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# Electrochemically-Induced CO-Substitution Reactions of $CoCp(CO)_2$: Manipulating the $[CoCp(CO)_2]^+/CoCp(CO)_2$ Radical/Substrate Coupling with $PR_3$ Nucleophiles (R = Ph or OMe)†

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Electrochemical oxidation of fundamentally and practically important half-sandwich compound $CoCp(CO)_2$, **1**, has been undertaken in benign solvent/electrolyte media, comprising $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$, in the presence of strong $PR_3$ nucleophiles ($PR_3 = PPh_3$ or $P(OMe)_3$). In the absence of $PR_3$, the electro-generated 17-electron cation $[CoCp(CO)_2]^+$, $\mathbf{1}^+$ is known to undergo fast coupling with neutral **1** to produce metal-metal bonded dimer cation, $[Co_2Cp_2(CO)_4]^+$, $2^+$ via an unprecedented radical-substrate (R-S) dimerization process. However, generation of $\mathbf{1}^+$ in the presence of 1 or 2 equiv of $PPh_3$ or $P(OMe)_3$ resulted in complete elimination of the R-S coupling and promoted CO-substitution reactions that afforded the corresponding mono- and di-substituted products. Thus, in the presence of $PPh_3$ and via implementation of the "electrochemical switch" approach both $[CoCp(CO)(PPh_3)]^+$ and $[CoCp(PPh_3)_2]^+$ have been successfully generated on synthetically useful timescale, with the former species being the major product. In a marked contrast, reaction of $\mathbf{1}^+$ with 1 equiv $P(OMe)_3$ ligand surprisingly yielded the tri-substituted dication, $[CoCp\{P(OMe)_3\}_3]^{2+}$ as a major product, along with small amount of the mono-substituted congener, $[CoCp\{P(OMe)_3\}(CO)]^+$. The outcomes of this study clearly show the importance of medium effects and the degree of metal-metal interactions in manipulating the properties and reactivity of the generated cation radicals towards nucleophilic attack and redox reactions.

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**Keywords:** Radical-substrate coupling, $CoCp(CO)_2$, CO-substitution, electrochemical switch mechanism, weakly coordinating anions (WCA).

†Dedicated to Prof. William E. Geiger, University of Vermont, USA in recognition of his outstanding contributions to the field of organometallic electrochemistry.

## 1. INTRODUCTION

The reaction chemistry of 17-electron radicals has recently received considerable interest due to their demonstrated high reactivity and their proposed roles in a variety of important stoichiometric and catalytic transformations [1-4]. The main principle that emerged from these studies is that these radicals are generally more reactive than their corresponding 18-electron counterparts in variety of reactions such as ligand substitution, insertion, and disproportionation. For example, the substitution reaction of $[Fe(CO)_3PPh_3]^+$ with nucleophiles occurs $10^9$ times faster than the substitution of its 18-electron analogue, $Fe(CO)_3PPh_3$ [5]. Moreover, many of these 17-electron radicals are proved to dimerize to the 18-electron metal-metal bonded dimers via coupling reactions such as the iron-centered radical, $FeCp(CO)_2$, which exceedingly dimerizes at a near-diffusion-controlled rate to give the corresponding metal-metal bonded dimer $[Fe_2Cp_2(CO)_4]$ [6].

Cyclopentadienyl cobalt dicarbonyl, $CoCp(CO)_2$, **1**, (Cp = $\eta^5$-$C_5H_5$) represents the parent of a historically and practically important family of 18-electron piano-stool metal carbonyl organometallic compounds $[CoCpL_2]$ [7]. It is a well-known catalyst for a variety of transformations including cycloaddition, intermolecular cyclization and ring opening of epoxy derivatives [8, 9]. It has been recently used as an activator in the cyclotrimerisation of alkynes in supercritical carbon dioxide ($scCO_2$) to form benzene derivatives [10]. The oxidative electrochemistry of $CoCp(CO)_2$, **1** is poorly developed due to a set of problems having to do not only with the susceptibility of $[CoCp(CO)_2]^+$, $\mathbf{1}^+$ to nucleophilic attack [11, 12] but also with the poor solubility of $\mathbf{1}^+$ in low-polarity and non-donor solvents such as dichloromethane [13]. These and related problems were overcome via utilization of solvent/electrolyte media of limited nucleophilicity, comprising weakly coordinating anion (WCA), $[B(C_6F_5)_4]^-$, in the supporting electrolyte [14-25]. Thus, in media comprised of $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$, we have previously shown [26, 27], based on voltammetric, spectroscopic, and DFT characterization, that the electrochemical oxidation of $CoCp(CO)_2$, **1**, occurs via unusual radical-substrate (R-S) dimerization in which the initially generated 17 $e^-$ cation, $[CoCp(CO)_2]^+$, $\mathbf{1}^+$, (Eq 1) reacts with the neutral 18 $e^-$ **1** to produce the unique dimer radical cation $[Co_2Cp_2(CO)_4]^+$, $\mathbf{2}^+$, (Eq 2) having unsupported metal-metal bond with bridging ligands. The dimer radical, $\mathbf{2}^+$ is subsequently oxidized to form the dimer dication $\mathbf{2}^{2+}$ (Eq 3). The overall mechanism proposed [27] for the oxidation of **1** in the absence of strong nucleophiles is described by equations 1-3.

$$\text{(Eq 1)}\qquad CoCp(CO)_2 \rightleftharpoons [CoCp(CO)_2]^+ + e^- \qquad E_{1/2}(1) = 0.37\ V$$

$$\text{(Eq 2)}\qquad \underset{\mathbf{1}^+}{[CoCp(CO)_2]^+} + \underset{\mathbf{1}}{CoCp(CO)_2} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\mathbf{2}^+}{[Co_2Cp_2(CO)_4]^+} \qquad K_{eq} = [\mathbf{2}^+]/[\mathbf{1}^+][\mathbf{1}]$$

$$\text{(Eq 3)}\qquad \underset{\mathbf{2}^+}{[Co_2Cp_2(CO)_4]^+} \rightleftharpoons \underset{\mathbf{2}^{2+}}{[Co_2Cp_2(CO)_4]^{2+}} + e^- \qquad E_{1/2}(2) = 0.47\ V$$

In this contribution, we have explored the feasibility of implementing electrochemical switch approach to perform CO-substitution reactions of the highly reactive $[CoCp(CO)_2]^+$ cation, $\mathbf{1}^+$ with donor nucleophiles such as $PPh_3$ and $P(OMe)_3$. Gieger *et al.* [28] have recently shown that the same electrochemical approach provides facile and alternative thermal and photochemical routes to undertake CO-substitution reaction by $PR_3$ nucleophiles, by taking advantage of kinetic stability and longevity of 17-electron cation of $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]^+$ , when generated in $CH_2Cl_2$ containing $[B(C_6F_5)_4]^-$ anion and $PPh_3$. Thus, under these conditions, generation of a quantitative yield of the mono-substituted $[Cr(\eta^6\text{-}C_6H_6)(CO)_2(PPh_3)]^+$ cation in synthetically-useful timescale has been accomplished.

Given that the electrophilicity of the cation, $[CoCp(CO)_2]^+$, makes it susceptible to nucleophilic attack by solvents, electrolytes, and even electron-rich neutral precursors, it is expect that these strong nucleophilies might limit or possibly eliminate reactions with weaker nucleophiles, including the neutral substrate, **1**. Importantly, the approaches and procedures developed in this study have proven efficient in manipulating the reactivity of the $[CoCp(CO)_2]^+$ cation, thereby minimizing or completely eliminating its tendency for dimerization via reaction with parent compound.

## 2. EXPERIMENTAL

A full description of the experimental procedures used in this work is available elsewhere [24, 27]. The other details are as follows.

All experiments were conducted under nitrogen using either standard Schlenk techniques or a Vacuum Atmospheres drybox at the laboratories of *Prof. William Geiger*, University of Vermont, USA. Reagent-grade $CH_2Cl_2$ is dried over $CaH_2$ and then vacuum distilled. $CoCp(CO)_2$, **1**, triphenylphosphine ($PPh_3$), trimethylphosphite ($P(OMe_3)$) were 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 [27]. Electrochemical measurements were undertaken in the 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 Buehler 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 of redox processes were obtained from cyclic voltammetry (CV) data. Diagnostic criteria such as shapes and scan rate responses of the CV curves were accomplished via procedures described elsewhere [29]. IR spectra were recorded with an ATI-Mattson Infinity Series FTIR interfaced to a computer employing Winfirst software at a resolution of 4 $cm^{-1}$.

## 3. RESULTS AND DISCUSSION

### *3.1. Reactions of the 17-electron Cation $[CoCp(CO)_2]^+$ with $PR_3$ Nucleophiles*

### *3.1.1. CO-Substitution Reaction by $PPh_3$*

### *(a) Cyclic Voltammetry*

Experimentally, the electrochemically-induced CO-substitution by $PPh_3$ can be observed directly by performing cyclic voltammetry of $CoCp(CO)_2$, **1**, in the presence of the added $PPh_3$ in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ solvent/electrolyte system. Figure 1(a) illustrates how the presence of 1 equiv of $PPh_3$ affects the CV behavior of **1**. Apparently, the two reversible waves observed for the oxidation of **1** (solid curve) are essentially disappeared or merged into one irreversible anodic wave (dashed curve) at $E_{pa}$ = 0.37 V in the presence of $PPh_3$, with concurrent appearance of new cathodic feature at ca -0.4 V. This new feature, which is shown by repeat scans to be a reversible process, is assigned to the mono-substituted product $[CoCp(CO)(PPh_3)]^+$, ($E_{1/2}$ = -0.38 V vs $Fc^{0/+}$). This assignment is confirmed by addition or measuring the $E_{1/2}$ for the oxidation of an authentic sample of $CoCp(CO)(PPh_3)$ under the same experimental conditions. Importantly, scanning the potential to more negative values, in the cathodic direction, reveals the existence of two additional irreversible waves at $E_{pc}$ = - 1.23 and - 2.10 V, respectively, as shown in Figure 1(b). The wave at $E_{pc}$ = - 1.23 V is assigned to reduction of the di-substituted product, $[CoCp(PPh_3)_2]^+$, to form neutral complex, as previously observed during the anodic oxidation of parent $CoCp(CO)(PPh_3)$ under similar solvent/electrolyte conditions [24].

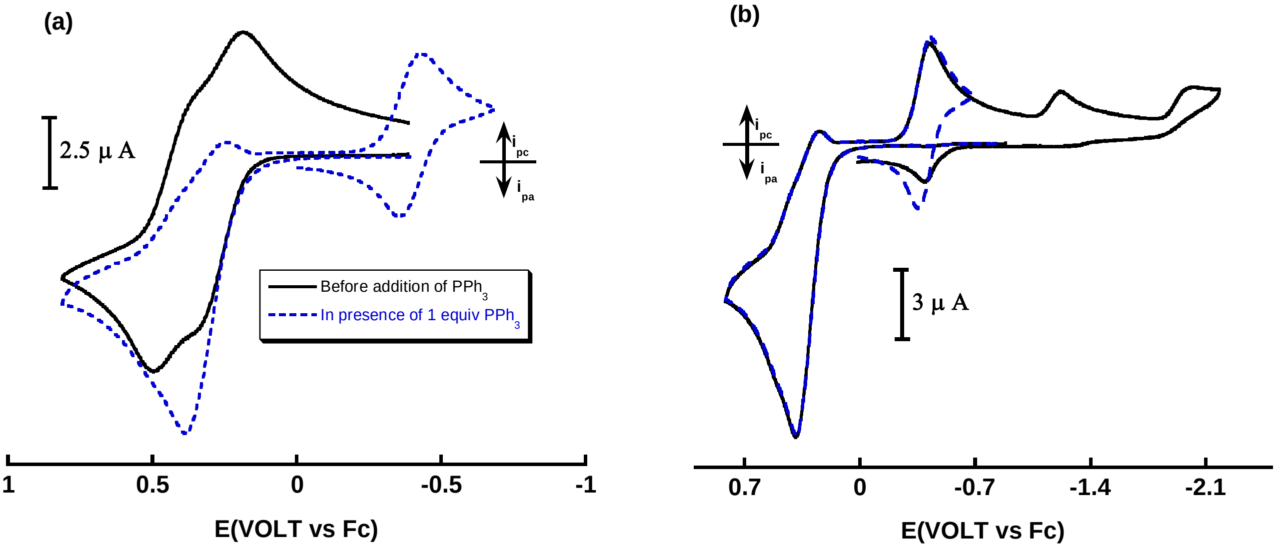


**Figure 1**. (a) Cyclic voltammograms of 1.55 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ at scan rate of 500 mV/s, 298K and 1 mm GC disk electrode, before (black curve) and after (blue curve) addition of 1 equiv of $PPh_3$. (b) CVs under the same conditions but at different switching potentials.

Careful inspection of the voltammetric behavior obtained in the presence of 1 equiv $PPh_3$ as a function of scan rate Figure 2(a) revealed that the second reversible wave of **1**, attributed to the oxidation of the dimer monocation to dimer dication ($[Co_2Cp_2(CO)_4]^{+/2+}$) did not vanish completely at slow scan rates (< 500 mV/s). The chemical reversibility of wave assigned to the $PPh_3$-substitution product is markedly enhanced upon increasing scan rate. This is evident from the current ratio ($i_{rev}/i_{fwd}$), measured for this wave, which increases from 0.73 to 0.97 upon increasing the scan rate from 0.2 V/s to 4 V/s, respectively. This behavior indicates that the $[CoCp(CO)(PPh_3)]^{+/0}$ redox couple is moderately stable under these conditions, and higher scan rates are required to outrun the follow-up chemical reactions. The combined findings of anodic oxidation of **1** in the presence of 1 equiv of $PPh_3$ implies that the R-S dimerization reaction may compete with the CO-substitution reaction at slow scan rates, thereby making the substitution product less stable under these conditions. However, at fast scan rates (≥ 1 V/s) the dimerization reaction is completely eliminated and the substitution product becomes more stable.

The substitution reaction with 2 equiv of $PPh_3$ was also undertaken in an attempt to simplify the chemistry involved in this reaction. Figure 2(b) compares the voltammetric behavior obtained in the presence of 1 and 2 equiv of $PPh_3$, respectively. It is obvious that the two anodic waves of **1** are now merged into one highly irreversible wave, even at low scan rates, in the presence of 2 equiv $PPh_3$ but, interestingly, the shape of the reversible wave of the mono-substituted product is somewhat different from that observed in the presence of 1 equiv of $PPh_3$. Notably, the cathodic part of the wave is shifted to more negative potential and has a plateau-looking shape. This wave shape can be accounted for by the fact that the generated mono-substituted monocation, $[CoCp(CO)(PPh_3)]^+$ might undergo further substitution by the excess $PPh_3$ in the reaction layer to generate the di-substituted product, $[CoCp(PPh_3)_2]^+$. This homogeneous reaction is expected to be a very fast and giving rise to this peculiar shape. Similar findings has been reported by Connelly et al [1, 12] in the chemical oxidation of $CoCp(CO)(PPh_3)$ by $[FeCp_2]^+$, which gave the di-substituted product $[CoCp(PPh_3)_2]^+$ even in absence of excess $PPh_3$. Furthermore, the marked difference in the voltammetric behavior of **1** in the absence and the presence of $PPh_3$ can be accounted for by considering the strong donor ability (basicity) of $PPh_3$ compared to neutral $CoCp(CO)_2$.

Unlike the $Cr(\eta^6\text{-}C_6H_6)(CO)_3$ congener, which gave rise to only one CO-substitution product when anodically oxidized under similar conditions, voltammetric behavior of **1** in the presence of 1 or 2 equiv $PPh_3$ is consistent with the generation of a mixture of the mono- and di-substituted products. The difference between the two conceptually and structurally related complexes could be attributed to the high reactivity of the 17-electron cation, $[CoCp(CO)_2]^+$, which known to undergo coupling reaction with its neutral counterpart, compare to the highly stable and long-lived $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]^+$ cation.

### *(b) Bulk Coulometry*

With the possibility of the “electrochemical switch mechanism” for performing CO-substitution reactions on the CV time scale of 10 s, it seemed also necessary to check the long-term stability and isolation of these substitution products. Therefore, bulk electrolysis experiments of **1** were carried out in the presence of either 1 or 2 equiv of $PPh_3$ at ambient temperature as well as 273 K. Initially oxidative bulk electrolysis at 298 K for 1-2 mM $CoCp(CO)_2$ in the presence of 1 equiv $PPh_3$ at $E_{appl}$ = 0.75 V vs $Fc^{0/+}$, using a Pt basket as the working electrode, released 1.2 F and generated a having a greenish-brown color. Subsequent cyclic (CV) and linear sweep (LSV) voltammetric scans showed the presence of several products from which the mono-substituted product, $[CoCp(CO)(PPh_3)]^+$, could not be identified. Given the expected kinetic stabilization of the generated product(s) at lower temperature, thereby simplify the substitution reaction, anodic bulk electrolysis of **1** in the presence of either 1 or 2 equiv of $PPh_3$ was conducted, at the similar experimental procedures but at 273 K. Specifically, for conditions of 1.55 mM **1**, and 2 equiv $PPh_3$ in $CH_2Cl_2$/0.05M $[NBu_4][B(C_6F_5)_4]$ and 273K, exhaustive electrolysis at $E_{appl}$ = 0.7 V gave the mono-substituted product, $[CoCp(CO)(PPh_3)]^+$, ($E_{1/2}$ = -0.38 V, see Fig. 3) in ~ 55 % yield, as evidenced by CV and LSV scans obtained after bulk electrolysis. Importantly, scanning the potential into more negative values (Figure 3) led to detection of the di-substituted monocation, $[CoCp(PPh_3)_2]^+$, which is identified by its characteristic $E_{1/2}$ value of -1.2 V together with regeneration of neutral starting material, **1**.

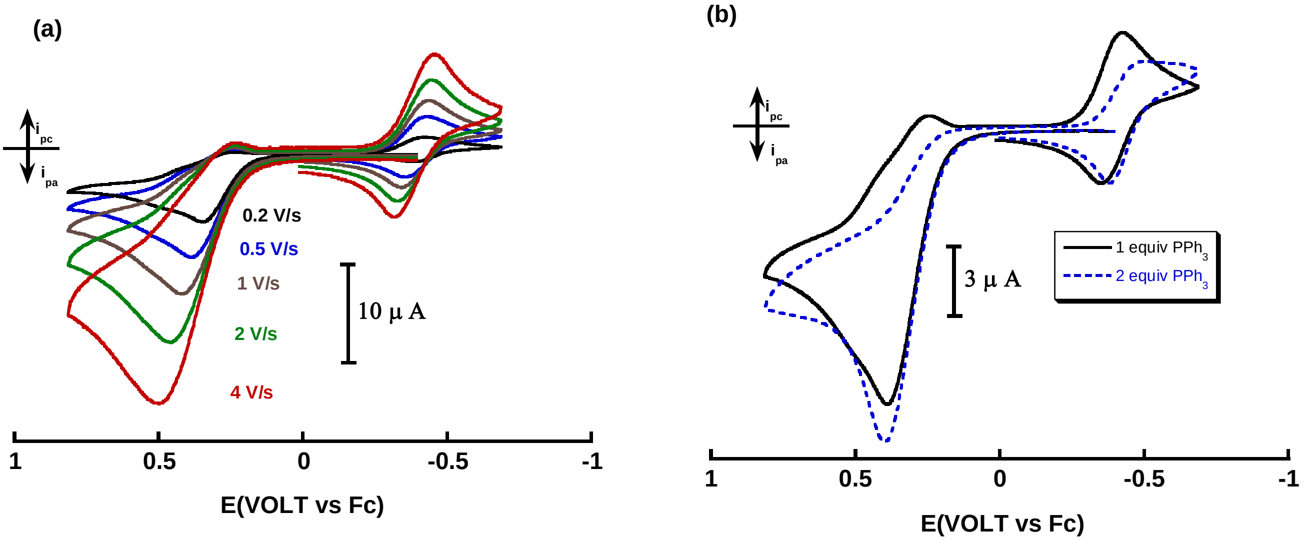


**Figure 2.** (a) Cyclic voltammograms obtained at different scan rates with 1 mm GC disk electrode for 1.55 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ in the presence of 1 equiv $PPh_3$ at 298K. (b) CVs of 1.55 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ in the presence of 1 and 2 equiv of $PPh_3$ at scan rate of 500 mV/s, 298K using 1 mm GC disk.

Virtually, the complexity of the bulk electrolysis experiments and the possible generation of more than one substitution product, even in the CV time scale, attest that application of the "electrochemical switch" method for promoting CO-substitution by $PPh_3$ is not quite simple for $CoCp(CO)_2$ complex as initially thought on the basis of the conceptually and structurally related $Cr(\eta^6\text{-}C_6H_6)(CO_3)$ and its facile and quantitative conversion into $[Cr(\eta^6\text{-}C_6H_6)(CO)_2(PPh_3)]^{0/+}$ via the same approach.

This complicated behavior is expected given the high reactivity of the 17-electron cation, $\mathbf{1}^+$, compared to the Cr counterpart, $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]^+$ which is persistent in solution for long time, whereas the former cation tends to rapidly react with its neutral parent, **1**. This means that the electro-generated $[CoCp(CO)_2]^+$ cation faces, in principle, a competitive attack by both $PPh_3$ and neutral **1**, which is the reason for formation of a mixture of products. Bearing in mind that the produced mono-substituted product will be in a cationic form, $[CoCp(CO)(PPh_3)]^+$, which is known, based on our previous work on the electrochemical oxidation of neutral $CoCp(CO)(PPh_3)$, to undergo $PPh_3$/CO “ligand exchange” reaction [24], it is likely to encounter such reaction in here. This assumption provides legitimate reason for the observation of different substitution including the mono-$[CoCp(CO)(PPh_3)]^+$ and di-substituted $[CoCp(PPh_3)_2]^+$ along with neutral **1**, particularly at longer time scale.

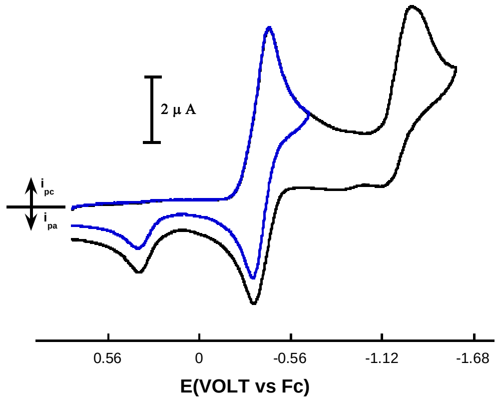


**Figure 3.** Cyclic voltammograms of the electrolysis products of 1.55 mM **1** in the presence of 2 equiv $PPh_3$ in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ at scan rate of 100 mV/s, 273 K, using 1 mm GC disk electrode.

### *3.1.2. Reaction of Electro-generated $[CoCp(CO)_2]^+$ with $P(OMe)_3$*

Since the electron density around the metal atom is influenced by the σ-basicity and π-acidity of the phosphorus ligands, it is expected that in bonding with transition metals, the $d_\pi$-$L_\pi$ back-bonding to phosphorus would produce a synergistic increase in the σ-donicity of the ligand [30]. This effect is anticipated to be stronger in phosphites, $P(OR)_3$, than in the phosphines, $PR_3$, (R = Ph or Me), owing to the presence of the more electronegative oxygen atom bonded to phosphorous in phosphites, thereby making $P(OMe)_3$ a stronger σ-donor and π-acceptor than $PPh_3$. Moreover, differences in the cone angle ($107^\circ$ in $P(OMe)_3$ versus $145^\circ$ in $PPh_3$) are expected to greatly affect their reactivities with electrophiles such as the 17-electron cation, $\mathbf{1}^+$. Based on these facts, along with the complexity observed in reaction of $\mathbf{1}^+$ with $PPh_3$, we sought out to apply the same electrochemical switch approach to induced CO-substitution reaction with $P(OMe)_3$ with the hope to cleanly generate the corresponding mono-substituted product, $[CoCp(CO)P(OMe)_3]^+$ as detailed below.

### *(a) Cyclic Voltammetry*

Figure 4 compares the cyclic voltammograms recorded for 2.25 mM **1** in $CH_2Cl_2$ /0.05 M $[NBu_4][B(C_6F_5)_4]$, before (Fig. 4(a)) and after (Fig. 4(b)) addition of 1 equiv of $P(OMe)_3$. Similar to the behavior in the presence of $PPh_3$, the two reversible oxidation waves of **1** (Figure 4(a)) are merged into one irreversible wave upon addition of $P(OMe)_3$, concurrent with the emergence of a new reversible wave detected in the cathodic scan direction at $E_{1/2}$ = -0.82 V vs $Fc^{0/+}$ (Figure 4(b)).

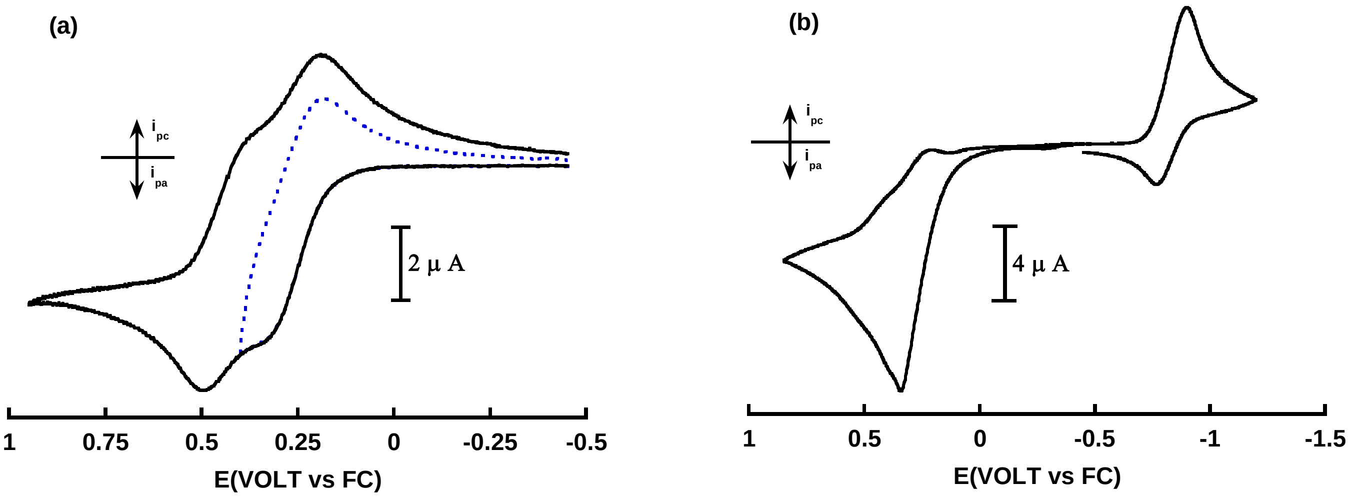


**Figure 4.** (a) Cyclic voltammograms of 2.25 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ at scan rate of 500 mV/s, 1 mm GC disk electrode. (b) Cyclic voltammograms recorded under same conditions as in (a) but after addition of 1 equiv $P(OMe)_3$ ligand.

The chemical reversibility of the product wave is highly dependent on scan rate as illustrated in Figure 5(a). The current ratio ($i_{rev}/i_{fwd}$), measured as a function of scan rate, increases from 0.45 to 0.8 upon increasing the scan rate from 0.2 to 8 V/s, respectively. This behavior implies a very high chemical reactivity and instability of the generated P(OMe)-based-substitution product, and therefore, scan rates higher than 10 V/s are required to surpass the follow-up chemical reactions and achieve full chemical reversibility of the process.

Mechanistically, although the CVs of **1** in the presence of $P(OMe)_3$ share the same voltammetric characteristics observed with $PPh_3$, careful analysis of the relevant voltammetric peaks discloses unexpected differences in both cases. A very obvious difference is noted upon comparing the $E_{1/2}$ values of the two produced substitution products, where $E_{1/2}$ of -0.815 V is measured for $P(OMe)_3$-containing product compare to -0.38 V for the $PPh_3$-based substituted product. The former $E_{1/2}$ value is, indeed, inconsistent with the expected ($E_{1/2}$ = ~ -0.27 V) value for the formation of the mono-substituted $[CoCp(CO)P(OMe)_3]^{+/0}$ couple, based on an expected shift of -0.60 V in substitution of CO by $PPh_3$ or a shift of -0.57 V in substitution of CO by $P(OMe)_3$ [31, 32], providing the $E_{1/2}$ of $\mathbf{1}^{0/+}$ is 0.3

V. This conclusion is further supported by the observation of an irreversible wave at $E_{pa}$ = -0.25 V, which can be clearly seen via a close-up view shown in Figure 5(b).

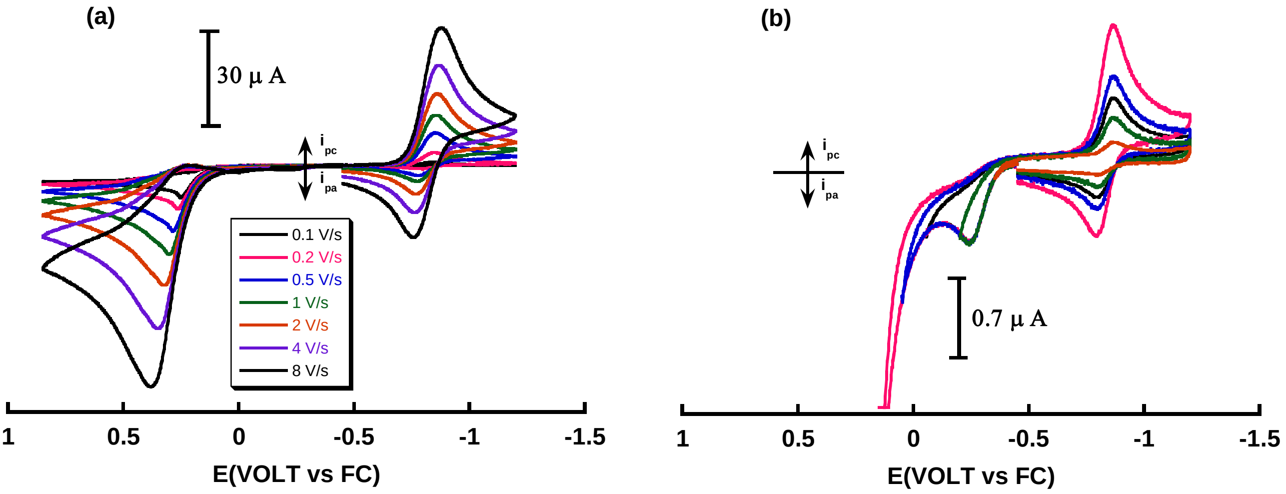


**Figure 5.** (a) Cyclic voltammograms of 2.25 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ and 1 equiv $P(OMe)_3$ at different scan rates, 1 mm GC disk electrode. (b) Cyclic voltammograms obtained under same condition as in (a), but at different switching potentials and scan rate of 500 mV/s

Careful analysis of CV curves obtained in the presence of 1equiv $P(OMe)_3$ at different switching potentials (Figure 6) emphasized that detection of the corresponding substitution product wave ($E_{1/2}$ = -0.82 V) depends dramatically on the switching potentials, and interestingly its formation does not require full generation of the monocation $\mathbf{1}^+$. Such behavior is a key feature in stoichiometric associative substitution reaction. Additionally, we found that the peak potential ($E_{pa}$) of the oxidation wave of **1** is shifted by a 100 mV to more positive and its anodic peak current is almost double that in the absence of $P(OMe)_3$. On this ground, it can be concluded that (i) the substitution reaction in the presence of $P(OMe)_3$ does not lead to formation of the mono-substituted cation, $[CoCp(CO)P(OMe)_3]^+$, as the major product, and (ii) the electrochemically-induced substitution process has a catalytic nature since application of positive potentials less than the $E_{1/2}$ of $\mathbf{1}^{0/+}$ and scanning back to more negative potentials results in appreciable generation of the substitution product at $E_{1/2}$ = -0.82 V as clearly depicted in Fig. 6.

Unlike the behavior with $PPh_3$, the data obtained for $P(OMe)_3$ strongly support an electrocatalytic CO-substitution reaction of the initially generated $[CoCp(CO)_2]^+$ cation to afford P(OMe)-substituted product that is, most likely, not the corresponding mono-substituted $[CoCp(CO)\{P(OMe)\}]^+$cation. Evidence from literature attest to this conclusion as chemical oxidation of $CoCp(CO)_2$ with $[FeCp_2][PF_6]$ in $CH_2Cl_2$ when undertaken in the presence of $P(OMe)_3$ afforded a high yield of the diamagnetic, cobalt(III) derivative, $[CoCp\{P(OMe)_3\}_3][PF_6]_2$ [1,12]. Connelly *et al.* [1, 12] explained the formation of product by assuming initial generation of a paramagnetic di-substituted bis(phosphite) complex, which is then undergone further oxidation upon coordination of a third $P(OMe)_3$ ligand to give rise to the tris(phosphite) dication.

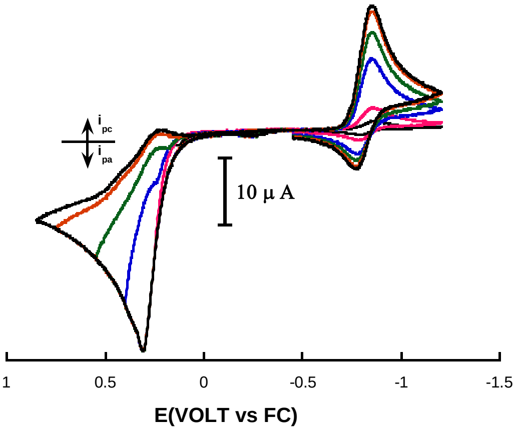


**Figure 6.** Cyclic voltammograms as at different switching potentials obtained for 2.25 mM **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ in the presence of 1 equiv of $P(OMe)_3$ at scan rate of 500 mV/s using 1 mm GC disk electrode.

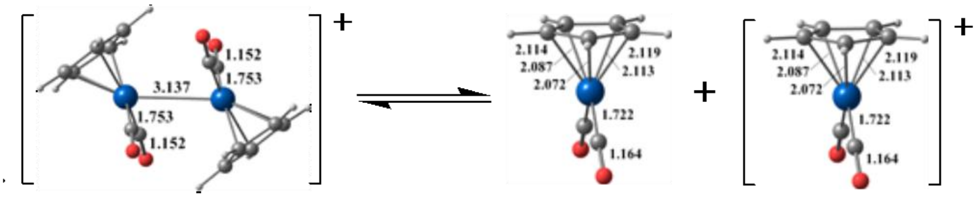
Thus, in view of these findings, we can confidently assign the product wave at $E_{1/2}$ = -0.82 V for the dication $[Co^{III}Cp\{P(OMe)_3\}_3][B(C_6F_5)_4]_2$ whereas the irreversible wave at $E_{pc}$ of -0.25 V is attributed to transient formation of the mono-substituted cation, $[CoCp(CO)\{P(OMe)_3\}][B(C_6F_5)_4]$. Nonetheless, to have solid proof of the species responsible for the product wave at $E_{1/2}$ = -0.82 V and to confirm whether it is truly for the dication $[CoCp\{P(OMe)_3\}_3]^{2+}$ or not, chemical oxidation of $CoCp(CO)_2$ complex with $[FeCp_2][B(C_6F_5)_4]$ in in the presence of 1 equiv of $P(OMe)_3$ was performed in $CH_2Cl_2$. The isolated pale-yellow solid CV, when checked electrochemically, under similar solvent/electrolyte conditions gave rise to only one reversible wave having identical $E_{1/2}$ (= -0.82 V) to that observed before. This finding provides clear-cut evidence and confirm the formation of $[CoCp(CO)\{P(OMe)_3\}][B(C_6F_5)_4]$ as the major product. Significantly, it is very important to emphasize that this electrochemically-activated CO-substitution reaction is operative only in the vicinity of the electrode (diffusion layer), since **1** in the presence of $P(OMe)_3$ is otherwise very stable in the bulk solution.

### *(b) Bulk Coulometry*

Anodic bulk electrolysis of **1** in $CH_2Cl_2$/0.05 M $[NBu_4][B(C_6F_5)_4]$ at ambient temperature and $E_{appl}$ = 0.7 V, in the presence of $P(OMe)_3$ revealed that electrolysis was completed upon consumption of approximately 1 F/mol. The color of the solution changed from yellow to light orange. Cyclic voltammograms obtained after electrolysis showed the presence of more than one. From these products, we were able to identify the neutral starting material, **1** ($E_{1/2}$ = 0.37 V), and the mono-and tri-substituted products with their respective characteristic $E_{1/2}$ values at - 0.25 and - 0.82 V. Two additional unidentified products at $E_{1/2}$ = -1.25 and -1.75 V are also seen in the CV. Importantly, cyclic and linear sweep voltammograms recorded after reductive back electrolysis at a potential that is more negative than the tri-substituted products ($E_{appl}$ = -0.85 V) afforded neutral $[CoCp\{P(OMe)_3\}_3]$ in ~ 70% yield along with minor formation of the mono-substituted product (~15%).

## 4. MECHANISTIC ASPECTS OF THE SUBSTITUTION PROCESS

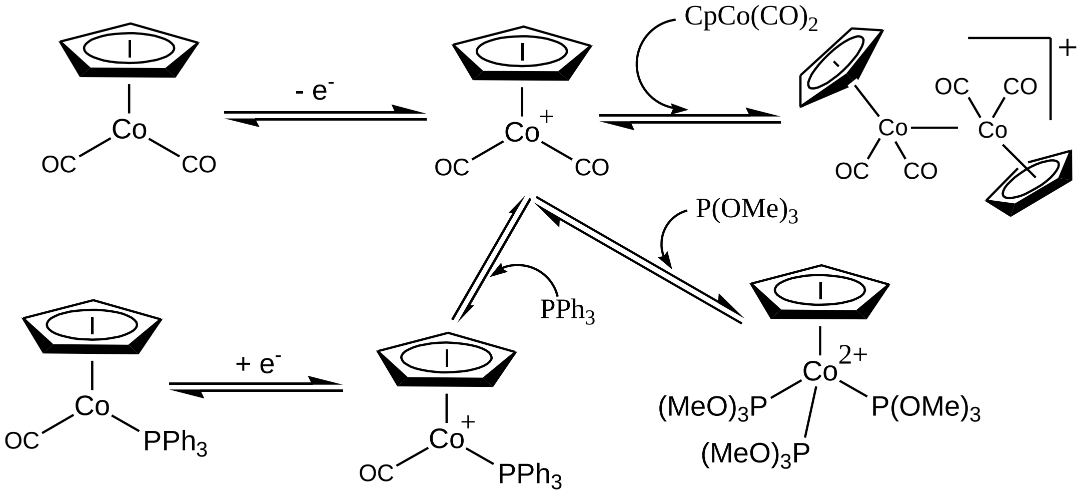
In view of our previous work [26, 27], it is clearly established that, in media containing solvents of low donor strength and anions of limited nucleophilicity, the electrochemically-generated 17-electron **$1^+$** undergoes radical-substrate (R-S) coupling with its neutral partner, **1**, giving rise to unsupported metal-metal bonded dimer cation, $[Co_2Cp_2(CO)_4]^+$. DFT calculation performed on this system implied weak metal-metal bond as a result of the long cobalt-cobalt distance of 3.14 Å. This is consistent with the fact that the dimer radical **$2^+$** partially dissociates in solution to give equilibrium amounts of neutral **1** and the cation **$1^+$** as illustrated in Scheme 1



**$2^+$** **1** **$1^+$**

**Scheme 1.** Structural representation of equilibrium dissociation of the R-S dimer, **$2^+$**

However, in the presence of strong $PR_3$ nucleophiles such as $PPh_3$ or $P(OMe)_3$ this radical-substrate reaction is presumably limited or eliminated by the homogeneous reaction of **$1^+$** with the added $PR_3$ as proposed in Scheme 2.



**Scheme 2.** Proposed mechanism for CO-substitution with $PR_3$ nucleophiles ($PR_3$ = $PPh_3$ or $P(OMe)_3$)

Voltammetrically, this substitution reaction should lead to only single irreversible oxidation wave for **1**, followed by emergence of the new reversible wave the substitution product at a potential that is less positive than the initial oxidation of **1**. As proposed in Scheme 2, reaction of $\mathbf{1}^+$ with $PR_3$ is expected to be the predominant pathway, since these two-electron donor ligands are considerably stronger nucleophiles than neutral **1**. It worthy to mention that this type CO-substitution reaction is extremely facilitated by the generation of $\mathbf{1}^+$, and as a result weakening of the Co-CO bond and increasing the susceptibility of the metal center towards nucleophilic attack by the nucleophiles would be the driving force for such reaction, otherwise the neutral **1** and the $PR_3$ ligands are not reacting together under normal conditions.

## 5. CONCLUSION

The overall findings of this work showed that the tendency of the 17-electron radical cation, $[CoCp(CO)_2]^+$, $\mathbf{1}^+$, to react with the parent compound, **1**, through “radical-substrate” dimerization to produce the unique metal-metal bonded dimer cation, $[Co_2Cp_2(CO)_4]^+$, $\mathbf{2}^+$, can be minimized or completely eliminated by stronger two-electron donor nucleophiles such as $PPh_3$ and $P(OMe)_3$. This has led also to facile CO-substitution reaction of the $[CoCp(CO)_2]^+$ cation and formation of the corresponding ($PR_3$)-containing substitution product(s), via utilization of what is known as “electrochemical switch approach". Thus, in the case of $PPh_3$, evidence derived from CV and oxidative bulk electrolysis showed that, although facile substitution of a single CO group by $PPh_3$ to afford the mono-substituted product, $[CoCp(CO)(PPh_3)]^+$ is achievable, chances for generation of a relatively low yield of the di-substituted product, $[CoCp(CO)(PPh_3)]^+$, is also possible. By way of contrast, substitution reaction with $P(OMe)_3$ has promoted loss of both carbonyl groups and formation of an unexpected tri-substituted dication, $[CoCp\{P(OMe)_3\}_3]^{2+}$ as the major product through an electrocatalytic reaction.

Significantly, the outcomes of this study together with our previous work in this area demonstrate clearly that using of media comprising $CH_2Cl_2$ and weakly coordinating $[B(C_6F_5)_4]^-$ anion is essential in increasing the kinetic stability and solubility of the electro-generated organometallic radical cations, thereby allow for their electrochemical and spectral characterization. The present study also underscores the role of weak metal-metal interactions between the generated radicals in controlling their stability and tendency to react with other nucleophiles present in solution.

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