

# Synthesis and electrochemistry of cobalt tetrabutanotriarylcorroles. Highly selective electrocatalysts for two-electron reduction of dioxygen in acidic and basic media

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Dedicated to Professor Kevin M. Smith on the occasion of his 70th birthday

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**ABSTRACT:** Three  $\beta$ , $\beta'$ -tetrabutano-substituted cobalt(III) triarylcorroles were synthesized and characterized by UV-vis, <sup>1</sup>H NMR spectroscopy and mass spectrometry as well as electrochemistry and spectroelectrochemistry. The examined compounds are represented as butano-(YPh)<sub>3</sub>CorCo(PPh<sub>3</sub>), where Cor represents the core of the corrole and Y is a CH<sub>3</sub>, H or Cl group on the *para*-position of each *meso*-phenyl ring of the macrocycle. Each corrole undergoes two stepwise cobalt-centered reductions leading to formation of Co(II) and Co(I) derivatives in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP. Three reversible one-electron oxidations were observed within potential, ranging from 0.16 to 1.40 V in CH<sub>2</sub>Cl<sub>2</sub>. The first oxidation generates a mixture of Co(III)  $\pi$ -cation radical and Co(IV), while the second oxidation is metal-centered to give the Co(IV) corrole. Each cobalt corrole was examined as a catalyst for electroreduction of O<sub>2</sub> when coated on an edge-plane pyrrolytic graphite electrode in acidic and basic solutions. The results indicate that the cobalt tetrabutanotriarylcorroles can act as selective catalysts for the 2e reduction of molecular oxygen to give H<sub>2</sub>O<sub>2</sub> as the final product under the given solution conditions.

KEYWORDS: cobalt corroles, butano-substitution, electrochemistry, dioxygen reduction.

## **INTRODUCTION**

Cobalt corroles can have potential applications as catalysts for a variety of reactions [1–10]. In this regard, part of our own research efforts have been directed towards the synthesis [6–8, 11–16] and characterization of substituted cobalt corroles as catalysts for the electroreduction of  $O_2$  in acid media [8, 15–18].

We have demonstrated that the addition of substituents on *meso*-phenyl and/or  $\beta$ -pyrrole positions of

triarylcorroles or tetraarylporphyrins containing iron, cobalt or manganese central metal ions can significantly affect the catalytic activity of the compound to act as an electrocatalyst for reduction of dioxygen [18-24]. However, to the best of our knowledge, it is still not known how the addition of butano-groups on the  $\beta$ , $\beta'$ pyrrole positions of a cobalt corrole will affect the electrocatalytic activity of these types of compounds when adsorbed on an electrode surface. This is investigated in the present paper where we have synthesized three cobalt corroles containing four  $\beta$ ,  $\beta'$ -butano substituents and characterized them as to their catalytic activity for reduction of molecular oxygen in acidic and basic solutions when adsorbed the corrole catalyst on an electrode surface. The number of electron transferred and the percentage of  $H_2O_2$  produced in the catalytic

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1a-CH<sub>3</sub>Ph

**2a-**Ph

3a-CIPh

(b) Non-butano-cobalt corroles



Chart 1. Structures of (a) butano-cobalt corroles and (b) non-butano-cobalt corroles

reduction of oxygen were calculated from cyclic and linear sweep voltammetry coupled with measurements at a rotating disk electrode (RDE).

The investigated compounds are represented as  $butano-(YPh)_3CorCo(PPh_3)$ , where Cor is the core of the corrole and Y is CH<sub>3</sub>, H or Cl group on the *para*-position of the phenyl rings of the compound, as seen in Chart 1 which also includes the structure of the related non-butano-substituted cobalt corroles.

Reduction/oxidation potentials and UV-visible spectra of each neutral, oxidized and reduced species were also measured in dichloromethane  $(CH_2Cl_2)$  containing 0.1 M tetra-*n*-butylammonium perchlorate. The effect of the butano substituents on redox potentials and the site of electron transfer is also discussed.

# **RESULTS AND DISCUSSION**

#### Synthesis and characterization

Synthesis of the free-base butano-triarylcorroles was carried out in a mixture of  $CH_3OH/H_2O$  [25]. The synthetic route of butano-(YPh)<sub>3</sub>CorCo<sup>III</sup>(PPh<sub>3</sub>) **1a–3a** 

is shown in Scheme 1. The functionalized pyrrole ring, 4,5,6,7-tetrahydroisoindole, which was synthesized according to a procedure described in the literature [26], was used as starting material to react with a corresponding arylaldehyde. The aldehyde and pyrrole (ratio 1/2) were dissolved in CH<sub>3</sub>OH/H<sub>2</sub>O and stirred for 15 min under N<sub>2</sub> before the addition of HCl as catalyst, and the resulting mixture was stirred for 3 h. The reaction mixture was extracted by CHCl<sub>3</sub> and then oxidized by *p*-chloranil in this solvent to give a mixture including the free-base tetrabutanocorrole. The freebase tetrabutanotriarylcorroles have been synthesized previously by Paolesse and co-workers [27], but due to their poor stability they were immediately oxidized to the corresponding tetrabenzocorroles. Our attempts to purify the mixture by chromatographic separation also failed. To avoid decomposition of the free-base corrole during the purification process, the mixture was directly utilized to react with the salt of cobalt acetate and the yield of cobalt tetrabutanocorroles 1a-3a was 7-8%.

<sup>1</sup>H NMR spectra of butano-(YPh)<sub>3</sub>CorCo(PPh<sub>3</sub>) **1a–3a** were measured in CDCl<sub>2</sub>. As an example, the spectrum of butano-(CH<sub>3</sub>Ph)<sub>3</sub>CorCo(PPh<sub>3</sub>) **1a** is shown in Fig. S1, which also includes the spectrum of (CH<sub>3</sub>Ph)<sub>3</sub>CorCo(PPh<sub>3</sub>)

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Scheme 1. Synthesis routes for compounds 1a–3a

**1b** for a comparison. As seen in Fig. S1a, the resonances at  $\delta = 7.73$ , 7.10 and 6.55 pm are assigned to the *meso*-phenyl protons while the resonances of the triphenylphosphine protons appear at 7.26, 6.72 and 5.07 ppm for **1a**. The resonances of protons on the *para*-position of the *meso*-phenyl appear at 2.51 ppm, while the signals at 3.42 and 2.10–1.12 ppm are attributed to the β-butano protons of **1a**. The δ of triphenylphosphine protons for **1a** are shifted downfield, as compared to the δ values of PPh<sub>3</sub> (7.06, 6.71 and 4.70 ppm) for (CH<sub>3</sub>Ph)<sub>3</sub>CorCo(PPh<sub>3</sub>) **1b** (Fig. S1b), indicating an effect of the β-butano-substituents on the chemical shifts of **1a**. The mass spectra of **1a–3a** display *m/z* peaks at 838.890, 798.433 and 900.609, respectively, which correspond in each case to [M-PPh<sub>3</sub>]<sup>+</sup> species.

The electronic absorption spectra of the butanosubstituted corroles 1a-3a and the related non-butanosubstituted compounds 1b-3b are illustrated in Fig. 1. As seen in the figure, one sharp single Soret band and one weak Q-band were observed for compounds 1b-3bin CH<sub>2</sub>Cl<sub>2</sub>. Compounds 1a-3a also exhibit a sharp Soret band and a weak Q-band in the same solvent. However, a shoulder peak at 408–414 nm can also be observed for 1a-3a, as seen from the solid lines in Fig. 1. The Soret band of 1a-3a was blue-shifted by 10–15 nm while the Q-band was red-shifted by 13–14 nm, as compared to the non-butano-substituted cobalt corroles 1b-3b.

#### Electrochemistry

Electrochemistry of compounds 1a-3a were carried out in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP as supporting electrolyte. Cyclic voltammograms showing the reductions and oxidations are illustrated in Figs 2 and 3, respectively, while the redox potentials of 1a-3a are summarized in Table 1, which also includes the potentials of 1b-3b obtained under the same experimental conditions.

As seen in Fig. 2, each compound undergoes two irreversible reductions in CH<sub>2</sub>Cl<sub>2</sub>. The first reduction peak potentials ( $E_{pc1}$ ) of **1a–3a** range from -1.09 to -0.97 V, while the second peak potentials ( $E_{pc2}$ ) range from -2.03 to -1.93 V vs. SCE. The difference in peak potentials between the first and the second reductions is listed in Table 1 as  $\Delta E_{(1r-2r)}$ , which ranges from 0.92 to 0.96 V. The values are 60–100 mV larger than the  $\Delta E_{(1r-2r)}$  for **1b–3b**.

The first reductions of butano-(YPh)<sub>3</sub>CorCo<sup>III</sup>(PPh<sub>3</sub>) **1a–3a** are assigned to metal-centered processes which involve an electrochemical *EC* mechanism to generate [butano-(YPh)<sub>3</sub>CorCo<sup>II</sup>(PPh<sub>3</sub>)]<sup>-</sup>, which undergoes a rapid



Fig. 1. UV-vis spectra of cobalt butano-corroles and nonbutano-corroles in  $CH_2Cl_2$ 

dissociation of the axialy bound PPh<sub>3</sub> to give fourcoordinate [butano-(YPh)<sub>3</sub>CorCo<sup>II</sup>]<sup>-</sup>. The four coordinate Co(II) species can be further reduced to its Co(I) form at more negative potentials or reoxidized at  $E_{pa} = -0.38$ , -0.37 and -0.29 V to give the neutral cobalt(III) corroles. A similar reduction mechanism was previously proposed for other related cobalt(III) triarylcorroles [16].

Three reversible one-electron oxidations are observed for compounds **1a–3a** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP and examples of cyclic voltammograms are illustrated in Fig. 3, which also includes a cyclic voltammogram of **3b** under the same solution conditions. The first oxidation of **1a–3a** is located at  $E_{1/2} = 0.16-0.26$  V, while the second and third are located at  $E_{1/2} = 0.78-0.81$  V and 1.38–1.40 V, respectively.

The difference in half-wave potentials between the first two oxidations and the second and third oxidations are listed as  $\Delta E_{1/2(2o-1o)}$  and  $\Delta E_{1/2(3o-2o)}$  in Table 1. Both sets of separations are close to 0.60 V for **1a–3a**.



Fig. 2. Cyclic voltammograms showing the reductions of butano-(YPh)<sub>3</sub>CorCo(PPh<sub>3</sub>) 1a-3a in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

Easier oxidations are observed in  $CH_2Cl_2$  for **1a–3a**, as compared to **1b–3b** in the same solvent. For example, the first oxidation of **3a** is shifted negatively by 0.31 V, while the second and third oxidations are negatively shifted by 0.17–0.19 V, as compared to **3b** (see Figs 3c and 3d). This result is consistent with an effect of the four electron-donating butano groups on the  $\beta$ , $\beta'$ -pyrrole positions of compounds **1a–3a**.

#### Spectroelectrochemistry

The singly and doubly reduced corroles in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP were characterized by thinlayer spectroelectrochemistry. The spectral changes of compounds 1a, 2a and 3a during the first and second controlled potential reductions are shown in Fig. 4. The first controlled potential reduction gives a product with a Soret band at 413-418 nm and two Q-bands at 544-547 and 610-626 nm. Generation of the first one-electron reduced product, a Co(II) corrole, in the thin-layer cell is accompanied by a decrease in intensity of the neutral Soret band as a new band grows in, which is red-shifted by 37-42 nm. The intensity of the Soret band for the first reduced corrole was slightly increased, while the peak is blue-shifted during the second controlled potential reduction to give a final Co(I) corrole product with an intense Soret band at 410-419 nm (Fig. 4).

Thin-layer UV-visible spectral changes were also measured for each Co(III) corrole during the first, second and third controlled potential oxidations in  $CH_2Cl_2$ 



**Fig. 3.** Cyclic voltammograms showing the oxidations of butano-(YPh)<sub>3</sub>CorCo(PPh<sub>3</sub>) **1a–3a** and (ClPh)<sub>3</sub>CorCo(PPh<sub>3</sub>) **3b** in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

Table 1. Half-wave potentials (V vs. SCE) of compounds 1a-3a and 1b-3b in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

Compound	Oxidation					Reduction <sup>a</sup>			Ref.
	$\Delta E_{1/2(30-20)}$	3rd	2nd	1st	$\Delta E_{1/2(2\text{o}-1\text{o})}$	Co <sup>III</sup> /Co <sup>II</sup>	Co <sup>II</sup> /Co <sup>I</sup>	$\Delta E_{\rm pc(1r-2r)}$	
1a-CH <sub>3</sub> Ph	0.60	1.38	0.78	0.16	0.62	-1.09	-2.03	0.94	tw
2a-Ph	0.59	1.39	0.80	0.20	0.60	-1.05	-1.97	0.92	tw
3a-ClPh	0.59	1.40	0.81	0.26	0.55	-0.97	-1.93	0.96	tw
1b-CH <sub>3</sub> Ph	0.60	1.54	0.94	0.52	0.42	-0.81	-1.65	0.84	16
<b>2b</b> -Ph	0.64	1.56	0.92	0.51	0.41	-0.75	-1.61	0.86	16
3b-ClPh	0.61	1.59	0.98	0.57	0.41	-0.65	-1.54	0.89	16

<sup>a</sup> Irreversible peak potentials at a scan rate of 0.10 V/s. tw = this work.



Fig. 4. Thin-layer UV-vis spectral changes of cobalt butano-corroles 1a-3a during the controlled potential reductions in  $CH_2Cl_2$  containing 0.1 M TBAP

containing 0.1 M TBAP. These spectral changes are shown in Fig. 5. As seen in the figure, the initial Soret bands of **1a–3a** decrease in intensity and blue-shifted during the first controlled potential oxidation at 0.50 V. The spectral data suggests that a mixture of Co(III) cation radical and Co(IV) are generated after a one-electron abstraction in the thin-layer cell.

The spectral changes shown in the middle of Fig. 5 suggest that a Co(IV) corrole was generated during the second controlled potential oxidation of the Co(III) corrole at 1.10 V. The third controlled potential oxidation at 1.60 V shows that the Soret band decreases in intensity as the oxidation proceeds, but the wavelengths of maximum absorption do not change upon generation of the triply oxidized species. These types of spectral

changes can be interpreted in terms of a corrole ringcentered process.

#### Electrocatalytic reduction of O<sub>2</sub>

The catalytic activity of **1a–3a** towards the reduction of  $O_2$  was examined by cyclic voltammetry and rotating ring-disk electrode voltammetry in aqueous solutions containing 1.0 M HClO<sub>4</sub>. As an example, Fig. 6a illustrates cyclic voltammograms for **2a** adsorbed on an EPPG disk electrode in 1.0 M HClO<sub>4</sub> under N<sub>2</sub> (dashed line) and under air (solid line). Two quasi-reversible reductions are observed under both solution conditions; the first reduction is located at 0.64 V (N<sub>2</sub>) and 0.60 V (air) while the second located at 0.21 V under both N<sub>2</sub>



Fig. 5. Thin-layer UV-vis spectral changes of cobalt butano-corroles during the controlled potential oxidations in  $CH_2Cl_2$  containing 0.1 M TBAP

and air within the potential window of 0.9~ -0.20 V. Similar behavior was previously reported for a cobalt  $\beta$ -brominated triarylcorrole [28]. As will be shown, the second reduction has a higher peak current in HClO<sub>4</sub> under air, which corresponds to the catalytic reduction of dissolved O<sub>2</sub> to give H<sub>2</sub>O<sub>2</sub> as the product.

The number of electrons transferred in the catalytic electroreduction of dioxygen was calculated at a rotating disk electrode (RDE). Each compound has similar RDE responses in air-saturated 1.0 M HClO<sub>4</sub> and an example of the linear sweep voltammograms is shown in Fig. 6b. From the magnitude of the steady-state limiting current values which was taken at a fixed potential (-0.10 V) on the catalytic wave plateau of the current-voltage curve. The slope of the diagnostic Koutecky–Levich plot [29] (Fig. 6c) obtained by linear regression was then used to estimate the average number of electrons (*n*) involved in the catalytic reduction of O<sub>2</sub>.

The Koutecky–Levich plots are interpreted on the basis on Equation 1, where  $j_{lim}$  is the measured limiting current density (mA.cm<sup>-2</sup>),  $j_k$  is the kinetic current, and  $j_{lev}$  is the Levich current which is used to measure the rate of the current-limiting chemical reaction as defined by Equation 2. The value of *n* in Equation 2 is the number of electrons transferred in the overall electrode reaction, *F* is

the Faraday constant (94,685 C.mol<sup>-1</sup>), *A* is the electrode area (cm<sup>2</sup>), *D* is the dioxygen diffusion coefficient (cm<sup>2</sup>.s<sup>-1</sup>), *c* is the bulk concentration of O<sub>2</sub> (M) in 1.0 M HClO<sub>4</sub>, *v* is the kinematic viscosity of the solution, and  $\omega$  is the angular rotation rate (rad.s<sup>-1</sup>) of the electrode.

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

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

The plot shown in Fig. 6c for **2a** indicates that the number of electrons transferred to  $O_2$  in the electroreduction process is 2. The same values of *n* are also obtained for compounds **1a** and **3a**, which are consistent with the catalytic electroreduction in a twoelectron process by using these corroles as catalysts.

Dioxygen can be cathodically reduced to give  $H_2O_2$  or  $H_2O$  in acidic media, which is 2e° or 4e° transfer process. In the current study, the number of electron transferred (*n*) is 2 for all three compounds, proving that the catalytic reduction of  $O_2$  gives  $H_2O_2$  under the given experimental conditions. This is consistent with the effect of the electron-donating and steric interactions involving the  $\beta$ , $\beta$ -butano-substituents of the corrole.

 $H_2O_2$  was the final product formed in the reduction of oxygen and it cannot be further electroreduced to  $H_2O$ 



**Fig. 6.** (a) Cyclic voltammorgams under  $N_2$  (----) and air (----), (b) linear sweep voltammograms at different rotating rate and (c) Koutecky–Levich plot for catalyzed reduction of  $O_2$  in 1.0 M HClO<sub>4</sub> saturated with air at a rotating EPPG disk electrode coated with compound **2a** at a potential scan rate of 50 mV/s

using the corrole as a catalyst. This was confirmed by recording cyclic voltammograms with and without added 0.2 mM  $H_2O_2$  in acidic solution under  $N_2$  using **2a** as the catalyst (Fig. S2).

Oxygen reduction was also carried out in a basic solution (pH = 10) using compound **2a** as catalyst which was adsorbed on an EPPG disk electrode. As seen in Fig. 7a, an irreversible reduction peak was observed at  $E_{pc} = -0.35$  V for both solutions saturated with nitrogen or air. However, a higher peak current is seen in the solution saturated with air, indicating that a catalytic reduction of dissolved O<sub>2</sub> occurred under the given solution conditions. The RDE responses for **2a** adsorbed on the electrode in air-saturated pH10 solution are shown in Fig. 7b and were used to calculate the number of electron transferred during oxygen reduction. The slope of the Koutecky–Levich plot for **2a** (Fig. 7c) indicates that the number of electrons



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Fig. 7. (a) Cyclic voltammograms, (b) linear sweep voltammograms at different rotating rate and (c) Koutecky–Levich plot for catalyzed reduction of  $O_2$  in pH10 solution saturated with air at a rotating EPPG disk electrode coated with compound 2a at a potential scan rate of 50 mV/s

transferred (*n*) for  $O_2$  electroreduction process is 2 in the basic solution.

# 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 an EG&G PAR Model 173 potentiostat or a BiStat electrochemistry station. Time-resolved UV-visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N<sub>2</sub> from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

All reported <sup>1</sup>H NMR spectra were recored on a Bruker Avanc II 400 MHz instrument. Chemical shifts ( $\delta$  ppm) were determined with TMS as the internal reference. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution instrument using alphacyano-4-hydroxy-cinnamic acid as the matrix.

All electrochemical measurements were carried out at 298 K using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat or a CHI-730C Electrochemistry Work Station. A three-electrode system was used and consisted of a graphite working electrode (Model MT134, Pine Instrument Co.) for cyclic voltammetry and rotating disk voltammetry. A platinum wire served as the auxiliary electrode and a home-made saturated calomel electrode (SCE) as the reference electrode, which was separated from the bulk of the solution by means of a salt bridge. The 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  $\alpha$ -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 HClO<sub>4</sub> until reproducible voltammograms are obtained [30, 31].

The corrole catalysts were irreversibly adsorbed on the electrode surface by means of a dip-coating procedure described in the literature [32]. The freshly polished electrode was dipped in a 1.0 mM catalyst solution of  $CH_2Cl_2$  for 5 s, transferred rapidly to pure  $CH_2Cl_2$  for 1-2 s, and then exposed to air where the adhering solvent rapidly evaporated leaving the corrole catalyst adsorbed on the electrode surface. All experiments were carried out at room temperature.

## Chemicals

Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was purchased from Sinopharm Chemical Reagent Co. or Aldrich Chemical Co. and used as received for electrochemistry and spectroelectrochemistry experiments. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika and used as received.

#### Synthesis

The 4,5,6,7-tetrahydroisoindole (8 mmol) and aldehyde (4 mmol) were dissolved in 200 mL CH<sub>3</sub>OH/  $H_2O$  (v/v = 1:1) and then HCl (36%, 2.5 mL) was

added into the solutions. The mixture was stirred under nitrogen for 3 h at room temperature and then extracted with CHCl<sub>3</sub>. The organic layer was collected, washed twice with  $H_2O$  and dried with  $Na_2SO_4$ . After filtered and diluted to 300 mL with CHCl<sub>3</sub>, p-chloranil (4 mmol) was added into the mixture and stirred for 1.5 h at room temperature. After evaporating the mixture to dryness, the residue containing the free-base tetrabutanocorrole was dissolved in a solution of  $CH_3OH$  with  $Co(OAc)_2 \cdot 4H_2O$ and triphenylphosphine. After refluxed for 1 h, the solvent was removed under vacuum, and the mixture was flash chromatographed using neutral alumina column (200~300 mesh) and dichloromethane/hexane (v/v = 1) as eluent. The red fraction was collected and evaporated to dryness. Pure compound was obtained after re-crystallizing in the mixed solvents of methanol and chloroform.

**Butano-(CH<sub>3</sub>Ph)<sub>3</sub>CorCo(PPh<sub>3</sub>) 1a.** Yield 112 mg (7%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm 378, 413, 572. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ, ppm 7.73 (br, 3H), 7.26 (s, 3H), 7.10 (br, 7H), 6.72 (t, 6H), 6.55 (s, 2H), 5.07 (t, 6H), 3.42 (br, 6H), 2.51 (d, 9H), 2.08–1.66 (m, 8H), 1.59 (br, 12H), 1.24 (s, 6H). MS (MALDI-TOF): *m/z* calcd. for [M – PPh<sub>3</sub>]<sup>+</sup> 838.890, found: 840.360.

 $\begin{array}{l} \textbf{Butano-(Ph)_3CorCo(PPh_3) 2a. Yield 122 mg (8\%).} \\ UV-vis (CH_2Cl_2): $\lambda_{max}$, nm 376, 408, 572. $^{1}H NMR (400 MHz, CD_2Cl_2): $\delta$, ppm 8.14 (s, 2H), 7.79 (s, 2H), 7.63 (s, 2H), 7.59–7.45 (br, 4H), 7.39 (d, 3H), 7.21 (s, 5H), 6.77 (s, 6H), 5.54 (s, 6H), 3.58 (br, 4H), 1.85 (brm, 14H), 1.47 (br, 10H), 1.26 (s, 4H). MS (MALDI-TOF): $m/z$ calcd. for [M – PPh_3]* 798.313), found: 798.433. \\ \end{array}$ 

**Butano-(CIPh)**<sub>3</sub>**CorCo(PPh**<sub>3</sub>) **3a.** Yield 112 mg (7%). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm 376, 414, 574. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ, ppm 8.07 (s, 2H), 7.64 (br, 6H), 7.43 (br, 4H), 7.22 (s, 3H), 6.75 (s, 6H), 5.46 (s, 6H), 3.56 (br, 4H), 1.95 (br, 8H), 1.74 (br, 10H), 1.48 (br, 10H). MS (MALDI-TOF): *m/z* calcd. for [M – PPh<sub>3</sub>]<sup>+</sup> 900.609, found: 900.196.

# CONCLUSION

Three cobalt  $\beta$ , $\beta'$ -butano-substituted triarylcorroles were synthesized and characterized as to their electrochemistry and spectroelectrochemistry. The butano-groups lead to easier oxidations and harder reductions of the compound as compared to the related non-butano corroles. The studied compounds are highly selective electrocatalysts for two-electron reduction of dioxygen in both acidic and basic solutions.

## **Supporting information**

<sup>1</sup>H NMR spectra for compound **1a**, **1b** and cyclic voltammorgams of compound **2a** absorbed on an EPPG electrode in 1.0 M HClO<sub>4</sub> with (—) or without 0.2 mM  $H_2O_2(- -)$  under N<sub>2</sub> (Figs S1 and S2) 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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