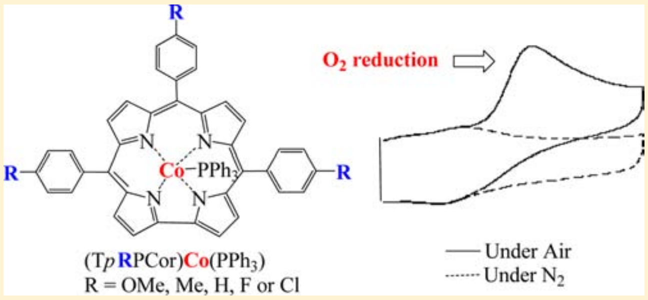
Inorganic Chemistry
Article
pubs.acs.org/IC

Molecular Oxygen Reduction Electrocatalyzed by *meso*-Substituted Cobalt Corroles Coated on Edge-Plane Pyrolytic Graphite Electrodes in Acidic Media

Zhongping Ou,*[†] Aixiang Lü,[†] Deying Meng,[†] Shi Huang,[†] Yuanyuan Fang,[†,‡] Guifen Lu,[†]
and Karl M. Kadish*[‡]

[†]School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China
[‡]Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States

Supporting Information



ABSTRACT: Five *meso*-substituted cobalt(III) corroles were examined as to their catalytic activity for the electoreduction of O_2 when coated on an edge-plane pyrolytic graphite electrode in 1.0 M $HClO_4$. The investigated compounds are represented as (T*p*RPCor)Co(PPh_3), where T*p*RPCor is the trianion of a *para*-substituted triphenylcorrole and R = OMe, Me, H, F, or Cl. Three electrochemical techniques, cyclic voltammetry, linear sweep voltammetry with a rotating disk electrode (RDE), and voltammetry at a rotating ring disk electrode (RRDE), were utilized to evaluate the catalytic activity of the corroles in the reduction of O_2. Cobalt corroles containing electron-withdrawing substituents were shown to be better catalysts than those having electron-donating groups on the three *meso*-phenyl rings of the triarylcorroles.

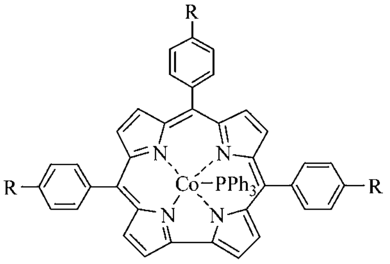
INTRODUCTION

Corroles and metallocorroles have attracted a great deal of interest in recent years[1−7] in part because of improved synthetic methods that make them more readily available than in the past[1,2,6,7] and in part because these compounds have potential applications as catalysts for a variety of reactions.[4,8−21] One of the most frequently studied groups of metallocorroles are the cobalt derivatives, which have been characterized as to their spectral and electrochemical properties under many different solution conditions.[1,2,6,22−39]

Part of our own research efforts have been directed toward the synthesis[13−17,22,24−26] and study of substituted monocobalt and bis-cobalt corroles as catalysts for the electroreduction of O_2 in acidic media.[13−16,20,21] We have demonstrated that substituents on the *meso*-phenyl positions of a triarylcorrole can significantly affect the electrocatalytic properties,[21] but no study has yet been reported on how a systematic change in the electron-donating or electron-withdrawing nature of these substituents will affect the electrocatalytic activity. This is examined in the present work where five cobalt corroles are characterized as O_2 or H_2O_2 reduction catalysts in 1.0 M $HClO_4$.

The investigated compounds are shown in Chart 1 and represented as (T*p*RPCor)Co(PPh_3), where T*p*RPCor is the trianion of *para*-substituted triphenylcorrole and R = OMe, Me, H, F, or Cl. Three electrochemical techniques, cyclic voltammetry, linear sweep voltammetry with a rotating disk electrode (RDE), and voltammetry at a rotating ring disk electrode (RRDE), were utilized to examine the catalytic activity of the corroles in the reduction of O_2. The number of electrons transferred and the percentage of H_2O_2 produced in the catalytic reduction of oxygen were calculated from currents at the disk and ring electrodes and also by using Koutecky−Levich plots.

Chart 1. Structures of Cobalt Corroles



R = OMe, (T*p*OMePCor)Co(PPh_3) **1**
R = Me, (T*p*MePCor)Co(PPh_3) **2**
R = H, (TPCor)Co(PPh_3) **3**
R = F, (T*p*FPCor)Co(PPh_3) **4**
R = Cl, (T*p*ClPCor)Co(PPh_3) **5**

RESULTS AND DISCUSSION

Electrochemistry in CH_2Cl_2, 0.1 M TBAP. Cobalt(III) triarylcorroles have been shown to undergo two one-electron

Received: May 1, 2012
Published: August 3, 2012

dx.doi.org/10.1021/ic300886s | *Inorg. Chem.* 2012, 51, 8890−8896

reductions and up to four one-electron oxidations in nonaqueous media, with the exact number of processes and half-wave potentials depending upon the type of electrochemical solvent, substituents on the macrocycle, and type of bound axial ligand.[21,23,40,41]

The first reduction of the neutral Co(III) compound is metal-centered in all cases and generates an anionic Co(II) corrole that can then be reduced to its Co(I) form at more negative potentials. The first oxidation of the Co(III) corrole might also be metal-centered to generate a Co(IV) corrole with an unoxidized macrocycle or it could be ring-centered and give a Co(III) corrole π-cation radical, the prevailing mechanism depending in part on solution conditions and the presence or absence of any coordinated axial ligands on the Co(III) central metal ion.

An evaluation of redox potentials for the first reduction and first oxidation of cobalt(III) corroles is needed to better understand the use of these compounds as catalysts in the reduction of O_2 and potentials for these two one-electron transfer processes. Compounds **1**−**5** were therefore examined in CH_2Cl_2 prior to carrying out investigations of catalytic O_2 reduction in acid media.

Examples of cyclic voltammograms for **1** and **5** in solutions of CH_2Cl_2 containing 0.1 M TBAP are illustrated in Figure 1. The first reduction is irreversible as previously shown for other five-coordinate cobalt(III) corroles with a bound triphenylphosphine (PPh_3) axial ligand.[23,25] The peak potential for this one-electron transfer process ranges between E_{pc} = −0.65 and −0.84 V depending upon the compound (Table 1). The mechanism is described by the "square scheme" illustrated in Scheme 1 where dissociation of the bound PPh_3 occurs after electron transfer to generate an anionic Co(II) corrole. This four-coordinate species can be further reduced to its Co(I) form at more negative potentials[23,41] or it can be reoxidized via an electrochemical *EC* type mechanism at more positive potentials to give back the neutral five-coordinate Co(III) corrole as shown in Scheme 1. The reoxidation process of the four-coordinate Co(II) corrole occurs at E_{pa} = −0.14 V (**1**) or −0.10 V (**5**) for the two compounds whose cyclic voltammograms are illustrated in Figure 1. Similar reduction and oxidation potentials were measured for the other three corroles (**2**, **3**, and **4**), and values of $E_{1/2}$ or E_p for all five compounds are listed in Table 1.

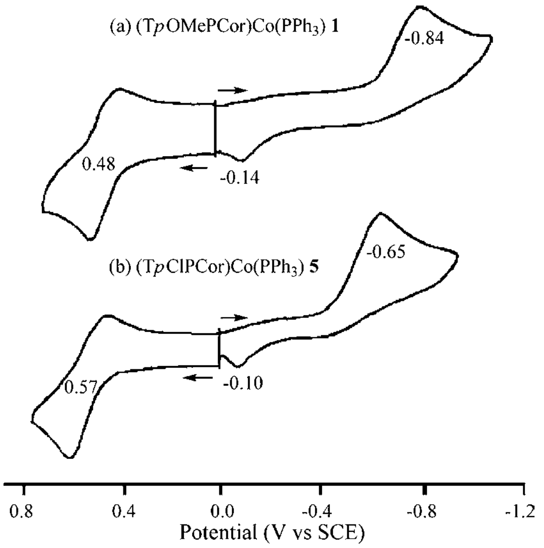
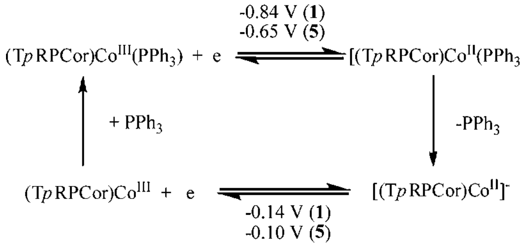


Figure 1. Cyclic voltammograms illustrating the first reduction and first oxidation of (a) (*Tp*OMePCor)Co(PPh_3) **1** and (b) (*Tp*ClPCor)Co(PPh_3) **5** in CH_2Cl_2 containing 0.1 M TBAP at a scan rate of 0.10 V/s. The direction of the scan is given by the arrows.

Scheme 1. Redox Mechanism of Co(III) Corroles in CH_2Cl_2[a]



[a] Redox potentials in the scheme are for compounds **1** and **5** and were taken from Figure 1.

The first oxidation of **1**−**5** is reversible in CH_2Cl_2 and occurs at an $E_{1/2}$ value which varies with the electron-donating or electron-withdrawing nature of substituents on the macrocycle. The reversible potentials are listed in Table 1 and located in a range of $E_{1/2}$ values between 0.48 and 0.57 V vs SCE. This one-electron abstraction is proposed to occur at the corrole π-ring system to give a Co(III) corrole π-cation radical, but a definitive evaluation of the electron tansfer site (metal or macrocycle) was not elucidated in the present study which is concerned with the electrocatalytic reduction of O_2 in acid media.

Electrocatalytic Reduction of O_2. Figure 2a illustrates examples of cyclic voltammograms for **1**, **3**, and **5** adsorbed on an EPPG disk electrode in 1.0 M $HClO_4$ under N_2 (dashed line) and under air (solid line), while Figure 2b shows the cyclic voltammogram obtained at an uncoated EPPG disk electrode under the same solution conditions. A surface reaction is seen at

Table 1. Potentials (V vs SCE) for Redox Reductions of Co(III) Corroles in CH_2Cl_2, 0.1 M TBAP and Catalytic Reduction of O_2 in 1.0 M $HClO_4$

		$[Co^{III}]^+/Co^{III}$,[b]	$Co^{III}/[Co^{II}]^-$,[b]		catalytic reduction of O_2 in acid			
compounds	3σ[a]	$E_{1/2}$	E_{pa}	E_{pc}	E_p, with O_2	$E_{1/2}$[c]	$\%H_2O_2$[d]	*n*
(*Tp*OMePCor)Co(PPh_3) **1**	−0.81	0.48	−0.14	−0.84	0.15	0.22	87.7	2.2
(*Tp*MePCor)Co(PPh_3) **2**	−0.51	0.52	−0.12	−0.81	0.10	0.22	75.6	2.4
(TPCor)Co(PPh_3) **3**	0.00	0.51	−0.10	−0.75	0.12	0.23	72.7	2.6
(*Tp*FPCor)Co(PPh_3) **4**	0.18	0.56	−0.08	−0.72	0.15	0.22	69.2	2.7
(*Tp*ClPCor)Co(PPh_3) **5**	0.69	0.57	−0.10	−0.65	0.15	0.21	64.9	2.8

[a] Sum of substituent constants on the *para*-position of the three phenyl rings. Substituent constants are from ref 46. [b] Data measured by regular cyclic voltammetry in CH_2Cl_2 under N_2. [c] Half wave potential at $i = 0.5i_{max}$, where i_{max} is the limiting current measured at 400 rpm of the RDE. [d] Calculated at $E_{1/2}$.

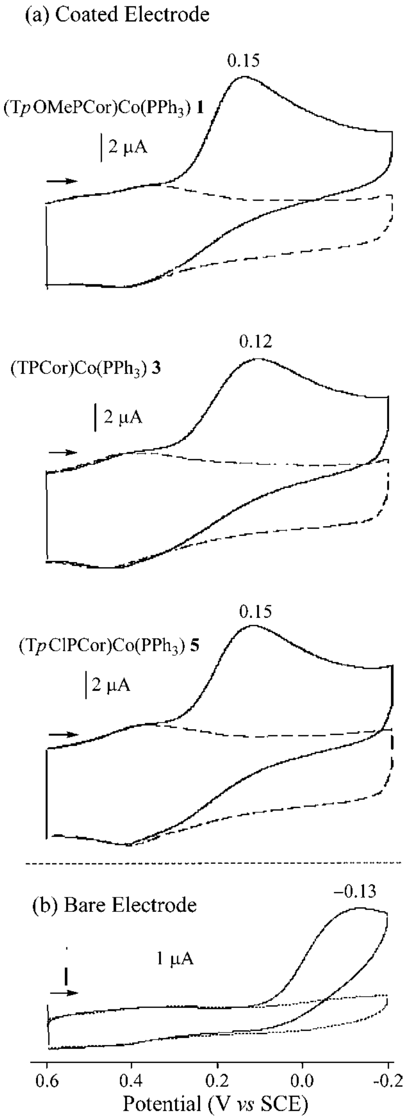


Figure 2. Cyclic voltammorgams of (a) corroles **1**, **3**, and **5** absorbed on an EPPG electrode in 1.0 M $HClO_4$ under N_2 (----) or air (—) and (b) uncoated electrode under N_2 (----) or air (—). Scan rate = 50 mV/s.

the bare or coated electrode at about 0.4 V, but no peaks assigned to the cobalt corrole can observed from 0.60 to −0.20 V. This contrasts with what has been reported for (TPFCor)Co, $(F_5PhMes_2Cor)Co$, $(Mes_3Cor)Co$, or $(Me_4Ph_5Cor)Co$ under the same solution conditions,[13,21] where well-defined processes are observed for the surface adsorbed corroles at $E_{1/2}$ values between 0.30 and 0.40 V vs SCE. The lack of a cobalt corrole reduction between +0.6 and −0.2 V under N_2 (dashed lines in Figure 2a) is consistent with the fact that PPh_3 coordination to Co(III) shifts the half-wave potential for the Co^{III}/Co^{II} process to more negative values located beyond −0.20 V.[42] A similar lack of a cobalt corrole redox process was earlier reported for $(mapc\text{-}t)Co(PPh_3)$, adsorbed on the electrode surface in acid media under N_2[17,43] (where mapc-t is the 5,15-bis-(pentafluorophenyl)-10-(2−3-(1-imidazolyl-methyl)-benzamido-phenyl)corrole).

A different situation occurs when the corrole-coated electrode is placed in 1.0 M $HClO_4$ under air. This is shown by the solid line in Figure 2a where irreversible but well-defined cathodic reduction peaks are exhibited at E_{pc} = 0.15 V (**1**), 0.12 V (**3**), or 0.15 V (**5**) for a scan rate of 50 mV/s. A similar reduction peak is also seen for **2** and **4** at 0.10 and 0.15 V, respectively (Table 1). As will be shown, the irreversible peaks obtained in $HClO_4$ under air correspond to the catalytic reduction of dissolved O_2 to give mainly H_2O_2 with some amount of H_2O. The oxygen in solution is also reduced at a bare EPPG electrode without the corrole, but this reduction occurs at a more negative potential of E_{pc} = −0.13 V for a scan rate of 50 mV/s (Figure 2b).

Peak potentials for the catalytic reduction of oxygen at the corrole-coated electrodes are almost identical for compounds **1** to **5**, which indicates that this reaction is not strongly influenced by differences in the substitution pattern between the catalysts. The O_2 reduction peak in Figure 2a varies from E_p = 0.12 to 0.15 V, and a similar potential (~0.14 V) has been reported when (mapc-t)Co is used as the catalyst for O_2 reduction[17] in an aqueous buffer solution of pH 7. These peak potentials are all significantly lower than what has been reported for O_2 reduction using a β-pyrrole-substituted monocobalt corrole such as $(Me_4Ph_5Cor)Co$[13] (0.38 V) or $(Br_8TF_5PCor)Co$[18] (0.56 V) as the catalyst. The O_2 reduction potentials in Figure 2a are also lower than when the catalyst is a hangman corrole (0.43−0.48 V)[19] or a *meso*-substituted corrole, such as (TPFCor)Co, $(F_5PhMes_2Cor)Co$, or $(Mes_3Cor)Co$.[21]

Measurements were also performed at a rotating disk electrode (RDE) to calculate the number of electrons transferred in the catalytic electroreduction of dioxygen. The RDE response was similar for all corroles (see Figure 3 for compounds **1** and **5**) in air-saturated 1.0 M $HClO_4$ and is characterized by a half-wave potential located at 0.21−0.23 V for **1**−**5**, where i_{max} is the limiting current measured at 400 rpm and $E_{1/2}$ is the potential when $i = 0.5i_{max}$.

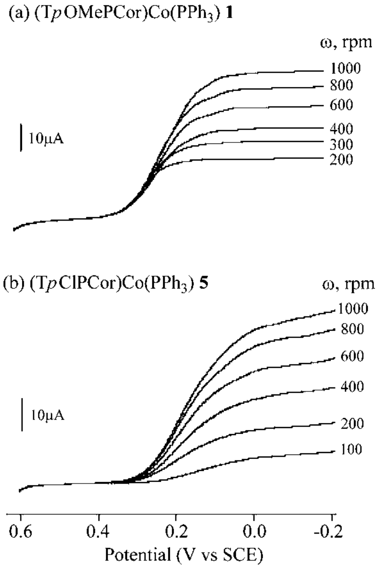


Figure 3. Current−voltage curve for catalytic reduction of O_2 in 1.0 M $HClO_4$ saturated with air at a rotating EPG disk electrode coated with (a) $(TpOMePCor)Co(PPh_3)$ **1** and (b) $(TpClPCor)Co(PPh_3)$ **5**. Electrode rotating rates (ω) are indicated on each curve. Potential scan rate = 50 mV/s.

The number of electrons transferred during oxygen reduction was calculated from the magnitude of the steady-state limiting currents that were taken at a fixed potential on the catalytic wave plateau of the current−voltage curves in Figure 3 (−0.10 V). 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 eq 1.[44]

$$j_{\text{lev}} = 0.62nFAD^{2/3}cv^{-1/6}\omega^{1/2} \quad (1)$$

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 (cm^2), D is the dioxygen diffusion coefficient (cm^2 s^{-1}), c is the bulk concentration of O_2 in 1.0 M $HClO_4$, 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 (Figure 4) obeys the Koutecky–Levich equation.[45]

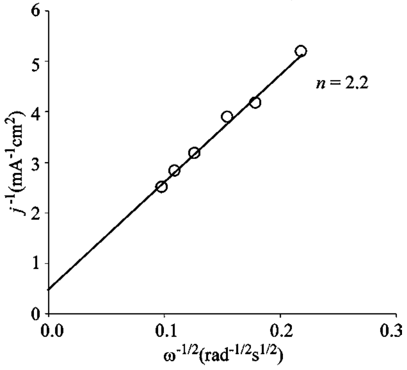
$$1/j = 1/j_{\text{lev}} + 1/j_{\text{k}} \quad (2)$$

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 line in Figure 4.

$$j_k = 10^3 knF\Gamma c \quad (3)$$

The value of k (M^{-1} s^{-1}) is the second-order 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.

(a) (T*p*OMePCor)Co(PPh$_3$) **1**



(b) (T*p*ClPCor)Co(PPh$_3$) **5**

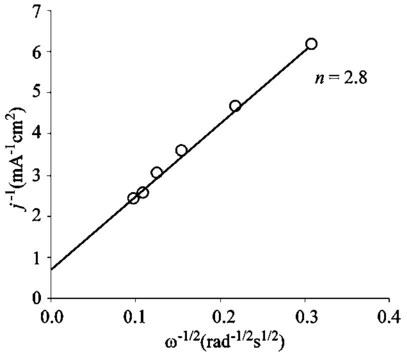


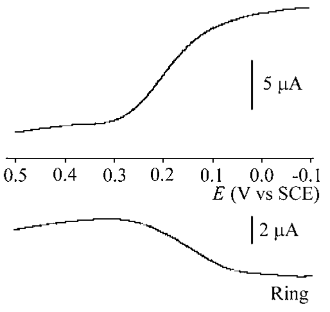
Figure 4. Koutecky–Levich plots for catalyzed reduction of O_2 in 1.0 M $HClO_4$ saturated with air at a rotating EPPG disk electrode coated with (a) (T*p*OMePCor)Co(PPh$_3$) **1** and (b) (T*p*ClPCor)Co(PPh$_3$) **5**.

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. This analysis was carried out, and the number of electrons transferred per dioxygen molecule (n) during the catalytic reduction of O_2 by corroles **1**–**5** was calculated. These values are summarized in Table 1 that also includes reduction potentials for **1**–**5** in air saturated $HClO_4$. The Koutecky–Levich plots for **1**–**5** indicate that the number of electrons transferred to O_2 in the electroreduction process ranges from 2.2 to 2.8 (Table 1), with the largest value being obtained for **5** (n = 2.8) and the smallest for **1** (n = 2.2). These values parallel the electron-donating ability of the *para*-phenyl substituents on the corrole as defined by the value of 3σ, which is taken from the literature.[46]

Dioxygen can be cathodically reduced by 4e to give H_2O or via 2e to give H_2O_2, after which the resulting H_2O_2 might be further reduced to H_2O, catalytically decomposed on the electrode surface, or removed into the bulk of the solution.[17,18] 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 show that the number of electrons transferred (n) ranges from 2.2 to 2.8 for compounds **1**–**5**, indicating that the catalytic electroreduction of O_2 is neither a simple 2e$^-$ transfer process to give H_2O_2 nor a 4e$^-$ process to produce H_2O but is consistent with the formation of both H_2O and H_2O_2 using compounds **1**–**5** as catalysts in acidic media.

The catalytic reduction of O_2 was also examined at an RRDE under the same solution conditions. The disk potential was scanned from 0.6 to −0.1 V at a rotation speed of 400 rpm while holding the ring potential constant at 1.0 V. This data is shown in Figure 5 for compounds **1** and **5** where the disk current begins to increase at about 0.20 V and a plateau is reached at about −0.10 V. The anodic ring current increases throughout the range of the

(a) (T*p*OMePCor)Co(PPh$_3$) **1**



(b) (T*p*ClPCor)Co(PPh$_3$) **5**

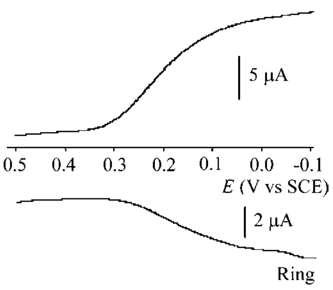


Figure 5. Rotating ring-disk electrode voltammograms of (a) (T*p*OMePCor)Co(PPh$_3$) **1** and (b) (T*p*ClPCor)Co(PPh$_3$) **5** in 1.0 M $HClO_4$ saturated with air and the potential of the ring electrode maintained at 1.0 V. Rotation rate = 100 rpm and scan rate = 10 mV/s.

disk potentials where the disk current rises. On the basis of eq 4,[47] the amount of H_2O_2 formed upon the reduction of dioxygen was calculated as 87.7%, 75.6%, 72.7%, 69.2%, and 64.9% for compounds **1**−**5**, respectively under the given experimental conditions.

$$\%H_2O_2 = 100(2I_R/N)/(I_D + I_R/N) \qquad (4)$$

These results indicate that more H_2O_2 (and less H_2O) is formed when the catalyst is a corrole containg electron-donating OMe groups and less H_2O_2 (and more H_2O) is produced when the utilized corrole has stronger electron-withdrawing substituents.

The j_k values obtained from the intercept of the line in Figure 4 were used to caculate the second-order rate constants k for the formation of (T*p*RPCor)$Co^{III}O_2$ complexes on the electrode surface. The values calculated under the given solution conditions using eq 4 range from 1.0×10^5 to 3.9×10^5 M^{-1} s^{-1}, which are comparable with the values obtained for the catalytic electroreduction of dioxygen at a (F_5PhMes_2Cor)Co (1.7×10^5 M^{-1} s^{-1})[21] or (diethylesterMe_2Et_2P)Co (1.4×10^5 M^{-1} s^{-1})[48] modified electrode.

Electrocatalysis of the Reduction of H_2O_2. Cyclic voltammetric and RDE experiments were carried out in N_2 saturated aqueous acid solutions containing 0.2 mM hydrogen peroxide. As an example, the cyclic and linear sweep voltammograms as well as the related Koutecky−Levich plots for the reduction of H_2O_2 at a rotating graphite electrode coated with (T*p*ClPCor)Co(PPh_3) **5** are shown in Figure 6. The measured peak potential for reduction of H_2O_2 (E_p = −0.02 V) is shifted negatively by 170 mV as compared to E_p for the catalytic reduction of O_2 (0.15 V, Table 1), while the cathodic current under the given experimental conditions is much lower than for the reduction of O_2. The result indicates that the catalytic activity of **5** toward H_2O_2 in 1.0 M $HClO_4$ is weaker than that for the O_2 reduction under the same solution conditions. The cathodic currents in Figure 6a and b should be due to the two-electron reduction of H_2O_2, giving H_2O, and this is confirmed by the Koutecky−Levich plot for the (T*p*ClPCor)Co(PPh_3)/H_2O_2 system where the value of n = 2.0 is consistent with what has been reported for H_2O_2 reduction catalyzed by related cobalt porphyrins.[49,50]

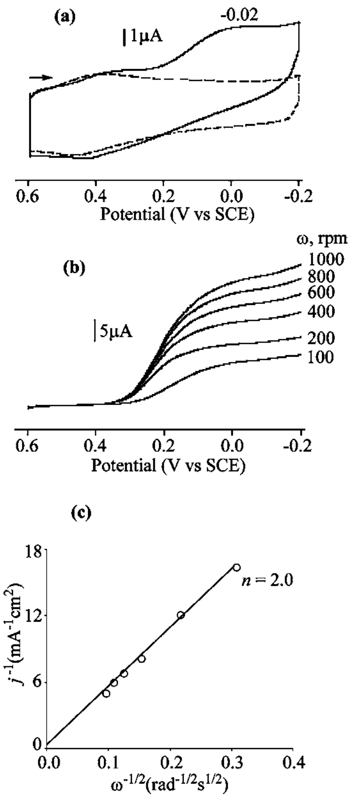


Figure 6. (a) Cyclic voltammorgams of (T*p*ClPCor)$CoPPh_3$ **5** under N_2 without (----) or with 0.2 mM H_2O_2 (—), (b) current−voltage curve for catalyzed reduction of H_2O_2 in 1.0 M $HClO_4$, and (c) the Koutecky−Levich plot. A rotating EPPG disk electrode coated with **5** was employed, scan rate = 50 mV/s.

Effect of the Substituents on the Catalytic Electroreduction of O_2. The nature of electron-donating or electron-withdrawing substituents on the corroles **1**−**5** can be related to the number of electrons transferred (n) as shown by the plot of n vs 3σ[46] in Figure 7. As shown in this figure, compounds **1** and **2**, which contain electron-donating OMe or Me substituents, produce more H_2O_2 than the parent compound **3** as indicated by the lower number of electrons transferred (n = 2.2 to 2.4), while compounds **4** and **5**, which contain electron-withdrawing F or Cl groups, produce less H_2O_2 and more H_2O as indicated by the higher n values of 2.6 to 2.8 under the same experimental conditions. These results indicate that cobalt corroles substituted with the electron-withdrawing groups may have a higher dioxygen-binding ability as was proposed for a series of porphyrins having a different structure.[51]

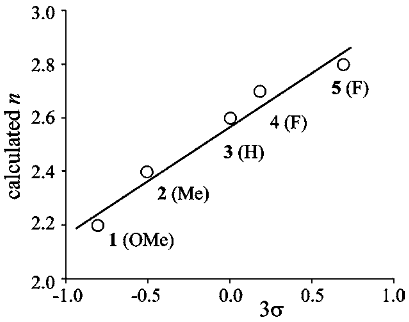


Figure 7. Correlation between the number of electrons transferred (n) during the catalytic reduction of O_2 in 1.0 M $HClO_4$ and the sum of the Hammett substituent constants (3σ) for the groups at the *para*-position of the three phenyl-rings on the corrole macrocycle.

Finally, it should be pointed out that the catalytic activity of the monocobalt corroles will depend not only on the nature of the substituents but also on steric interactions involving bulky substituents on the *meso*-phenyl rings. We previously demonstrated that *ortho*-substituents on phenyl rings of a triphenylcorrole can lead to steric hindrance as indicated by changes in the UV−visible spectra and redox potentials.[52]

With this in mind, monocobalt corroles were divided into three different groups of catalysts on the basis of their structure and catalytic activity (Table 2). The first group of compounds comprises cobalt corroles that contain methyl or fluoro groups on the *ortho*-position of the *meso*-phenyl rings. With one exception, the catalytic electroreduction of O_2 by this type of corrole produces only H_2O_2 via a two-electron transfer pathway (n = 2.0). Hangman corrole in the first group, which contains two *ortho* F groups on the phenyl rings of the compound, was reported to give a mixture of H_2O and H_2O_2 as a product of the O_2 reduction (n > 2.0), and it was proposed that this occurs

Table 2. Number of Electrons Transferred for Catalytic Reduction of O_2 by Different Co(III) Corroles in Acid media

type	catalyst	*ortho*-group[a]	*β*-group[b]	n[c]	ref
I	(mapc-t)Co(PPh_3)	F	none	2.0	17
	(TPFCor)Co	F	none	2.0	21
	(F_5PhMes_2Cor)Co	F, Me	none	2.0	21
	(Mes_2Cor)Co	Me	none	2.0	21
	(hangman)Co[e]	F	none	2.5−2.9	19
II	(T*p*OMePCor)Co(PPh_3) **1**	none	none	2.2	*tw*
	(T*p*MePCor)Co(PPh_3) **2**	none	none	2.4	*tw*
	(TPCor)Co(PPh_3) **3**	none	none	2.6	*tw*
	(T*p*FPCor)Co(PPh_3) **4**	none	none	2.7	*tw*
	(T*p*ClPCor)Co(PPh_3) **5**	none	none	2.8	*tw*
	(Me_4Ph_5Cor)Co	none	Ph,Me	2.9	13
III	(Br_8TF_5PCor)Co	F	Br	4.0[d]	18

[a]Substituents on *ortho*-position of phenyl rings on the corrole macrocycle. [b]Substituents on *β*-pyrrole positions of the corrole macrocycle. [c]Number of electron transferred during the reduction of O_2 catalyzed by cobalt corroles under the given experimental conditions. [d]Measured at pH 4. [e]Hangman represents one of the five macrocycles in ref 19.

because of the presence of an intramolecular proton transfer network in this compound.[19]

The second group of corroles are the nonsterically hindered corroles that have no substituents at the *ortho*-positions of the phenyl rings. The currently investigated compounds **1**−**5**, as well as (Me_4Ph_5Cor)Co[13], which gives H_2O and H_2O_2 through processes involving both two-electron and four-electron transfer reactions (n = 2.2−2.9).

The third group of corroles are the *β*-bromonated derivities of the form of (Br_8TF_5PCor)Co. This compound seems to be the best catalyst reported to date in that it shows a 4e reduction to produce H_2O, even though it also has F substituents on the *ortho*-position.[18] This result indicates that substituents at the *ortho*-positions of the phenyl rings or at the *β*-positions of the corrole macrocycle may significantly affect pathways for the reduction of O_2 via a two- or four-electron transfer process.

In summary, we have examined the electrocatalytic activity of five *meso*-phenyl-substituted cobalt corroles toward the reduction of dioxygen in 1.0 M $HClO_4$. The corroles that contain electron-donating substituents at the *meso*-phenyl ring, when coated on an EPPG electrode, lead mainly to a two-electron reduction of O_2 and the formation of H_2O_2. However, corroles with electron-withdrawing groups on the three *meso*-phenyl rings may catalyze the reduction of O_2 to produce a mixture of H_2O and H_2O_2 under the same solution conditions. The corroles with electron-withdrawing groups on both the three *meso*-phenyl rings and the eight *β*-pyrrole positions are better catalysts than the corroles with electron-donating groups.

EXPERIMENTAL SECTION

Materials. Dichloromethane and perchloric acid and were purchased from Sigma-Aldrich Co. and used as received. The cobalt corroles were synthesized according to procedure reported elsewhere.[53]

Electrochemical Apparatus and Procedures. All electrochemical measurements were carried out with a Chi-730C Electrochemistry Workstation. 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 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 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 μm 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 $HClO_4$ until reproducible voltammograms are obtained.[54,55]

The corrole catalysts were irreversibly adsorbed on the electrode surface by means of a dip-coating procedure described in the literature.[13,56] 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 1−2s, 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 under room temperature.

ASSOCIATED CONTENT

Supporting Information

Cyclic voltammorgams of cobalt corroles **1** and **5** absorbed on an EPPG electrode in 1.0 M $HClO_4$ under N_2 or air at a scan rate of 50 mV/s after the PPh_3 axial ligand of the compound was removed. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zpou2003@yahoo.com (Z.O); kkadish@uh.edu (K.M.K.). Tel: +86 511-88791928 (Z.O); 01-713-7432740 (K.M.K.). Fax: +86 511-88791800 (Z.O.); 01-713-7432745 (K.M.K.)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by grants from the Robert A. Welch Foundation (K.M.K., Grant E-680) and the Natural Science Foundation of China (Grant 21071067 and 21001054).

REFERENCES

(1) Paolesse, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. *2*, pp 201−232.

(2) Erben, C.; Will, S.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. *2*, pp 233−300.

(3) Gross, Z.; Gray, H. B. *Comm. Inorg. Chem.* **2006**, *27*, 61−72.

(4) Aviv, I.; Gross, Z. *Chem. Commun.* **2007**, *20*, 1987−1999.

(5) Aviv-Harel, I.; Gross, Z. *Chem.—Eur. J.* **2009**, *15*, 8382−8394.

(6) Guilard, R.; Barbe, J. M.; Stern, C.; Kadish, K. M. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2003; Vol. *18*, pp 303−349.

(7) McGown, A. J.; Badiei, Y. M.; Leeladee, P.; Prokop, K. A.; DeBeer, S.; Goldberg, D. P. In *Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: Signapore, 2011; Vol. *14*, pp 525−599.

(8) Simkhovich, L.; Luobeznova, I.; Goldberg, I.; Gross, Z. *Chem.—Eur. J.* **2003**, *9*, 201−208.

(9) Mahammed, A.; Gray, H. B.; Meier-Callahan, A. E.; Gross, Z. *J. Am. Chem. Soc.* **2003**, *125*, 1162−1163.

(10) Simkhovich, L.; Goldberg, I.; Gross, Z. *J. Porphyrins Phthalocyanines* **2002**, *6*, 439−444.

(11) Mahammed, A.; Gross, Z. *J. Am. Chem. Soc.* **2005**, *127*, 2883−2887.

(12) Gao, Y.; Liu, J.; Wang, M.; Na, Y.; Akermark, B.; Sun, L. *Tetrahedron.* **2007**, *63*, 1987−1994.

(13) Kadish, K. M.; Fremond, L.; Ou, Z.; Shao, J.; Shi, C.; Anson, F. C.; Burdet, F.; Gros, C. P.; Barbe, J. M.; Guilard, R. *J. Am. Chem. Soc.* **2005**, *127*, 5625−5631.

(14) Kadish, K. M.; Fremond, L.; Burdet, F.; Barbe, J. M.; Gros, C. P.; Guilard, R. *J. Inorg. Biochem.* **2006**, *100*, 858−868.

(15) Guilard, R.; Jerome, F.; Gros, C. P.; Barbe, J. M.; Ou, Z.; Shao, J.; Kadish, K. M. *C. R. Acad. Sci., Ser. IIC: Chim.* **2001**, *4*, 245−254.

(16) Kadish, K. M.; Shao, J.; Ou, Z.; Fremond, L.; Zhan, R.; Burdet, F.; Barbe, J. M.; Gros, C. P.; Guilard, R. *Inorg. Chem.* **2005**, *44*, 6744−6754.

(17) Collman, J. P.; Kaplun, M.; Decreau, R. A. *Dalton Trans.* **2006**, *4*, 554−559.

(18) Schechter, A.; Stanevsky, M.; Mahammed, A.; Gross, Z. *Inorg. Chem.* **2012**, *51*, 22−24.

(19) Dogutan, D. K.; Stoian, S. A.; McGuire, R.; Schwalbe, M.; Teets, T. S.; Nocera, D. G. *J. Am. Chem. Soc.* **2011**, *133*, 131−140.

(20) Kadish, K. M.; Fremond, L.; Shen, J.; Chen, P.; Ohkubo, K.; Fukuzumi, S.; El Ojaimi, M.; Gros, C. P.; Barbe, J. M.; Guilard, R. *Inorg. Chem.* **2009**, *48*, 2571−2582.

(21) Kadish, K. M.; Shen, J.; Fremond, L.; Chen, P.; El, Ojaimi, M.; Chkounda, M.; Gros, C. P.; Barbe, J. M.; Ohkubo, K.; Fukuzumi, S.; Guilard, R. *Inorg. Chem.* **2008**, *47*, 6726−6737.

(22) Will, S.; Lex, J.; Vogel, E.; Adamian, V. A.; Van, Caemelbecke., E.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 5577−5583.

(23) Adamian, V. A.; D'Souza, F.; Licoccia, S.; Di Vona, M. L.; Tassoni, E.; Paolesse, R.; Boschi, T.; Kadish, K. M. *Inorg. Chem.* **1995**, *34*, 532−540.

(24) Kadish, K. M.; Adamian, V. A.; Van, Caemelbecke, E.; Gueletti, E.; Will, S.; Erben, C.; Vogel., E. *J. Am. Chem. Soc.* **1998**, *120*, 11986−11993.

(25) Kadish, K. M.; Koh, W.; Tagliatesta, P.; Sazou, D .; F.; Paolesse, R.; Licoccia, S.; Boschi, T. *Inorg. Chem.* **1992**, *31*, 2305−2313.

(26) Kadish, K. M.; Shao, J.; Ou, Z.; Gros, C. P.; Bolze, F.; Barbe, J. M.; Guilard, R. *Inorg. Chem.* **2003**, *42*, 4062−4070.

(27) Paolesse, R.; Licoccia, S.; Fanciullo, M.; Morgante, E.; Boschi, T. *Inorg. Chim. Acta* **1993**, *203*, 107−114.

(28) Paolesse, R.; Licoccia, S.; Bandoli, G.; Dolmella, A.; Boschi, T. *Inorg. Chem.* **1994**, *33*, 1171−1176.

(29) Licoccia, S.; Paolesse, R. *Struct. Bonding (Berlin, Ger.)* **1995**, *84*, 71−133.

(30) Grodkowski, J.; Neta, P.; Fujita, E.; Mahammed, A.; Simkhovich, L.; Gross, Z. *J. Phys. Chem. A* **2002**, *106*, 4772−4778.

(31) Guilard, R.; Jerome, F.; Barbe, J. M.; Gros, C. P.; Ou, Z.; Shao, J.; Fischer, J.; Weiss, R.; Kadish, K. M. *Inorg. Chem.* **2001**, *40*, 4856−4865.

(32) Kadish, K. M.; Ou, Z.; Shao, J.; Gros, C. P.; Barbe, J. M.; Jerome, F.; Bolze, F.; Burdet, F.; Guilard, R. *Inorg. Chem.* **2002**, *41*, 3990−4005.

(33) Guilard, R.; Gros, C. P.; Bolze, F.; Jerome, F.; Ou, Z.; Shao, J.; Fischer, J.; Weiss, R.; Kadish, K. M. *Inorg. Chem.* **2001**, *40*, 4845−4855.

(34) Guilard, R.; Burdet, F.; Barbe, J. M.; Gros, C. P.; Espinosa, E.; Shao, J.; Ou, Z.; Zhan, R.; Kadish, K. M. *Inorg. Chem.* **2005**, *44*, 3972−3983.

(35) Kadish, K. M.; Shao, J.; Ou, Z.; Zhan, R.; Burdet, F.; Barbe, J. M.; Gros, C. P.; Guilard, R. *Inorg. Chem.* **2005**, *44*, 9023−9038.

(36) Barbe, J. M.; Burdet, F.; Espinosa, E.; Guilard, R. *Eur. J. Inorg. Chem.* **2005**, *6*, 1032−1041.

(37) Barbe, J. M.; Canard, G.; Brandes, S.; Guilard, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3103−3106.

(38) Barbe, J. M.; Canard, G.; Brandes, S.; Guilard, R. *Chem.—Eur. J.* **2007**, *13*, 2118−2129.

(39) Barbe, J. M.; Canard, G.; Brandes, S.; Jerome, F.; Dubois, G.; Guilard, R. *Dalton Trans.* **2004**, 1208−1214.

(40) Mahammed, A.; Giladi, I.; Goldberg, I.; Gross, Z. *Chem.—Eur. J.* **2001**, *7*, 4259−4265.

(41) Kadish, K. M.; Koh, W.; Tagliatesta, P.; Sazou, D.; Paolesse, R.; Licoccia, S.; Boschi, T. *Inorg. Chem.* **1992**, *31*, 2305−2313.

(42) Song, E.; Shi, C.; Anson, F. C. *Langmuir* **1998**, *14*, 4315−4321.

(43) The PPh$_3$ axial ligand is replaced by pyridine when the corrole is dissolved in a mixed solvent system containing CH$_2$Cl$_2$ and pyridine,[40] and the bound pyridine molecule is then removed when the corrole-coated electrode is inserted into an acidic solution. This proceedure was carried out for compounds **1** and **5**, which were examined on the coated graphite electrode by cyclic voltammetry. The current−voltage curves are illustrated in Figure S1 of the Supporting Information. As shown in this figure, a reversible reduction of the Co(III) corrole is observed under N$_2$. The reduction peak potentials for the two examined compounds under air are positively shifted as compared to E_p values for the same corroles containing bound PPh$_3$ (Figure 2a), thus indicating that the PPh$_3$ axial ligand influences $E_{1/2}$ for reduction.

(44) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, Inc: New York, 2001.

(45) Oyama, N.; Anson, F. C. *Anal. Chem.* **1980**, *52*, 1192−1198.

(46) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(47) In the equation, I_D and I_R are the Faradic currents at the disk and ring electrodes, respectively (see Lefevre, M.; Dodelet, J. P. *Electrochim. Acta* **2003**, *48*, 2749−2760). 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.

(48) Durand, R. R.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710−2718.

(49) Liu, H. Y.; Abdailmuhdi, I.; Chang, C. K.; Anson, F. C. *J. Phys. Chem.* **1985**, *89*, 665−670.

(50) Collman, J. P.; Hendricks, N. H.; Leidner, C. R.; Ngameni, E.; L'Her, M. *Inorg. Chem.* **1988**, *27*, 387−393.

(51) Shi, Z.; Zhang, J. *J. Phys. Chem. C* **2007**, *111*, 7084−7090.

(52) Shen, J.; Shao, J.; Ou, Z.; E. W.; Koszarna, B.; Gryko, D. T.; Kadish, K. M. *Inorg. Chem.* **2006**, *45*, 2251−2265.

(53) Paolesse, R.; Nardis, S.; Sagone, F.; Khoury, R. G. *J. Org. Chem.* **2001**, *66*, 550−556.

(54) Conway, B. E.; Angerstein-Kozlowska, H.; Sharp, W. B. A.; Criddle, E. E. *Anal. Chem.* **1973**, *45*, 1331−1336.

(55) Hsueh, K. L.; Conzalez, E. R.; Srinivasan, S. *Electrochim. Acta* **1983**, *28*, 691−697.

(56) Shi, C.; Anson, F. C. *Inorg. Chem.* **1998**, *37*, 1037−1043.