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An investigation of electron transfer properties of (Cp)Mn(CO)$_3$ and substituted Cp derivatives

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Abstract

The results of an electrochemical investigation of the reduction of (η^5-C_5H_5)Mn(CO)$_3$, (η^5-$C_5H_4COOCH_3$)Mn(CO)$_3$, (η^5-$C_5H_4CH_3$)Mn(CO)$_3$ and (η^5-C_5H_4Cl)Mn(CO)$_3$ are reported. Each compound was characterized with at least a single one-electron EC process. However, for (η^5-$C_5H_4COOCH_3$)Mn(CO)$_3$ and (η^5-C_5H_4Cl)Mn(CO)$_3$ additional reduction processes were also observed. The first reduction potential of these compounds exhibits a potential range of 340 mV and a correlation with the Hammett parameter (σ_p). Voltammetric and IR analysis of the reduced solutions indicate that several species are formed upon reduction. A possible reaction scheme is suggested, although isolation of the proposed products and intermediates for identification has not been possible.

Key words: Electron transfer; Manganese complexes; Cyclopentadienyl complexes; Carbonyl complexes

Introduction

Substitutent effects on physical and chemical properties of organometallic compounds have been investigated for many different systems. However, the substituted cyclopentadienyl system remains less studied than other substituted ligands; substituted phosphine [1], substituted arylisocyanide [2], etc. The most thoroughly studied substituent effect for substituted Cp systems is the effect of the substituents on ligand substitution reactions. These studies have yielded information about the relative ability of the substituted Cp ligands to stabilize ring-slipped intermediates [3, 4]. Little is known about the substituents' effects on the electron transfer properties in a series of compounds containing a single Cp ligand. The focus of this investigation is to determine the electron transfer properties of (η^5-C_5H_5)Mn(CO)$_3$ and the chloro-, carbomethoxy- and methyl-Cp derivatives. An investigation of (η^5-C_9H_7)Mn(CO)$_3$ reports two reversible reduction processes, while our investigation shows that the substituted Cp derivatives have less different electrochemical properties [5]. Furthermore, the reduced substituted compounds undergo rearrangement reactions to form several different species, which probably include dimers.

Experimental

Materials

(η^5-C_5H_5)Mn(CO)$_3$ and (η^5-$C_5H_4CH_3$)Mn(CO)$_3$ were obtained from Strem Chemical Company and Aldrich, respectively. Tetrahydrofuran (THF) and acetonitrile (MeCN) were purified by distilling from Na (THF) and P_2O_5 (MeCN) according to published procedures [6]. However, benzophenone was not used in the purification of THF due to its interference in the electrochemical investigations. The purified solvents were then stored in serum bottles or in Kontes solvent collection flasks.

Synthesis of (η^5-$C_5H_4COOCH_3$)Mn(CO)$_3$ (CarCp)

1.9 g (6.9 mmol) pentacarbonyl manganese bromide and 2.26 g (6.9 mmol) carbomethoxycyclopentadienyl thallium(I) (synthesized according to published procedures [7, 8]) were combined in 150 ml of freshly distilled THF and refluxed for 4 h. Filtration and solvent removal resulted in an oily residue, which was dissolved in pentane and cooled in dry ice/acetone. Yellow crystals were collected in the air by filtration. IR (cyclohexane)

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ν(CO): 2034, 1957, 1739 cm^{-1}; (THF) ν(CO): 2028, 1945, 1731 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.80 (s, 3H), 4.78 (t, 2H) and 5.43 (t, 2H).

Synthesis of (η^5-C_5H_4Cl)$Mn(CO)_3$ (ClCp)

This compound was prepared following published procedures [9]. However, further purification was necessary. The oily residue which results was sublimed at 25 °C followed by column chromatography using 10% dichloromethane/pentane and silica gel to remove unreacted pentacarbonyl manganese bromide. IR (cyclohexane) ν(CO): 2032, 1953 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.62 (t, 2H) and 4.88 (t, 2H).

Equipment and techniques

The electrochemical data were collected using an EG&G Princeton Applied Research potentiostat/galvanostat model 273 interfaced to a 12 MHz PC-AT computer with an IEEE-488 bus, using the model 270 version 3.0 software. The three-electrode system for the cyclic voltammetric measurements (CV) consisted of a Pt disk working electrode, area 0.02 cm^2, a Pt disk counter electrode and an Ag/AgCl reference electrode separated from the solution with a bridge. In the bulk electrolysis (BE) experiments, the three-electrode system consisted of a Pt mini-grid working electrode, approx. area 0.025 cm^2, and an Ag/AgCl reference electrode separated from the solution by a bridge in one compartment of a two compartment cell. A Pt wire counter electrode is placed in the second compartment and the two sides of the cell are separated by a frit. All potentials are reported normalized to a ferrocene $E_{1/2}$ of 0.40 V, unless otherwise noted, to allow for comparison between systems. The CV measurements were made using approx. 5 mM compound with 0.5 M tetra(n-butyl)ammonium tetrafluoroborate (TBABF$_4$) while the BE experiments used approximately 1 mM compound with 0.1 M TBABF$_4$. All sample preparations were completed in the dry box to avoid air contamination and all procedures were performed using standard Schlenk [10] methods. All the voltammograms are 90% IR compensated and run under argon at room temperature using an inert atmosphere CV cell. The electrochemical abbreviations used throughout the text are standard terms, see ref. 12, pp. vii–xvii.

The IR data were obtained using a Matteson Galaxy 2020 IR spectrometer and a KBr solution cell with a pathlength of approx. 0.02 mm. The electrolyzed solutions were transferred for IR analysis in a glove box to avoid air oxidation of the reduced material. The IR solution cell was rinsed several times with the sample before analysis. The spectra were run versus a solvent/supporting electrolyte background to eliminate peaks due to either species. A Varian VXR300 NMR was used to collect the NMR data of the synthesized compounds.

Results

Reduction of (η^5-C_5H_5)$Mn(CO)_3$ (HCp)

Figure 1 is a representative cyclic voltammogram of the reduction of (η^5-C$_5$H$_5$)Mn(CO)$_3$ at a scan rate of 100 mV/s in THF/TBABF$_4$, which demonstrates the presence of a single reduction process (wave 1). E_{pc} of wave 1 is −2.46 V versus Ag/AgCl with an $E_p - E_{p/2}$ of 74 mV and the presence of four return oxidation processes (waves 4–7, Fig. 1). The value of $E_p - E_{p/2}$ of 74 mV is slightly larger than the expected [11] 59 mV for a simple one-electron process*. Wave 1 shifts to negative potentials with increasing scan rate (Table 1) and is diffusion controlled, as evidenced by a constant $i_p/\nu^{1/2}$.

The oxidation processes (waves 4, 5, 6 and 7, Fig. 1) are coupled to wave 1 since they are present only after scanning wave 1. The values of the oxidation potentials are −2.12, −0.99, −0.61 and −0.23 V (waves 4, 5, 6 and 7, respectively) versus Ag/AgCl. Although these oxidations are coupled to wave 1, this is not a reversible process since ΔE_p is 206 mV between wave 1 and wave 4 and i_{p1}/i_{p4} has a value of 6.6. The ratio of current of wave 1 to the currents of waves 4–7 is 2.8, indicating that additional chemical reactions are occurring. However, since waves 4–7 are very small, there is much error in the analysis of these waves.

These observations are all indicative of an EC mechanism [11–13] which is evident from the negative shift in potential** combined with the larger value of $E_p - E_{p/2}$ than expected. A possible mechanism for the one electron reduction is presented in Scheme 1.

Bulk electrolysis negative of wave 1 results in 1.06±0.04 electrons transferred. IR analysis of HCp in THF/TBABF$_4$ prior to electrolysis results in ν(CO) at 2020 and 1933 cm^{-1} (bands A1 and A2, Fig. 2, I), while the spectrum after BE (Fig. 2, II) results in bands located at 1864, 1775, 1971, 1896 and 1828 cm^{-1}, labeled B1, B2, C1, C2 and C3, respectively. These new bands clearly indicate the formation of several species upon reduction as demonstrated by the CV in the presence of waves 4–7. In Fig. 2, II, the appearance of bands A1 and A2 indicates that some product does re-oxidize before the IR can be obtained. For this reason and based on previous work [5], the bands labeled B1 and B2 are most likely due to [(η^5-Cp)Mn(CO)$_3$]$^-$, while

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*The internal standard of ferrocene has a value of $E_p - E_{p/2}$ of 56 mV.

**Data analysis of FeCp$_2$ under the same IR compensation and solution conditions results in a deviation of ±2 mV.

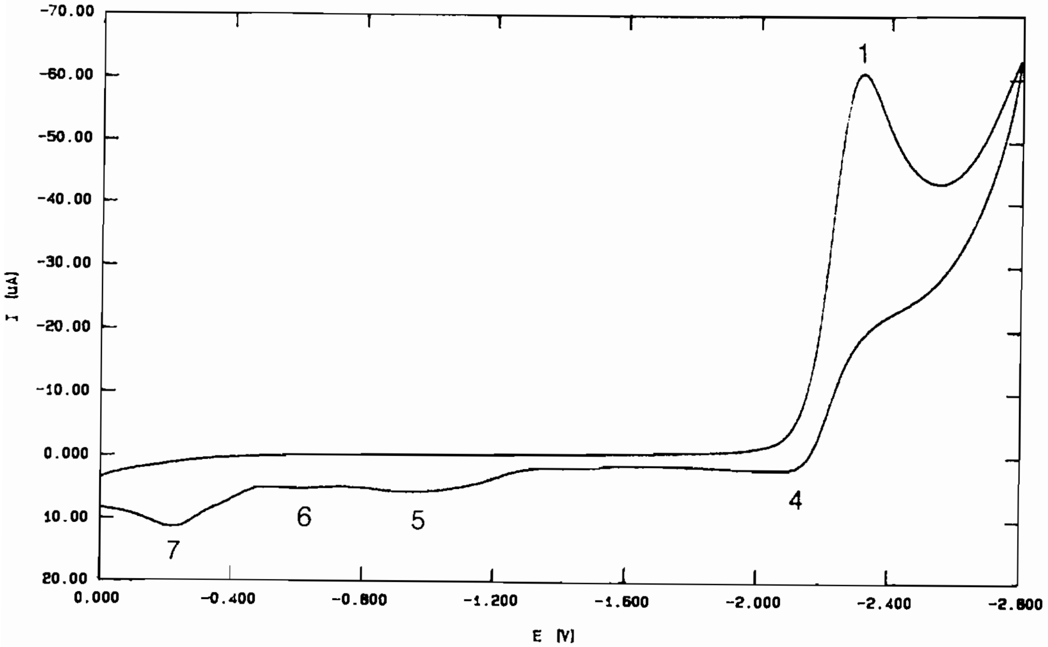
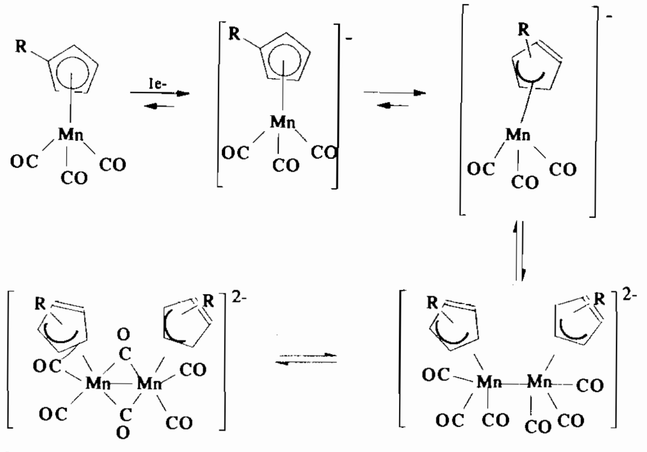


Fig. 1. Cyclic voltammogram of a 5 mM solution of (η^5-C_5H_5)Mn(CO)$_3$ in 0.5 M THF/TBABF$_4$ at a scan rate of 100 mV/s with a Pt working electrode and Ag/AgCl reference.

TABLE 1. Scan rate dependence of CpMn(CO)$_3$ reduction in THF/TBABF$_4$ vs. Ag/AgCl

Scan rate, ν (mV/s)	E_{pc}[a] (V)	$E_p - E_{p/2}$ (mV)	i_{pc} (μA)
30	−2.44	52	18
60	−2.45	65	32
100	−2.48	74	27
250	−2.49	77	41
500	−2.50	90	52
1000	−2.52	103	66

[a] Potentials were standardized to a ferrocene $E_{1/2}$ of 0.4 V.



R = H, CO_2CH_3, Cl, CH_3

Scheme 1.

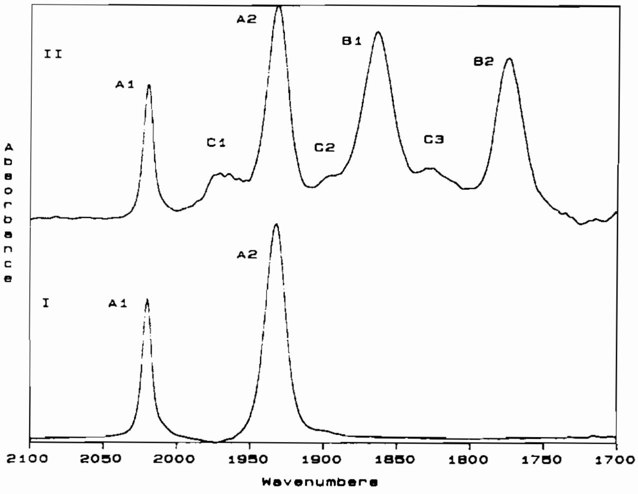


Fig. 2. IR spectrum of (η^5-C_5H_5)Mn(CO)$_3$ vs. THF/TBABF$_4$ background. (I) Solution before electrolysis. (II) One-electron reduced solution.

the small intensity bands (C1, C2 and C3, Fig. 2, II) are evidence of an additional chemical reaction. However this assignment is not definite, B1 and B2 could also be due to a chemical product of [(η^5-Cp)Mn(CO)$_3$]$^-$. Further identification and isolation was not possible due to extreme air sensitivity. Upon any exposure to air, the original bands A1 and A2 increase while all others decrease, indicating the return of HCp upon air oxidation.

Reduction of (η^5-$C_5H_4COOCH_3$)Mn(CO)$_3$ (CarCp)

A representative cyclic voltammogram of CarCp in THF/TBABF$_4$ at 100 mV/s is shown in Fig. 3(a), which demonstrates a total of three reduction processes (waves 1, 2 and 3, Fig. 3(a)) and seven return oxidations. Waves 1, 2 and 3 are located at −2.15, −2.40 and −2.78 V versus Ag/AgCl, respectively, with an $E_p - E_{p/2}$ of 74 mV for wave 1. Analysis of the oxidations beyond determining the peak potentials was not attempted.

A cyclic voltammogram that has more reversible characteristics is obtained if the scan is cycled to potentials just negative of wave 1 but positive of wave 2 (Fig. 3(b)). Under these conditions, an E_{pc} of −2.12 V and an E_{pa} of −1.95 V results, yielding a ΔE_p of 170 mV and i_{p1}/i_{p4} of 1.25. The ΔE_p of 170 mV is still larger than the expected [11] 59 mV for a reversible process, but the ratio of the peak currents is closer to unity. These data demonstrate that the first reduction on the CV timescale is more reversible for CarCp than

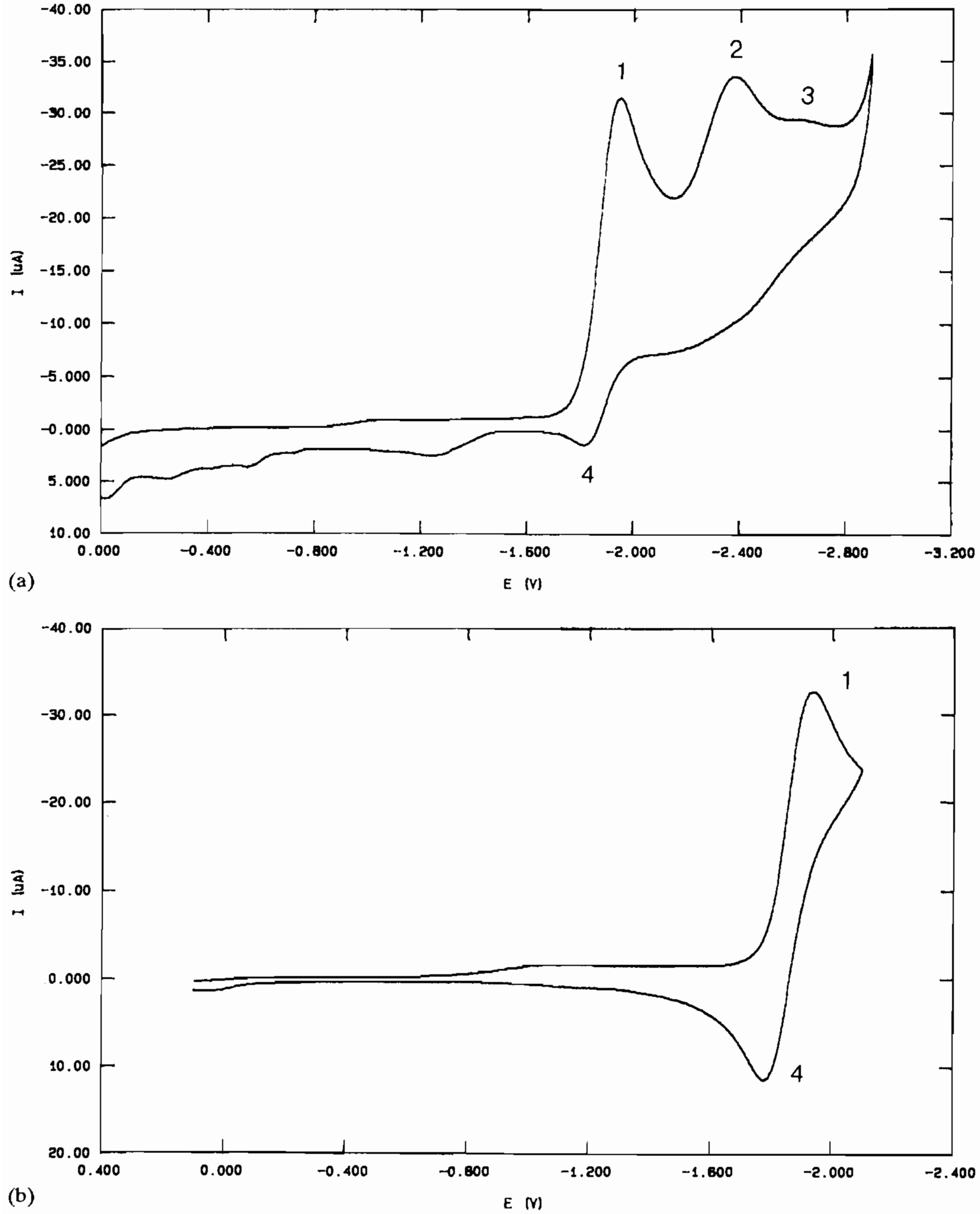


Fig. 3. Cyclic voltammogram of a 5 mM solution of (η^5-$C_5H_4COOCH_3$)Mn(CO)$_3$ in 0.5 M THF/TBABF$_4$ at a scan rate of 100 mV/s with a Pt working electrode and Ag/AgCl reference. (a) Range of 0.0 to −2.9 V. (b) Range of 0.0 to −2.1 V.

HCp. A 30 s time delay at the switching potential results in the generation of six return oxidation processes, and an increase in the current ratio (i_{p1}/i_{p4}) to 2.1. Under these conditions, the presence of six oxidation waves indicates that the one-electron reduced species undergoes chemical reactions with time.

Data analysis indicates an EC(E) mechanism [11–13] is occurring with the reduction of CarCp unlike what was observed for HCp. The EC(E) mechanism is characterized by the negative shift in potential of waves 1, 2 and 3 with increasing scan rate and the larger value of $E_p - E_{p/2}$. The CV of the first reduction process indicates that CarCp is able to approach reversibility on the CV timescale. However, coupled chemical reactions following the electron transfer do occur.

Bulk electrolysis of CarCp negative of wave 1 and wave 2 results in 1.0 ± 0.1 and 2.1 ± 0.2 electrons transferred, respectively. IR analysis of CarCp in THF/TBABF$_4$ prior to electrolysis results in ν(CO) at 2028, 1945 and 1731 cm^{-1} (bands A1, A2 and A3, Fig. 4, I), while the spectra of solutions of the one-electron reduced (Fig. 4, II) and two electron reduced (Fig. 4, III) species are more complicated. Figure 4, II shows no evidence of the original bands A1, A2 and A3 but the presence of at least three new species. This could indicate the ability of the carbomethoxy substituent to stabilize a ring-slipped geometry, as demonstrated in Scheme 2. Similar stabilization has been suggested in other works involving the generation of a ring-slipped intermediate in studies of Co and Rh cyclopentadienyl complexes [3, 14]. The two-electron spectrum (Fig. 4, III) shows evidence of unreduced CarCp and five additional species, labeled B through E. Isolation of either the one-electron or the two-electron species was not possible making the exact assignment of ν(CO) difficult.

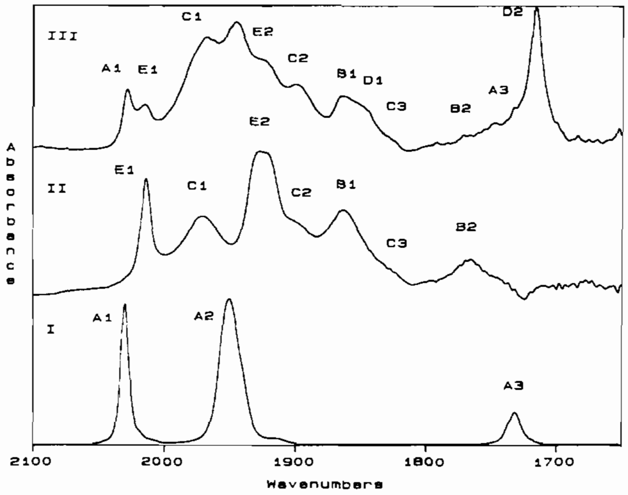
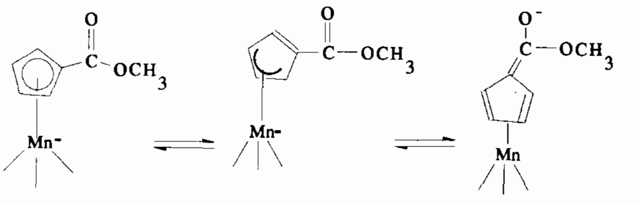


Fig. 4. IR spectrum of (η^5-C$_5$H$_4$COOCH$_3$)Mn(CO)$_3$ vs. THF/TBABF$_4$ background. (I) Solution before electrolysis. (II) One-electron reduced solution. (III) Two-electron reduced solution. The spectra were autoscaled and absorbances may not be comparable between (I), (II) and (III).



Scheme 2.

Reduction of (η^5-C$_5$H$_4$Cl)Mn(CO)$_3$ (ClCp)

Cyclic voltammograms of ClCp are similar to those obtained for CarCp. However, for ClCp there are only two reduction processes (waves 1 and 2) followed by one return oxidation. Waves 1 and 2 are located at −2.26 and −2.49 V versus Ag/AgCl, respectively, with an $E_p - E_{p/2}$ of 89 mV for wave 1. Waves 1 and 2 are both one-electron diffusion-controlled processes that shift negative with increasing scan rate. The return oxidation has an E_{pa} of −0.25 V versus Ag/AgCl with a very small current.

As with HCp, the reduction mechanism for ClCp is an EC mechanism [11–13]. Unfortunately, with the small difference in ΔE_{pc} and poor resolution between waves 1 and 2, a study of the reversibility of wave 1 was not possible as it was with CarCp.

Similar bulk electrolysis results were seen with ClCp (Table 2) as with the other compounds in this series. Electrolysis negative of wave 1 resulted in 0.9 ± 0.1 electrons transferred, while negative of wave 2 resulted in 2.0 ± 0.1 electrons transferred. However, IR analysis of both the one-electron and two-electron reduced species of ClCp was unsuccessful due to rapid loss of product before the analysis.

Reduction of (η^5-C$_5$H$_4$CH$_3$)Mn(CO)$_3$ (MeCp)

The cyclic voltammogram of MeCp in THF/TBABF$_4$ at 100 mV/s is similar to that obtained for HCp, in that there is only one reduction process and four return oxidations. Wave 1 has an E_{pc} of −2.49 V versus Ag/AgCl and $E_p - E_{p/2}$ of 90 mV. As with all the other compounds in this investigation, wave 1 shifts to negative potentials upon increasing scan rate and is diffusion controlled.

The oxidation potentials are found at −2.27, −1.24, −0.84 and −0.60 V versus Ag/AgCl. The return oxidations are coupled to wave 1 since they are present only after scanning through wave 1. However, as with HCp, this is not a reversible process since ΔE_p is 220 mV between wave 1 and the first oxidation with a ratio of peak currents of 5.6. As demonstrated by the other compounds, the reduction of MeCp is characterized as an EC process [11–13].

TABLE 2. Reduction data of $(XC_5H_4)Mn(CO)_3$ in THF/TBABF$_4$ vs. Ag/AgCl

X	E_{pc1}^{a} (V)	Q_{obs}/Q_{theor}	E_{pc2}^{a} (V)	Q_{obs}/Q_{theor}	E_{pc3}^{a} (V)
H	−2.46 (±0.04)	1.06 (±0.04)			
$COOCH_3$	−2.15 (±0.04)	1.0 (±0.1)	−2.40 (±0.03)	2.1 (±0.2)	−2.78 (±0.05)
Cl	−2.26 (±0.02)	0.9 (±0.1)	−2.49 (±0.05)	2.0 (±0.1)	
CH_3	−2.49 (±0.02)	1.0 (±0.1)			

^{a}All potentials are taken at a scan rate of 100 mV/s, with 90% IR compensation and standardized to a ferrocene $E_{1/2}=0.4$ V.

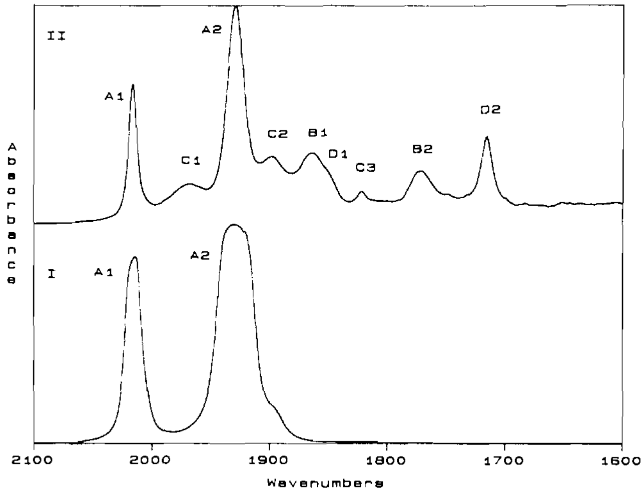


Fig. 5. IR spectrum of $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ vs. THF/TBABF$_4$ background. (I) Solution before electrolysis. (II) One-electron reduced solution. The spectra were autoscaled and absorbances may not be comparable between (I) and (II).

The bulk electrolysis data can be found in Table 2. The IR of the one-electron reduced MeCp (Fig. 5, II) shows evidence of three species present in addition to the unreduced MeCp (Fig. 5, I), similar to what was observed with HCp. A second chemical reaction product is represented by D1 and D2 that is not present with HCp. The exact nature of this species is unknown. These bands could indicate the presence of an Mn dimer with bridging carbonyls as shown in Scheme 1, as is known to occur with several Mn complexes.

Discussion

The substitution of a hydrogen on the Cp ring yielded a reduction potential range of 0.34 V for the compounds in this study. This range is larger than the 0.18 V range found [2] in a series of hexakis(arylisocyanide)-chromium(0) compounds for the one-electron reduction process with *para* substituents of chloro, hydrogen, methyl and methoxy substituents. It can also be noted that in the arylisocyanide investigation, the 0.18 V range could be divided by six, since all six ligands undergo the substituent change. At first inspection, the difference in the potential range between these two studies appears quite significant. However, there is a difference in the bonding of these systems that is important in understanding the trend. In the arylisocyanide system, a single lone pair of electrons is involved in the metal–ligand σ bond, which is not directly conjugated with the added substituents. One of the π-accepting orbitals of the isocyanide is directly conjugated with the substituent, but the relative importance of this bonding is small [15, 16]. In our system, the orbitals that are involved in the metal–Cp bonds, as well as the LUMO of the molecule, are affected directly by the substituents as demonstrated in theoretical and PES investigations of the substituted-Cp complexes [17, 18]. Consequently, the larger potential range for the substituted-Cp system is not surprising.

When considering the electronic effects of the added substituents the shifts in the reduction potentials for the compounds in this study follow the expected trends. For example, the electron-withdrawing groups (chloro and carbomethoxy) are expected to stabilize any added charge. This ability is reflected in the 310 mV positive shift of wave 1 (CarCp) and the 200 mV positive shift of wave 1 (ClCp) with respect to HCp (Table 2). However, the shift in potentials caused by the electron-donating methyl group is less dramatic. This group is expected to shift the potential to more negative potentials, which it does. However, its potential lies within the experimental error of wave 1 for HCp.

The largest difference in the voltammograms for this series is in the number of reduction processes observed. With CarCp three reduction processes are observed and with ClCp two reduction processes are observed. However, both HCp and MeCp show evidence of only one reduction process. This difference is explained by the effects of the added substituents. Both CarCp and ClCp have observable second reduction processes because of the stabilizing effect of the electron-withdrawing substituents, which shift the reduction potentials farther away from the solvent edge. Second reduction processes would be observed for both the HCp and MeCp if the solvent/supporting electrolyte allowed more negative potentials to be observed.

There have been reports of a linear relationship between the Hammett parameter, σ_p, and both electrochemical and spectroscopic parameters [2, 3]. At first, using σ_p does not seem appropriate for our work, since *para* substitution has no literal meaning in these compounds. However, σ_p relates the inductive and resonance effects of the different substituents in aromatic systems, whereas σ_m includes only inductive effects. For cxample, a linear relationship was found between ν(CO) and σ_p for a series of ring-substituted $CpRh(CO)_2$ compounds [3]. In support of this previous investigation, we have found a similar linear correlation between the ν(CO) (i.e. A1 and A2 in Figs. 2, 4 and 5) of each compound* studied and σ_p with correlation coefficients of 0.984 and 0.993, respectively [19]. Additionally, the compounds in this series also have a linear correlation between E_{pc} and σ_p as illustrated in Fig. 6 with a correlation coefficient of 0.979. This was not expected in a system that has an EC mechanism since E_{pc} should depend on both thermodynamic and kinetic parameters [11]. However, there are at least two examples reported where E_p has been related to thermodynamic and spectroscopic parameters [1, 20]. In each of these systems, the correlation indicated that E_p depends mainly on the thermodynamic difference within a series of compounds and not the rate of electron transfer. This must hold true for the compounds investigated in our work, since we also find linear correlations. Our work and others [1] suggest that E_p will correlate with thermodynamic parameters, if a few conditions are met. The chemical system must not structurally deviate with substituent and have a metal-centered electron transfer.

As stated earlier, an investigation of the reduction of (η^5-indenyl)$Mn(CO)_3$ demonstrated the presence of two reversible reduction processes in THF/TBAP using a glassy carbon working electrode [5]. However, in our investigation we only see evidence of reversibility with wave 1 of CarCp and no evidence of reversibility** with the other complexes in this series. The indenyl complex has an E_{pc} for the first reduction† of -2.12 V which is within experimental error of the value of wave 1 for CarCp in our investigation. It is not clear why the compounds in this work seem to be more prone to chemical reactions following electron transfer even though the indenyl system is more likely to ring-slip. One reason might be that the indenyl ring could limit access to one side of the metal complex due to the additional bulk of the six-membered ring, while the Cp ring does not have this restriction. A second difference between the two studies is the temperature of the system during the reductions. During the indenyl investigation, a low temperature was used in the chemical reductions. This low temperature might slow the dimerization illustrated in Scheme 1, and any other chemical reactions that would be coupled to the electron transfer.

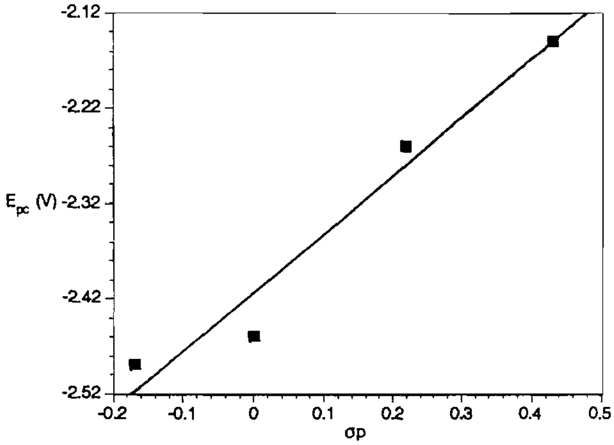


Fig. 6. Correlation of E_{pc} vs. Hammett parameter (σ_p) for the complexes in this series.

The species formed after the one-electron reduction are stable towards additional electrochemical processes. The BE results of the compounds indicate the species formed upon reduction are not easily reduced further, since a larger number of electrons transferred would be expected due to the additional reduction reactions. Furthermore, the formed species are oxidized at more positive potentials indicating a greater stability towards oxidation.

The formation of dimeric species is not uncommon for manganese compounds [21]. There have been several Mn dimers reported in the literature [22–24] including $Cp_2Mn_2(CO)_5$, (μ-diphosp)$_2Mn(CO)_6$ and $(Cp^*)_2Mn_2$-(μ-CO)$_3$. Although bridging carbonyls are not common in manganese compounds there are some examples of this occurring. Generally, examples of bridging carbonyls in Mn dimers occur in order to achieve 18-electron configurations as with other metal centers. For example, a short-lived transient, $Cp_2Mn_2(CO)_4(\mu\text{-}CO)$, is formed during the reaction of $CpMn(CO)_2S$ with $CpMn(CO)_3$, where S is solvent [25]. The dimers shown in Scheme 1 are suggested rearrangements that would enable the metal centers to obtain the desired 18-electron configuration.

The reactivity of the reduced species in this study prevents both their isolation and purification. Clearly, other reactions are possible than those suggested in Scheme 1. A few reactions, including protonation of the Cp, have been reported with reduced manganese

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*ν(CO) was taken in cyclohexane solution not THF.

**This includes changing to a GCE electrode from Pt. Under these conditions, we do see a second reduction for HCp that was not observed with the platinum electrode.

†This potential has been corrected for our conditions.

species [5, 26]. Also, our investigation has lead only to the assignment of the bands B1 and B2 (Figs. 2, 4 and 5) to the 19-electron $[(\eta^5\text{-}C_5H_4X)Mn(CO)_3]^-$ species where X is H, carbomethoxy and methyl, respectively. This is an analogous assignment to the indenyl system [5]*. The other observed ν(CO) bands are reasonable for the formation of the dimers illustrated in Scheme 1 and other ring-slipped species. Unfortunately, definite assignments cannot be made for all the observed peaks, based solely on the results from this investigation. Even our grouping of the IR peaks (other than B1 and B2) may be questioned. Certainly, other methods could yield information about the proposed structures.

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*Definite identification has not been possible. It has been suggested that bands B1 and B2 could also be due to a chemical reaction product of $[(\eta^5\text{-}C_5H_4X)Mn(CO)_3]^-$.