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Chemical and electrochemical studies on metal carbonyl/cobaltocene systems

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Abstract

The chemical and electrochemical behaviour of compounds of the type $[Co(C_5R_5)_2][M(CO)_n]$ (R = H, Me; M = Mn; $n = 5$; R = H; M = Co, $n = 4$; M = V; $n = 6$) was studied. A relationship between the chemical behaviour and the redox potentials of the components of the complexes was obtained. The reduction of $[MnX(CO)_5]$ (X = Cl, Br or I) by cobaltocene in different solvents was studied by both chemical and electrochemical methods.

Key words: Cobalt; Manganese; Vanadium; Electrochemistry; Carbonyl; Cobaltocene

1. Introduction

In binuclear metal carbonyls such as $[Mn_2(CO)_{10}]$ or $[Co_2(CO)_8]$ with a metal–metal bond, the potentials for the reduction and reoxidation of the reduced species differ by as much as 1.5 V. Thus the cyclic voltammetry of such complexes is characterized by an irreversible reduction with E_p in the range -1.0 to -1.6 V (*vs.* SCE) [1*,2] and a concomitant irreversible oxidation of the resulting carbonylate anion at about 0 V. In most instances, oxidation leads to a neutral radical that rapidly dimerizes [3], reforming the starting neutral dimeric carbonyl as exemplified for $[Mn_2(CO)_{10}]$ in Scheme 1.

Since both electrode reactions involve one-electron transfer followed by rapid bond rupture or bond formation, respectively, electrochemical peak potentials are a poor measure of a true or "effective" redox potential of the $2M^-/M_2$ pair. Since the anion M^- is stable at an electrode potential $E_2 > E > E_1$, the question arises as to whether a chemical reductant for M_2 needs to have a reversible potential close to E_1 or whether a more positive reduction potential (still cathodic of E_2) would suffice for generating the anion M^-. However, if the "effective" potential for reductive metal–metal bond cleavage in M_2 can be shown to lie negative of E_2, at least part of the free energy for dimerization, ΔG_{dim}, enters into this potential ($E_{eff} \approx E_2 - \Delta G_{dim}/F$). Answering these questions is relevant in the context of, for example, electron-transfer-catalysed chain reactions [4], where an endoergonic step in the reaction sequence must be balanced frequently by coupled exoergonic steps.

In this paper we describe the investigation of a redox couple where one component has a well-defined redox potential about midway between the peak potentials E_p^a (anodic) and E_p^c (cathodic) for the $2M^-/M_2$ component, which should make an ideal system for addressing the above questions. It has been known for many years that cobaltocene is a reductant towards a number of organometallic compounds [5]. Moreover, $[CoCp_2]$ reacts readily with metal carbonyls such as $[Co_2(CO)_8]$ [6,7] and $[V(CO)_6]$ [8] to afford the "con-

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* Reference numbers with asterisks indicate notes in the list of references.

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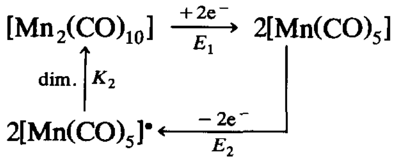

Scheme 1.

tact ion pairs" [7] $[CoCp_2][Co(CO)_4]$ and $[CoCp_2][V(CO)_6]$, respectively. The other component is the couple $[Mn(CO)_5]^-/\frac{1}{2}[Mn_2(CO)_{10}]$. The inertness of the neutral carbonyl compound towards Lewis bases compared with $[Co_2(CO)_8]$ or $[V(CO)_6]$ [9] allowed us to study the chemical or electrochemical reduction of $[Mn_2(CO)_{10}]$ both in hydrocarbons and in polar solvents.

2. Experimental details

Unless stated otherwise, all operations were carried out in an atmosphere of prepurified argon. The reaction vessels were oven dried before use. Solvents were dried by conventional methods.

IR spectra were recorded with Perkin-Elmer 283 or FT 1725X instruments equipped with gratings, in solutions or Nujol mulls of the compounds prepared under rigorous exclusion of moisture and dioxygen.

EG & G/PAR electrochemical equipment described previously [10] was used for recording cyclic voltammograms at Pt bead or vitreous carbon electrodes. Rapid scan ($v > 1$ V s^{-1}) voltammograms were sampled with a Nicolet 3091 digital storage oscilloscope and transferred to a PC. A saturated calomel electrode (SCE) was the reference electrode and was calibrated against the ferrocene/ferrocenium couple in the appropriate solvent. Potentials quoted in the Tables are normalized to a ferrocene/ferrocenium potential of 0.4 V *vs.* SCE, *i.e.*, addition of 0.4 V (the potential of the ferrocene/ferrocenium couple *vs.* SCE in CH_2Cl_2) to the quoted value refers the value to SCE. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAH).

Commercially available $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$ were sublimed *in vacuo* before use. $[V(CO)_6]$ [11], $[CoCp_2]$ [12] and $[CoCp^*{}_2]$ ($Cp^* = C_5Me_5$) [13] were prepared according to literature methods.

2.1. Reaction of $[CoCp_2]$ with $[Mn_2(CO)_{10}]$; preparation of $[CoCp_2][Mn(CO)_5]$

A solution of $[Mn_2(CO)_{10}]$ (0.2 g, 0.5 mmol) in acetonitrile (5 ml) was treated with $[CoCp_2]$ (0.19 g, 1.0 mmol). A golden yellow solution was immediately obtained on mixing the reagents. An IR spectrum of the solution in the carbonyl stretching region revealed $[Mn(CO)_5]^-$ as the only carbonyl species. Addition of heptane (10 ml) caused the separation of a violet oil which crystallized when the volatiles were removed under reduced pressure, affording 0.37 g (94% yield) of $[CoCp_2][Mn(CO)_5]$ as a dioxygen-sensitive violet solid. Anal. Found: C, 46.7; H, 2.7. Calc. for $C_{15}H_{10}CoMnO_5$: C, 46.9; H, 2.6%. IR spectrum (Nujol mull): 3020m, 1838vs-br, 1465m-s, 1010m, 860s, 675s, 650s, 455m-s cm^{-1}; (CH_3CN): 1900s, 1863vs cm^{-1}; (THF): 1893s, 1863vs, 1849sh cm^{-1}.

When the reaction was performed in THF, $[CoCp_2][Mn(CO)_5]$ was the only carbonyl compound present in solution after 30 min but in toluene $[Mn_2(CO)_{10}]$ (*ca.* 20% with respect to the starting amount) was still present in solution after 48 h.

When preformed $[CoCp_2][Mn(CO)_5]$ was treated with toluene, the absorptions typical of $[Mn_2(CO)_{10}]$ [14] were observed in solution after stirring for 10 min at room temperature.

2.2. Reaction of $[CoCp^*_2]$ with $[Mn_2(CO)_{10}]$ in toluene

A solution of $[CoCp^*_2]$ (0.7 g, 2.1 mmol) in toluene (50 ml) was treated with $[Mn_2(CO)_{10}]$ (0.4 g, 1 mmol). Precipitation of an orange solid was observed immediately upon mixing the reagents. After stirring for 30 min at room temperature, the solid was filtered off washed with toluene (2 × 5 ml) and dried *in vacuo*, affording $[CoCp^*_2][Mn(CO)_5]$ (0.92 g, 85% yield) as a dioxygen-sensitive orange solid. Anal. Found: C, 57.0, H, 5.8. Calc. for $C_{25}H_{30}CoMnO_5$: C, 57.3; H, 5.8%. IR spectrum (Nujol mull): 1880s, 1850vs, 1430m, 1080m, 1025m-s, 680s, 650s, 440m-s cm^{-1}; (THF): 1895s, 1861vs cm^{-1}.

2.3. Thermal treatment of $[Co(\eta^5\text{-}C_5R_5)_2][M(CO)_n]$ ($R = H$: $M = Co$, $n = 4$; $M = Mn$, $n = 5$; $M = V$, $n = 6$; $R = Me$: $M = Mn$)

$[CoCp_2][Mn(CO)_5]$ (0.1 g, 0.26 mmol) was introduced into a sublimation apparatus and warmed at 25°C/0.01 mmHg for 15 h. Large orange crystals which were identified as $[Mn_2(CO)_{10}]$ (0.03 g) from its IR spectrum in the carbonyl-stretching region formed on the cold finger. When the bath temperature was raised to 40°C, slow sublimation of $[CoCp_2]$ (0.03 g, IR) was observed. The residue was quickly heated to 100°C, which caused the sublimation of a violet solid shown by infrared spectroscopy (THF; carbonyl-stretching region) to be $[CoCp_2][Mn(CO)_5]$ contaminated with small amounts of $[Mn_2(CO)_{10}]$.

When the experiment was repeated with $[CoCp_2][V(CO)_6]$, $[CoCp_2][Co(CO)_4]$ or $[CoCp^*_2][Mn(CO)_5]$, decomposition occurred on heating the samples *in vacuo* and no sublimate was obtained.

2.4. Reaction of $[MnX(CO)_5]$ ($X = Cl$ or Br) with $CoCp_2$

2.4.1. In toluene

A solution of $[CoCp_2]$ (0.24 g, 1.3 mmol) in toluene (20 ml) was treated with $[MnBr(CO)_5]$ (0.36 g, 1.3 mmol). After 10 min a bright yellow solid was present in a yellow–orange solution. The solid was filtered off and dried *in vacuo*, affording $[CoCp_2]Br$ (0.32 g, 92% yield), identified by IR spectroscopy and elemental analysis. The solution was evaporated to dryness and the residue was sublimed at 80°C/0.1 mmHg, affording 0.2 g (80% yield) of $[Mn_2(CO)_{10}]$, identified by its IR spectrum in heptane.

By treating $[MnCl(CO)_5]$ with $[CoCp_2]$ under similar experimental conditions, $[CoCp_2]Cl$ and $[Mn_2(CO)_{10}]$ were obtained in 85 and 87% yields, respectively.

2.4.2. In acetonitrile

A solution of $[MnBr(CO)_5]$ (0.24 g, 0.9 mmol) in acetonitrile (20 ml) was treated with $[CoCp_2]$ (0.17 g, 0.9 mmol). An IR spectrum of the solution in the carbonyl-stretching region recorded after 10 min showed absorptions typical of $[MnBr(CO)_5]$ (2039w, 2046s cm^{-1}), $[Mn_2(CO)_{10}]$ (2009vs, 1980m cm^{-1}) and $[Mn(CO)_5]^-$ (1900s, 1863vs cm^{-1}). On addition of 0.17 g (0.9 mmol) of $[CoCp_2]$, a yellow solution was obtained, the IR spectrum of which in the carbonyl-stretching region showed that $[CoCp_2][Mn(CO)_5]$ was the only carbonyl compound present.

3. Results and discussion

$[CoCp_2]$ reacts readily with $[Mn_2(CO)_{10}]$ at room temperature according to the equation

$$[CoCp_2] + [Mn_2(CO)_{10}] \xrightarrow{CH_3CN \text{ or } THF} \underset{\mathbf{1}}{2[CoCp_2][Mn(CO)_5]} \quad (1)$$

the course of the reaction being dependent on the solvent. In acetonitrile, reaction (1) is fast and compound **1** can be isolated in almost quantitative yield. On the other hand, the reaction of $[CoCp_2]$ with $[Mn_2(CO)_{10}]$ in toluene is not complete even after prolonged stirring at room temperature, the absorptions of $[Mn_2(CO)_{10}]$ still being observable after 48 h. Moreover, when preformed $[CoCp_2][Mn(CO)_5]$ was suspended in toluene, $[Mn_2(CO)_{10}]$ was detected spectroscopically in solution, suggesting that an equilibrium is probable under these conditions.

Stabilization of the "solvent-separated ion pairs" [7(b)] by the solvent showing the higher dielectric constant (CH_3CN; $\epsilon = 37.5$; THF: $\epsilon = 7.58$; toluene: $\epsilon = 2.39$ [15] is presumably responsible for the observed reactivity.

The preparation of $[CoCp_2][Mn(CO)_5]$ in eq. (1) represents the first synthesis of such a derivative from the corresponding neutral precursors, $[CoCp_2]$ and $[Mn_2(CO)_{10}]$. The cobalticinium derivative is generally obtained from the performed ions [7,16] through a metathesis reaction:

$$[CoCp_2]X + Na[Mn(CO)_5] \xrightarrow[\substack{X=OH;\ S=H_2O\ [16] \\ X=Br;\ S=CH_3CN\ [7]}]{S} [CoCp_2][Mn(CO)_5] + NaX \quad (2)$$

Compound **1** is not completely stable as a solid $[CoCp_2]$ and $[Mn_2(CO)_{10}]$ may be isolated from preformed $[CoCp_2][Mn(CO)_5]$ by fractional sublimation at 25–40°C *in vacuo*. A similar situation was encountered by Hieber and Schropp [16(a)] on the attempted sublimation of the green ion pair $[Cr(\eta^6\text{-}C_6H_6)_2][Mn(CO)_5]$. However, compound **1** may be sublimed rapidly without excessive decomposition at 100–150°C *in vacuo* (see also ref. 16). Moreover, $[CoCp_2][Mn(CO)_5]$ is stable in THF (green solution) and in CH_3CN or acetone (yellow solution). The change of colour of carbonyl metallate derivatives on going from the solid state to polar solvents has been extensively studied and it has recently been demonstrated [7,17] that the colours are associated with the interionic charge-transfer interactions of carbonyl metallates acting as electron donors,

TABLE 1. Peak and redox potentials for cobalticinium and decamethylcobalticinium salts of V, Mn and Co carbonyls ($v = 100$ mV s^{-1})

Entry	Compound	Solvent	$E_{1/2}$ $[CoCp_2^*]$	E_p^c $[M_2(CO)_{2n}]/2[M(CO)_n]^-$	E_p^a $[M(CO)_n]^-/[M(CO)_n]^\bullet$
1	$[CoCp_2][Mn(CO)_5]$	CH_3CN	−0.93	−1.52	−0.09
2	$[CoCp_2^*][Mn(CO)_5]$	THF	−1.43	−1.33	−0.31
3	$[CoCp_2][Co(CO)_4]$	THF	−0.93	−0.63	0.02
4	$[CoCp_2][Co(CO)_4]$	CH_2Cl_2	−0.93	−0.63	−0.01
5	$[CoCp_2][V(CO)_6]$	CH_2Cl_2	−0.92	−0.14 [a]	

All potentials are referred to the potential of a ferrocene/ferrocenium couple at 0.400 V *vs.* SCE, which is close to the actual value found in CH_2Cl_2 with our reference electrodes.

[a] $E_{1/2}$ $\{V(CO)_6/[V(CO)_6]^-\}$.

TABLE 2. Peak potentials for the reduction and radical reoxidation of $[Mn_2(CO)_{10}]$ and $[MnX(CO)_5]$ (X = Cl, Br or I) ($v = 100$ mV s^{-1})

Entry	(a) $[Mn_2(CO)_{10}]$			
	Solvent		E_p^c $[Mn_2(CO)_{10}]/2[Mn(CO)_5]^-$	E_p^a $[Mn(CO)_5]^-/[Mn(CO)_5]^\bullet$
1	CH_3CN		−1.51	−0.1
2	THF		−1.33	−0.26
3	CH_2Cl_2		−1.55	−0.30
	(b) $MnX(CO)_5$			
	X	Solvent	E_p^c $[MnX(CO)_5]/[Mn(CO)_5]^-$	E_p^a $[Mn(CO)_5]^-/[Mn(CO)_5]^\bullet$
4	Cl	CH_3CN	−1.68	−0.16
5	Br	CH_3CN	−1.59	−0.13
6	I	CH_3CN	−1.35	−0.13
7	I	CH_2Cl_2	−1.32	−0.30

All potentials are referred to the potential of a ferrocene/ferrocenium couple at 0.400 V *vs.* SCE, which is close to the actual value found in CH_2Cl_2 with our reference electrodes.

the cations being electron acceptors. Moreover, it has been demonstrated that a linear correlation exists between the redox potential of both the cation and the anion involved in the ion-pair interaction and the charge-transfer band observed in the UV–visible spectrum. In other words, the easier the oxidation of the anion, the higher is the energy of the absorption band [7(b)].

To elucidate further the behaviour of **1**, this compound and as other cobalticinium carbonylmetallates together with $[Mn_2(CO)_{10}]$ itself were investigated by cyclic voltammetry in various solvents. Potentials are quoted *vs.* SCE but are referred to the ferrocene couple (see Experimental section). Data are collected in Table 1 and 2.

Focusing on **1** in acetonitrile (entry 1, Table 1) as an example in the potential range near −0.5 V, *i.e.* anodic from the $CoCp_2^{+/0}$ couple and cathodic from the $[Mn(CO)_5]^-$ oxidation peak, no current flows when the cell is switched on (Fig. 1(A)). Current flow is observed when the potential is set cathodic of the $CoCp_2^{+/0}$ transition. By sweeping anodically through the peak at E_2 and then reversing the potential, a peak (small because of diffusive loss of species during the backward scan) is observed at E_1 due to the reduction of $[Mn_2(CO)_{10}]$ that had been generated at E_2 in the previous anodic sweep of the cycle. The assignment was confirmed by addition of $[Mn_2(CO)_{10}]$ to the solution. Thus the only species detectable electrochemically, in CH_3CN solution are $[CoCp_2]^+$ and $[Mn(CO)_5]^-$. Note that under these conditions, owing to a large excess of $(Bu_4N)PF_6$, the supporting electrolyte, no contact ion pairs are present in solution, rather solvated ions [7].

From the results obtained with **1**, it is evident that reaction (1) is thermodynamically favoured from left to right, at least in polar solvents. In non-polar solvents, where an equilibrium situation is attained, **1** is in partly reconverted to $[CoCp_2]$ and $[Mn_2(CO)_{10}]$. Since the change in reduction/oxidation potentials of $[CoCp_2]$ and $[Mn_2(CO)_{10}]$ with solvent is significant though not dramatic (see Tables 1 and 2(a)) [18], the driving force

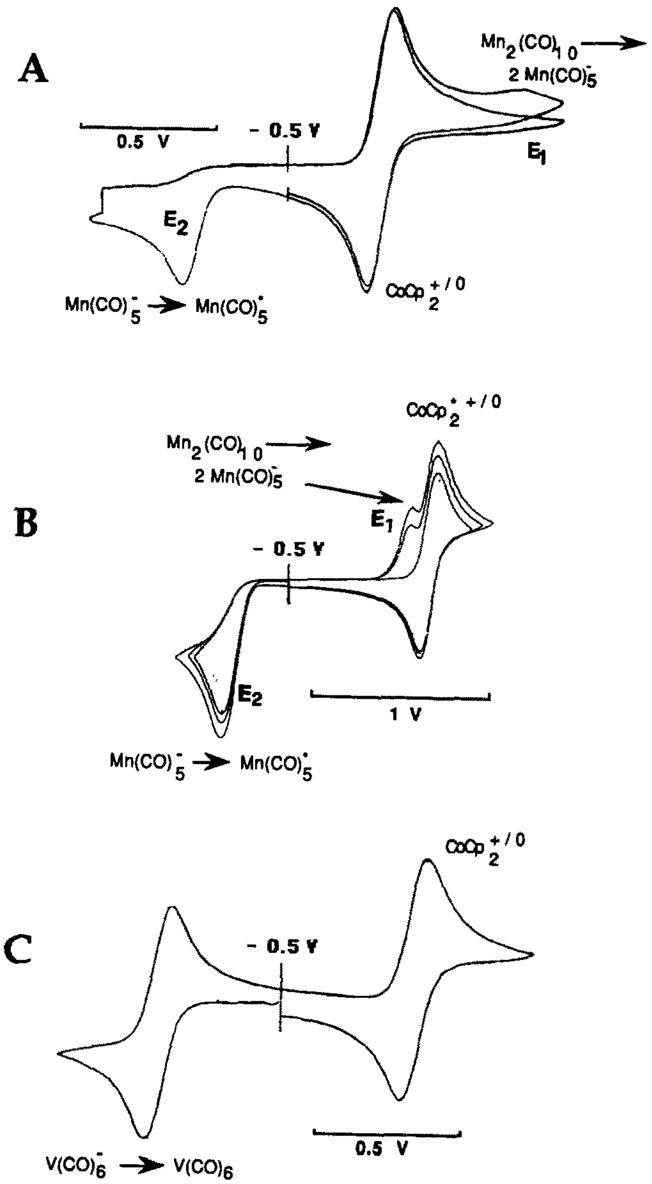

Fig. 1. Cyclic voltammograms of (A) $[CoCp_2][Mn(CO)_5]$, CH_3CN, TBAH, $v = 200$ mV s^{-1}; (B) $[CoCp^*_2][Mn(CO)_5]$, THF, TBAH, $v = 100$ mV s^{-1}; (C) $[CoCp_2][V(CO)_6]$, THF, TBAH, $v = 100$ mV s^{-1}.

for reaction (1) cannot be high in any solvent. However, if the manganese-dependent redox potential relevant to eqn. (1), E_1 (Scheme 1) were close to the $[Mn(CO)_5]^-/[Mn(CO)_5]^\bullet$ potential E_2, reaction (1) would be highly exoergonic under all circumstances. As the value of E_1 is in fact considerably negative of E_2, it is concluded that the free energy of dimerization of $[Mn(CO)_5]^\bullet$, ΔG_{dim}, in fact makes a substantial contribution to E_1 [19].

This result should be compared with that obtained with $[CoCp^*_2][Mn(CO)_5]$ where cobaltocene is replaced by the fully methylated derivative (entry 2, Table 1), a stronger reducing agent than $[CoCp_2]$ [20]. In this case the $[Mn_2(CO)_{10}]$ reduction peak after sweeping through the $[Mn(CO)_5]^-$ oxidation peak appears on the *anodic* side of the $[CoCp_2]^{+/0}$ couple (Fig. 1(B)). A similar situation is encountered with $[CoCp_2][Co(CO)_4]$ and $[CoCp_2][V(CO)_6]$ (Table 1). In each case the reduction of the carbonyl compound is at less negative potential from the $[CoCp_2]^{+/0}$ couple. Thus, for $[CoCp_2][Co(CO)_4]$ the cyclic voltammogram is similar to that shown in Fig. 1(B), the follow-up $[Co_2(CO)_8]$ reduction peak being at −0.63 V, anodic of the cobaltocene couple. The cyclic voltammogram of $[CoCp_2][V(CO)_6]$ (Fig. 1(C)) consists solely of the reversible patterns of the $[CoCp_2]^{+/0}$ and $[V(CO)_6]^{0/-}$ couples with no current flowing in the potential range in between.

We investigated the reduction of the halopentacarbonyl derivatives of manganese(I) chemically and electrochemically. In toluene $[MnI(CO)_5]$ is reduced by $[CoCp_2]$ to $[Mn_2(CO)_{10}]$ [5]. We extended this to the chloro and bromo derivatives and confirmed that in toluene $[Mn_2(CO)_{10}]$ and $[CoCp_2]X$ are formed quantitatively according to the stoichiometry of the equation

$$[CoCp_2] + [MnX(CO)_5] \longrightarrow [CoCp_2]X + \tfrac{1}{2}Mn_2(CO)_{10} \quad (3)$$

$$X = Cl, Br$$

When a 2:1 Co:Mn molar ratio was used, the products were the same, leaving one equivalent of cobaltocene unreacted. However, in acetonitrile the addition of one equivalent of $[CoCp_2]$ to $[MnX(CO)]_5$ afforded $[CoCp_2][Mn(CO)_5]$ and $[CoCp_2]X$. Addition of a second equivalent of $[CoCp_2]$ caused the disappearance of the IR absorptions due to $[Mn_2(CO)_{10}]$, suggesting that in acetonitrile the correct stoichiometry is that of the equation

$$2[CoCp_2] + [MnX(CO)_5] \longrightarrow [CoCp_2][Mn(CO)_5] + [CoCp_2]X \quad (4)$$

$$X = Cl \text{ or } Br$$

Electrochemical reduction of $[MnX(CO)_5]$ (X = Cl, Br or I) follows a pattern similar to that observed for $[Mn_2(CO)_{10}]$, where E_1 is now referred to the equation

$$[MnX(CO)_5] + 2e^- \longrightarrow [Mn(CO)_5]^- + X^- \quad (5)$$

The E_p values given in Table 2 show that the chloride and bromide carbonyl derivatives are reduced with a peak potential negative of that of $[Mn_2(CO)_{10}]$ whereas $[MnI(CO)_5]$ has a slightly more positive peak potential at the same scan speed, consistent with the weaker Mn–I bond as compared with Mn–Cl and Mn–Br [21]. As judged by peak potentials, reduction of $[MnX(CO)_5]$ is not very different from the analogous reaction of $[Mn_2(CO)_{10}]$ rationalizing the feasibility of reaction (4).

The course of the reaction between $CoCp_2$ and $MnX(CO)_5$ in toluene deserves special note. The formation of $[Mn_2(CO)_{10}]$ exclusively in this istance must be far kinetic rather thermodynamic reasons in the light of the above considerations. The generally accepted two-step reaction sequence between cobaltocene and an organic halide [22], transferred to $[MnX(CO)_5]$ would suggest eqn. (6) as the initial step, following by the competing reactions (7) and (8). The formation of the dimerization product $[Mn_2(CO)_{10}]$ only shows that in toluene $k_7 \gg k_8$, despite the high thermodynamic driving force for reaction (8) of about 0.8 V (Table 1).

$$[CoCp_2] + [MnX(CO)_5] \xrightarrow{k_6} [Mn(CO)_5]^\bullet + [CoCp_2]X \quad (6)$$

$$2[Mn(CO)_5]^\bullet \xrightarrow{k_7} [Mn_2(CO)_{10}] \quad (7)$$

$$[Mn(CO)_5]^\bullet + [CoCp_2] \xrightarrow{k_8} [CoCp_2][Mn(CO)_5] \quad (8)$$

4. Conclusions

This paper has shown that a dimeric derivative containing a metal–metal bond can be reduced by compounds with a potential very positive (0.6 V) of the peak potential corresponding to the electrochemical reductive cleavage of the metal–metal bond. Given that the free energy of the overall reaction (1) is close to zero, this means that the "effective" redox potential for the half-reaction $[Mn_2(CO)_{10}]/2[Mn(CO)_5]^-$ lies half way between peak potentials of the relevant couples. In terms of activation theory, this result is interpreted as follows. Cleavage of the metal–metal bond takes place in the radical anion $[Mn_2(CO)_{10}]^{-\bullet}$, which can be viewed as a transition state. Once formed, it rapidly decays to $[Mn(CO)_5]^-$ and $[Mn(CO)_5]^\bullet$ in a highly exothermic reaction, with the radical $[Mn(CO)_5]^\bullet$ being subject to further reduction, homogeneous or at the electrode surface [23*]. Such a course could explain why overall cleavage is feasible even if only a small number of molecules are converted to the radical anion. In terms of stationary electrode reduction, the peak potential consequently has the meaning of an overpotential with respect to the thermodynamic potential of the $[Mn_2(CO)_{10}]/2[Mn(CO)_5]^-$ half reaction. To quantify this, complementary investigations of the homogeneous kinetics by chemical reductants and by pulse radiolysis will be the subject of future research.

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References and Notes

1 Since both electron transitions are irreversible and followed by rapid chemical reactions, peak potentials E_p are related to $E_{1/2}$ by $E_p = E_{1/2} - 0.02 + (RT/nF)\log(k/v)$, where v is the sweep rate in V s^{-1} and k is a first-order rate constant [2].

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23 Note that rapid follow-up reaction and slow heterogeneous electron transfer in stationary electrode electrochemistry have the same effect of displacing the peak potential in the direction of scan [2] and are phenomenologically indistinguishable.