Electrochemical studies of hexahapto-dibenzo[a,e]cyclooctatetraene complexes of chromiumtricarbonyl and cationic manganesetricarbonyl

By

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Electrochemical behavior of mono- and bimetallic chromiumtricarbonyl and cationic manganese(tricarbonyl) of fluxional dibenzo[a,e]cyclooctatetraene (DBCOT) complexes were studied via cyclic voltammetry over a range of scan rates (20 – 2000 mV/s) and temperatures (0 °C and 25 °C). The presented work displays electrochemical reduction mechanisms associated with eight-membered ring coordinated M(CO)₃ systems that undergo rapid ring inversion in solution.

The electrochemical studies of these complex systems exhibit comparatively similar behaviors, which suggest relatively undifferentiated mechanisms. Slight differences between the chromium and isoelectronic cationic manganese are seen in their chemical reactions in solution and the potential at which they reduce.

The significance of the electrochemical studies of these complexes are justified by their potential contribution to nanotechnology considering the possibility of generating a cylindrical nanostructure containing the tub-shaped eight-membered ring π-coordinated M(CO)₃ system. The high probability of a haptotropic shift to the eight-membered ring upon reduction could prove to be beneficial to electrocatalysis.
Keywords: Dibenzocyclooctatetraene, cyclic voltammetry,
arenechromiumtricarbonyl, organometallic synthesis,
arenemanganesetricarbonyl, bischromiumtricarbonyl
DEDICATION

I would like to dedicate this thesis to my late grandmother (Mattie Rivers) and late sister (Chiquanna Byrd) for who I know would be very proud of my accomplishments and success thus far. I would like to give a special thanks to my loving wife (Jennifer), my grandfather (Willie), the coolest mom in the world (Ca-shia), my brother (Kwazone), my sister (Cherokee) and my grandmother (Virginia). I would also like to express my gratitude to my aunts (Shati and Nica), all of my little cousins (Demia, Shalandria, Ashante, Jzamere, Tania), and my nephew (Jacob). Special thanks to my mother and father-in-law (Cindy and Joey). I would like to thank all of my family and friends, with a special thanks to Jason Miller, for a lifelong friendship and inspiration. I thank God for blessing me with each and every one of you!

_Do not be anxious about anything, but in everything by prayer and supplication with thanksgiving let your requests be made known to God. And the peace of God, which surpasses all understanding, will guard your hearts and your minds in Christ Jesus._

_Philippians 4:6-7_
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First and foremost I would like to thank God for blessing me with this opportunity. During the duration of my graduate studies I have been blessed with a great support system, because of whom, this opportunity became possible. The work presented is dedicated to the memory of Dr. William P. Henry, for guiding, encouraging, and believing in my educational goals. I would like give the greatest thanks to my committee members, Dr. David O. Wipf, Dr. Joseph P. Emerson, and Dr. Todd E. Mlsna for their support and patience throughout the years. I would also like to thank the Department of Chemistry for hosting an encouraging and welcoming environment. Thanks to the Department of Chemistry Teaching Assistantship and The GAANN Fellowship from the US Department of Education for their financial support. I would like to extend a special thanks to my mentor (Dr. Shannon Davis) for providing me with my first opportunity to indulge in a satisfying craft and encouraging me to make the most of every opportunity given.
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<tr>
<td>Ag/AgCl</td>
<td>Silver/Silver Chloride reference electrode</td>
</tr>
<tr>
<td>AN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>ArH</td>
<td>Hydrocarbon arene</td>
</tr>
<tr>
<td>BCOT</td>
<td>Benzocyclooctatetraene</td>
</tr>
<tr>
<td>COT</td>
<td>Cyclooctatetraene</td>
</tr>
<tr>
<td>COTDMC</td>
<td>cyclooctatetraenyl-2,3,4,5,6,7-d6-dimethylcarbonol</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry (voltammogram)</td>
</tr>
<tr>
<td>DBCOT</td>
<td>Dibenzo[a,e]cyclooctatetraene</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>E</td>
<td>Potential</td>
</tr>
<tr>
<td>E_{pa}</td>
<td>Anodic peak potential</td>
</tr>
<tr>
<td>E_{pc}</td>
<td>Cathodic peak potential</td>
</tr>
<tr>
<td>Fc+/Fc</td>
<td>Ferrocenium/Ferrocene redox couple</td>
</tr>
<tr>
<td>I_{pa}</td>
<td>Anodic peak current</td>
</tr>
<tr>
<td>I_{pc}</td>
<td>Cathodic peak current</td>
</tr>
<tr>
<td>K^+OtBu^-</td>
<td>Potassium tert-butoxide</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td>xi</td>
<td></td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal Hydrogen Electrode</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Angle between the planes</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene Carbonate</td>
</tr>
<tr>
<td>$R_u$</td>
<td>Uncompensated Resistance</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard Calomel Electrode</td>
</tr>
<tr>
<td>TBAP</td>
<td>Tetrabutylammonium perchlorate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrafuran</td>
</tr>
<tr>
<td>V</td>
<td>Volts</td>
</tr>
<tr>
<td>MTT</td>
<td>Manganese tricarbonyl transfer</td>
</tr>
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</table>
CHAPTER I
INTRODUCTION

1.1 Introduction

The redox behavior of organometallic complexes has been studied since the discovery of ferrocene, in 1952, by Wilkinson et al." and the unique chemical and electrochemical redox properties associated with organometallic complexes continues to be of interest. The research presented in this thesis aims to provide insightful information on the electrochemical redox behavior of “piano stool” oriented metaltricarbonyl complexes of the dibenzo[a,e]cyclooctatetraene (DBCOT) ligand (Figure 1.1). The coordination of metaltricarbonyls to DBCOT affords an organometallic complex with unique intramolecular interactions and geometrical behaviors in solution. Specifically, $\eta^6$-DBCOTchromiumtricarbonyl ($2a-b$), cationic $\eta^6$-DBCOTmanganesetricarbonyl ($3a-b$) and $\eta^6,\eta^6$-DBCOT bischromiumtricarbonyl ($4a-b$)systems are investigated.

DBCOT, $C_{16}H_{12}$, was first synthesized by Feiser almost 70 years ago." Its structure was determined by X-ray diffraction in 1981 by Irngartinger." This organic hydrocarbon contains a central non-aromatic cyclooctatetraene (COT) fused with two benzene rings at opposite ends of the COT. DBCOT binds more strongly to metal centers than its cyclooctadiene (COD) counterpart." This has led to the use of DBCOT as a poison for homogeneous catalysts." DBCOT could be used to bind the homogeneous catalyst’s metallic active site to prevent any transformation that may cause the metal to
precipitate out of the solution. Transformation is inhibited due the fact that the DBCOT cannot be hydrogenated in aqueous solutions because of the rigidness in its tub conformation. The first coordination compound successfully synthesized with DBCOT as a ligand dates back to 1960, where it was in $\eta^4$ conformation to silver and palladium.\(^8\)

The electrochemical reductive dynamics of the $\eta^6$-DBCOTM(CO)\(_3\) system are rather interesting: unique ring inversion, geometric isomerization, haptotropic shifts and the dynamic intramolecular forces associated with the chromiumtricarbonyl and cationic DBCOT manganesetricarbonyl systems (Figure 1.2). This chapter will review previous literature that has provided useful electrochemical information on the redox chemistry of arene metal complexes for this study.

Figure 1.1 Dibenzo[\(a,e\)]cyclooctatetraene,\(\textbf{1}\)
1.2 Electrochemical studies of chromium complexes

This section will highlight the literature reporting the reductive electrochemistry of Cr(CO)$_3$ and Mn(CO)$_3^+$ arene complexes using electrochemical techniques in non-aqueous solvents. The fact that these metaltricarbonyl groups are isoelectronic one would assume that their electrochemical behavior is relatively similar. It is well known that the cyclic voltammetric behavior of most monoaromatic compounds produce irreversible
reductive waves at room temperature. The irreversibility is due to the metastable behavior of the arene cation radical that is subject to fast secondary reactions. On the other hand, most polyaromatic rings, like naphthalene, produce reversible waves. The anodic peak potential varies dramatically depending upon the hydrocarbon substituent(s) on the aromatic ring. The complex formed by the coordination of a transition metal to the naphthalene not only exhibits a reduction peak, but also causes a significant positive shift in the reduction peak potential. A variety of conditions and effects control the electrochemical reversibility or irreversibility of the compounds, which will be thoroughly discussed in this chapter.

1.2.1 Electrochemical studies of monochromium arene complexes

Rieke et al. carried out electrochemical studies on various (arene)chromiumtricarbonyl complexes using normal pulse polarography. He determined that there is a significant difference in the electrochemical reversibility of (benzene)Cr(CO)₃ complexes compared to (naphthalene)Cr(CO)₃ complexes. In order to determine the chemical reversibility, the polarographic slope was reported. The polarographic slope was obtained by plotting the $E$ vs. $\log\left(\frac{id-i}{i}\right)$ (described as the sample current). Polarographic analysis revealed an irreversible system for the (benzene)Cr(CO)₃ complexes with polarographic slopes of 60 mV, indicating a one-electron, irreversible process. Polarographic analysis revealed a reversible system for (naphthalene)Cr(CO)₃ complexes polarographic slopes of approximately 30 mV indicative of a two-electron, reversible process (Table 1.1). Contrary to polarographic studies cyclic voltammetry suggested that both benzene and naphthalene complexes
undergoes a two-electron reduction, the difference in their reversibility is based on their follow-up chemical kinetics.

Table 1.1 Pulse Polarographic Data for (Arene)Cr(CO)₃

<table>
<thead>
<tr>
<th>Structure</th>
<th>E½ (V vs SCE)</th>
<th>Slope (mV)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>(benzene)Cr(CO)₃</td>
<td>-2.25</td>
<td>60</td>
<td>AN</td>
</tr>
<tr>
<td>(benzene)Cr(CO)₃</td>
<td>-2.50</td>
<td>60</td>
<td>AN</td>
</tr>
<tr>
<td>(naphthalene)Cr(CO)₃</td>
<td>-1.66</td>
<td>30</td>
<td>AN/PC</td>
</tr>
<tr>
<td>(benzene)Cr(CO)₃</td>
<td>-1.72</td>
<td>30</td>
<td>PC</td>
</tr>
</tbody>
</table>

Notes: AN (Acetonitrile) PC (Propylene Carbonate)

The explanation for this dramatic shift in potential (Table 1.1), comparing (benzene)Cr(CO)₃ to the (naphthalene)Cr(CO)₃, is suggested to be solely based on the chemical process that takes place in solution. Naphthalene is displaced from the coordinated chromium at approximately 10³ to 10⁴ times faster than benzene under normal conditions.¹⁴,¹⁵ This chemical process involves geometric isomerization of the Cr(CO)₃ coordinated to the naphthalene, where there is a rearrangement from an η⁶ arene coordination to an η⁴ butadiene coordination.¹⁴,¹⁶ Scheme 1.1 shows the suggested ECE mechanism for the two-electron reduction of (naphthalene)Cr(CO)₃ with a single reduction peak at -1.68 V vs. Ag/AgCl reference electrode. Rieke proposed a scheme based on the idea, originally proposed by Bard, that the reduction is a two-electron, two-step mechanism, where the second electron is positive to the first.¹¹,¹⁶ The 18 e⁻ system undergoes electrochemical reduction to generate an extremely unstable 19 e⁻ anion. This system stabilizes via geometric isomerization resulting in ring slippage of the Cr(CO)₃,
affording a more stable 17 e\textsuperscript{-} system, which is expected to readily reduce to an 18 e\textsuperscript{-} dianion.\textsuperscript{16,17}

![Scheme 1.1 Reduction of (Naphthalene)Cr(CO)\textsubscript{3}](image)

Howell et al., 1984, reported data relating the oxidation potentials of ArH aromatic rings ($E_{Ar}^o$) with that of their (η\textsuperscript{6}-ArH)chromiumtricarbonyl ($E_{ArCr}^o$) corresponding complexes.\textsuperscript{10} Howell discovered that upon coordination of Cr(CO)\textsubscript{3} to the ArH aromatic rings, there is a noticeable negative shift in the oxidation potential as well as an increase in reversibility of the wave (Table 1.2). If the Howell was interested in knowing if the electron detachment from the (arene)Cr(CO)\textsubscript{3} is affected by the donor properties of the arene ligand. To determine if there is an effect, a relationship between the slopes associated with the vertical ionization potentials of the arene ligands and the energy of the highest occupied molecular orbital (HOMO), calculated by the Hückel model of π-systems, were compared to the correlation of the oxidation potentials of the free arenes ($E_{Ar}^o$) and their Cr(CO)\textsubscript{3} counterparts ($E_{ArCr}^o$). The slopes of the vertical ionization potentials vs. HOMO energy of $E_{Ar}^o$ vs. $E_{ArCr}^o$ are similar (0.12 and 0.18,
respectively). This indicates that electron detachment from the Cr-arene is not affected by the donating ability of the arene ligand.

Table 1.2 Standard Oxidation Potentials of Free Arene versus (Arene)Cr(CO)₃

<table>
<thead>
<tr>
<th>Arene</th>
<th>Free Arene</th>
<th>2.64</th>
<th>2.53</th>
<th>2.30</th>
<th>2.38</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Arene)Cr(CO)₃</td>
<td>1.06</td>
<td>1.05</td>
<td>1.02</td>
<td>1.03</td>
<td></td>
</tr>
</tbody>
</table>

Notes: All potentials related to the free arenes are in volts (V) versus SCE and converted to NHE by the relationship \( E_{NHE} = E_{SCE} + 0.24 \) V. Solvent is trifluoroacetic acid containing 0.1 M TBAP. All potentials related to the (arene)Cr(CO)₃ are in volts (V) versus SCE and converted to NHE by the relationship \( E_{NHE} = E_{Ag/AgClO} + 0.66 \) V. Solvent is 7% by volume trifluoroacetic anhydride containing 0.1 M TBAP.

1.2.2 Bimetallic chromium complexes

In 1986, Rieke et al.\(^{18,19}\) reported significant electrochemical polyarene bimetallic chromium tricarbonyl complex results. He hypothesized that in molecules that have little restriction to the conjugation of the arenes, relatively good interaction of the conjugated phenyl rings are expected. When comparing the bimetallic chromium complex (B) to its monometallic counterpart (A) (Figure 1.3), as a result of the interaction of the conjugated phenyl rings, there is a positive shift in the reduction potential of about 300 mV. It is suggested that the bimetallic (polyarene)Cr(CO)₃ complex undergoes a two-step, two-electron reduction process by the addition of an electron to one (arene)Cr(CO)₃ followed by an addition to the other (Scheme 1.2).
In 1992, Geiger and others\textsuperscript{20} presented data for \textit{bis} chromiumtricarbonyl complexes that contain arenes bonded by polynorbornyl-type bridges of different chain lengths 1, 2, and 3 (Figure 1.4).

All of the \textit{bis} complexes adopt an \textit{exo,exo} configuration 4, 5, and 6 (Figure 1.5). The tunneling polynorbornyl bridge helps facilitate intramolecular electron transfer via through-bond mechanisms or long range coupling between the benzene rings.\textsuperscript{21} Oxidative voltammetry was carried out on the \textit{bis} chromiumtricarbonyl coordinated complexes of 1,
2, and 3. For complex 4, Geiger reported observing two 1-electron reversible oxidations at scan rates >1 V/s with $E_{1/2}^1 \approx +0.37$ and $E_{1/2}^2 \approx +0.51$ V vs. Fe$^{+}$/Fe in CH$_2$Cl$_2$/0.1 [Bu$_4$N][PF$_6$]. Complex 5 exhibited broader peaks, but also expressed reversible two 1-electron CV waves with $E_{1/2}^1 \approx +0.37$ and $E_{1/2}^2 \approx +0.51$ V. Complex 6 only produced one wave assumed to be a one-electron process ($E_{1/2} = +0.29$ V), this is due to the dication passivating the electrode after each scan. The fact that significantly fast scan rates had to be used in order to observe reversibility, which indicates weak coupling of the metal centers. This weak coupling proved to be independent of the length of the chain.

Figure 1.5  *bis* chromiumtricarbonyl polynorbornyl-type complexes

### 1.2.3  DBCOT chromium complexes

In 1969, Müller et al.$^{22}$ published the synthesis of the *mono* chromiumtricarbonyl complex of DBCOT. However, structural characterization and analysis of the complex was not available until presented by Bandara et al.$^9$ in 2011. Bandara presented data relating the angle between planes ($\phi$) of C$_{1-3,8,13-16}$ and C$_{4-7,9-12}$ of the parent DBCOT and
its mono and bis chromiumtricarbonyl complexes (Figure 1.6). It was determined that the ligand of the bis complex had a flattened DBCOT framework with an angle of 106.70° when compared with DBCOT at an angle of 98.70° and the mono complex unexpectedly exhibiting an angle of 91.70°. The larger angle corresponding to the bimetallic complex is due to the congestion caused by the syn Cr(CO)₃ moiety. The smaller angle of the anti-mono complex is due to the C-H—π interactions between the β-hydrogens and the arene ring of a neighboring mono complex in the crystal lattice. DFT calculations confirmed the lowest energy confirmations of the complexes as anti for DBCOTCr(CO)₃, syn for DBCOTMn(CO)₃, and syn,anti for DBCOT[Cr(CO)₃]₂.

Figure 1.6  Measured angles between the planes of DBCOT, the anti DBCOTCr(CO)₃ and syn,anti DBCOTCr(CO)₃

In 2000, Henry et al.²³ published the first crystal structure of the bis chromiumtricarbonyl complex of DBCOT. Upon obtaining the crystal structure, it was discovered that the Cr(CO)₃ entities were bound in a syn,anti conformation. Henry discovered that four molecules existed, differing in anti Cr(CO)₃ rotational tripod orientation to the benzene ring (Figure 1.7).
Figure 1.7  Possible tripod rotational orientations of Cr(CO)₃

Notes: θ indicates the angle away from the imaginary center line perpendicular to the bond shared by the fused ring

To understand ring inversion for the *bis* complex, the ring inversion for COT must first be understood. Ring inversion relates the conformational mobility and isodynamics of COT. Conformation mobility refers to the process by which rotation around a single bond occurs and the isodynamics relate the synchronicity of the bond rotation.²⁴ The basis of ring inversion is the regeneration of the starting material (Figure 1.9, **Ring 1**). During the process of regeneration, the COT goes through a delocalized planar transition state.²⁴,²⁵ The ground state tub conformation along with the alternating single and double bonds of the COT ring inversion allows this to occur. This same idea is applied to the DBCOT and η⁶,η⁶-DBCOT-*bis*-Cr(CO)₃ complex.

Bandara proposed that in solution, this *syn,anti* conformation undergoes a planar transition state (Figure 1.8).⁹ It was also suggested that intermolecular C-H···O hydrogen bonds between the oxygen of the Cr(CO)₃ and the neighboring arene provide extra stability to the complex in its solid state.
Figure 1.8  Inversion of η⁶,η⁶-DBCOT-syn,anti-Cr(CO)₃

Henry et al. reported the crystal structure of the anti,anti conformation of the bis-chromiumtricarbonyl DBCOT complex. DFT calculations suggest that the anti,anti isomer possesses a higher energy than the syn,anti isomer, which suggests that under thermodynamic conditions this conformation is not as stable as its syn,anti counterpart. Theoretical analysis confirmed that the minimum energy orientations for all Cr(CO)₃ moieties are exo-staggered. Henry proposed that the destabilization caused by the syn-Cr(CO)₃ is counteracted by the interaction between the syn-Cr(CO)₃ and the neighboring arene of the syn,anti complex in solution.

1.3  Electrochemistry of manganesetricarbonyl complexes

1.3.1  Arene manganesetricarbonyl

Sun et al. gave the most efficient (arene)Mn(CO)₃⁺ synthetic procedure to date (Scheme 1.3). This procedure involves the use of manganese tricarbonyl transfer (MTT) reagents to generate (arene)Mn(CO)₃⁺ complexes. Electrochemical reduction studies of
(arene)Mn(CO)$_3^+$ complexes typically reveal a chemically irreversible process at room temperature in CH$_2$Cl$_2$.

$$\text{arene} + \text{Mn(CO)}_3^+ \rightarrow (\text{arene})\text{Mn(CO)}_3^+ + \text{arene}$$

Scheme 1.3  Use of MTT [(naphthalene)Mn(CO)$_3^+$] to synthesize (arene)Mn(CO)$_3^+$

Neto et al.\textsuperscript{28} published cyclic voltammetric data on various (arene)Mn(CO)$_3^+$ complexes, which shows that hydrocarbon (arene)Mn(CO)$_3^+$ ion complexes produce an irreversible primary reduction peak near -1 V relative to Fc$^+/\text{Fc}$ couple, with a reversible peak near 0 V that is a result of the product formed by the reduced species. Neto proposed a mechanism for the electrochemical reduction of hydrocarbon (arene)Mn(CO)$_3^+$. The 18 e$^-$ cationic complex is reduced to a neutral 19 e$^-$ complex. This 19 e$^-$ complex can dissociate CO followed by dimerization or to the dicarbonyl anion complex. The dicarbonyl anion complex is expected to react with the cationic starting complex to generate a bimetallic Mn complex.\textsuperscript{28}

1.4 Cyclooctatetraene

1.4.1 Structural and dynamic behavior of COT

Cyclooctatetraene (COT) was first synthesized by Willstater in 1911.\textsuperscript{29} COT is nonplanar and has a tub-shaped geometry with D$_{2d}$ symmetry. It is well known to undergo two dynamic processes, ring inversion and bond shift.\textsuperscript{30,31} Anet et al. concluded that there are two possible planar transition states associated with these COT reactions.\textsuperscript{32}
Ring 1 has unequal bond lengths and has a D_{4h} symmetry. Ring 2 possesses equal bond lengths having a D_{8h} symmetry. Figure 1.9 gives the relationship between the ring inversion and bond shift of the COT to their respective planar transition state.

Figure 1.9  
Ring inversion (**Ring 1**, top) and bond shift (**Ring 2**, bottom) of COT and the respective planar transition states

Figure 1.10 gives the molecular orbital diagrams of the respective planar COT transition states. This figure shows the D_{8h} COT, associated with bond shifting dynamic, which has a HOMO containing two half-filled orbitals that are degenerate nonbonding orbitals. The MO diagram on the right suggests that there is a Jahn-Teller effect of the D_{4h} transition state of the ring inversion process that causes a split in the HOMO and LUMO into two non-degenerate orbitals placing both π-electrons in one orbital. Steiner suspects that the transition states of COT are interconnected with the small energy gap of the D_{4h} planar transition state being generated by Jahn-Teller distortion associated with the D_{8h}. Jahn-Teller distortion is due to additional transitions during bond rotation, which produces an energy gap and poor overlap. Geometric
distortion splits the rotational pair across a small energy gap which allows for
paramagnetism. Steiner suggests that the energy gap is relatively small, which is
indicative of the anti-aromaticity of COT. Although the $D_{8h}$ planar transition state is
accepted by some as the transition state of the ring inversion process, the question of the
degree of its destabilization still lingers.$^{25}$

![Molecular orbital diagrams for bond shift (1) and ring inversion (2) of the COT transition states](image)

**Figure 1.10** Molecular orbital diagrams for bond shift (1) and ring inversion (2) of the COT transition states

### 1.4.2 Electrochemical studies of COT

Electrochemical studies suggest that COT can undergo planarity upon
reduction.$^{25,31,35,36}$ COT is reduced in 2 one–electron steps. The first step is rate limiting
and results in a planar monoanion, while the second step is very rapid and generates the
dianionic COT species. Planarity of the COT transition state was confirmed by the
comparison of the specific rates of bond shift in cyclooctatetraenyl-2,3,4,5,6,7-d6-dimethylcarbonol (COTDMC) to COT itself at the same temperature (-10 °C). The rate of bond shift in COTDMC is significantly lower than that of COT (0.04 s⁻¹ and 0.26 s⁻¹). This smaller rate is due to the repulsive interaction of the DMC group with the adjacent CH group.

In 1962, Katz et al.³⁵ reported the electrolytic reduction of COT in 96% dioxane-water. Oscilopolarographic analysis revealed a reversible addition of two electrons to the hydrocarbon followed by an irreversible pseudo-first-order reaction of the dianion with the water molecules. This led to the proposal that the COT anion is unlike the COT hydrocarbon in geometry. The high degree of stabilizations from the π-electron delocalization as observed in COT anions is not observed in the COT hydrocarbon. On the basis of prior anthracene studies³⁷, it was suggested that the monoanion and dianion of COT is affected by solvent ions, such as hydrogen from the water molecules, resulting in an irreversible chemical reaction. In this publication, a series of quantitative electroanalysis suggests a geometrical change from a tub-shaped COT hydrocarbon to a planar COT anion that occurs during the reduction process (Scheme 1.4). Computational studies indicated that there was a very small change in free energy between the monoanion and dianion, which suggests that there is no or very little change in geometry.

\[
\text{Scheme 1.4 COT electrochemical reduction process}
\]
In 1965, Allendoerfer et al.\textsuperscript{36} resolved the issue pertaining to the water molecule interaction with the anionic COT moieties, using DMF as the solvent. Immediately after the absorbing the first electron to generate the COT monoanion, a very rapid formation of the dianion occurs without protonation from residual water molecules. The half-wave potentials vs. SCE of the COT reduction processes were determined to be -1.62 and -1.86 V with reciprocal slope values of 0.063 and 0.056 V in DMF, respectively.\textsuperscript{36} The values are distorted by protonation through interaction with water, causing a slight cathodic shift in the observed potentials.

With the help of the MO diagrams of the planar transition state shown in Figure 1.10, predicted MO diagrams of the electrochemical reduction process of COT can be drawn (Figure 1.11). The addition of an electron causes a change from the tub geometry of the ground state COT to the more energetically favorable planar geometry of the anionic COTs. There are six $\pi$ electrons filling the lower $\pi$-bonding molecular orbitals. The monoanion is anti-aromatic due to the delocalized electron while the dianion is aromatic having 10 paired $\pi$-electrons, thus fulfilling Hückel’s rule. The negative charge associated with the monoanion impedes the addition of another electron needed to form the dianion.
1.5 Fused benzo COT derivatives

1.5.1 Characteristics and behavior

The first fused COT derivatives were synthesized in the early 1940’s, although the first attempts to synthesize fused COT derivatives pre-dates the synthesis of COT itself. The idea behind the synthesis of fused COT derivatives was that it was possible to generate a more stable COT species. Fused benzo COT derivatives share many of the same characteristics as the parent COT such as: 1) no aromaticity in their ground state, 2) fluxional behavior in solution and 3) planar transition states.

1.5.2 Theoretical analysis of ring inversion

In collaboration with Dr. Steven Gwaltney and previous studies carried out by Bachrack, theoretical studies of the ring inversion of COT and its fused derivatives...
(BCOT and DBCOT) have been extensively studied. The energy barrier of ring inversion for each organic moiety was determined using DFT studies (Figure 1.12).

![Energy barrier of ring inversion calculated using DFT studies](image)

Figure 1.12  Energy barrier of ring inversion calculated using DFT studies

It is obvious that as once benzene is fused to the COT (BCOT), the energy barrier for ring inversion decreases. This is indicative of a decrease in anti-aromaticity, thus increasing stability.24 As a second benzene (DBCOT) is added opposite the first benzene, the energy barrier for ring inversion is slightly increased. This can be due to a slight repulsion between the two benzenes in their tub conformation.

### 1.5.3  Electrochemical studies of BCOT

In 1972 Anderson et al.30 carried out electrochemical studies on BCOT and DBCOT. Anderson concluded that BCOT and DBCOT cannot be electrochemically reduced past their radical anion stage. With the assumption that the moieties are in a “puckered” confirmation, their half-wave potentials (E$_{1/2}$) are reversible with reduction potentials vs. SCE determined to be -2.13 and -2.29 V in the aprotic solvent THF (0.2 M TBAP), respectively (Scheme 1.5).30 Anderson noted that the solution contained a relatively small concentration of water, which resulted in a protonated species capable of
undergoing reduction, but was considered to be negligible because the concentration of the water was assumed to be extremely low.

Scheme 1.5  Electrochemical reduction of BCOT according to Anderson

In 1975, Jensen et al. re-investigated Anderson’s work by collecting data using THF. THF was dried by careful purification and by passing THF over neutral alumina immediately before use. Under these conditions, Jensen noticed that the BCOT showed two distinct peaks, indicating two 1-electron transfers to give the dianion of the BCOT with $E_p$ values of -1.75 and -1.9 V vs. SCE in THF containing 0.2M [Bu$_4$N][BF$_4$] (Scheme 1.6). Upon protonation by residual water, the peak of the second electron transfer merges with the peak of the first electron transfer. Jensen suggested that the residual water protonates BCOT$_2^-$, resulting in a merger with the first peak.

Scheme 1.6  Electrochemical reduction of BCOT according to Jensen
1.5.4 Electrochemical studies of DBCOT

In 1972, Anderson\textsuperscript{30} carried out polarographic electrochemical reduction studies on DBCOT. The studies revealed that DBCOT underwent a single electron reduction to its radical anion at -2.29 V vs. SCE. It was concluded that the radical anion was rapidly protonated by water molecules that were present in the solution, which prevented further reduction. This result was synonymous to that of the BCOT polarographic study presented in the previous section.

Bard et al\textsuperscript{42} were the first to report cyclic voltammetric studies for the redox chemistry of DBCOT. It is noteworthy to mention that prior to this cyclic voltammetric analysis, the majority of the electrochemical studies had been polarographic or analyzed using a two electrode cell system. The direct current (dc) polarogram showed an $E_{1/2}$ of -1.95 V vs. SCE in a 0.5 M TBAP/DMF solution. It was determined to be a two-electron wave from the limiting current and diffusion current constant. The diffusion current constant is obtained by relating the radius, mass flow rate of the mercury from orifice of capillary, and life of the drop and density of mercury under the experimental conditions to the semi-infinite linear diffusion current.\textsuperscript{12} Experiments carried out at slow scan rates (0.02-0.5 V/s) exhibited a quasi-reversible one-electron reduction wave with a corresponding oxidation wave. The width of the reduction peak is 150 mV, which suggests that it is actually a combination of two reduction peaks. This indicated that the reduction of DBCOT consisted of two 1-electron transfer reactions. The sharp cathodic peak and the broad anodic peak observed for the first electron transfer is the rate limiting step. Scheme 1.7 shows the two-step reduction process that mimics that of the COT.
1.6 Research Objectives

From data obtained from the comprehensive electrochemical analysis of chromium and manganese arene complexes, it is generally accepted that these species can be reduced. This research will provide detailed electrochemical analysis of the DBCOTM(CO)₃ complexes with respect to the free DBCOT ligand. It will seek to answer questions on how ring inversion, free rotation and inhibited rotation of the M(CO)₃ affect its redox behavior. It will be determined if coordination of the M(CO)₃ to the fluxional DBCOT ligand plays a major role in reduction mechanism of the complex. The likelihood of the occurrence of haptotropic shifts of the metal(tricarbonyl) due to geometrical isomerization of DBCOT will be investigated. It will be determined if polymerization occurs during the reduction process of the DBCOTM(CO)₃ systems. Understanding the redox behavior of these complexes will provide valuable information on how this unique system can be used in catalysis, nanotechnology and supramolecular organometallic chemistry.

Scheme 1.7 Electrochemical reduction of DBCOT

\[
\text{DBCOT} \xrightarrow{e^-} \text{DBCOT}^+ \xrightarrow{e^-} \text{DBCOT}^{2-}
\]
CHAPTER II
EXPERIMENTAL

This chapter summarizes the synthetic and electrochemical procedures utilized. The synthesis section gives a brief and generic synthesis of the ligand and the organometallic complexes of interest and highlights important tasks that ensured quality products. The electrochemical section emphasized on cyclic voltammetry and the experimental manipulations involved in producing efficient data.

2.1 Material and Methods

Acetone-\textit{d}6 (CD$_3$COCD$_3$), carbon tetrachloride (CCl$_4$), chloroform (CHCl$_3$), chromium(0)hexacarbonyl (Cr(CO)$_6$), \( \alpha,\alpha'-\text{dibromo-o-xylene} \) (C$_8$H$_8$Br$_2$), dimethylformamide [DMF, (CH$_3$)$_2$NC(O)H], lithium wire (Li), N-bromosuccinimide (NBS, C$_4$H$_4$BrNO$_2$), pentane (C$_5$H$_{12}$), potassium tert-butoxide (K'OtBu, C$_4$H$_9$OK), tetrahydrofuran (THF, C$_4$H$_8$O), and tetramethylsilane [TMS, Si(CH$_3$)$_4$] were purchased form Sigma Aldrich. Acetone (CH$_3$COCH$_3$), ethanol [EtOH, C$_2$H$_5$], ethyl acetate (C$_4$H$_8$O$_2$), and isopropanol (C$_3$H$_7$OH) were purchased from VWR. Celite, dry hexanes (C$_6$H$_{14}$), \( d \)-chloroform (CDCl$_3$), ethyl ether ((C$_2$H$_5$)$_2$O), methylene chloride (CH$_2$Cl$_2$), and sea sand were purchased from Fisher Chemicals. n-Butyl ether (C$_8$H$_{18}$O) was purchased from Alfa-Aesar. Tetrabutylammonium perchlorate [TBAP, (C$_4$H$_9$)$_4$N(ClO$_4$)] was
purchased from Eastman Kodak Chemicals. Chromatographic silica gel was purchased from Silicycle. Ferrocene [Fc, Fe(C₅H₅)₂] was purchased from Strem Chemicals.

All air-sensitive materials were manipulated under a hood using ultra-pure argon gas supplied through a double manifold. Before use the double manifold is flushed with Ar for 5-10 min. Various schlenk techniques were used for the purpose of transferring, reacting and storing the air-sensitive moieties.⁴³ Commercial grade solvents were purified via distillation under Ar over a drying agent (Na/K alloy or P₂O₅), if they were not available in their anhydrous form. All solvents were purged with Ar prior to immediate use. NBS was purified by recrystallization in deionized water. The NBS was dried for 2-3 h under vacuum with applied heat. Dry hexanes and THF were purified over a Na/K alloy via distillation under Ar. Dichloromethane was distilled over P₂O₅ via distillation under Ar. TBAP was recrystallized three times from an ethyl acetate/pentane solution and dried under vacuum for 3-5 h before use. Anhydrous DMF was bubbled with Ar for 0.5-1 h before use to rid of any moisture.

2.2 Synthetic Procedures

2.2.1 DBCOT synthesis

Chaffin et al.⁷ proposed the following synthetic procedure the primary organometallic ligand, DBCOT. ¹H NMR was used as the primary spectroscopic technique.
2.2.1.1 Preparation of lithium sand

Lithium sand was made by carefully cutting lithium wire (in mineral oil) into ≈0.5” pieces into a 100 ml beaker containing silicon oil. The mixture was transferred to a 500 ml 3-neck round bottom flask, which also contained silicon oil under an argon atmosphere via mechanical stirrer. Lithium particles were observed after vigorous convection at ≈200 °C for 3 h. After obtaining the proper size particles the silicon oil was removed via teflon cannula and the particles were washed three times with dry hexanes to remove any remaining oil before use.
2.2.1.2 Synthesis of 5, 6, 11, 12-Tetrahydrobibenz [a, e] cyclooctadiene

Lithium sand and α,α’-dibromo-o-xylene in anhydrous THF were sonicated for 5-6 h at 60 min intervals with the exchange of the warm water, caused by the exothermic reaction, with cold water to prevent boiling of solvent. Completion was indicated by a blood red solution. Soxhlet extraction with hexanes was used to purify the desired product.

2.2.1.3 Synthesis of 5, 11-Dibromo-5, 6, 11, 12-tetrahydribenz [a, e] cyclooctadiene

5, 6, 11, 12-Tetrahydribenz [a, e] cyclooctadiene was added to a solution NBS in anhydrous CCl₄ and brought to reflux for 3 h. The remaining succinimide was removed via filtration and the solvent was removed by rotary evaporation.

2.2.1.4 Synthesis of Dibenzo [a,e]cyclooctatetraene

5, 11-Dibromo-5, 6, 11, 12-tetrahydribenz [a, e] cyclooctadiene was dissolved in anhydrous THF and brought to 0 °C using an ice bath. Upon obtaining the desired
temperature 1M K’OtBu/THF solution was added very slowly via canula and allowed to stir for 8 h up to room temperature.

2.2.2 Synthesis of chromiumtricarbonyl complexes

Henry et al.²⁶ proposed the following synthetic procedure of the primary organometallic complexes under investigation.

DBCOT and Cr(CO)₆ were added to a Schlenk flask and cooled to 0 °C using ice bath. The Schlenk flask was filled and evacuated with ultra high purity Ar five times before solvent was added. Dry n-butylether and THF in an 18:2 ratio was added as
solvent and allowed to reflux at 130 °C for 3 d to obtain mono DBCOT Cr(CO)₃; for 7 d
to obtain bis DBCOTCr(CO)₃.

2.2.3 Synthesis of η⁶-dibenzo [a,e]cyclooctatetraene(tricarbonyl)manganese (I)
tetrafluoroborate

DBCOT and η⁶-naphthalene(tricarbonyl)manganese(I) tetrafluoroborate were added to a schlenk flask with vacuum and reflux condenser adaptations. The apparatus was evacuated and filled with high purity argon gas three times. CH₂Cl₂ was added to the mixture and allowed to reflux for approximately 8 h. After cooling to room temperature, the volume was reduced to 10 mL via vacuum evaporation. Zero degree anhydrous diethyl ether was added to the solution to yield a light yellow precipitate (η⁶-dibenzo[a,e]cyclooctatetraene(tricarbonyl)manganese(I) tetrafluoroborate).

Full details on the synthesis and purification are given in Nilantha Bandara’s dissertation.⁹,²⁶ Briefly, the complexes were purified by column chromatography on oven dried silica gel using hexanes:diethyl ether at a 7:3 ratio as eluent. The complexes were indicated on the column by a yellow band. Upon solvent removal, a yellow solid remained which was verified via melting point and ¹H NMR.⁹,²⁶
2.3 **Cyclic Voltammetry: Three Electrode System**

A cyclic voltammetric three electrode cell system was used to effectively study the analyte at the working electrode surface by monitoring both the potential and the current. The electronic behavior of the analyte is studied by applying a potential to the working electrode and measuring the current that is displaced. Since potential is being applied to the working electrode a reference electrode is needed because it maintains a standard constant potential, thus giving a comparable entity. An auxiliary electrode is necessary to complete the current necessary to supply the current required at the working electrode. These three electrodes work together to afford unique and valuable information on the electronic behavior of the analyte under investigation.

2.3.1 **Experimental Procedure**

The three electrode system was constructed allowing a constant flow of Ar through-out the cell. Parafilm was used to ensure a seal around the rubber top of the cell as an extra precaution to prevent any moisture from penetrating the solution. A platinum disk with an area of 0.01 cm² (working electrode), platinum wire (auxiliary electrode), and Ag wire with liquid junction reference electrode were used in each experiment. To ensure a quality CV the following steps were taken before each experiment: 1) A glass cell was washed thoroughly with acetone and dried for at least 24 h before use 2) The surface of each electrode was sanded lightly with P800 SiC sandpaper and rinsed with acetone 3) 0.85 g (0.00248 mol) of supporting electrolyte TBAP was added to a 100 ml Schlenk flask and dried under vacuum for approximately 3 h 4) Solvent was bubbled with Ar for approximately 30 min to remove any remaining oxygen. All analyte solutions were 3 mM.
10 ml of anhydrous solvent was added via glass syringe to the 0.85 g of TBAP to obtain a 0.25 M solution of supporting electrolyte. The supporting electrolyte solution is transferred to the cell using the glass syringe and needle. Stirring and Ar were applied to the solution for 20-25 min and both removed from the solution before background scans were run. The uncompensated resistance ($R_u$) associated with the system was corrected for manually before scanning began. Background scans are obtained for both the anodic and cathodic potentials of the supporting analyte solution. After obtaining the background voltammograms, the analyte was added to the solution and a series of scans at scan rates ranging from 20 to 2000 mV s$^{-1}$ and various potential ranges. All potentials were recorded versus Ag wire reference electrode with a double junction and reported recorded versus a ferrocenium/ferrocene redox couple (Fc$^+/Fc$). Ferrocene is used as a non-interactive internal standard that is added at the end of the experimental acquisition to provide a reliable internal reference potential. Electrochemical analysis will be further discussed in the next chapter.

2.4 Cyclic Voltammetry Instrumentation and Software

Experimental CV was carried out using an EG&G PAR, potentiostat/galvanostat 273A with Model 250 Research Electrochemistry Software version (M270). Digital simulations were generated using software Digisim v 2.1, Bioanalytical Systems, Inc.

2.4.1 CV Experimental Parameters

The table below shows the experimental parameters, abbreviation, value, and unit used for in a typical CV experiment.
Table 2.1  Standard experimental CV conditions

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CHAPTER III
RESULTS AND DISCUSSION

This chapter will present the results of cyclic voltammetric analysis of the η⁶-DBCOTmonochromiumtricarbonyl, η⁶-DBCOTmanganesetricarbonyl cation, and η⁶, η⁶-DBCOT-syn,anti-bischromiumtricarbonyl. This section will discuss the electrochemical behavioral similarities and differences of each complex and their possible reductive electrochemical mechanism, which would facilitate conclusions drawn about each complexes behavior. Digital simulation software (Digisim) will be used to support the proposed mechanism of each complex.

3.1 Electrochemical studies of η⁶-DBCOTmonochromiumtricarbonyl

3.1.1 Cyclic Voltammetry of η⁶- DBCOTmonochromiumtricarbonyl (25 ºC)

![Graphs of cyclic voltammetry](image)

Figure 3.1 CV of η⁶- DBCOTmonochromiumtricarbonyl at room temperature A) Direct B) Normalized
Figure 3.2  Peak current as a function of the square root of the scan rate of Figure 3.1A

Figure 3.1A shows a series of cyclic voltammograms (CVs) for η6-DBCOTmonochromiumtricarbonyl plotted against a ferrocene reference potential at 25 °C. Figure 3.1B shows presents the normalized current by dividing the current by the square root of the scan rate to give the “current function”. Theory for diffusion limited current predicts a linear relation between the peak current and square root of the scan rate, which means the quotient of the peak current at its corresponding scan rate should be relatively the same. Figure 3.1B clearly displays this for the initial reductive peak of the voltammogram. The shift in the peak as the scan rate is increased is most likely due to aggravation at reference electrode. The linear slope (Figure 3.2) suggests a near diffusion controlled initial electron transfer step. By plotting the current function, the relative peak positions and shapes are more easily distinguished. There is a negative potential shift as the scan rate is increased. This is most likely due the shift of the second electrochemical reduction because of its slower electron transfer kinetics, thus broadening the peak and decreasing the current height.

The first narrow reduction peak ($E_{pc} = -2.3$ V) is assumed to be two one-electron reductions occurring at nearly the same potential or with the 2nd reduction more positive
than the first, assuming this system follows similar electrochemical reduction processes as previous literature describes for DBCOT and other polyarene chromium complexes.\textsuperscript{14,42-36} This peak is associated with that of the parent complex. The broad peak that trails the narrow reduction peak ($E_{pc} = -2.5$ V) is assumed to be that of the protonated dianion of the complex. The smaller reduction peak ($E_{pc} = -2.8$ V) is indicative of the DBCOT ligand. The presence of this peak indicates either the decomposition of the complex in the solution or unreacted ligand from synthesis. If the cause of the production of the ligand reduction peak is due to decomposition, a possible explanation is the very negative potentials used during scanning.

The two oxidation peaks ($E_{pa} = -2.03$ V, $E_{pa} = -1.5$ V) observed on the reverse scan could occur based on two possibilities, the first being the corresponding oxidation peak of the initial two one-electron reductions. The second and more likely process is that the first oxidation peak (-2.03 V) is due to the quasi-reversible reduction of the complex of interest and the second oxidation peak (-1.5 V) could be due to the product of a chemical reaction of one of the reduced species (could be dimerization of the monoanionic radical complex or decomposition or the protonated species). From the assumptions made, a generic mechanism was predicted.

\begin{align*}
    A + e &= B \quad (3.1) \\
    B + e &= C \quad (3.2) \\
    C &= D \quad (3.3) \\
    D + e &= E \quad (3.4) \\
    E &= F \quad (3.5)
\end{align*}
The proposed mechanism of $\eta^6$-DBCOTCr(CO)$_3$ (Scheme 3.1) is constructed on Bard’s$^{42}$ assumption of generating a monoanionic radical upon the first reduction and a dianionic aromatic DBCOT ligand upon the second reduction in consecutive electrochemical reduction reactions. The justification for applying this conceptual outlook of Bard’s suggested mechanism is simply that Cr does not possess the electron withdrawing ability or the positive charge of isoelectronic Mn$^+$, therefore, the DBCOT is responsible for all electron accepting abilities of the complex. The reductive process (Scheme 3.1) begins with mono $\eta^6$-DBCOTCr(CO)$_3$ (A) accepting an electron at the COT center to generate a 19 e$^-$ monoanion radical B, which immediately accepts the second electron to form the 20 e$^-$ semi-tub shaped $\eta^6$ coordinated complex C.$^{42}$ It is suggested that the electron withdrawing capability of the metal enhanced by the carbonyls slight inhibits the delocalization of the electrons which is the reason behind the tub shaped dianion. The repulsion between the Cr(CO)$_3$ and the now 10 e$^-$ COT center forces the geometrical isomerization and haptotropic shift to produce the $\eta^4$ coordinated complex D.$^{11,12,13,16,18}$ A third heterogeneous reaction of D is believed to produce an unknown complex E, which is suggested to produce the trailing reduction peak at -2.6 V. This unknown product is suggested to undergo a homogeneous reaction to produce an irreversible species F, (-1.5 V).
Scheme 3.1  Electrochemical reduction mechanism of η⁶-DBCOTchromiumtricarbonyl at 25 °C

Digisim Electrochemistry software was used to simulate and compare the predicted EECEC mechanism (Figure 3.3) to the experimental voltammogram at various scan rates. It important to note that the simulations are not corrected to the ferrocene reference, therefore a difference of 0.909 V is unaccounted for. The area of the platinum disk electrode was 0.01 cm². The digital simulation of the proposed mechanism mimicked the overall shape of the 0.003 M complex solution under the following parameters that are manipulated based on Bard’s digital parameters of DBCOT⁴²: $E_0^1 = -1.44$ V; $k_s^1 = 0.025$ cm/s; $\alpha = 0.6$; for the first reduction; $E_0^2 = -1.14$ V; $k_s^2 = 0.01$ cm/s; $\alpha = 0.5$ for the second reduction and $E_{1/2}^3 = -0.68$ V; $k_s^3 = 0.06$ cm/s; $\alpha = 0.7$ for the third reduction. D was assumed to be relatively close to the ligand, $5.00 \times 10^{-6}$ cm²/s, for all
species. All parameters listed remained constant over the various scan rates for the heterogeneous reactions. This suggested that the proposed mechanism and estimated parameters appear to be valid. The chemical reactions that are assumed to be taking place have parametric values of: $K_{eq1} = 1$; $k_{f1} = 0.3 \text{ s}^{-1}$; $k_{b1} = 0.3 \text{ s}^{-1}$ for the first chemical reaction and $K_{eq2} = 1 \times 10^6$; $k_{f2} = 0.1 \text{ s}^{-1}$; $k_{b2} = 1 \times 10^{-7} \text{ s}^{-1}$ for the second chemical reaction.

Figure 3.3  Digital simulation of 3 mM η6- DBCOTmonochromiumtricarbonyl at in 0.25 M TBAP/DMF solution at 25 °C
To justify the inequality of \( k_s^1 > k_s^2 \) the idea and ability of the predicted haptotropic shift of the \( \text{Cr(CO)}_3 \) and geometrical isomerization of the ligand must be discussed. In the introduction the electrochemical reduction mechanism of the ligand (DBCOT) was referenced.\(^{42}\) It was suggested that \( k_s^2 > k_s^1 \) due to the geometrical isomerization of DBCOT from a tub to a more planar geometry after the first electron is accepted at the 8-electron center, thus allowing for a much faster electron transfer of the second electron. This assumption CANNOT be made for the complex under investigation. The most cogent reasoning for the larger \( k_1 \) for the reduction of the complex is that the coordinated \( \text{Cr(CO)}_3 \) facilitates the accepting ability of the 8-electron COT center by accepting some of the electron density of ligand.

Notice the dramatic difference in the \( K_{eq} \) values of the chemical reactions. The first chemical reaction (\( K_{eq}^1 = 1 \)) suggests reversibility of the chemical reaction, which could contribute to the quasi-reversible behavior of the complex. While the second chemical reaction (\( K_{eq}^2 = 1 \times 10^6 \)) is indicative of a heavily favored product, which can be associated the irreversible nature of the oxidation peak at -1.50 V. The digital simulation cannot be representative of an overall depiction of the experimental voltammogram due to inconclusive theoretical and computation studies of the complex. Information of the rate constant, equilibrium constant, diffusion coefficient and etc. are necessary in order to produce confident \( I_{pc}, I_{pa}, E_{pc}, \) and \( E_{pa} \) values.

The scan rate dependence of the peak current was studied for the oxidation peaks (\( E_{pa} = -2.05 \) V, \( E_{pa} = -1.50 \) V) of the complex (Figure 3.4). The analysis yielded complicated results, which are suggested to be contributed by complications in the kinetics of the heterogeneous electron transfer, or chemical changes due to homogeneous
reactions. When compared to the scan rate versus current analysis of the reduction the plots were inconsistent. The room temperature studies presented a linear relationship for the both oxidation peaks. The studies at 0 °C show what seems to be an inverse relationship. This could be indicative of the quasi-reversible nature of the DBCOTCr(CO)₃ complex and the irreversible properties of the unknown generated species. As the temperature is increased the linearity is regenerated but the currents do not resemble those at the initial room temperature scans. An explanation for this unusual discrepancy in the data is unknown but under investigation.

3.1.2 Cyclic Voltammetry of η⁶- DBCOTmonochromiumtricarbonyl (0ºC)

Figure 3.4 CV of η⁶- DBCOTmonochromiumtricarbonyl (0 °C) A) Direct B) Normalized
Figure 3.5  Peak current as a function of the square root of the scan rate of Figure 3.5A

The primary purpose for decreasing the temperature is to determine if there are two separate reduction peaks that can be observed to support the suggested 2 one-electron processes. The most obvious characteristics of Figure 3.5A is the decrease in the peak current as well as the more broad and less defined peaks. The normalized plot (Figure 3.5B) shows a clear increase in the potential of the reduction peak. The decrease in the peak current is expected considering that as temperature is decreased, electron transfer rate becomes smaller. The dramatic shift in potential can possibly be due to passivation on the electrode surface, which becomes more prominent as the scan rate is increased. A shift in the cathodic peak potential as the scan rate is increased is unexpected, but not uncommon, considering the reduced species at 0 °C is expected to be the same species at 25 °C. If a plot the peak current as function of the square root of the scan rate (Figure 3.6) is generated, just as observed at 25 °C, a straight line is obtained with an R² value of 0.9993. This data suggests a diffusion controlled reaction and not necessarily fast heterogeneous kinetics due to the decrease in temperature. With the electron transfer kinetics remaining relatively fast, it leaves the question “Does the chemistry in solution differ from 25 °C to 0 °C or is there a specific orientation of the complex that is favored?”
The overall shape of cyclic voltammogram is similar to that at room temperature, so it is assumed that their electrochemical reduction mechanism is the same.

3.1.3 Cyclic Voltammetry of \( \eta^6 \)-DBCOTmonochromiumtricarbonyl (0 °C - 25 °C)

![Figure 3.6](image)

**Figure 3.6** CV of \( \eta^6 \)-DBCOTmonochromiumtricarbonyl (0 °C - 25 °C) A) Direct B) Normalized

![Figure 3.7](image)

**Figure 3.7** Peak current as a function of the square root of the scan rate

The voltammogram obtained as the temperature is increased from 0 °C to 25 °C (Figure 3.7A) exhibited peaks that surprisingly mimic that at 0 °C. Since the conditions
are the same as the initial 25 °C CV experiment (Figure 3.1A) it would be expected that the voltammograms would have been relatively similar. Figure 3.7 further magnifies the varying potential of the cathodic potential as scan rate is increased. The theory of why the current did not increase to the same or relatively close to that of the 25 °C scans is that the complex is slowly undergoing decomposition producing a product in solution that passivates the electrode. This is not seen at 25 °C because the rate of fluxionality may be too fast for this decomposition to occur. This could be a reason why increasing the temperature back to 25 °C did not yield the expected results. The \( I_{pa} \) and \( I_{pc} \) increase insignificantly as the temperature increased but their broadness remains. It is also noticeable that the intensity of the ligand peak has increased.

Figure 3.9 gives a direct visual of each temperature scan plotted against to each other. The broadening of all peaks as well as the shift in the oxidation peaks at 0 °C and 0 °C - 25 °C is noticeable. This is suggested to be the result of passivating at the electrode to an unknown irreversible species that is produced after reduction at 0 °C. The third reduction (Equation 3.4) is assumed to still be present at 0 °C and 0 °C - 25 °C but merged into their broad reduction peak.
Figure 3.8  η⁶-DBCOTmonochromiumtricarbonyl temperature comparisons at 200 mV/s

3.2  Electrochemical studies of η⁶-DBCOTmanganeseetracarbonyl

3.2.1  Cyclic Voltammetry of η⁶-DBCOTmanganeseetracarbonyl (25 °C)

Figure 3.9  CV of η⁶-DBCOTmanganeseetracarbonyl (25 °C) A) Direct B) Normalized
Figure 3.10 and 3.11 show that the manganese complex cation reduces between -1.375 and -1.4 V and oxidizes between -1.1 and -1.15 V depending on the scan rate applied. It is also assumed that this is 2 one-electron reduction processes. It is obvious to notice that this complex reduces more easily than the neutral, isoelectronic Cr(CO)_3 counterpart. Of course, the initial explanation for this would be its cationic nature, which greatly increases its electron accepting ability. Figure 3.10B clearly shows the reduction peaks of the manganese complex have minimal shift as the scan rate is increased as well as a reduction peak at ≈1.37 V. This suggests complex’s electron accepting ability is not altered by potential solution chemistry. The quasi-reversibility suggests that is a minor chemical reaction taking place in solution, which could be responsible the slight reduction peak at -1.9 V. the shift on the oxidation peaks of the normalized plots suggests a complex issue with the kinetics than is under further investigation. Based on the information obtained from the voltammogram it is assumed that the generic electrochemical mechanism is as follows:

\[ A + e = B \]  \hspace{1cm} (3.6)
\[ B + e = C \]  \hspace{1cm} (3.7)

\[ C = D \]  \hspace{1cm} (3.8)

The reductive pathway of \( \eta^6\text{-DBCOTMn(CO)}_3^{+} \) (A) seems to follow a similar reductive pathway as its Cr(CO)_3 derivative. The initial heterogeneous reaction results in a neutral 19 e\(^{-}\) species (B). Upon obtaining its neutral form the second electron addition follows producing the monoanionic 20 e\(^{-}\) species (C). Electrostatic repulsion of the Mn(CO)_3 with the COT center results in a change in conformation to the planar isomer that resembles conformation of the Cr(CO)_3 complex at the same stage. The heterogeneous electron transfer reaction is almost simultaneously followed by a homogeneous reaction resulting in the haptotropic shift of the Mn(CO)_3 producing an \( \eta^4 \) COT coordinated Mn(CO)_3 18 e\(^{-}\) species (D) (Scheme 3.2). The CV does not indicate any further present reaction during the reduction process as seen in \( \eta^6\text{-DBCOTCr(CO)}_3 \).
Scheme 3.2  Electrochemical reduction mechanism of $\eta^6$-DBCOTmanganese tricarbonyl at 25 °C

Digisim Electrochemistry software was also used to simulate the predicted EEC mechanism to the experimental voltammogram of the manganese complex at 25 °C (Scheme 3.2). Once again these values are not plotted against the Fe$^+/Fe$ couple, therefore 0.685 V must be accounted for. The simulation constant parameters are as follows: $E_0^1 = -0.725$ V; $k_s^1 = 0.025$ cm/s; $\alpha = 0.7$ for the first reduction; $E_0^2 = -0.43$ V; $k_s^2 = 0.01$ cm/s; $\alpha = 0.5$ for the second reduction. D was assumed to be the same as its chromium counterpart, $5.00 \times 10^{-6}$ cm$^2$/s, for all species. The chemical reactions that are assumed to be taking place have parametric values of: $K_{eq}^1 = 1 \times 10^6$; $k_f^1 = 1$ s$^{-1}$; $k_b^1 = 1 \times 10^{-6}$ s$^{-1}$. Notice that the $I_{pa}$, $I_{pc}$, $E_{pa}$ and $E_{pc}$ are not exact due to the same reasons mentioned for its chromium counterpart (Figure 3.3). As theorized, the digital simulation did mimic the
overall shape of the experimental voltammogram. As the scan rate of the digital is increased the reversibility of the complex reduction becomes more prominent. The digital simulation does not exhibit the slight shift in the oxidation peak clearly seen in C and D. One must take into consideration that the digital simulation does not account for solvent affects which is the primary reason for the differing of signals.

Figure 3.11  Digital simulation of 3 mM η⁶- DBCOTmanganese-tricarbonyl in 0.25 M TBAP/DMF solution at 25 °C

Oxidative analysis of the √ν vs. I_{pa} was carried out to determine if the unusual behavior was consistent with its chromium counterpart. The non-linear plot was shown
to be characteristic of the DBCOTMn(CO)₃ oxidation peak \( (E_{pa} = -1.1 \text{ V, Figure 3.10}) \). In comparison with the DBCOTCr(CO)₃ complex, the initial 25 °C scans and 0 - 25 °C resembles the chromium complex. The 0 °C analysis for the manganese complex exhibited an upward slope, opposing the downward slope of the chromium complex. Although, the 0 °C studies show different results, the complexity of the kinetics at the electrode is still assumed to the most logical reasoning for the non-linear plot.

![Graph](image_url)

Figure 3.12 Variable temperature oxidative kinetic studies η⁶-DBCOTmanganese-tricarbonyl at 25 °C

### 3.2.2 Comparative oxidative studies of \( \sqrt{\nu} \) vs. \( I_{pa} \) of η⁶-DBCOTmonochromium-tricarbonyl and η⁶-DBCOTmanganese-tricarbonyl

If the oxidative analysis of the \( \sqrt{\nu} \) vs. \( I_{pa} \) of η⁶-DBCOTmonochromium-tricarbonyl (Figure 3.4) and η⁶-DBCOTmanganese-tricarbonyl cation (Figure 3.13) are compared the inconsistency of the plots for the chromium complex does not emulate those of the manganese complex. The erratic oxidative behavior of the DBCOTCr(CO)₃ complex is
not unexpected considering the intense broadening at the various temperatures and the unexplainable electrochemical behavior from 0 °C to 25 °C. Although the $\sqrt{\nu}$ vs. $I_{pa}$ does not present a linear plot, each temperature study presented a plot that is consistent with the previous. This suggests the manganese complex is more stable in solution and no obvious passivating is seen like in case of the chromium complex. These studies further support the simplistic behavior of the manganese complex and the intricate behavior of its chromium counterpart.

3.2.3 Cyclic Voltammetry of η⁶- DBCOTmanganesetricarbonyl (0 °C)

![Cyclic Voltammetry of η⁶- DBCOTmanganesetricarbonyl (0 °C)](image)

Figure 3.13 CV of η⁶- DBCOTmanganesetricarbonyl (0 °C) A) Direct B) Normalized
There is very little change in the potential as well as the current of the reduction peaks as the temperature of the solution is cooled from 25 °C to 0 °C (Figure 3.14) and fast electron transfer kinetics as well as reversibility are still assumed (Figure 3.15). The reduction peaks of the manganese complex show minimal shift as the scan rate is increased compared to the chromium complex. The oxidation peaks shown present an interesting trend compared to its Cr(CO)₃ counterpart. As we decreased to temperature of the solution containing the Cr(CO)₃ complex, there is a direct relationship associated with the current of the oxidation peak. On the other hand, the Mn(CO)₃ complex under the same conditions exhibit an inverse relationship. The expectation was that this complex would have been very similar to the Cr(CO)₃ considering that Mn and Cr have very similar electrochemical properties. The question “Why doesn’t this complex exhibit the same electrochemical behavior as the Cr(CO)₃ complex at 0 °C?” immediately arises.

The digital simulation (Figure 3.16) of the 0 °C scans were carried out under the following parameters: \( E_0^1 = -0.725 \); \( k_s = 0.025 \); \( \alpha = 0.7 \); for the first reduction and \( E_0^2 = -0.43 \); \( k_s = 0.01 \text{ s}^{-1} \); \( \alpha = 0.5 \) for the second reduction. D was assumed to be slightly
smaller than the complex at 25 °C, 4.00 × 10⁻⁶ cm²/s. The chemical reaction has parametric values of: \( K_{eq} = 1 \times 10^6 \); \( k_f = 0.4 \) s⁻¹; \( k_b = 4 \times 10^{-7} \) s⁻¹. The smaller \( k_f \) is predicted because of the temperature decrease which suggests a slower chemical reaction.

Figure 3.15  Digital simulation of 3 mM \( \eta^6 \)-DBCOTmanganesetricarbonyl in 0.25 M TBAP/DMF solution at 0 °C
3.2.4 Cyclic Voltammetry of η₆-DABCOTmanganese(III)tricarbonyl (0 °C to RT)

Figure 3.16 CV of η₆-DABCOTmanganese(III)tricarbonyl (0 °C - 25 °C) A) Direct B) Normalized

Figure 3.17 Peak current as a function of the square root of the scan rate of Figure 3.17A

As mentioned previously the change in electrochemical behavior based on the obtained voltammograms for room temperature and 0 °C are relatively indifferent. The electrochemical behavior as the temperature is increased from 0 °C to 25 °C resembles mostly that of the initial room temperature trial. The current of the oxidation peaks are mimics of those obtained at the initial room temperature trial which opposes what is
observed for the chromium complex. Overall the electrochemical behavior is relatively unchanged except for small shifts in the potentials of the oxidation peak at 0 °C and the reduction peak at 0 °C - 25 °C when comparing the various temperatures (Figure 3.)

Figure 3.18 CV temperature comparisons of η⁶- DBCOTmonomanganesetricarbonyl

3.3 Electrochemical studies of η⁶,η⁶-DBCOT-syn,anti-bischromiumtricarbonyl

CV Studies of DBCOT-bis-Cr(CO)₃ were carried out as dubious studies. The reason being is that there was decomposition of the bis complex to an unknown isomer, verified by ¹H NMR (Figure 3.20), under the stored conditions before an accurate and direct voltammogram could be generated.
Though further studies are needed to support the suggested isomer formation, $^1$H NMR shows a clear splitting of the vinyl hydrogens from a single peak (6.65 ppm, C$_5$-C$_6$, C$_{11}$-C$_{12}$) to two well separated peaks (6.64 ppm and 6.52 ppm) (Figure 3.20 A and B). Observation of the chemical shifts shows that the single peak at 6.65 ppm (C$_5$-C$_6$, C$_{11}$-C$_{12}$) of A and the more deshielded peak at 6.64 ppm (C$_5$, C$_{12}$) of B are relatively the same. Thus, it is safe to assume that their environments are similar. On the other hand, the peak at 6.52 ppm (C$_6$, C$_{11}$) of B is indicative of more shielding. The most logical explanation for this split is a haptotropic rearrangement of the anti Cr(CO)$_3$ from an $\eta^6$ coordination to an $\eta^4$ coordination (Figure). The $\eta^4$ coordinated Cr(CO)$_3$ would provide a similar shielding effect as the anti, $\eta^6$ coordinated Cr(CO)$_3$ with minimal difference in the
chemical shift of the vinyl hydrogens located on C5 and C12. The vinyl hydrogens located on C6 and C11 are more shielded from the effects of the η⁴ coordinated Cr(CO)₃ and the syn η⁶ coordinated Cr(CO)₃ which results in the upfield shift.

Each experimental voltammogram shows three distinct reduction peaks with quasi-reversible characteristic. The first two peaks ($E_{pc} = -2.45$ V, $E_{pc} = -2.6$ V) are assumed to be related to the bis complex, while the third ($E_{pc} = -2.9$ V) is most likely due to unreacted ligand from the synthesis. One oxidation is observable with behavior similar to that of the mono chromium complex. The bis complex shows a reduction and oxidation wave that is similar to what is exhibited by the mono complex ($E_{pc} = -2.45$ V) and the ligand ($E_{pc} = -2.9$ V). This could indicate decomposition of the bis complex. The instability of the bis complex could be related to that of the unstable mono complex, which is seen by the passivation process. This complex is of current interest and is being thoroughly investigated.

Figure 3.20  CV of η⁶,η⁶-DBCOT-syn,anti-bischromiumtricarbonyl (25 °C) A) Direct B) Normalized
Figure 3.21  CV of \( \eta^6,\eta^6\)-DBCOT-syn,anti-bischromiumtricarbonyl (0 °C) A) Direct B) Normalized

Figure 3.22  CV of \( \eta^6,\eta^6\)-DBCOT-syn,anti-bischromiumtricarbonyl (0 °C - 25 °C) A) Direct B) Normalized
CHAPTER IV
CONCLUSION

The electrochemical analysis of the DBCOTM(CO)₃ system has proven to be difficult to interpret considering all of the complex reductive pathway and orbital interaction possibilities. From knowledge acquired from the previous works of a variety of authors, a strong attempt was made to understand this system and plausible mechanistic pathways of η⁶-DBCOTCr(CO)₃ and its isoelectronic counterpart η⁶-DBCOTMn(CO)₃ have been proposed. η⁶, η⁶- bis-DBCOTCr(CO)₃ failed to sustain stability under the stored condition, thus and in dept electrochemical analysis of the complex was not ideal and is under further investigation.

The proposed mechanisms of η⁶-DBCOTCr(CO)₃ and its cationic derivative η⁶-DBCOTMn(CO)₃⁺ is constructed mainly on Bard’s assumption of generating an aromatic DBCOT ligand upon reduction and the idea that M(CO)₃ undergo a change in hapticity during or immediately after this geometrical isomerization. Though the predicted mechanisms for the complex are obviously more complicated than that of the DBCOT ligand, the justification for applying this conceptual outlook of Bard’s suggested mechanism is that the η⁶-DBCOTM(CO)₃ are assumed to reduced the DBCOT ligand and not the metal.

For η⁶-DBCOTCr(CO)₃ the reductive process produces a radical with the addition of the first electron, which immediately undergoes a second reduction at the ligand.
Almost synchronously after the second electron is accepted there is suggested to be a geometrical isomerization of the DBCOT which allows for a haptotropic shift of the Cr(CO)$_3$ to produce the $\eta^4$ coordinated complex. CV indicates that there are multiple homogenous reactions involved in the reduction process of this complex that produces a second reduction wave and second oxidation wave. These waves have not yet identified and are under further analysis. 0 °C analyses show an unexplainable behavior of the reduction, which is irreversible when the temperature is increased from 0 °C - 25 °C. This behavior is currently under investigation.

DBCOTMn(CO)$_3$$^+$ electrochemical studies present a more simple reduction process compared to its Cr(CO)$_3$ derivative. None-the-less it follows the same reductive process as $\eta^6$-DBCOTCr(CO)$_3$ to produce the $\eta^4$ coordinated complex. DBCOTMn(CO)$_3$$^+$ is easier to reduce which is assumed to be due to its cationic nature and fact that Mn(CO)$_3$$^+$ has a greater electron withdrawing capability compared to Cr(CO)$_3$.

Digital simulation supports the mechanistic predictions but much analysis is needed to confirm the predictions with confidence. Due to insufficient information it cannot be concluded that the fluxionality of these complexes partake in a major role of the reduction process. Future work will consist of a series of computational, theoretical and more electrochemical studies to further understand these unique systems.
REFERENCES


(9) Bandara, N. Dissertation, Mississippi State University, Mississippi State, MS, 2011.


APPENDIX A

DIGITAL SIMULATION PARAMETERS
Table A.1  η^6-DBCOTCr(CO)_3 digital simulation parameters at 25 °C

<table>
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<th>Charge transfer reactions</th>
<th>Charge transfer parameters</th>
<th>Species parameters</th>
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<td>parameters</td>
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<td></td>
</tr>
<tr>
<td>K_{eq}^1: 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_f^1: 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_b^1: 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K_{eq}^2: 1 × 10^6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_f^2: 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_b^2: 1 × 10^{-7}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: To correct simulation potentials to the Fe⁺/Fe reference couple, subtract -0.909 V
Table A.2  \( \eta^6\)-DBCOTMn(CO)\(_3\) digital simulation parameters at 25 °C

<table>
<thead>
<tr>
<th>Charge transfer reactions</th>
<th>Charge transfer parameters</th>
<th>Species parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1: A + e = B</td>
<td>( E_0^1 ) (V): -0.725</td>
<td>( C_{\text{anal}}[A] ) (M/l): 0.003</td>
</tr>
<tr>
<td></td>
<td>( \alpha^1 : 0.7 )</td>
<td>( C_{\text{init}}[A] ) (M/l): 0.003</td>
</tr>
<tr>
<td></td>
<td>( k_s^1 ) (cm/s): 0.025</td>
<td>( D[A] ) (cm(^2)/s): 5.00 \times 10^{-6}</td>
</tr>
<tr>
<td>Reaction 2: B + e = C</td>
<td>( E_0^2 ) (V): -0.43</td>
<td>( C_{\text{anal}}[B] ) (M/l): 0</td>
</tr>
<tr>
<td></td>
<td>( \alpha^2 : 0.5 )</td>
<td>( C_{\text{init}}[B] ) (M/l): 1.6762 \times 10^{-15}</td>
</tr>
<tr>
<td></td>
<td>( k_s^2 ) (cm/s): 0.01</td>
<td>( D[B] ) (cm(^2)/s): 5.00 \times 10^{-6}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Homogeneous chemical reactions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1: C=D</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{\text{start}} ) (V): 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{\text{switch}} ) (V): -1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_{\text{end}} ) (V): 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( v ) (V/s): 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K): 298.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R_u ) (Ohms): 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{\text{dl}} ) (F): 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycles: 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrode geometry: planar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area (cm(^2)): 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion: semi-infinite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-equilibrium: enabled for all reactions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical reaction parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{\text{eq}}^1 ): 1 \times 10^6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_f^1 ): 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_b^1 ): 1 \times 10^{-6}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Species parameters:

\( C_{\text{anal}}[C] \) (M/l): 0
\( C_{\text{init}}[C] \) (M/l): 9.0545 \times 10^{-23}
\( D[C] \) (cm\(^2\)/s): 5.00 \times 10^{-6}
\( C_{\text{anal}}[D] \) (M/l): 0
\( C_{\text{init}}[D] \) (M/l): 9.0485 \times 10^{-17}
\( D[D] \) (cm\(^2\)/s): 5.00 \times 10^{-6}

Note: To correct simulation potentials to the Fc\(^+\)/Fc reference couple, subtract -0.685 V
Table A.3  \( \eta^6\text{-DBCOTMn(CO)}_3 \) digital simulation parameters at 0 °C

<table>
<thead>
<tr>
<th>Charge transfer reactions</th>
<th>Charge transfer parameters</th>
<th>Species parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction 1:</strong> A + e = B</td>
<td>( E_0^1 ) (V): -0.725</td>
<td>( C_{\text{anal}}[A] ) (M/l): 0.003</td>
</tr>
<tr>
<td><strong>Reaction 2:</strong> B + e = C</td>
<td>( \alpha^1 ) : 0.7</td>
<td>( C_{\text{init}}[A] ) (M/l): 0.003</td>
</tr>
<tr>
<td></td>
<td>( k_s^1 ) (cm/s): 0.025</td>
<td>( D[A] ) (cm(^2)/s): ( 4 \times 10^{-6} )</td>
</tr>
<tr>
<td><strong>Homogeneous chemical reactions</strong></td>
<td>( E_0^2 ) (V): -0.43</td>
<td>( C_{\text{anal}}[B] ) (M/l): 0</td>
</tr>
<tr>
<td><strong>Reaction 1:</strong> C=D</td>
<td>( \alpha^2 ) : 0.5</td>
<td>( C_{\text{init}}[B] ) (M/l): ( 1.2608 \times 10^{-16} )</td>
</tr>
<tr>
<td></td>
<td>( k_s^2 ) (cm/s): 0.01</td>
<td>( D[B] ) (cm(^2)/s): ( 4 \times 10^{-6} )</td>
</tr>
<tr>
<td><strong>Experimental parameters</strong></td>
<td></td>
<td>( C_{\text{anal}}[C] ) (M/l): 0</td>
</tr>
<tr>
<td>( E_{\text{start}} ) (V): 0</td>
<td></td>
<td>( C_{\text{init}}[C] ) (M/l): ( 1.4681 \times 10^{-24} )</td>
</tr>
<tr>
<td>( E_{\text{switch}} ) (V): -1.5</td>
<td>( K_{eq}^1 : 1 \times 10^6 )</td>
<td>( D[C] ) (cm(^2)/s): ( 4 \times 10^{-6} )</td>
</tr>
<tr>
<td>( E_{\text{end}} ) (V): 0</td>
<td>( k_f^1 : 0.4 )</td>
<td>( C_{\text{anal}}[D] ) (M/l): 0</td>
</tr>
<tr>
<td>( v ) (V/s): 2</td>
<td>( k_b^1 : 4 \times 10^{-7} )</td>
<td>( C_{\text{init}}[D] ) (M/l): ( 1.4671 \times 10^{-18} )</td>
</tr>
<tr>
<td>Temperature (K): 273.15</td>
<td></td>
<td>( D[D] ) (cm(^2)/s): ( 4 \times 10^{-6} )</td>
</tr>
<tr>
<td>( R_u ) (Ohms): 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{dl} ) (F): 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycles: 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrode geometry: planar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area (cm(^2)): 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion: semi-infinite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pre-equilibrium: enabled for all reactions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:** To correct simulation potentials to the Fe\(^{3+}/\text{Fe} \) reference couple, subtract \(-0.685 \) V