Int. J. Electrochem. Sci., 9 **(2014)** 8131 - 8144

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Probing Solvation and Ion-Pairing Effects on the Redox Behavior of Cyclopentadienyl Cobalt Dicarbonyl, $CpCo(CO)_2$, in the presence of $[B(C_6F_5)_4]^-$ anion

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Received: 14 September 2014 / *Accepted:* 19 October 2014 / *Published:* 28 October 2014

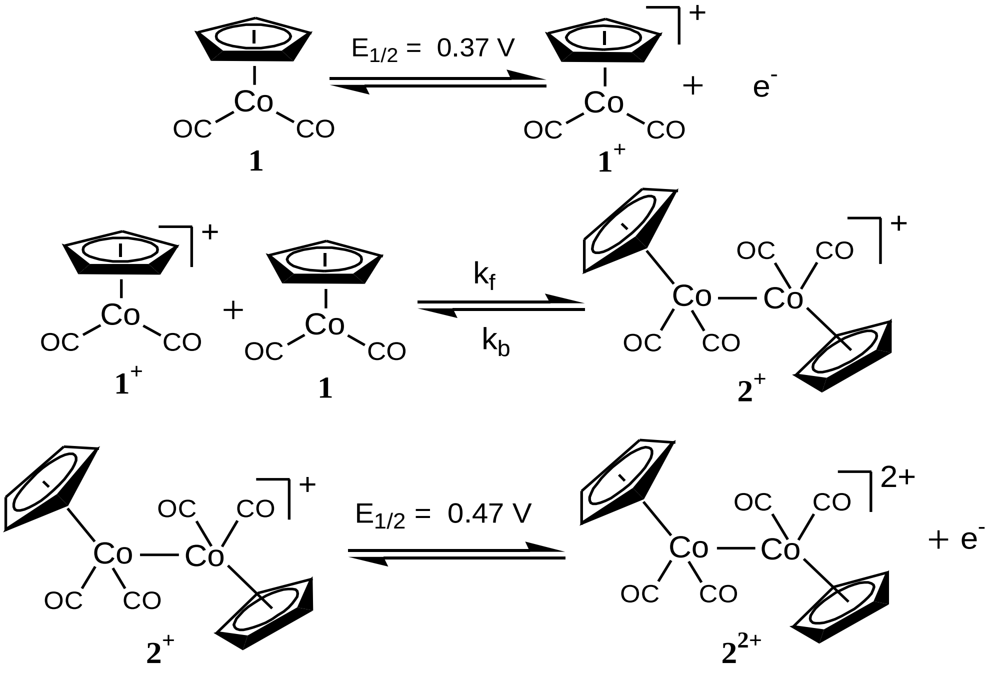
The redox behavior of $CpCo(CO)_2$, **1**, (Cp = η^5-C_5H_5) has been investigated in a number of organic solvents having different polarity and donor strength, in the presence of $[B(C_6F_5)_4]^-$ as the supporting electrolyte anion. Voltammetric oxidation in weakly-donor (donor number, DN_{solv}, ~ 0) and low dielectric (ε) solvents such as benzotrifluoride (BTF, ε = 9.2), 1,2-dichloroethane (DCE, ε = 10.36), and 1,2-difluorobenzene (DFB, ε = 13.8) is identical to that observed in dichloromethane (DCM, ε = 8.9)/$[NBu_4][B(C_6F_5)_4]$ media. Thus, in these gentle solvent/electrolyte media, the electrochemically generated 17e$^-$ cation, $[CpCo(CO)_2]^+$, **1**$^+$, is postulated to undergo "radical-substrate" (R-S) dimerization via reaction with its neutral counterpart, **1**, to eventually form, upon further one-electron oxidation $[Cp_2Co_2(CO)_4]^{2+}$, **2**$^{2+}$. However, this R-S coupling reaction is eliminated when the strongly donor tetrahydrofuran (THF, DN_{solv} = 20) or the highly polar nitromethane (NM, ε = 37.3) are used with $[NBu_4][B(C_6F_5)_4]$, owing to rapid attack by solvent molecules on **1**$^+$ and formation of solvated species that dissociate into different oxidation products such as Cp_2Co. These results attest that the redox behavior of $CpCo(CO)_2$ is highly affected by the sequential changes in solvation energies and/or ion pairing, which can be manipulated via utilization of different solvent/electrolyte media.

Keywords: electrochemical oxidation, Radical-substrate dimerization, $CpCo(CO)_2$, solvation effect, weakly coordinating anions (WCA), and ion-paring.

1. INTRODUCTION

Cyclopentadienyl cobalt dicarbonyl, $CpCo(CO)_2$, **1**, (Cp = η^5-C_5H_5) represents the parent of a historically and practically important family of 18-electron piano-stool metal carbonyl organometallic compounds [1-6]. It is a well-known catalyst for a variety of transformations including cycloaddition, intermolecular cyclization and ring opening of epoxy derivatives [7, 8]. It has been recently used as an activator in the cyclotrimerisation of alkynes in supercritical carbon dioxide (scCO_2) to form benzene derivatives [9]. In spite of these various applications, the oxidative electrochemistry of $CpCo(CO)_2$, **1**, is poorly developed owing to problems arising from either the poor solubility of electrochemically generated 17-electron cation, $[CpCo(CO)_2]^+$, **1**$^+$, in low-polarity and weakly-donor solvents such as dichloromethane (DCM) [10] or the susceptibility of **1**$^+$ to undergo nucleophilic attack [10-12] with solvent and/or supporting electrolyte anions such as $[PF_6]^-$ and $[BF_4]^-$. Enhanced radical stability, however, has been achieved using structural variations of the parent complex through either replacement of one or more of the COs by a donor ligand such as a triphenylphosphine (PPh_3) or by substitution at the Cp ring [13]. In this context, Gennett and co-workers [10] reported that electrochemical oxidation of $CpCo(CO)_2$, **1**, in $CH_2Cl_2/[NBu_4][PF_6]$ using a Pt electrode was complicated by adsorption of **1** and/or the generated product(s) on the electrode surface. This behavior has limited the electrochemical characterization of the generated product(s) at platinum surfaces.

Our previous work on the electrochemical oxidation of $CpCo(CO)_2$ [14-16] showed that overcoming the problems that arise from the poor solubility and/or kinetic stability of the generated products via utilization of gentle solvent/electrolyte media comprising $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$ has enabled the discovery of a unique radical-substrate (R-S) coupling reaction. On the basis of voltammetric, spectroscopic and DFT calculations, it is confirmed that the initially generated 17 e^- cation $[CpCo\ (CO)_2]^+$, **1**$^+$, ($E_{1/2}$ = 0.37 V) reacts with one molecule of its neutral 18 e^- substrate, **1**, via R-S dimerization to form the unsupported Co-Co bond dimer radical cation $[Cp_2Co_2(CO)_4]^+$, **2**$^+$ as shown in Scheme 1. This dimer radical, **2**$^+$, is subsequently oxidized at a potential that is more positive (E_{12} = 0.47) than the initial oxidation of **1** to produce the dimer dication **2**$^{2+}$ (Scheme 1) [14, 15].



Scheme 1. R-S dimerization reaction of **1**

This unique and unexpected oxidative behavior of **1** in CH_2Cl_2 in the presence of the weakly coordinating $[B(C_6F_5)_4]^-$ anion (WCA) has highlighted the importance of solvation and ion-pairing effects in tipping the thermodynamic balance to favor the formation of the dimer radical, thereby allowing its direct voltammetric and spectroscopic observation. Given the important role played by WCA-containing supporting electrolytes in increasing the solubilities of the generated cations and minimizing their ion-pairing effects, we sought out to utilize the same supporting electrolyte, $[NBu_4][B(C_6F_5)_4]$, with other solvents having donor number (DN_{solv}) and dielectric (ε) close to those of dichloromethane (DCM: DN ~ 0, $\varepsilon = 8.9$) such as benzotrifluoride (BTF: DN ~ 0, $\varepsilon = 9.2$), 1,2-dichloroethane (DCE: DN ~ 0, $\varepsilon = 10.36$), and 1,2-difluorobenzene (DFB: DN ~ 0, $\varepsilon = 13.8$) [17] in order to support and generalize the redox behavior observed in DCM to the known family of low polarity and weakly coordinating solvents.

Importantly, the ability of $[B(C_6F_5)_4]^-$ anion to enhance the thermodynamic and kinetic stability of electrogenerated 17 e^- organometallic cations, thereby making them more persistent, particularly in WC solvents as DCM [18-21], is also pursued in both strongly donor (tetrahydrofuran THF: $DN_{solv} = 20$, $\varepsilon = 7.52$) and highly polar (nitromethane NM: $DN_{solv} = 2.7$, $\varepsilon = 37.3$) solvents. The finding of this study underscores the important role of solvation and ion-pairing effects in tuning the thermodynamic and kinetic stability of the electrochemically-generated oxidation product(s) of **1**, thereby allowing for direct voltammetric comparison with the results observed in low nucleophilicity media [14, 15]. Thus, shutting off ion-pairing effects through highly polar solvents and/or inducing nucleophilic attack on $\mathbf{1}^+$ by strongly coordinating solvents is expected to eliminate or outrun the R-S dimerization reaction and therefore generation of different oxidation products.

2. EXPERIMENTAL

This work was undertaken at Prof. W. E. Geiger's laboratory at the University of Vermont, USA. Detailed description of the experimental procedures is available elsewhere [14, 15]. The other details are as follows.

All experiments were conducted under nitrogen using either standard Schlenk techniques or a Vacuum Atmospheres drybox. Reagent-grade dichloromethane (DCM), 1,2-dichloroethane (DCE), benzotrifluoride (BTF), 1,2-difluorobenzene (DFB), tetrahydrofuran (THF), and nitromethane (NM) are dried over CaH_2 and then vacuum distilled. $CpCo(CO)_2$, **1**, was purchased from Strem and used as received. $[NBu_4][B(C_6F_5)_4]$ was prepared by metathesis of $[NBu_4]Br$ with $K[B(C_6F_5)_4]$ (Boulder Scientific, Boulder, Co) and purified as detailed elsewhere [22]. Electrochemical measurements were conducted inside a drybox using a standard three-electrode cell configuration and a PARC 273A potentiostat interfaced to a personal computer. The glassy carbon working electrodes (1.5 mm diameter, Cypress, or 1 mm diameter, from Bioanalytical Systems) are routinely polished with diamond paste, followed by washings with nanopure water, and dried under vacuum. The working electrode for bulk electrolysis was a Pt-basket.

All potentials given in this paper are referenced versus ferrocene/ferrocenium ($Fc^{0/+}$) couple. Mechanistic aspects associated with the redox processes were obtained via cyclic voltammetry (CV) and linear sweep voltammetric (LSV) data. Diagnostic criteria such as shapes and scan rate responses of the CV curves were accomplished via protocols described in reference [23]. IR spectra were recorded with an ATI-Mattson Infinity Series FTIR interfaced to a computer, employing Winfirst software at a resolution of 4 cm^{-1} [24].

3. RESULTS AND DISCUSSION

*3.1. Voltammetric oxidation of $CpCo(CO)_2$, **1**, in DCM/$[NBu_4][B(C_6F_5)_4]$*

Consistent with Gennett's work [10], electrochemical oxidation of $CpCo(CO)_2$ in CH_2Cl_2 solution containing the traditional $[PF_6]^-$ anions is complicated by severe adsorption process as illustrated in inset (a) of Figure 1. Under these conditions, the sharp cathodic peak in the reverse direction of the scan is attributed to adsorption of presumably the electrogenerated $[CpCo(CO)_2][PF_6]$ or other related oxidation product onto the GC electrode surface. This oxidative behavior is drastically changed when the large and weakly coordinating $[B(C_6F_5)_4]^-$ anion is used in the supporting electrolyte. As can be seen in Figure 1b, simple diffusion-controlled oxidation processes are observed at different scan rates when low concentration of $CpCo(CO)_2$, **1**, is used [14, 15]. However, at higher concentration of **1** the voltammetric behavior becomes more complicated by a follow-up second order reaction. This is evidenced by the transformation of the one-electron reversible oxidation process, observed at low concentrations and assigned to $[CpCoCO)_2]^{0/+}$ redox couple ($E_{1/2}$ = 0.37 V *vs* $Fc^{0/+}$) into a two closely-spaced waves as shown in Fig. 2.

On the basis of the electrochemical, IR and ESR data, the oxidative behavior of $CpCo(CO)_2$ was interpreted in terms of a coupling reaction between the 17 e^- cation radical, $[CpCo(CO)_2]^+$, $\mathbf{1}^+$, and the 18e^- starting material, $CpCo(CO)_2$ to initially form a Co-Co bonded dimer radical $[Cp_2Co_2(CO)_4]^+$, $\mathbf{2}^+$ [15]. This intermediate is also electroactive and undergoes further oxidation at a slightly more positive potential ($E_{1/2}$ = 0.47 V*vs* $Fc^{0/+}$), giving rise to the new oxidation feature in the CV curve. Reaction mechanism involving an $EC_{dim}E$ has been proposed as depicted in Scheme 1. Significantly, data obtained from DFT calculations suggested that the long Co-Co distance (3.137 Å) in the dimer cation $[Cp_2Co_2(CO)_4]^+$, $\mathbf{2}^+$, is consistent with its existence as a dissociative equilibrium with its radical/substrate ($[CpCo(CO)_2]^+$/ $CpCo(CO)_2$) partners. However, removal of another electron from the dimer monocation, $\mathbf{2}^+$ caused shortening of the bond between the two cobalt centers in the resulting $[Cp_2Co_2(CO)_4]^{2+}$, $\mathbf{2}^{2+}$ to ~ 2.637 Å, consistent with formation of a “full” metal–metal bond in the dimer dication [15].

Virtually, a very unusual aspect of the oxidative behavior of $CpCo(CO)_2$ system in weakly coordinating CH_2Cl_2/$[NBu_4][B(C_6F_5)_4]$ solvent/electrolyte media was the voltammetric observation of the dimer monocation intermediate ($[Cp_2Co_2(CO)_4]^+$, $\mathbf{2}^+$). Generally, this species has not been observed in other analogous half-sandwich metal carbonyls such as $CpRh(CO)_2$, $CpMn(CO)_3$ and $CpRe(CO)_3$ when their oxidative behavior studied under the same conditions [1]. Indeed, all these systems, without exception, have been confirmed to undergo EC_{dim} reactions upon oxidation in CH_2Cl_2/$[NBu_4][B(C_6F_5)_4]$, where the C_{dim} represents radical/radical dimerization. The marked difference in the $CpCo(CO)_2$ case is explained in terms of sequential changes in solvation energies that enable direct voltammetric detection of the radical/substrate dimerization product. This important finding is the driving force for pursuing the present study to explore the influence of other solvent on the redox behavior of $CpCo(CO)_2$ in the presence of $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte.

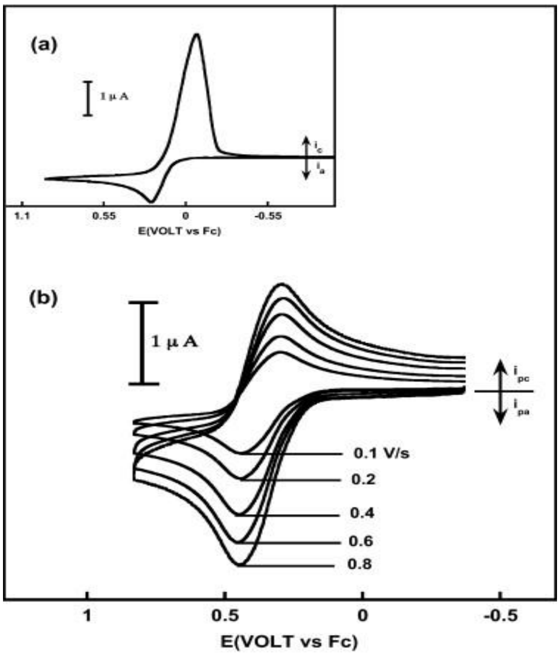


Figure 1. (a) Cyclic Voltammogam of 2 mM **1** in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ at scan rate of 0.1 V/s, 298 K on a 1mm GC disk. (b) Cyclic voltammogams of 0.25 mM **1** in CH_2Cl_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ at different scan rates, 298 K on a 1mm GC disk.

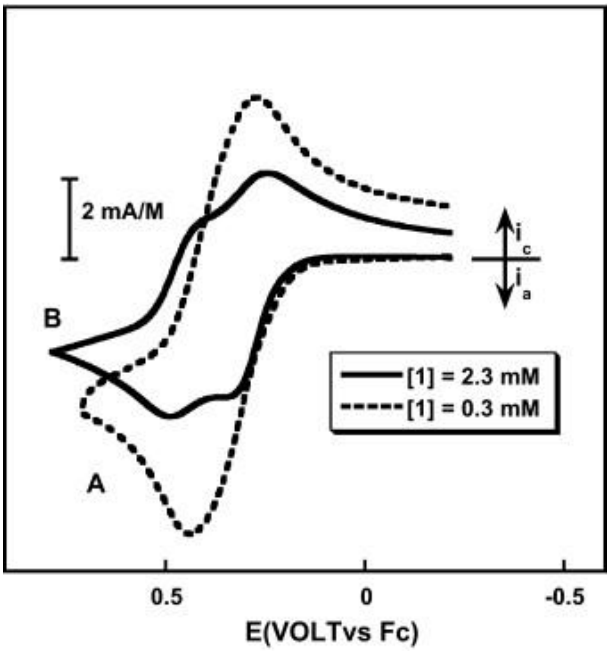


Figure 2. Cyclic voltammograms of **1** in CH_2Cl_2/ 0.05 M $[NBu_4][B(C_6F_5)_4]$ at 298 K, 1 mm GC disk and scan rate of 0.5 V/s at two different concentrations; y-axis is concentration-normalized current.

3.2. Voltammteric oxidation of $CpCo(CO)_2$ in weakly donor solvents containing $[NBu_4][B(C_6F_5)_4]$

The voltammetric behavior of $CpCo(CO)_2$ has been explored in another three low polarity and weakly coordinating solvents including benzotrifluoride (BTF, ε = 9.2), 1,2-dichloroethane (DCE, ε = 10.36), and 1,2 difluorobenzene (DFB, ε= 13.8) containing $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte. As seen in gentle DCM/$[NBu_4][B(C_6F_5)_4]$ media, two closely-spaced reversible oxidation processes are observed (Fig. 3). In spite of the fact that the overall oxidation behavior in the four solvents is very similar, virtually the best voltammetric behavior was noted in DCM. However, the trend implies that the sequential changes in solvation energies and ion pairing effects, which are the apparent reason for direct voltammetric detection of the unusual radical/substrate dimerization products, are qualitatively similar in all these solvents. This finding is important as it reflects that R-S coupling can be detected in other low polarity solvents rather than DCM.

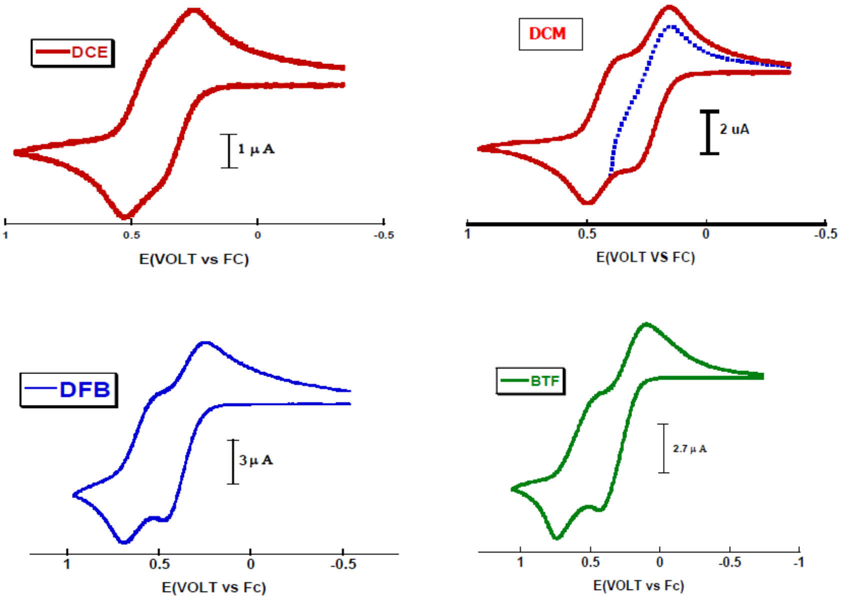


Figure 3. Cyclic voltammogams obtained at scan rate of 0.1 V/s and 1mm GC disk electrode for oxidation of ~ 1.5 mM $CpCo(CO)_2$ using designated solvent and 0.05 M $[NBu_4][B(C_6F_5)_4]$.

3.3. Voltammetric Oxidation of $CpCo(CO)_2$ in THF/$[NBu_4][B(C_6F_5)_4]$

Previous work by McKinney [11] on the chemical oxidation of $CpCo(CO)_2$ with 1 equiv of $AgBF_4$ in tetrahydrofuran (THF) showed that the oxidation process is accompanied by evolution of gas and deposition of silver metal, leading to isolation of air stable off-white solid. IR spectra of that solid suggested the presence of Cp, BF_4^-, and THF but no carbonyl bands. This implies that in THF, the oxidized species is unstable and undergoes loss of the two carbonyl groups, giving rise to non-carbonyl containing product.

The electrochemical behavior of precursor **1** in THF (ε = 7.52, DN_{solv} = 20) containing 0.05 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte shows an irreversible oxidation process at E_{pa} = 0.47 V vs

$Fc^{0/+}$ and a reversible reduction process at a far negative potential, $E_{1/2}$ = -2.30 V vs $Fc^{0/+}$ (Figure 4a). The one-electron nature of the irreversible oxidation wave was estimated by direct comparison of the "steady state" linear sweep voltammogram (LSV) of this wave with that of the known one-electron [25] reduction wave of $CpCo(CO)_2$ to its monoanionic radical,$[CpCo(CO)_2]^-$ as illustrated in Figure 4b. Moreover, as illustrated in Figure 5, the peak potential (E_{pa}) of the oxidation wave is strongly dependent on the scan rate and shifted by about 95 mV to more positive per tenfold increase in the scan rate. This behavior testifies that the oxidation of $CpCo(CO)_2$ in THF is highly irreversible, even in the presence of the $[B(C_6F_5)_4]^-$ anion and using faster scan rates (e.g. 20 V/s) were not enough to obtain a reversible CV. On view of the oxidative behavior of analogous cobalt-polyolefin compounds in THF [26], the irreversible oxidation of **1** is explained in terms of a rapid attack by solvent molecules (THF) on the initially generated 17 e^- radical cation, $[CpCo(CO)_2]^+$, **1**$^+$, followed by breaking of the cobalt-CO bond and formation of the solvated complex, $[CpCo(THF)_2]^+$. Thus, on the CV time scale, it is clearly evident that presence of strongly donor solvents such as (THF) is essential to eliminate the postulated R-S dimerization reaction. However, this solvent (THF) failed to provide the suitable media to obtain persistent solution of the 17 e^- $[CpCo(CO)_2]^+$, even in the presence of $[B(C_6F_5)_4]^-$ anion and using very fast scan rates and/or low temperatures.

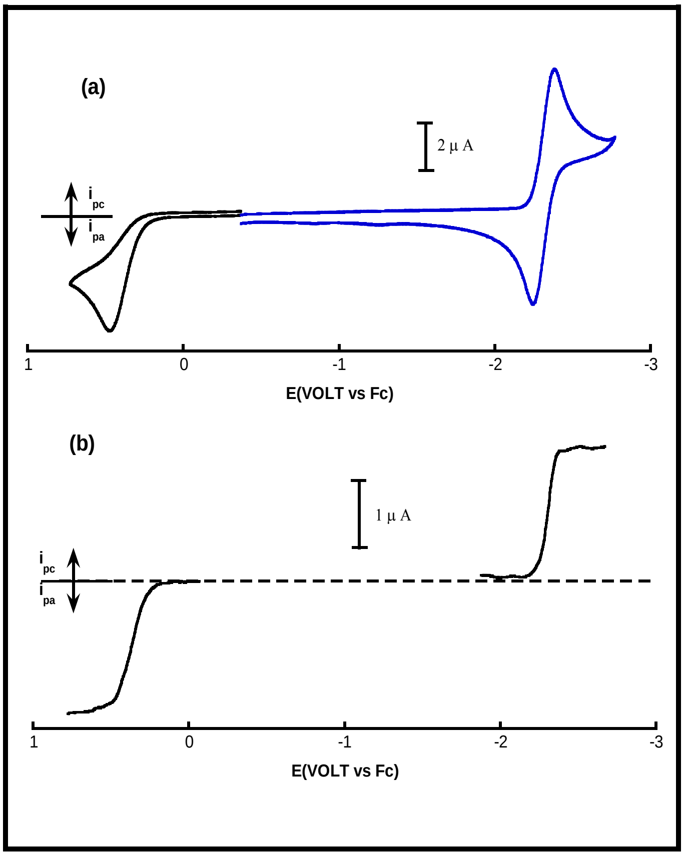


Figure 4. (a) Cyclic voltammograms of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ at scan rate of 200 mV/s, 298K and 1 mm GC disk electrode. (b) Linear sweep voltammograms recorded under the same conditions, scan rate of 5 mV/s.

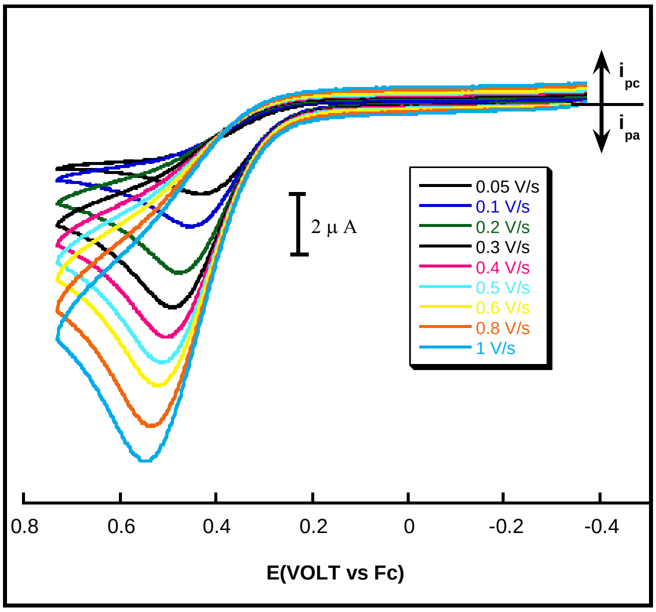


Figure 5. Cyclic voltammograms of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ at different scan rates, 298K and 1 mm GC disk electrode.

In order to gain more insights on the mechanism and to characterize the long-term oxidation products of **1** in this medium, bulk electrolysis of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ was undertaken at applied potential (E_{app}) of 0.75 V vs $Fc^{0/+}$. The measured coulomb count (2.63 C) was consistent with n_{app} = 2.10 e^-/mole, and so reflects the transfer of two electrons/molecule. The color of the solution changed from yellow to light brown. Cyclic and linear sweep voltammetry performed after bulk electrolysis demonstrated the absence of any electroactive products in the anodic direction (from 0 to +2 V) but revealed the existence of two waves in the cathodic direction at $E_{1/2}$ = -1.34 and -2.54 V vs $Fc^{0/+}$, respectively. Apparently, the second wave is indeed chemically and electrochemically reversible, whereas the reversibility of the first process is complicated by a pre-adsorption wave as shown in Figure 6. IR spectra obtained before and after bulk electrolysis (Figure 7) revealed the disappearance of the two carbonyl bands of the starting material, **1** (2021 and 1956 cm^{-1}) as well as the absence of any new carbonyl stretches, thereby indicating the absence of any carbonyl-containing products under these conditions.

Back electrolysis of this solution at a potential that is more negative than the first reduction wave (E_{app} = -1.60 V) was completed with 92% efficiency (2.42 C), based on the amount of charge passed during the forward electrolysis. Cyclic voltammograms recorded after this back electrolysis (Figure 8a) revealed the presence of only two reversible waves at $E_{1/2}$ = -1.34 and -2.54 V vs $Fc^{0/+}$, respectively over the entire potential window of THF (i.e., +1.5 to –2.7 V). These two waves have $E_{1/2}$ values that match those of $[Cp_2Co]^+$ in this medium, thereby tentatively assigned to formation of only cobaltocene under these condition. Interestingly, LSV scans (Figure 8b) obtained after back electrolysis showed an anodic current for the first wave and a totally cathodic current for the second one. This LSV behavior indicates the reduction of $[Cp_2Co]^+$ cations (formed in the forward bulk electrolysis) to neutral Cp_2Co (upon back electrolysis), which is responsible for the first anodic wave, whereas the second cathodic LSV wave represents the reduction of neutral Cp_2Co into the corresponding monoanion $[Cp_2Co]^-$.

The assignment of the two reversible waves for the one-electron oxidation of $[Cp_2Co]^+$ and one-electron reduction of Cp_2Co, respectively, was further supported by different additives of an authentic sample of Cp_2Co to the electrolyzed solution (Fig. 9). This resulted in an increase in the current of the two waves, which was proportional to the added amount of Cp_2Co. Taken together, the combined voltammetric and bulk electrolysis findings in THF/$[NBu_4][B(C_6F_5)_4]$ clearly demonstrate that changing the solvation and ion-pairing effects through increasing the donor strength of the solvent (DN_{solv} = 20) dramatically affects the redox chemistry and the stability of the 17-e^- cation,$[CpCo(CO)_2]^+$, owing to the rapid displacement of the carbonyls by THF molecules to form the corresponding solvated complex, $[CpCo(solv)_2]^{2+}$, which eventually forms the very stable cobaltocenium ion, $[Cp_2Co]^+$, as the final product instead of the proposed R-S dimer radicals, $[Cp_2Co_2(CO)_4]^{+/2}$. This finding is also consistent with the oxidative behavior of **1** in weakly coordinating solvents (bulk electrolysis), regarding the generation of $[Cp_2Co]^+$ as a side product, thereby indicating that this solvent reaction also might occur in low polarity solvents such as CH_2Cl_2 but at much slower rates.

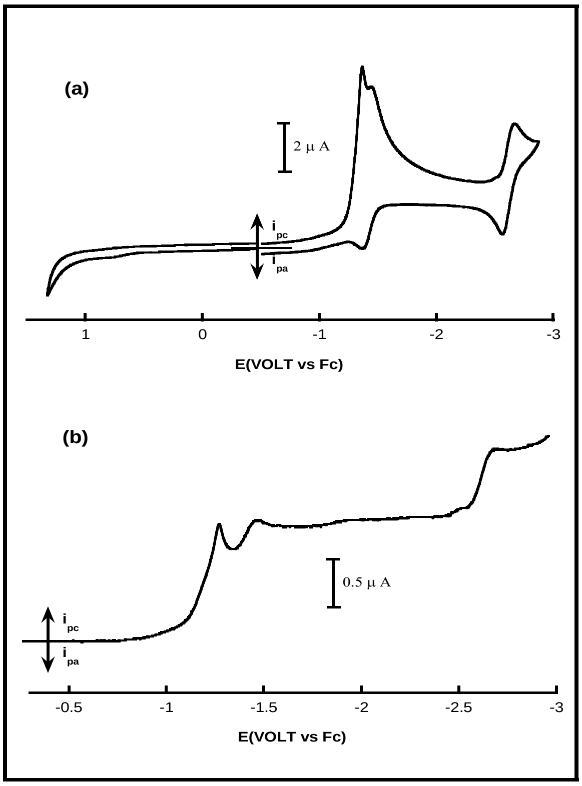


Figure 6. (a) Cyclic voltammograms recorded after bulk electrolysis of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ at E_{app} = 0.75 V, scan rate = 200 mV/s, 298K and 1 mm GC disk electrode. (b) Linear sweep voltammograms recorded under the same conditions, scan rate of 5 mV/s.

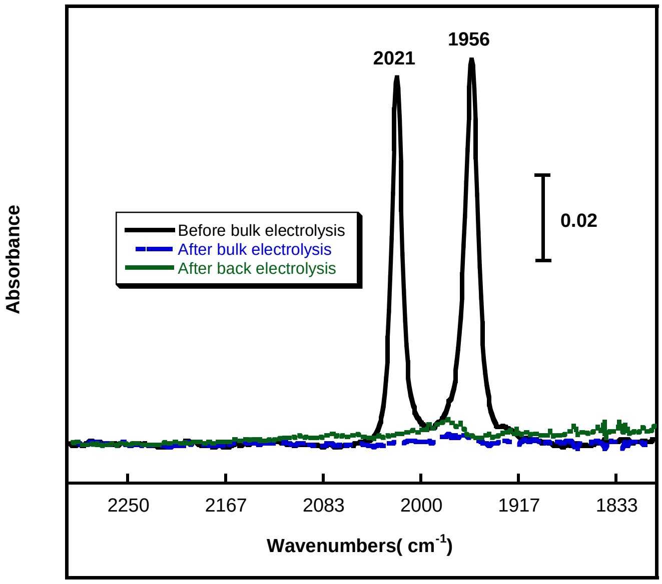


Figure 7. IR spectra of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ obtained before and after bulk electrolysis and after back electrolysis.

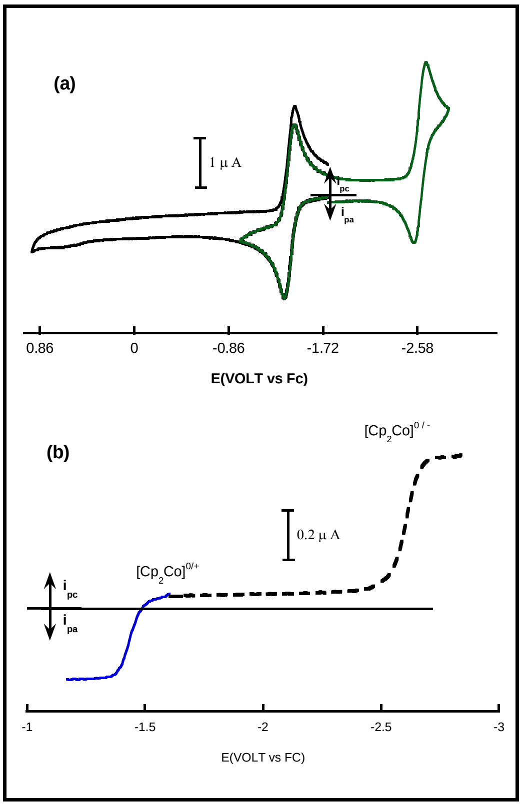


Figure 8. (a) Cyclic voltammograms recorded after back electrolysis of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ at E_{app} = -1.6 V, scan rate = 200 mV/s, 298K and 1 mm GC disk electrode. (b) Linear sweep voltammograms recorded under the same conditions, scan rate of 5 mV/s.

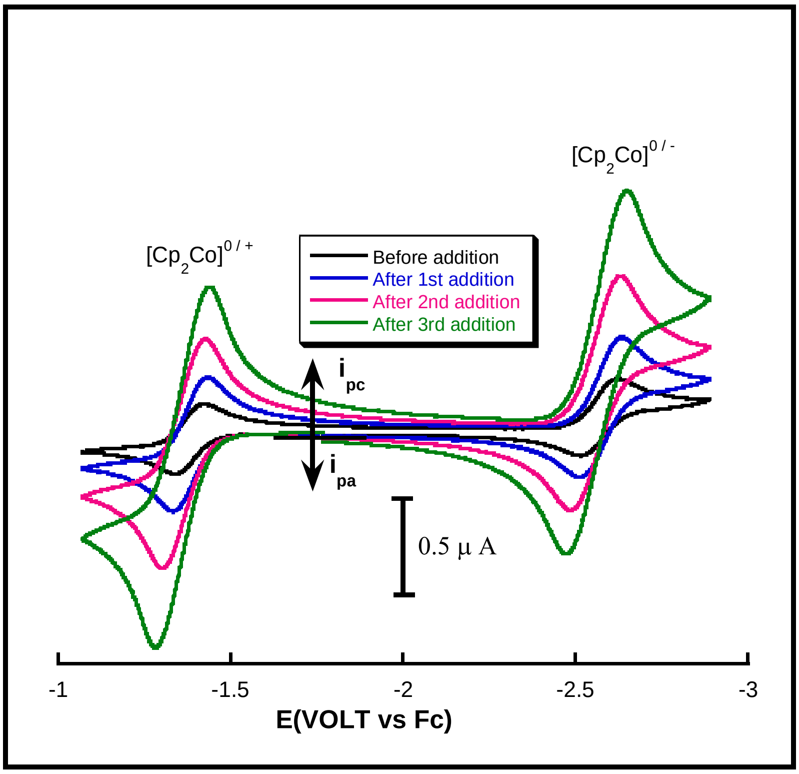


Figure 9. Cyclic voltammograms recorded after back electrolysis of 1.3 mM **1** in THF/0.05 M $[NBu_4][B(C_6F_5)_4]$ at E_{app} = -1.6 V, scan rate = 200 mV/s, 298K and 1 mm GC disk electrode and after addition of successive amounts of Cp_2Co.

3.4. Voltammetric oxidation of CpCo(CO)$_2$ in Nitromethane/[NBu$_4$][B(C$_6$F$_5$)$_4$]

The choice of nitromethane as a solvent for exploring the redox behavior of $CpCo(CO)_2$ is based on the fact that this solvent combines extremely high polarity (ε = 37.3) with relatively weak donor (DN_{solv} = 2.7) strength. These properties are expected to affect the thermodynamic and kinetic stability of the electrochemically generated oxidation products of **1**. As shown in Figure 10, the cyclic voltammograms obtained for **1** in CH_3NO_2 /0.05 M $[NBu_4][B(C_6F_5)_4]$ media exhibit a quasi-reversible oxidation process having an oxidation peak potential (E_{pa}) at 0.24 V and a reduction counterpart (E_{pc}) at -0.1 V. Furthermore, scanning the potential to more negative in the cathodic direction enabled the detection of an additional irreversible wave at E_{pc} of -0.56 V vs $Fc^{0/+}$. Although the overall oxidative behavior is somewhat different from those observed in DCM and THF, it is qualitatively similar to that reported for the structurally analogous $CpRe(CO)_3$, which undergoes radical-radical dimerization, giving rise to a metal-metal bonded dimeric dication $[Cp_2Re_2(CO)_6]^{2+}$ in DCM/$[NBu_4][B(C_6F_5)_4]$ media [18, 27]. Thus, changing the solvation energy while shutting off the ion pairing effects by the high polarity of CH_3NO_2 allowed the radical-radical dimerization reaction to be the favorable pathway for the initially generated $[CpCo(CO)_2]^+$ cation, at least on the CV time scale.

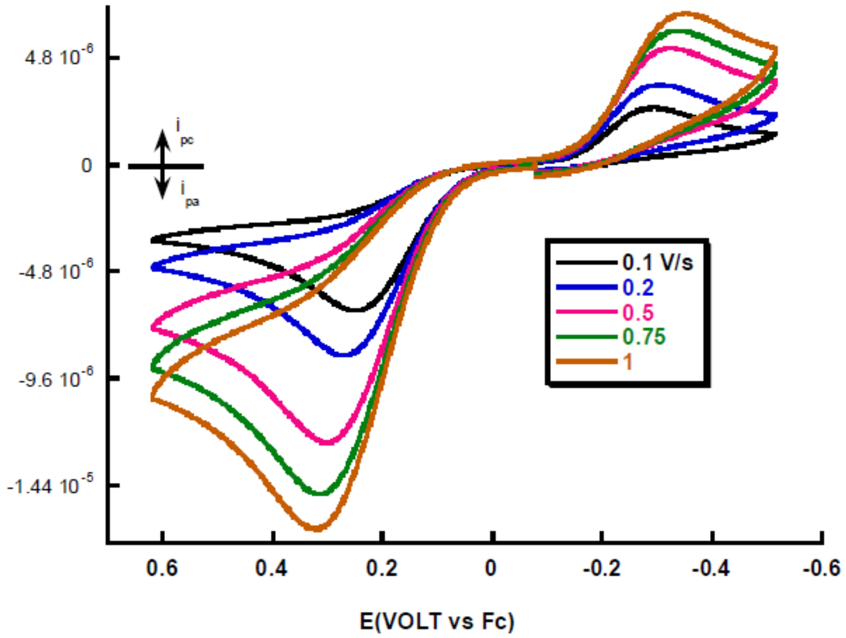


Figure 10. Cyclic voltammograms of 1.5 mM **1** in CH_3NO_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ at designated scan rates, 298K and 1 mm GC disk electrode.

To identify the long-term oxidation products in nitromethane, bulk electrolysis of 1.5 mM $CpCo(CO)_2$, **1**, in CH_3NO_2/0.05 M $[NBu_4][B(C_6F_5)_4]$ was conducted at the potential of the anodic wave, E_{app} = 0.6 V. The passed charge is ~2 F/equiv, as expected for the transfer of 2 electrons per molecule. This is indeed different from the transfer of only one-electron/molecule upon bulk oxidation of $CpRe(CO)_3$ in DCM/$[NBu_4][B(C_6F_5)_4]$ [27], which indicates that the long term oxidation product in CH_3NO_2 might not be the R-R dimer dication, $[Cp_2Co_2(CO)_4]^{2+}$. This is evident by the fact that the cyclic voltammograms obtained after bulk electrolysis did not show the waves characteristic for the dimer dication, as there is no electroactive products have been detected in the anodic direction. Whereas in the cathodic direction, two irreversible reduction waves (E_{pc} = -0.28 and -1.0 V) together with another reversible wave at $E_{1/2}$ = -1.37 V were seen.

On the basis of its formal redox potential, the reversible couple is confidently assigned to the generation of the stable $[Cp_2Co]^+$ cation, which undergoes reduction to form the neutral species Cp_2Co at $E_{1/2}$ = -1.37 V. In order to check the possible formation of any carbonyl-containing products, IR spectra of the solution before and after bulk electrolysis were recorded. Interestingly, as seen in THF, the two carbonyl bands of $CpCo(CO)_2$ at 2023 and 1966 cm^{-1} in CH_3NO_2 were completely disappeared upon bulk oxidation without the appearance of any new bands at higher energy as expected if either $[CpCo(CO)_2]^+$ or $[Cp_2Co_2(CO)_4]^{2+}$ were formed. This behavior is probably consistent with the possibility of nucleophilic attack by the solvent and therefore formation of the solvated species as seen with acetonitrile and THF. Back electrolysis at the potential of the first reduction wave, E_{app} = -0.3 V did not give back any of the starting material, as illustrated by both CVs and IR recorded after back reduction. Taken together, these data indicate that the oxidation of $CpCo(CO)_2$ in nitromethane containing $[NBu_4][B(C_6F_5)_4]$ is not quite simple, as initially thought based on the CV behavior, and most likely involved loss of carbonyl from the oxidized species upon the two-electron oxidation to afford the solvated complex $[CpCo(NM)_3]^{2+}$ as the major product detected at $E_{pc} = -0.3$ V.

The strong dependence of the redox chemistry of $CpCo(CO)_2$ on the nature of solvent, even in the presence of the large and weakly coordinating $[B(C_6F_5)_4]^-$ anion, clearly underscores the crucial role of solvation and ion-paring in controlling the stability and longevity of the one-electron oxidation product of $CpCo(CO)_2$. Thus, in low polarity/weakly coordinating solvents such as DCM, BTF, DCE and DFB, R-S coupling is favored and formation of cobalt-cobalt bonded dimer dication, $[Cp_2Co_2(CO)_4]^{2+}$, is anticipated as the final product under these conditions. In stark contrast, shutting off the ion-pairing effects by a more polar solvents such as CH_3NO_2 or introducing nucleophilic attack on the radical cation by solvents having highly donor strength such as THF allowed for a dramatic change in the overall redox chemistry of $CpCo(CO)_2$, thereby giving rise to different oxidation products.

4. CONCLUSION

The redox behavior of the fundamentally and practically important half-sandwich $CpCo(CO)_2$ has been investigated in media comprising the large and weakly coordinating $[B(C_6F_5)_4]^-$ as the supporting electrolyte anion, and a wide range of nonaqueous solvents, having different polarity and coordinating abilities. The results of this study emphasize that simple alterations in the solvent/electrolyte conditions could lead to new and unexpected redox chemistry of the electrochemically generated $[CpCo(CO)_2]^+$ radical. Thus, increasing the kinetic stability and solubility of the 17 e^- cation, $[CoCp(CO)_2]^+$, along with its tendency to react with the parent, $CpCo(CO)_2$, through "radical-substrate" dimerization pathway to afford the dimer dication, $[Cp_2Co_2(CO)_4]^{2+}$, occurred only in low polarity/nucleophilicity solvents such as DCM, DCE, BTF, and DFB owing to their preferential solvation and ion-pairing effects. Whereas increasing solvent polarity as in CH_3NO_2 or coordinating ability as is the case of THF dramatically affects the thermodynamic and kinetic stability of the radical, thereby leading to formation of solvated complex having the general formula $[CpCo(solv)_n]^{2+}$. Thus, shutting off ion-pairing effects and/or increasing tendency for nucleophilic attack on the generated cation can cause elimination of the R-S dimerization reaction observed in DCM and formation of different redox products.

ACKNOWLEDGEMENT
King Saud University, Deanship of Scientific Research, College of Science Research Center is gratefully acknowledged for supporting this work.

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