C(16)–N(4)	1.376(5)
N(1)–C(4)	1.364(5)	C(4)–C(19)	1.368(4)
C(4)–C(5)	1.398(6)	C(1)–C(19)	1.408(6)
C(5)–C(6)	1.417(5)		
P–Co–N(1)	95.9(1)	C(9)–C(10)–C(11)	125.8(3)
P–Co–N(2)	98.4(1)	C(10)–C(11)–N(3)	123.3(3)
P–Co–N(3)	101.4(1)	C(11)–N(3)–Co	125.5(2)
P–Co–N(4)	98.1(1)	Co–N(3)–C(14)	126.9(2)
N(1)–Co–N(2)	90.0(1)	N(3)–C(14)–C(15)	124.3(3)
N(1)–Co–N(3)	161.0(2)	C(14)–C(15)–C(16)	123.4(4)
N(1)–Co–N(4)	80.3(1)	C(15)–C(16)–N(4)	119.5(3)
N(2)–Co–N(3)	95.2(1)	C(16)–N(4)–Co	131.1(3)
N(2)–Co–N(4)	161.5(2)	Co–N(4)–C(19)	117.8(3)
N(3)–Co–N(4)	89.4(1)	N(4)–C(19)–C(1)	111.7(3)
Co–N(1)–C(4)	133.5(3)	C(19)–N(1)–C(1)	111.4(3)
N(1)–C(4)–C(5)	120.2(3)	C(1)–N(1)–Co	117.9(3)
C(4)–C(5)–C(6)	123.1(4)	C(1)–N(1)–C(4)	108.5(3)
C(5)–C(6)–N(2)	124.4(4)	C(6)–N(2)–C(9)	107.5(3)
C(6)–N(2)–Co	126.6(2)	C(11)–N(3)–C(14)	107.3(3)
Co–N(2)–C(9)	124.6(2)	C(16)–N(4)–C(19)	108.8(3)
N(2)–C(9)–C(10)	123.2(4)		

Nitrogen atoms are labeled N(1), N(2), N(3), and N(4) and correspond respectively to N(21), N(22), N(23), and N(24) in the "classical" numbering scheme shown in Figure 1.

Additional data, including a full presentation of data collection parameters and refinement information, anisotropic thermal parameters, hydrogen atom coordinates, nonessential bond lengths and angles, some geometrical entities (least-square planes, dihedral angles, torsion angles,

and square-pyramid edge lengths), and a listing of the observed/calculated structure factors are available from the Cambridge Crystallographic Data Centre.

Results and Discussion

Synthesis. The most efficient synthetic procedure leading to the corrole ring consists in the photochemical or metal-assisted, base-catalyzed cyclization of a linear tetrapyrrolic precursor, 1,19-dideoxybiladiene-*ac* dihydrobromide.[5–7,19]

Unfortunately it has been impossible to prepare *meso*-substituted corrolates following such procedure because of the problems involved in the synthesis of the corresponding *meso*-functionalized linear precursors.

In order to overcome this problem, we have developed a new method for the functionalization of the *meso* position[15] which involves the reaction of 2 equivalents of an (α-hydroxybenzyl)-pyrrole with a dipyrromethane unit. We have been unable to isolate the linear tetrapyrrolic intermediate, but an *in situ* cyclization reaction afforded [Co(OMTPC)PPh₃] in good yield.

The interesting properties of [Co(OMTPC)PPh₃][15] lead us to extend this synthetic approach to the preparation of [Co(5,15-OMDPC)PPh₃], in order to study in detail the influence of the number of *meso* substituents on the properties of the corresponding complex.

The first approach to the preparation of a *meso*-disubstituted corrole has been the application of the synthetic procedure used to obtain the triphenyl derivative. However, when a stoichiometric amount of 3,4-dimethyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid is added to an ethanolic solution of 3,3′,4,4′-tetramethyl-dipyrromethane-5,5′-dicarboxylic acid, the major product of the reaction is surprisingly [Co(OMTPC)PPh₃] with only a minor amount of a mixture of two different isomers of [Co(OMDPC)-PPh₃].

Self-condensation of (α-hydroxybenzyl)pyrroles, obtained for reduction of acylpyrroles, has been recently reported to be an efficient route to synthesize *meso*-tetraphenyl porphyrins.[20] Thus, in order to ascertain that the unexpected formation of triphenylcorrole derives from self-condensation of the mono-pyrrole unit we have reacted 3,4-dimethyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid under similar conditions in the absence of the dipyrromethane unit, and the only product of the reaction is again [Co(OMTPC)PPh₃], instead of the expected porphyrin.

The reaction conditions do not allow a detailed study of its mechanism, but the formulation of a plausible pathway is possible for some experimental evidences and a such pathway is reported in Scheme 1.

The first step of the reaction is, most probably, the formation of a porphyrinogen-like species in acidic ethanol. In fact, when trifluoroacetic acid is added to the ethanolic solution of the pyrrole, the optical spectrum of the mixture does not show the two absorptions typical of a linear tetrapyrrole (540 and 450 nm) but a major absorption centered at 220 nm which may be considered as indicative of the formation of a porphyrinogen structure.[21] A weaker band at 500 nm is also present; its intensity increases with time so that it is probably due to some oxidation product.

The solution is buffered with an excess of sodium acetate, and an equimolar mixture of triphenylphosphine and cobalt acetate is then added: the formation of cobalt corrolate may be followed by monitoring the electronic spectrum of the reaction mixture. The increase of a Soret-like absorption centered at 370 nm with the concomitant decrease of the band at about 500 nm reveals the formation of the complex.

Scheme 1
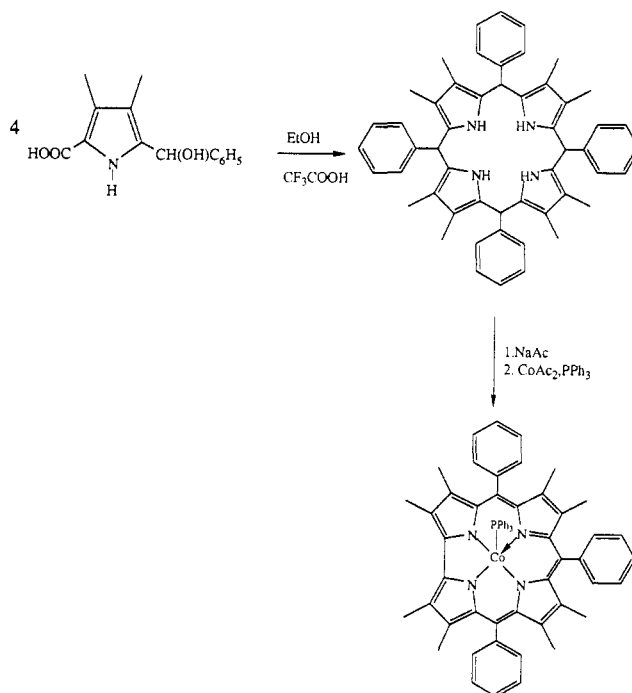
Coordination of the cobalt atom probably catalyzes a ring contraction reaction of the porphyrinogen species leading, after oxidation, to the final corrole ring.

This conversion represents a model for the uroporphyrinogen–corrin transformation that is a crucial step of the vitamin B₁₂ biosynthesis.

A similar catalytic activity of the Co atom has also been reported by Eschenmoser's group:[22] an hydroporphyrin cobalt complex undergoes a rearrangement to a corresponding corrin on melting. However, the reaction we report here is the first example of an interconversion between a porphyrinoid and a corrolic structure.

The reactivity pattern of other metals also confirm such key role of the cobalt atom: in fact Mn, Fe, or Rh fail to catalyze the ring contraction reaction, and in the presence of such metals, the products of the reactions are mixtures of metal complex and free base *meso*-tetraphenyloctamethylporphyrin. Although both cobalt and nickel are known to generate contracted macrocycles in natural systems, we have not observed such a contraction reaction even in the presence of nickel salts. A possible explanation is that in nickel corrolates the metal exists in the +2 oxidation state, and the resulting complexes are nonplanar with one of the inner core hydrogens displaced from nitrogen to carbon in such a way to interrupt the chromophore.[23] The retention of aromaticity seems to be then the driving force that favors the formation of nickel porphyrinate.

The cobalt atom is then essential to drive the reaction toward the formation of the direct link between the A and D pyrrole rings of the macrocycle. However, a question that is still unanswered is why the porphyrinogen rearranges to the final structure.

A plausible hypothesis is that the steric release allowed by the corrole ring drives this conversion. In fact [Co(OMTPC)PPh₃] has a planar structure, while analogous complexes, such as (*meso*-tetraphenyloctaethylporphyrinato)zinc(II), suffer significant deviations from planarity which have been attributed to the steric interactions between β-alkyl and *meso*-phenyl groups.[14]

(19) Pandey, R. K.; Zhou, H.; Gerzeveske, K.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 183.
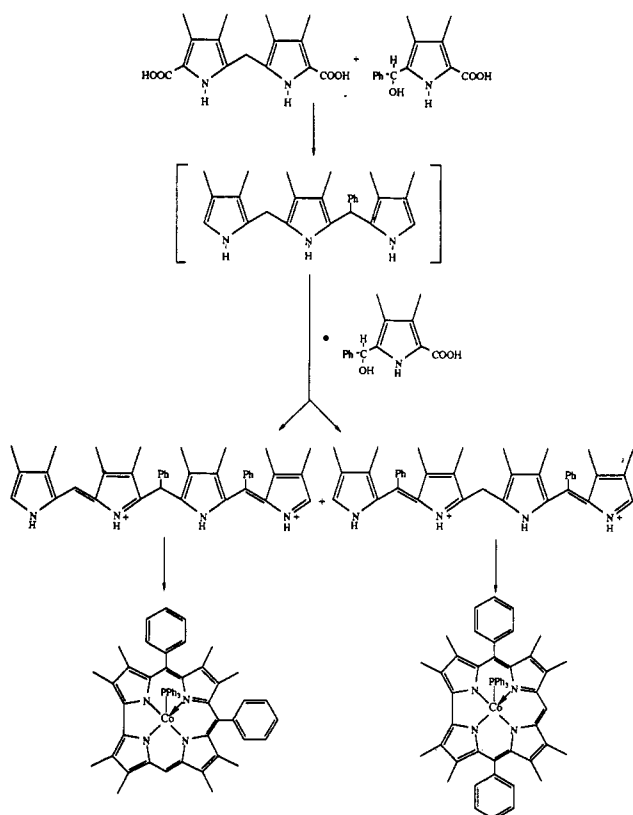(20) Kuroda, Y.; Murase, H.; Suzuki, Y.; Hogoshi, H. *Tetrahedron Lett.* **1989**, *30*, 2411.
(21) Mauzerall, D. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. IIB.

(22) Rasetti, V.; Pfaltz, A.; Kratky, C.; Eschenmoser, A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 16.
(23) Melent'eva, T. A. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 641 and references therein.

Scheme 2

(a)

(b)

Figure 2. (a) Simplified diagram of [Co(OMTPC)PPh₃]·CH₂Cl₂ with phenyl groups indicated by Ph. The Co---Cl(1) contact is shown. (b) ORTEP view of [Co(OMTPC)PPh₃]·CH₂Cl₂ showing the atom labeling. The thermal ellipsoids are drawn at a 40% probability level, and hydrogen atoms have been omitted for clarity.

Another piece of evidence supports this hypothesis: we have in fact reacted under similar conditions the β-unsubstituted α-(2-hydroxybenzyl)pyrrole, and the product obtained is not the corresponding corrole complex but the free base *meso*-tetraphenylporphyrin.

In order to complete the series of cobalt mono-, di-, and triphenylcorrolates and verify that the peculiar features of [Co(OMTPC)PPh₃] are independent from the number of *meso* substituents, the synthesis of diphenylcorrolates has also been carried out.

The major problem to overcome in order to obtain such derivatives is the high tendency of (α-hydroxybenzyl)pyrrole to self-condense. In order to avoid the competitive formation of [Co(OMTPC)PPh₃] we have then carried out the reaction by slowly adding a diluted ethanolic solution of 3,4-dimethyl-2-(α-hydroxybenzyl)pyrrole-5-carboxylic acid to an excess of 3,3′,4,4′-tetramethyldipyrromethane-5,5′-dicarboxylic acid and obtained a 2:1 mixture of two isomers: [Co(5,15-OMDPC)PPh₃] and [Co-(5,10-OMDPC)PPh₃]. Scheme 2 shows a possible pathway leading to the formation of the two isomers. If the condensation occurs stepwise, a tripyrryl-like species would be an intermediate of the reaction. At this point two equivalent positions might react with a second (α-hydroxybenzyl)pyrrole, leading to the mixture of isomers. Such a scheme does not however explain the different yields in the two species.

An hypothesis more consistent with the experimental results is then that the formation of the 5,15-diphenyl isomer occurs by the "normal" pathway that leds to corroles, *i.e.* through the formation of a 5,15-diphenylbiladiene-*ac* salt by reaction of two pyrrolic units with a dipyrromethane. However, the high tendency of the (α-hydroxybenzyl)pyrrole to self condense even at low concentration can generate a 2-(α-hydroxybenzyl)-*meso*-phenyldipyrromethane that can react with the other dipyrrolic unit present in excess.

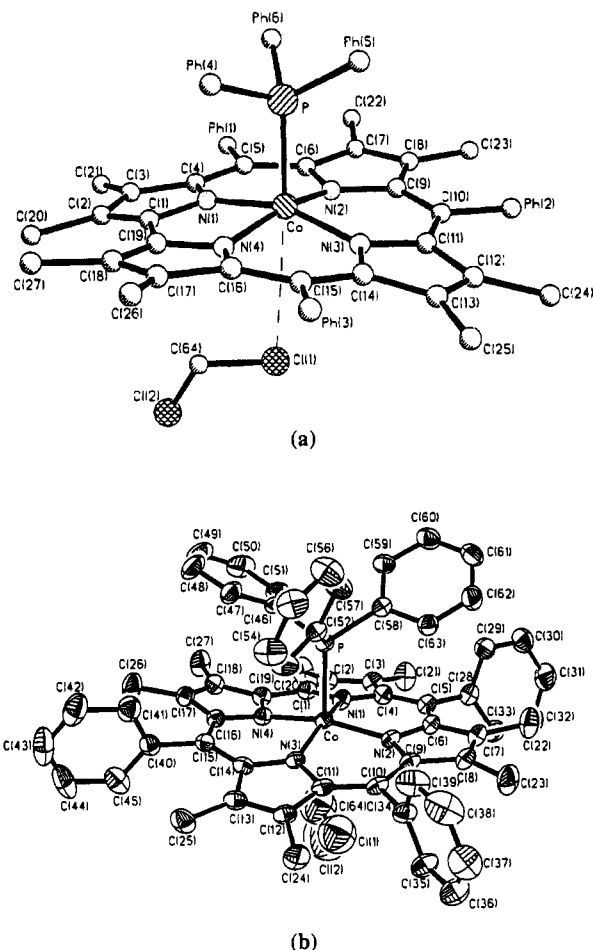Careful fractional crystallization from *n*-pentane at –30 °C allowed the separation of the two isomers.

Crystallography. We have previously reported[15] spectral evidence indicating a planar structure for [Co(OMTPC)PPh₃] in solution. An unambiguous characterization of the conformation of this complex is at this point necessary and we have carried out an X-ray analysis on a single-crystal obtained by slow diffusion of a dichloromethane solution in methanol.

Figure 2 illustrates the geometry and the numbering scheme for the complex [Co(OMTPC)PPh₃]·CH₂Cl₂. The tetraazamacrocyclic corrole moiety acts as a trianionic ligand to the Co(III) atom, which resides in an approximately square pyramidal coordination environment. The nitrogens occupy the four coordination sites of the basal plane, while the apex of the pyramid is occupied by the phosphorus atom. The steric requirements of the phosphine group severely distort the geometry of the complex and result in nonorthogonal angles at cobalt (Table 4).

In addition the Co atom is displaced 0.28 Å out of the equatorial plane toward the phosphorus. This displacement is comparable with the value of 0.26 Å found in the similar complex [(triphenylarsine)(2,3,7,8,12,13,17,18-octamethylcorrolato)rhodium-(III)], [Rh(OMC)AsPh₃].[6]

The structure of the present complex exhibits close geometrical resemblance with the structure of the corrole complexes [Rh-(OMC)AsPh₃] and [(triphenylphosphine)(corrolato)complex-(III)], [Co(C)PPh₃][10] (where an approximately 2-fold disorder is present). In particular, in order to compare the extent of this similarity with [Rh(OMC)AsPh₃], the 23-atom core of the corrole moiety was fitted and the weighted rms deviation of 0.22 Å, derived from the BMFIT program,[24] confirms that the two structures are roughly superimposible. Bond lengths and angles

(Table 4) do not differ from the expected values and there only the following remarks are worthy to be made: (i) the Co–N(1) and Co–N(4) bonds (1.878 and 1.879 Å, respectively) are slightly shorter than Co–N(2) and Co–N(3) (1.900 and 1.894 Å, respectively); (ii) the four planar (within 0.01Å) A, B, C, and D pyrrole rings exhibit rather narrow ranges for N—C_α, C_α—C_β, C_β=C_β distances (1.364–1.397, 1.432–1.459, and 1.363—1.377 Å, respectively) with mean C_α–N–C_α angle of 108.0°; (iii) in the (5,6,6,6) chelation ring system the N(4)–Co–N(1) angle (80.3°) is definitely narrower (up to 15°) than the other bite angles in the six-membered rings, which deviate significantly from coplanarity (mean deviation of 0.08 Å).

The 23-atom core of the corrole has a substantially planar conformation (mean deviation from the plane of best fit of 0.14 Å, with the largest deviations of +0.33 and –0.33 Å for C(2) and C(12), respectively).

The cobalt atom is displaced from this mean plane by 0.29 Å (0.31 Å in [Rh(OMC)PPh₃]), while it is out from the A, B, C, and D planes by +0.12, –0.40, –0.07, and –0.49 Å, respectively.

Of interest is the rather long intramolecular contact Co---Cl-(1) of 3.73 Å, but with the chlorine atom filling the vacant sixth coordination site of a distorted octahedron (the pertinent P–Co–Cl(1) angle is 171.2°).

The crystal structure of the complex consists of discrete monomeric units and the closest non-hydrogen interactions occur between C(60)---C(13) (at x – 1, y, z) (3.42 Å) and C(61)---C(12) (at x – 1, y, z) (3.44 Å), while the shortest separation involving the solvent molecule is 3.64 Å [Cl(2)---C(23) at x, 1 + y, z).

Spectroscopy. Spectral features of these isomers are summarized in Table 1 and are very similar to those of the previously reported mono- and triphenyl analogs.[15]

Despite the poor solubility of cobalt corrolates in deuteriated benzene, the 400-MHz ¹H NMR spectra of the complexes have been recorded using such a solvent in order to avoid the decomposition phenomena observed in chlorinated solvents.

All the resonances show a strong shift due to the macrocycle ring current.[25] The existence of such a shift confirms that aromaticity is retained despite the presence of *meso*-substituents. No significant difference has been observed in the chemical shift values of the resonances due to the protons of the axial phosphine ligand indicating the similarity of the geometry of the three complexes.

The identification of the spectra due to the 5,10- and 5,15-diphenyl derivatives, respectively, has been made by comparing the chemical shift values of the *meso*-protons resonances with those observed in the spectrum of the *meso*-unsubstituted complex.[15] Such an identification is confirmed by the observation of the data relative to the low-field region of the spectra where the eight peripheral methyl groups generate seven signals (1:1:1:1:1:1:2) for the 5,10-diphenyl isomer, while only two resonances of equal intensity are present in the spectrum of the symmetric 5,15-diphenyl derivative.

Symmetry considerations and the shielding effect of the *meso*-phenyl substituents led to the assignments reported in Table 1.

The assignment of all the resonances in the spectrum of [Co-(OMTPC)PPh₃] has been previously discussed.[15]

The electronic spectra of diphenylcorrolates present a Soret-like absorption at 375 nm, while the Q band is centered at 572 nm. Only a small red shift observed in the series unsubstituted and mono-, di-, and triphenyl *meso*-substituted complexes: this is very different from the corresponding series of porphyrinates where the increase of the number of *meso*-substituents induces a very significant red shift that demonstrated the higher sensitivity of the porphyrin ligand to substitution.

Mass spectra have been obtained by electron impact or fast atom bombardment techniques. The spectra obtained by EI show a parent peak corresponding to [M – PPh₃]⁺, that indicates the loss of the axial ligand from the molecular peak, which is not observed. In addition, a [M – PPh₃]²⁺ peak is revealed and the fragmentation patterns show the consecutive loss of the *meso*-phenyl groups.

The FAB technique, using *p*-nitrobenzyl alcohol as matrix, allows identification of the molecular peak.

Conclusions

In the present paper the first synthetic method for the preparation of a corrole ring from a monopyrrolic precursor has been presented.

Several evidences indicate that [Co(OMTPC)PPh₃] is produced by a ring-contraction reaction of a porphyrinogen-like species, and this is, to the best of our knowledge, the first example of a similar conversion.

The key factors of this reaction seem to be the catalytic activity of the cobalt atom and the steric release allowed by a corrole moiety. In fact the X-ray analysis of [Co(OMTPC)PPh₃]·CH₂-Cl₂ confirms that the complex retains a substantially planar structure in the solid state.

Despite the postulated steric constraints of its molecular skeleton, attributed to the direct pyrrole–pyrrole link, corrole is capable to assume a planar conformation as well in the presence of both β- and *meso*-substitution.

This behavior of corrole is then very different from that of other tetrapyrrolic macrorings and anticipates for this macrocycle new interesting applications as a model compound for biological systems or as catalyst.

Supplementary Material Available: A full presentation of data collection parameters and refinement information (Table S*I*), anisotropic thermal parameters (Table S*II*), hydrogen atom coordinates (Table S*III*), nonessential bond lengths (Table S*IV*) and angles (Table S*V*), and some other geometrical entities (least-square planes, dihedral angles, torsion angles and square-pyramid edge lengths) (Table S*VI*), Figure A, showing the superimposition of the 23-atom core in the present complex and in [Rh(OMC)AsPh₃], and Figure B, showing a packing diagram (8 pages). Ordering information is given on any current masthead page.

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(25) Scheer, H.; Katz, J. J. In *Porphyrins and Metalloporphyrins*; Smith K. M., Ed.; Elsevier: Amsterdam, 1975.