

Synthesis and electrochemistry of A₂B type mono- and bis-cobalt triarylcorroles and their electrocatalytic properties for reduction of dioxygen in acid media

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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> **ABSTRACT:** Two A_2B mono-cobalt corroles and the corresponding bis-cobalt derivatives linked by a xanthene acyl group were synthesized, characterized as to their electrochemistry and spectroelectrochemistry in nonaqueous media and then examined as catalysts for the electroreduction of O_2 in 1.0 M HClO₄. The investigated mono- and bis-corroles are represented as $(NH_2Ph)(YPh)_2CorCo(PPh_3)$ and $[(YPh)_2CorCo(PPh_3)]_2Xac$, respectively, where Cor is the trianion of the corrole, Y is a CH₃ or Cl substituent on the *para*-position of the 5- and 15-*meso*-phenyl rings of the macrocycle and Xac is the xanthene acyl group linking the two macrocycles in a face-to-face arrangement. The neutral compounds were characterized by cyclic voltammetry while thin-layer spectroelectrochemistry was used to elucidate UV-visible spectra of the compounds in their electrooxidized or electroreduced forms. Rotating disk and rotating ring-disk electrode measurements were also utilized to examine the electrocatalytic activity for reduction of O_2 when the face-to-face corroles were adsorbed on the electrode surface in 1.0 M HClO₄. The number of electrons transferred in the catalytic electroreduction of dioxygen was calculated from currents at the disk electrode using Koutecky–Levich plots. The effect of linking the two cobalt corrole macrocycles on UV-visible spectra, redox potentials and electrocatalytic activity for the reduction of dioxygen is discussed.

> **KEYWORDS:** A_2B type of cobalt triarylcorrole, bis-cobalt corrole, synthesis, electrochemistry, electrocatalytic reduction of oxygen.

INTRODUCTION

Cobalt corroles have attracted a great deal of interest, in part because of their unique spectral and electrochemical properties [1, 2] and in part because they can be utilized as catalysts for a variety of reactions [3-12]. In this regard, a number of mono- and bis-cobalt

linked face-to-face corroles have been synthesized and electrochemically characterized by our groups over the last two decades [13–26], with some of these compounds being examined as catalysts for the electroreduction of O_2 in acid media [13–17, 22–24].

Bis-copper and bis-manganese face-to-face corroles connected by a xanthene Xac linker were synthesized and electrochemically characterized by Sun, Liu and coworkers [27]. The bis-manganese corrole was also examined as to its catalytic activity for the oxidation of water. However, to the best of our knowledge, bis-cobalt face-to-face corroles containing the same Xac linker have never been synthesized and it was therefore of interest to

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Chart 1. Structures of examined mono- and bis-cobalt corroles

know if these compounds with two closely spaced redox active metal centers might function as efficient catalysts for the electroreduction of dioxygen in acid media.

This is addressed in the present manuscript where two mono-cobalt A_2B corroles and the corresponding biscobalt derivatives linked by a xanthene acyl group were synthesized, and characterized as to their electrochemistry and spectroelectrochemistry in nonaqueous media and then examined as catalysts for the electroreduction of O_2 in 1.0 M HClO₄.

The structures of the investigated mono- and biscorroles are shown in Chart 1 and represented as (NH_2Ph) $(YPh)_2CorCo(PPh_3)$ and $[(YPh)_2CorCo(PPh_3)]_2Xac$, respectively, where Cor is the trianion of the corrole macrocycle, Y is a CH₃ or Cl substituent on the *para*-position of the 5- and 15-*meso*-phenyl rings of the compound and Xac is a xanthene acyl group linking the two macrocycles in a face-to-face arrangement. The number of electrons transferred and the percentage of H₂O₂ produced in the catalytic reduction of O₂ was calculated from measurements performed at a rotating disk and/or rotating-ring disk electrode in 0.1 M HClO₄.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic routes for obtaining the two types of A_2B corroles are described in Scheme 1a. The procedure for the mono-corroles follows a procedure reported in the literature [28, 29] while synthesis of the bis-cobalt corroles was according to the route shown in Scheme 1b. The progress of the reaction was monitored by thinlayer chromatography and the purity of the final corrole product was confirmed by UV-visible spectroscopy and mass spectrometry.



Scheme 1a. Synthesis routes for mono-corroles 1a and 1b



Scheme 1b. Synthesis routes for bis-corroles 2a and 2b

The ¹H NMR spectrum of each compound was measured in CDCl₃ or CD₂Cl₂ and examples of the spectra for (NH₂Ph)(CH₃Ph)₂CorCo(PPh₃) **1a** and [(CH₃Ph)₂-CorCo(PPh₃)]₂Xac **2a** are shown in Fig. S1. The protons of the *para*-NH₂ group on **1a** appear as a broad resonance at 3.57 ppm while resonances of the two NH protons of **2a** are sharp and shifted to 9.20 ppm. Resonances of the six *para*-CH₃ protons of **1a** are located at 2.59 ppm while the 12 *para*-CH₃ protons of **2a** give peaks at 2.02 ppm and are characterized by a stronger absorption as compared to **1a**.

UV-visible spectra

UV-visible spectra of the four neutral corroles in CH_2Cl_2 are illustrated in Fig. S2. As seen in the figure, all four compounds are characterized by a Soret band at 392–394 nm and a single Q-band absorption at 562–566 nm. Almost identical UV-visible spectra are seen for the mono- and bis-corroles, indicating that neither the substituents on the *para*-positions of the *meso*-phenyl rings nor the face-to-face arrangement of the two metallomacrocycles has a significant effect on the UV-visible spectra.

Electrochemistry

Three reversible one-electron oxidations are observed for the mono-corroles **1a** and **1b** in CH₂Cl₂ containing 0.10 M TBAP. The first oxidation of compound **1a**, which contains two electron-donating CH₃Ph substituents, is located at $E_{1/2} = 0.48$ V while the second and third oxidations of this mono-cobalt corrole are located at $E_{1/2} = 1.02$ and 1.48 V, respectively (Fig. S3). The first two oxidations of **1b**, which contains two electronwithdrawing *meso*-ClPh substituents, are positively shifted by 80 and 30 mV as compared to that of compound **1a**. Similar oxidation behavior has been reported for other cobalt triarylcorroles containing a variety of electron-donating or electron-withdrawing substituents on the *meso* and/or β -pyrrole positions of the macrocycle [13, 16, 17, 26].

Different redox behavior is observed for the bis-cobalt corroles 2a and 2b, as compared to the related monocobalt corroles under the same solution conditions. As seen in Figs 1 and S3, compounds 2a and 2b exhibit four reversible oxidations, the first two of which are located at $E_{1/2} = 0.44$ and 0.53 V for **2a** and 0.50 and 0.63 V for 2b. The first two oxidations of the bis-cobalt corroles have a peak to peak separation consistent with one-electron transfer but each process has a current which is reduced by about 50% as compared to that of the other electron abstractions. This suggests the stepwise formation of $\{[(YPh)_2CorCo(PPh_3)]_2Xac\}^+$ and $\{[(YPh)_2CorCo(PPh_3)]_2Xac\}^{2+}$ in the first two oxidations, followed by the formation of {[(YPh)₂CorCo(PPh₃)]₂-Xac⁴⁺ and {[(YPh)₂CorCo(PPh₃)]₂Xac}⁶⁺ in the last two redox processes. The difference in $E_{1/2}$ between the first two oxidations of 2b is 130 mV (see Figs 1 and S3), consistent with a weak to moderate interaction between the two face-to-face macrocycles of this bis-corrole. A smaller $\Delta E_{1/2}$ of 90 mV is seen between the first two one-electron oxidations of 2a under the same solution conditions (Fig. S3), indicating a weaker interaction between the



Fig. 1. Cyclic voltammograms showing stepwise oxidations of the bis-cobalt corrole **2b** in CH₂Cl₂ containing 0.1 M TBAP

two face-to-face corroles in this compound. However, large values of $\Delta E_{1/2}$ (170–280 mV) have been reported for other previously examined face-to-face cobalt corrole dyads [19, 21], which are consistent with a stronger interaction between the two corrole macrocycles of these dyads.

The third oxidations of **2a** and **2b** are negatively shifted by 80–90 mV in potential as compared to the corresponding $E_{1/2}$ values of **1a** and **1b**, while the fourth oxidation of the two bis-corroles occurs at an $E_{1/2}$ which is positively shifted by 110–130 mV from $E_{1/2}$ values for oxidation of the structurally related mono-corroles under the same solution conditions (see Fig. S3).

Examples of the UV-visible spectral changes obtained during controlled potential oxidation of **1b** and **2b** in CH₂Cl₂ are illustrated in Fig. 2. The Soret and Q-bands of **1b** both decrease in intensity upon the first one-electron oxidation at 0.80 V (top left illustrations in Fig. 2), suggesting formation of a Co(III) π -cation radical rather than a Co(IV) corrole in the thin-layer cell. The Soret band further decreases in intensity when the applied oxidizing potential is set at 1.25 V (lower left illustration in Fig. 2) and this is consistent with generation of a Co(III) dication under the given solution conditions. Similar spectral changes were recorded for the bis-cobalt corrole **2b** and these are shown in the right hand side of Fig. 2. The spectral changes accompanying oxidation of **1b** and **2b** indicate



Fig. 2. Thin-layer UV-vis spectral changes of (a) mono-cobalt corrole 1b and (b) bis-cobalt corrole 2b during the oxidations in CH_2Cl_2 containing 0.1 M TBAP



Fig. 3. Cyclic voltammograms showing the reductions of (NH₂Ph)(CH₃Ph)₂CorCo(PPh₃) 1a and [(CH₃Ph)₂CorCo(PPh₃)]₂Xac 2a in CH₂Cl₂ containing 0.1 M TBAP

that the first three redox processes are all macrocyclecentered to give stepwise, $\{(ClPh)_2CorCo^{III}(PPh_3)\}_2Xac\}^+$, $\{[(ClPh)_2CorCo^{III}(PPh_3)]_2Xac\}^{2+}$ and $\{[(ClPh)_2CorCo^{III-}(PPh_3)]_2Xac\}^{4+}$ in CH₂Cl₂.

Two irreversible reductions are observed for the investigated corroles in CH_2Cl_2 containing 0.1 M TBAP and examples of cyclic voltammograms for **1a** and **2a** are illustrated in Fig. 3. The irreversibility of the first reduction is due to the known dissociation of the bound triphenylphosphine (PPh₃) axial ligand upon generation of the Co(II) corrole [13, 26] and this four coordinate species can then be further reduced to its Co(I) form at a more negative potential. The electrogenerated Co(II) corroles can also be irreversiblely reoxidized at anodic peak potentials of -0.04 to -0.21 V (see Table 1) to give short lived Co(III) four-coordinate corroles which then coordinate again the PPh₃ ligand to give back the original species.

The second irreversible reduction of **1a–2b** is assigned as a Co^{II}/Co^I process in CH₂Cl₂ and is associated with a following coupled chemical reaction leading to the proposed formation of an unstable σ -bonded product, [CorCo^{III}(CH₂Cl)]⁻, as previously described in the literature for Co(I) porphyrins and corroles [26, 30].



Scheme 2. Proposed reduction mechanism for the examined corroles in CH_2Cl_2 containing 0.1 M TBAP. The given potentials are for 1a

It should be noted that a second reoxidation peak is observed at -0.01~0.06 V for compounds **1a–2b** in CH₂Cl₂ when the potential scan is reversed after initially scanning beyond the second reduction potential of the neutral compounds (see Table 1 and Fig. 3). These "new" reactions are assigned to a re-oxidation of the proposed σ -bonded corrole as shown in Scheme 2.

A similar reduction mechanism as shown in Scheme 2 is also proposed to occur in PhCN containing 0.1 M TBAP and with added CH₃I. Examples of the cyclic

Solvent	Cpd	Oxidation			Re-oxidation		Reduction	
		3rd	2nd	1st	2nd	1st	1st	2nd
CH ₂ Cl ₂	1a	1.48	1.02	0.48	-0.01	-0.21ª	-0.77 ^a	-1.69ª
	2a	1.57	0.94	0.53, 0.44	0.01	-0.09 ^a	-0.88 ^a	-1.78 ^a
	1b	1.47	1.05	0.56	0.03	-0.13 ^a	-0.73 ^a	-1.64ª
	2b	1.60	0.96	0.63, 0.50	0.06	-0.04 ^a	-0.81 ^a	-1.69ª
PhCN	1a	1.50	1.01	0.61	0.10	-0.16 ^a	-0.73 ^a	-1.67
	2a	1.57	0.93	0.56, 0.50		-0.10 ^a	-0.87 ^a	-1.75

Table 1. Redox potentials (V vs. SCE) of the mono-(1a, 1b) and bis-cobalt corroles (2a, 2b) in CH₂Cl₂, 0.1 M TBAP

^a Irreversible peak potentials at a scan rate of 0.10 V/s.







Fig. 4. Cyclic voltammograms of (a) (NH₂Ph)(CH₃Ph)₂CorCo(PPh₃) 1a and (b) [(CH₃Ph)₂CorCo(PPh₃)]₂Xac 2a in PhCN containing 0.1 M TBAP (a) without and (b) with added CH₃I

voltammograms for 1a and 2a under these conditions are illustrated in Fig. 4. The first reduction is irreversible for both corroles in PhCN (again due to the loss of the PPh₃ ligand after generation of Co(II)), but the second reduction becomes reversible when the solvent is changed from CH₂Cl₂ to PhCN, indicating that the doubly reduced form of the compound is stable in PhCN which does not react with the electrogenerated Co(I) corrole. However, after adding 1-8 equivalents CH₃I to the PhCN solution the second reduction becomes irreversible and a new re-oxidation peak is observed, as is also the case in CH₂Cl₂. This new oxidation peak is assigned to a reaction of the transient σ -bonded cobalt corrole as shown in Scheme 2. The peak currents for the re-oxidation in PhCN containing CH₃I significantly increase when the potential is held at a negative potential (-1.80 for 1a and -1.95 V



Fig. 5. Cyclic voltammograms of the mono- and bis-cobalt corroles coated on EPPG electrode in 1.0 M HClO₄ under air (\longrightarrow) and N₂ (-----). Scan rate = 50 mV/s

for **2a**) for 20 s before reversing the scan and sweeping in a positive direction. The resulting voltammograms under this condition is illustrated in the lower part of Fig. 4 and is consistent with larger quantities of the σ -bonded corrole being generated at the electrode surface under the given experimental conditions.

Electrocatalytic reduction of dioxygen

Figure 5 illustrates cyclic voltammograms for the four corroles adsorbed on an EPPG disk electrode in 1.0 M HClO₄ under N_2 (dashed line) and under air (solid line). A surface reaction is seen at about 0.4 V in the N₂-saturated solution, but no peaks assigned to the electrode reactions of cobalt corrole can be detected from 0.6 to -0.2 V. The lack of a cobalt corrole electrode reaction between 0.6 and -0.2 V under N₂ is consistent with the fact that PPh₃ coordination to Co(III) shifts the potential for the Co^{III}/Co^{II} process to more negative

values located beyond -0.2 V, as described in earlier publications [13, 14].

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A different situation occurs when the corrole-coated electrode is placed in air-saturated 1.0 M HClO₄. This is shown by the solid lines in Fig. 5 where irreversible but well-defined cathodic reduction peaks are observed at $E_{\rm pc} = 0.25$ V for **1a**, 0.24 V for **1b**, 0.19 V for **2a** and 0.22 V for **2b**, at a scan rate of 50 mV/s. As will be shown, these irreversible peaks in the air-saturated HClO₄ solutions correspond to the catalytic reduction of dissolved O₂ to give only H₂O₂.

Peak potentials for the catalytic reduction of oxygen at the corrole-coated electrodes are similar for the two mono-corroles **1a** and **1b** and they are also similar for the two bis-corroles **2a** and **2b**. However, the reduction of O_2 occurs at more negative potentials when the bis-corroles are used as catalysts (Fig. 5).

Measurements were also performed at a rotating disk electrode (RDE). The RDE response in air-saturated 1.0 M HClO₄ is similar for all four examined corroles (Fig. 6a) and is characterized by a half-wave potential located at 0.24–0.29 V.

The number of electrons transferred during the reduction of oxygen was calculated from the magnitude of the steady-state limiting currents that were taken at a fixed potential (-0.1 V) on plateau of the current–voltage curves for the catalytic waves in Fig. 6a. When the amount of O_2 reduction at the corrole-modified electrode is controlled by mass transport alone, the relationship between the limiting current and rotation rate should obey the Levich equation given in Equation 1.

$$j_{\rm lev} = 0.62 n FAD^{2/3} c v^{-1/6} \omega^{1/2}$$
(1)

where j_{lev} is the Levich current, *n* is the number of electrons transferred in the overall electrode reaction, *F* is the Faraday constant (96485 C.mol⁻¹), *A* is the electrode area (cm²), *D* is the dioxygen diffusion coefficient (cm².s⁻¹), *c* is the bulk concentration of O₂ in 1.0 M HClO₄, *v* is the kinematic viscosity of the solution, and ω is the angular rotation rate of the electrode (rad.s⁻¹).

When the reciprocal of the limiting current density is plotted against the reciprocal of the square root of the rotation rate, the resulting straight line (Fig. 6b) obeys the Koutecky–Levich equation (Equation 2).

$$1/j = 1/j_{\rm lev} + 1/j_{\rm k} \tag{2}$$

where *j* is the measured limiting current density $(mA.cm^{-2})$ and j_k is the kinetic current which can be obtained experimentally from the intercept of the Koutecky–Levich plot in Fig. 6b.

$$j_{\rm k} = 10^3 kn F \Gamma c \tag{3}$$

The value of k (M⁻¹.s⁻¹) in Equation 3 is the secondorder rate constant of the reaction that limits the plateau current, Γ (mol.cm⁻²) is the surface concentration of the corrole catalyst, and the other terms have their usual significance as described previously.



Fig. 6. (a) Linear sweep voltammograms at different rotating rate and (b) Koutecky–Levich plots for catalytic reduction of O_2 in air-saturated 1.0 M HClO₄ at a rotating EPPG disk electrode coated with compounds **1a**, **1b** and **2a**, **2b** at a scan rate of 50 mV/s



Fig. 7. Rotating ring-disk electrode voltammograms of (a) **1a**, (b) **1b**, (c) **2a** and (d) **2b** in air-saturated 1.0 M HClO₄ and the potential on the ring electrode maintained at 1.0 V. Rotation rate = 400 rpm and scan rate = 10 mV/s

The slope of a plot obtained by linear regression can then be used to estimate the average number of electrons (*n*) involved in the catalytic reduction of O_2 . As seen in Fig. 6b, the slope of the Koutecky–Levich plots indicates that the number of electrons transferred in the electroreduction process of O_2 is 2.0.

When the products of O_2 reduction consist of a mixture of H_2O_2 and H_2O , values of *n* between 2 and 4 will be

calculated. In the current study, the Koutecky–Levich plots in Fig. 6b show that n = 2.0 for all four investigated

compounds, indicating that the catalytic electroreduction

of O₂ is a simple 2e⁻ transfer process to give only H₂O₂

an RRDE under the same solution conditions. The disk

potential was scanned from 0.5 to -0.2 V at a rotating rate

of 400 rpm while holding the ring potential constant at

1.0 V. This data is shown in Fig. 7 for **1a**, **1b** and **2a**, **2b**,

where the disk current begins increasing at about 0.4 V

and a plateau is reached at about 0.1 V. The ring current

increases throughout the range of the disk potentials

where the disk current rises. The number of electrons

transferred (n) calculated, on the basis of Equation 4 (see

Experimental section), is 2.2 for mono-cobalt corroles

(1a and 1b) and 2.0 for bis-cobalt derivatives (2a and

2b). Based on Equation 5 (see Experimental section), the

calculated amount of H₂O₂ formed upon the reduction of

dioxygen is 90-92% for 1a and 1b, and 100% for 2a and

electron reduction occurres and only H_2O_2 is formed as

the final products when the bis-cobalt corrole is utilized

The RDE and RRDE results both indicate that a two-

2b under the given experimental conditions.

The catalytic reduction of O_2 was also examined at

in acidic media.

as the catalyst in 1.0 M HClO₄. This could be attributed to the lack of a strong face-to face interaction between the two corrole macrocycles on the EPPG electrode surface.

EXPERIMENTAL

Instrumentation

Thin-layer UV-visible spectroelectrochemical experiments were performed with a home-built thin-layer cell which has a light transparent platinum net working electrode. Potentials were applied and monitored with Chi-730C Electrochemical Work Station. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N₂ was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment. Infrared spectra were recorded with Nicolet Nexus 470. MALDI-TOF mass spectra were carried out on a Bruker BIFLEX III ultrahigh resolution.

Cyclic voltammetry was carried out at 298K by using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat or CHI-730C Electrochemical Workstation. A homemade three-electrode cell was used for all electrochemical measurements. A threeelectrode system was used in each case and consisted of a glassy carbon or graphite working electrode (Model MT134, Pine Instrument Co.) for cyclic voltammetry and voltammetry at an RDE and a platinum-ring, graphitedisk electrode combination for voltammetry at the RRDE. A platinum wire served as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode, which was separated from the bulk of the solution by means of a salt bridge of low porosity which contained the solvent/supporting electrolyte mixture. The potential of the SCE is 0.241 V vs. NHE.

The rotating ring-disk electrode (RRDE) was purchased from Pine Instrument Co. and consisted of a platinum ring and a removable edge-plane pyrolytic graphite (EPPG) disk ($A = 0.196 \text{ cm}^2$). A Pine Instrument MSR speed controller was used for the RDE and RRDE experiments. The Pt ring was first polished with 0.05 micron α -alumina powder and then rinsed successively with water and acetone before being activated by cycling the potential between 1.20 and -0.20 V in 1.0 M HClO₄ until reproducible voltammograms were obtained [31, 32].

The corrole catalysts were adsorbed on the electrode surface by means of a dip-coating procedure described in the literature [15, 33]. In this procedure, the freshly polished electrode was dipped in a 1.0 mM catalyst solution of CH_2Cl_2 for 5s, transferred rapidly to pure CH_2Cl_2 for 1–2 s, and then exposed to air where the adhering solvent was rapidly evaporated, leaving the porphyrin catalyst adsorbed on the electrode surface. All experiments were carried out at room temperature. The average number of electrons transferred (*n*) and the amount of H_2O_2 formed in the catalytic reduction of O_2 were determined by the Koutecky–Levich plot [34] and calculated with Equations 4 and 5.

$$n = 4I_{\rm D}/(I_{\rm D} + I_{\rm R}/N) \tag{4}$$

$$\% H_2 O_2 = 100(2I_R/N)/(I_D + I_R/N)$$
 (5)

where $I_{\rm D}$ and $I_{\rm R}$ are the Faradic currents at the disk and ring electrodes, respectively. The intrinsic value of the collection efficiency (N) was determined to be 0.24 using the [Fe(CN)₆]³-/[Fe(CN)₆]⁴ redox couple in 1.0 M KCl.

Chemicals

Reagents and solvents (Sigma-Aldrich or Sinopharm Chemical Reagent Co.) for synthesis and purification are of analytical grade and used as received. Dichloromethane (CH₂Cl₂, 99.8%) was purchased from Sinopharm Chemical Reagent Co. and freshly distilled prior to use. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma-Aldrich Chemical, recrystallized and used as received.

Synthesis of mono-cobalt corroles

5-(4-Methylphenyl)dipyrromethane (475 mg, 2 mmol) or 5-(4-chlorophenyl)dipyrromethane (500 mg, 2 mmol) and 4-nitrobenzaldehyde (150 mg, 1 mmol) were dissolved in CH₃OH (100 mL) and, after which 100 mL HCl ((0.9%)) were added to the solution which was stirred at room temperature for 1 h, after which the products were then extracted with CHCl₃. The organic layer was

collected and washed twice with H_2O , then dried with Na_2SO_4 , filtered and diluted to 200 mL with CHCl₃. After the addition of *p*-chloranil (490 mg, 2 mmol), the mixture was refluxed for 1 h and then chromatographed on a silica column using CH₂Cl₂/hexane as eluent. The free-base nitrocorrole was obtained by evaporating the solvent to dryness.

The nitrocorrole was added into a flask containing $SnCl_2 \cdot 2H_2O$ (450 mg, 2 mmol) in concentrated HCl (50 mL), after which the mixture was stirred at 75 °C for 2 h, then neutralized with ammonia solution (25%) to pH 7. The product was extracted with ethyl acetate and the organic layer was collected and washed three times with water, dried with Na_2SO_4 and then chromatographed on basic alumina column to afford the free-base amino corrole.

The amino-substituted free-base corrole was dissolved in 30 mL CH₃OH containing excess $Co(OAc)_2$ ·4H₂O and triphenylphosphine. The mixture was heated to reflux for 1 h and the progress of the reaction monitored by thinlayer chromatography until the amino containing corrole was consumed. The sample was evaporated to dryness and chromatographed on a basic alumina column using ethyl acetate/hexane as an eluent. The red fraction was collected and the solvent evaporated to dryness.

(**NH**₂**Ph**)(**CH**₃**Ph**)₂**CorCo**(**PPh**₃) **1a.** Yield 33.8 mg, 5.4%. UV-vis (CH₂Cl₂): λ_{max} , nm 394, 564. ¹H NMR (400 MHz, CDCl₃): δ , ppm 8.61 (d, *J* = 12.4 Hz, 2H), 8.36 (m, 2H), 8.16 (s, 2H), 8.04 (s, 4H), 7.85 (s, 2H), 7.70 (m, 2H), 7.44 (s, 6H), 7.05 (d, *J* = 6.6 Hz, 3H), 6.71 (m, 6H), 4.75 (m, 6H), 3.57 (m, 2H), 2.59 (s, 6H). MS (MALDI-TOF): *m/z* calcd. for C₅₇H₄₃CoN₅P 887.26, C₃₉H₂₈CoN₅ 625.61; found [M – PPh₃]⁺ 625.10.

(NH₂Ph)(CIPh)₂CorCo(PPh₃) 1b. Yield 30.0 mg, 4.5%. UV-vis (CH₂Cl₂): λ_{max} , nm 396, 565. ¹H NMR (400 MHz, CDCl₃): δ , ppm 8.62 (d, J = 4.4 Hz, 2H), 8.29 (d, J = 4.8 Hz, 2H), 8.20 (d, J = 4.7 Hz, 2H), 7.99 (d, J = 4.2 Hz, 2H), 767 (m, 4H), 7.54 (m, 4H), 7.47 (m, 6H), 7.04 (m, 3H), 6.68 (m, 6H), 4.66 (m, 6H). MS (MALDI-TOF): *m/z* calcd. for C₅₇H₃₇Cl₂CoN₅P 927.15, C₃₇H₂₂Cl₂CoN₅ 665.06; found [M – PPh₃]⁺ 665.01.

Synthesis of bis-cobalt corroles

A mixture of SOCl₂ (2.5 mL) and 2,7-di-*tert*-butyl-9,9-dimethylxanthenes-4,5-dicarboxylic acid (20 mg, 0.05 mmol) was refluxed for 2 h. After removing excess SOCl₂ by distillation, the corresponding acid chloride was obtained. The amino-substituted free-base monocorrole (57 mg, 0.10 mmol), which was dissolved in CH₂Cl₂ (20 mL), was added to a flask containing Xac and 2 drops of TEA. The mixture was stirred for 2 h at room temperature and then purified by column chromatography on basic alumina with a mixture of ethyl acetate/hexane as eluent to give the final free-base bis-corrole product. Cobalt acetate was reacted with the free-base bis-corrole according to the above described procedure for the synthesis of **1a** and **1b** to yield the bis-cobalt corroles. [(CH₃Ph)₂CorCo(PPh₃)]₂Xac 2a. Yield 41.8 mg, 51.5%. UV-vis (CH₂Cl₂): λ_{max} , nm 396, 563. ¹H NMR (400 MHz, CD₂Cl₂): δ , ppm 9.20 (s, 2H), 8.51 (d, *J* = 4.1 Hz, 4H), 8.25 (m, 4H), 8.03 (m, 6H), 7.70 (m, 8H), 7.53 (d, *J* = 4.3 Hz, 4H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 28.3 Hz, 8H), 6.81 (m, 6H), 6.46 (m, 12H), 6.28 (s, 4H), 5.64 (s, 4H), 4.51 (m, 12H), 2.02 (d, *J* = 31.0 Hz, 12H), 1.82 (s, 6H), 1.46 ppm (s, 18H). MS (MALDI-TOF): *m/z* calcd. for C₁₀₃H₈₂N₁₀O₃Co₂ 1624.52; found 1621.78.

[(CIPh)₂CorCo(PPh₃)]₂Xac 2b. Yield 39.1 mg, 45.9%. UV-vis (CH₂Cl₂): λ_{max} , nm 396, 567. ¹H NMR (400 MHz, CDCl₃): δ, ppm 9.15 (s, 2H), 8.55 (d, *J* = 4.3 Hz, 4H), 8.32 (d, *J* = 8.1 Hz, 2H), 8.23 (d, *J* = 7.9 Hz, 2H), 8.14 (d, *J* = 2.0 Hz, 2H), 8.00 (d, *J* = 4.6 Hz, 4H), 7.77 (d, *J* = 2.2 Hz, 2H), 7.68 (m, 6H), 7.38 (d, *J* = 4.7 Hz, 4H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.13 (s, 4H), 7.00 (d, *J* = 12.3 Hz, 4H), 6.82 (m, 6H), 6.46 (m, 12H), 5.96 (s, 4H), 5.76 (s, 4H), 4.44 (m, 12H), 1.87 (s, 6H), 1.49 ppm (d, *J* = 9.9 Hz, 18H). MS (MALDI-TOF): *m/z* calcd. for C₉₉H₇₀N₁₀O₃Cl₄Co₂ 1704.31; found 1703.27.

CONCLUSION

Two irreversible one-electron reductions were observed for the investigated mono- and bis-cobalt corroles, leading to the formation of a four-coordinate Co(II) corrole and a Co(I) corrole or a transient σ -bonded Co(III) derivatives in CH₂Cl₂ and PhCN containing added CH₃I. The potentials for oxidation of the two bis-cobalt corroles suggest a weak interaction exists between the two corrole macrocycles in their neutral form and each of which undergoes a one-electron abstraction at a different half-wave potential. RDE and RRDE data indicate that the bis-cobalt corroles can be utilized as selective catalysts for the two-electron reduction of dioxygen to give H_2O_2 but no H_2O product is observed either with the mono-cobalt corrole or the face-to-face bis-cobalt derivatives.

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Supporting information

¹H NMR spectra for compounds **1a** and **2a**, UV-visible spectra of the four corroles measured in CH₂Cl₂, cyclic voltammograms showing the oxidations of investigated compounds in CH₂Cl₂ containing 0.1 M TBAP (Figs S1–S3) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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