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Communication

Evidence for Reactivity of Decamethylcobaltocene with Dichloromethane

Emily R. Mikeska and James D. Blakemore*

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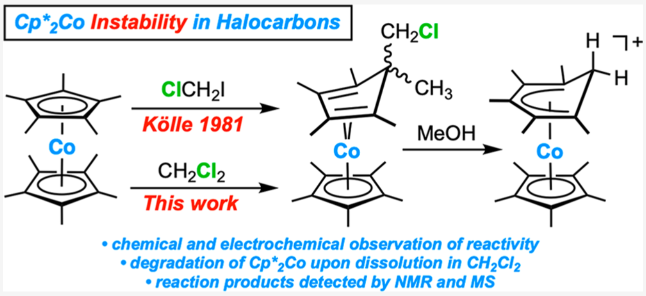

• chemical and electrochemical observation of reactivity
• degradation of Cp^*_2Co upon dissolution in CH_2Cl_2
• reaction products detected by NMR and MS

ABSTRACT: Decamethylcobaltocene (Cp^*_2Co) is commonly encountered in organometallic chemistry, where it is often used as a one-electron reductant under inert atmosphere and considered to be a stable metallocene in both its reduced [Co^{II}] and oxidized [Co^{III}] forms. Here, we report that Cp^*_2Co is not stable in dichloromethane (CH_2Cl_2), a finding that contrasts markedly with the robustness of this compound in other solvents used for redox chemistry, such as neat acetonitrile (CH_3CN). Parallel chemical and electrochemical studies show that when Cp^*_2Co comes into contact with CH_2Cl_2, both $[Cp^*_2Co]^+$ (**A**) and $Cp^*Co(\eta^4\text{-}C_5Me_5CH_2Cl)$ (**B**), a species in which a chloromethyl group has been added to one Cp* ring, are generated. **B** subsequently undergoes a ring-expanding rearrangement if exposed to MeOH, yielding $Cp^*Co(\eta^5\text{-}C_6Me_5CH_2)$ (**C**) that is detectable by mass spectrometry (MS). $[Cp^*Co]_3(\mu_3\text{-}CH)_2$ (**D**) could also be detected by MS, adding to the array of products arising from Cp^*_2Co that do not maintain the expected metallocene motif. Taken together, these findings suggest that Cp^*_2Co should be used with caution in CH_2Cl_2, particularly in cases in which one-electron transfer and/or clean reactivity are desired.

Metallocenes are ubiquitous in organometallic chemistry and have long been noted for their reliable redox behaviors under a variety of conditions. Decamethylcobaltocene (Cp^*_2Co, where Cp* is η^5-pentamethylcyclopentadienyl) is among the most well-known in this realm, as it features a rather negative reduction potential ($E_{1/2} = -1.91$ V vs ferrocenium/ferrocene in acetonitrile (CH_3CN)).[1] This negative potential makes Cp^*_2Co useful as a stoichiometric reductant; the two [η^5-Cp*] rings typically impart high stability to both the reduced and oxidized forms of the compound. However, in the course of recent studies in redox chemistry, we have found that Cp^*_2Co is not stable in the common polar, noncoordinating solvent dichloromethane (CH_2Cl_2).

For context, we note that the results described here are related to a wealth of literature on the reactivity of cobaltocene, Cp_2Co, with alkyl halides. The majority of this work was published in German in the 1960s−1980s and deserves more attention than it has received in recent years. In particular, Herberich and co-workers led the field, finding that although Cp_2Co does not react with CH_2Cl_2 at room temperature, it does react with halomethanes (CH_3X) with rates that (i) strongly depend on the identity of X and (ii) increase in the order Cl < Br < I.[2] Evidence was gathered for follow-up reactivity leading to a distinctive ring expansion of cyclopentadienyl,[3] as well as for the reactions with Cp_2Co being radical in nature.[4] Building on this prior work, we describe in this paper the reactivity of Cp^*_2Co with CH_2Cl_2 and identify four products arising from this reactivity.

We identified the reactivity of Cp^*_2Co with CH_2Cl_2 in the course of studies we have been conducting on reduction of uranyl (UO_2^{2+}) complexes by chemical and electrochemical means. In particular, we were focusing on the reduction of a monometallic uranyl complex[5] (**U**; see Figure S17) that displays a single one-electron reduction event in acetonitrile (CH_3CN) electrolyte at $E_{1/2} = -1.55$ V vs ferrocenium/ferrocene (denoted hereafter as $Fc^{+/0}$) (see Figure S17). We wished to generate the reduced form of the compound in both CH_3CN and CH_2Cl_2, and thus began comparative work in electrolytes based on both solvents. **U** undergoes a quasi-reversible reduction at $E_{1/2} = -1.59$ V vs $Fc^{+/0}$ in CH_2Cl_2 (see Figure S19), and spectroelectrochemical studies show the generation of similar reduced forms in both CH_3CN and CH_2Cl_2 (see Figures S53 and S54). On the basis of these promising findings, our work turned to chemical studies focused on the generation of $[U]^-$ in both solvents using Cp^*_2Co as a chemical reductant. This choice was based on the

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anticipated ability of the reagent to undergo electron transfer to **U** in both solvents, since the Co^{III}/Co^{II} potential has been reported to be −1.94 V vs $Fc^{+/0}$ in CH_2Cl_2.[1] With these values in mind, the driving force for generation of $[\mathbf{U}]^-$ in this case could be estimated at 8.1 kcal mol^{-1}.

In CH_3CN, **U** does undergo clean reduction by $Cp^*{}_2Co$, a process that we monitored using UV−visible spectroscopy. Isosbestic behavior was encountered, consistent with rapid stoichiometric electron transfer from Co^{II} to **U**. Comparison of our spectroelectrochemical data with spectra from the chemical reduction study in CH_3CN revealed similar isosbestic points at 348 and 404 nm, along with a significant increase in absorbance near 300 nm arising due to the anticipated cogeneration of $[Cp^*{}_2Co]^+$ (**A**) (see Figure S38). When the chemical reduction of **U** with $Cp^*{}_2Co$ was attempted in CH_2Cl_2, however, absorption near 300 nm attributable to **A** was observed but the features associated with $[\mathbf{U}]^-$ measured in spectroelectrochemical work were not observed (see Figure S47). Upon observing the lack of electron transfer to **U**, we investigated the stability of $Cp^*{}_2Co$ in CH_2Cl_2 solvent.

Taking an electro-analytical approach first, we began by investigating the cyclic voltammetric behavior of $[Cp^*{}_2Co][PF_6]$ at a graphite working electrode in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). We took this approach hoping that the product(s) of the reaction of electrogenerated $Cp^*{}_2Co$ with CH_2Cl_2 would be redox active, giving us the opportunity to use the measured redox chemistry as an insight into the composition of species present in solution. Notably, $[Cp^*{}_2Co][PF_6]$ is stable in CH_2Cl_2 on the basis of NMR spectra (see Figure S3) as well as control UV−visible spectroscopic studies (see Figure S52), setting the stage for this work.

The CV profile of $[Cp^*{}_2Co][PF_6]$ in CH_2Cl_2 electrolyte shows a quasi-reversible couple at $E_{1/2}$ = −1.97 V vs $Fc^{+/0}$ with a peak-to-peak separation (ΔE_p) of 165 mV at a scan rate of 100 mV/s (see Figure S21). However, determination of the ratio of anodic to cathodic peak current ($i_{p,a}/i_{p,c}$) as a function of scan rate reveals a significant diminishment of chemical reversibility at slower scan rates (see Figure S23). Such a loss of reversibility is consistent with EC-type reactivity in which the nascent reduced compound (here, $Cp^*{}_2Co$) undergoes a chemical reaction that depletes this species from near the electrode, resulting in the decreased current flowing in the reoxidation wave.[6]

Following excursion to reducing potentials at which $Cp^*{}_2Co$ was generated, we also observed a new irreversible oxidation wave at $E_{p,a}$ = −0.5 V vs $Fc^{+/0}$. This feature was absent when the switching potential of the voltammogram was set to be positive of the onset of the $Co^{III/II}$ reduction of $[Cp^*{}_2Co][PF_6]$, meaning that electrogeneration of $Cp^*{}_2Co$ results in formation of the new species undergoing oxidation at −0.5 V. Current associated with this feature at −0.5 V increased as the switching potential was extended more negative, providing further support to the notion that the feature at −0.5 V corresponds to the reoxidation of a product resulting from reactivity of Co^{II} with CH_2Cl_2 (see Figures 1, S25, and S26). Similar electrochemical behavior was observed at a platinum disk electrode, suggesting that the observed reactivity is independent of electrode material (see Figures S31−S36).

The irreversible oxidation wave at −0.5 V in our data is notably reminiscent of Co^{II}/Co^{I} redox waves that have been measured for metallocene-derived cobalt complexes supported by η^4-pentamethylcyclopentadiene (η^4-Cp*H) or η^4-hexamethylcyclopentadiene (η^4-C_5Me_6) ligands. In the case of Cp*Co(η^4-Cp*H), an anodic wave can be found at −0.61 V vs $Fc^{+/0}$ in butyronitrile, while in the case of Cp*Co(η^4-C_5Me_6) the wave is found at −0.62 V in acetonitrile.[7] On the basis of the similarity of the potentials for these processes to that of the wave observed in our data (as well as other evidence, *vide infra*), we conclude that one product of the reaction of $Cp^*{}_2Co$ with CH_2Cl_2 is Cp*Co(η^4-$C_5Me_5CH_2Cl$) (**B**), a ring-activated species featuring a chloromethyl group appended to the Cp* ring. Consistent with this general situation, the potential for the Co^{II}/Co^{I} wave of **B** appears at a more positive potential than those of its analogues from prior work due to the inductive effect of the chloro-containing substituent.

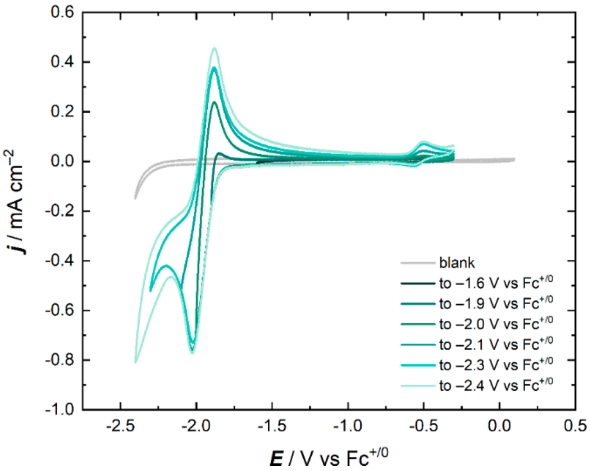
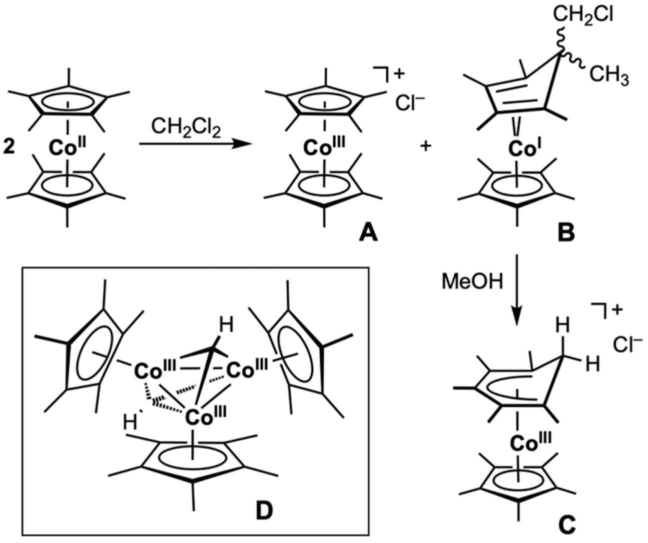


Figure 1. Cyclic voltammetry of $[Cp^*{}_2Co][PF_6]$ (2 mM) in CH_2Cl_2 electrolyte. Shift of the switching potential to more negative values results in growth of the redox wave near −0.5 V, corresponding to $\mathbf{B}^{+/0}$ redox cycling. Oxidation of **B** at −0.5 V is not observed with switching potentials set positive of the Co^{III}/Co^{II} reduction of $[Cp^*{}_2Co][PF_6]$, supporting EC-type reactivity in which **B** is a product of reaction of electrogenerated $Cp^*{}_2Co$ with CH_2Cl_2. Conditions: electrolyte, 0.1 M $TBAPF_6$ in CH_2Cl_2; scan rate, 100 mV/s; working electrode, HOPG.

Formation of **B** could occur under our conditions (see Scheme 1) by generation of a chloromethyl radical following electron transfer from Co^{II} to CH_2Cl_2 that results in cogeneration of Cl^-.[8] This electron transfer from electrogenerated $Cp^*{}_2Co$ to CH_2Cl_2 followed by reaction of a second equivalent of $Cp^*{}_2Co$ with the chloromethyl radical to generate **B** would thus correspond to the reaction cascade giving rise to the EC-type behavior observed in the cyclic voltammetry.

Evidence for such a reactivity manifold comes from the classic work of Kölle and co-workers with metallocenes.[8] This group reported the generation of Cp*Co(η^4-$C_5Me_5CH_2Cl$) (**B**) from $Cp^*{}_2Co$ in 1981, relying on chloroiodomethane ($ClCH_2I$) as the source of the chloromethyl radical in place of the CH_2Cl_2 involved here. Kölle and co-workers found that reaction of $Cp^*{}_2Co$ with $ClCH_2I$ to form **B** occurred in high yield, consistent with the high propensity of $ClCH_2I$ to release I^- upon reduction. We prepared **B** with Kölle's method (see Figures S8−S11 and Table S2), and in accord with our expectations, cyclic voltammetry data revealed an irreversible oxidation event with $E_{p,a}$ = −0.5 V corresponding to generation of $\mathbf{B}^+$ from **B** (see Figure S27). There is also a large, reversible wave corresponding to $\mathbf{B}^{0/-}$ cycling at $E_{1/2}$ = −1.70 V. The

Scheme 1. Reactivity Pathway of Cp*$_2$Co in CH_2Cl_2 Showing the Identities of Products A−D That Can Be Generated from Cp*$_2$Co



excellent reversibility of the **B**$^{0/-}$ event and poor reversibility of the **B**$^{+/0}$ event are consistent with observations from Chalkley and Peters on the redox properties of Cp*Co(η^4-Cp*H).[7] Extended reductive polarization experiments with [Cp*$_2$Co]$^+$ also show evidence of generation of **B** via direct measurement of the **B**$^{0/-}$ cycling (see Figure S30), further supporting the formation of **B** under conditions where Cp*$_2$Co is electrogenerated in CH_2Cl_2-based electrolyte.

Notably, Kölle and co-workers also reported that **B** undergoes a ring-expanding rearrangement in methanol (MeOH) at room temperature to yield Cp*Co(η^5-$C_6Me_5CH_2$) (**C**), a species which features the monoanionic η^5-$C_6Me_5CH_2$ ligand (see Scheme 1) and supports a cobalt metal center in the +III oxidation state.[8,9] This ring-expanding reaction is conceptually related to the prior work on Cp_2Co reactivity carried out by Herberich.[3] Exposure of our synthesized **B** to MeOH resulted in a rapid color change and generation of the chloride salt of **C**. Our NMR data, however, are not consistent with clean generation of **C** (see Figure S13−S15 and Table S3), suggesting that the ring-expanding reaction may be sensitive.

Electrospray ionization mass spectrometry (MS) was used to confirm the generation of both **A** and **C** *in situ* from Cp*$_2$Co in CH_2Cl_2 and MeOH. Consistent with the speciation measured by voltammetry and the favorability of the ring-expanding rearrangement of **B** in MeOH (which is required as solvent in our mass spectrometer), the m/z (M$^+$) peaks for both **A** and **C** were detected by mass spectrometry in a ratio of approximately 3:1 from a solution of Cp*$_2$Co in CH_2Cl_2 diluted with MeOH. The observed isotopic distributions in the mass peaks corresponding to **A** and **C** are in good agreement with values predicted for these cations (see Figures S55−S58). Additionally, execution of this experiment with CD_2Cl_2 revealed m/z peaks for **A** that were unchanged from those measured in CH_2Cl_2, but peaks for **C** that were shifted by two m/z units to higher mass values, corresponding to incorporation of 1 equiv of (CD_2) into product **C** (see Figures S59−S62). This isotope incorporation is consistent with the established mechanism of the ring-expansion that forms **C** from **B**.[3,8,9]

The mass spectra also revealed another species with m/z (M$^+$) = 608.1689. This signal corresponds to [Cp*Co]$_3$(μ_3-CH)$_2$ (**D**), a species first reported by Smith and Andersen in 1996 as a control compound in studies of the related [Cp*Co]$_3$(μ_3-CH)(μ_3−H).[10] While **D** was not previously prepared from Cp*$_2$Co and CH_2Cl_2, our observation of **D** by MS provides evidence that it can form from these reagents. Its formation is also consistent with the apparent tendency for this reactivity to give rise to species with ligands more labile than Cp*.[11] No isotope incorporation was measured when substituting CH_2Cl_2 for CD_2Cl_2, suggesting that formation of **D** may involve loss of the η^5-$C_6Me_5CH_2$ ligand from **C** or direct conversion from **A**. These possibilities have not been further explored at this time, but appear worthy of investigation.

We also probed the tendency of Cp*$_2$Co to undergo reaction with dilute CH_2Cl_2. The UV−visible spectral profile of Co*$_2$Co in CH_3CN is virtually stable on time scales of >5 min, but addition of 1 eq. of CH_2Cl_2 to the solution of Cp*$_2$Co promptly results in reactivity. This can be observed by appearance of the profile of [Co*$_2$Co]$^+$, which absorbs strongly at 294 nm (see Figures S41 and S42). Reactivity is fast when Cp*$_2$Co is dissolved in neat CH_2Cl_2, but clearly much slower in the case where a small amount of CH_2Cl_2 is added to CH_3CN. To probe this further, we carried out a CH_2Cl_2-concentration-dependent study of the consumption of Cp*$_2$Co in CH_3CN. As expected we found the reaction rate was linearly dependent on CH_2Cl_2 concentration, with an estimated pseudo-first-order rate constant of $8.3\ (\pm 0.4) \times 10^{-6}\ \mathrm{s}^{-1}$ (see Figures S43−S45). All attempts to obtain a clean spectrum of Cp*$_2$Co in CH_2Cl_2 were unsuccessful; the resulting data display strong absorption at ca. 300 nm, corresponding to generation of [Co*$_2$Co]$^+$ (see Figures S48−S50).

NMR studies confirm the reactivity sequence described above. ^{1}H NMR spectra of Cp*$_2$Co in CD_3CN display a single broad and paramagnetically shifted peak at ca. 47 ppm (see Figure S1). Conversely, the ^{1}H NMR spectrum obtained after dissolving Cp*$_2$Co in CD_2Cl_2 shows an intense singlet at 1.73 ppm, corresponding to **A** (see Figure S4) as well as approximately 15 other less-intense peaks that correspond to other products. Comparison of data for pure **B** show that this compound is present in the reaction mixture (see Figure S12). In neat CD_2Cl_2, **C** is not detected, consistent with the need for MeOH to induce formation of this species (see Figure 12). **D** was also not detected, suggesting it may form from **C** or via other chemistry. We note that **A** is the major species generated (~60−65% yield; see Figures S5−S7 and Table S1), and thus **B**, **C**, and **D** could be considered minor products under some conditions. Studies at elevated temperature (approaching 100 °C for nearly 3 h) also do not yield compounds **C** or **D** in quantifiable amounts, and thus at this stage, we cannot discount the possibility that these are formed preferentially under only certain conditions and may not be "general" products of Cp*$_2$Co reactivity with CH_2Cl_2 (see Figure S16).

In conclusion, we have found that Cp*$_2$Co is not stable in CH_2Cl_2, but instead displays reactivity leading to at least four detectable products. Chloromethylated species **B** is generated upon electrochemical generation of Cp*$_2$Co from **A** in CH_2Cl_2 and is observable via distinctive redox waves in voltammetry. However, **B** undergoes a ring-expanding rearrangement that occurs rapidly in the presence of MeOH. This evidence suggests that stoichiometric one-electron reactivity cannot be obtained from Cp^*_2Co in CH_2Cl_2, in agreement with Kölle's work using $ClCH_2I$ and Herberich's studies of Cp_2Co. However, we note that several literature examples show that Cp^*_2Co can be used as a reductant in CH_2Cl_2 when a one-electron acceptor that can undergo fast electron transfer is preloaded into the solvent before Cp^*_2Co dissolution.[12,13] We anticipate that the kinetics of the organometallic reactivity reported here are sluggish compared to simpler electron transfers. Moreover, available electrochemical data suggest that the products of degradation are themselves redox active, further complicating use of Cp^*_2Co as an outer-sphere reductant in CH_2Cl_2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00176.

> Experimental details; UV−vis, NMR, electrochemical, spectroelectrochemical and mass spectrometry data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

James D. Blakemore − *Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States;* orcid.org/0000-0003-4172-7460; Phone: +1 (785) 864-3019; Email: blakemore@ku.edu

Author

Emily R. Mikeska − *Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States;* orcid.org/0000-0001-5149-0132

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.3c00176

Notes

The authors declare no competing financial interest.

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