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Electrochemical generation of 17-electron cation radicals from arene–$M(CO)_3$ (M = Cr, Mo, W) and thiophene–$Cr(CO)_3$ complexes in MeCN: Conventional cyclic voltammetric studies with digital simulation and microelectrode voltammetry in the absence of supporting electrolyte

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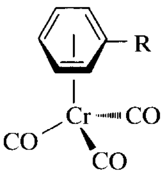
Abstract

One-electron electrochemical oxidation of arene–$M(CO)_3$ (M = Cr, Mo, W) and thiophene–$M(CO)_3$ complexes in acetonitrile produces 17-electron cations $(MeCN)_nM(CO)_{6-n}{}^+$. Thus oxidation of $LCr(CO)_3$, (L = C_6H_6, PhCl, $PhNMe_2$, thiophene, 3-methylthiophene) in acetonitrile leads to a rapid follow-up reaction in which the intermediate $(MeCN)_3Cr(CO)_3{}^+$ is detected by cyclic voltammetry. Oxidations in MeCN are not affected by redox catalysis, confirming a simple substitution mechanism. Increasing the concentration of the complex has no effect on the yield of MeCN substituted product, again ruling out bimolecular decomposition pathways. The reaction is very rapid and quite distinct from photochemical or thermal substitution of these complexes. Microelectrode steady-state voltammetry shows that all the arene complexes undergo two successive one-electron transfers in MeCN. Reproducible microelectrode voltammograms could only be obtained in MeCN in the absence of supporting electrolyte; addition of supporting electrolyte rapidly diminished the electrode response owing to electrode coating.

Introduction

Considerable progress has been made in the study of the electrochemistry of organometallic compounds [1–3]. This progress had led to a greater awareness of the role of odd-electron (17e and 19e) species in the reactions of organometallics. These intermediates are conveniently generated and kinetically monitored using electrochemical methods. The electrochemistry of arene chromium tricarbonyl complexes I continues to attract a great deal of attention. There has been much debate concerning the reactivity of the electrogenerated cations, which appear to produce free arene ligand and Cr^{III} in the presence of nucleophiles [4–7]. Recently, these complexes have also become important in organic synthesis [8–10].

For example, the coordinated arene is activated towards nucleophilic attack. After the reaction the arene ligand may be readily removed from the $Cr(CO)_3$ moiety by mild I_2 oxidation. We were interested to see how this oxidation related to the electrochemistry of these complexes. Secondly, we wished to learn more about the greatly increased lability and catalytic activity of electrogenerated 17e and 19e radicals [11,12]. Our results below provide new insight into the fate of the oxidized arene complexes. In addition to the arene complexes we also report the electrochemistry of thiophenechromium complexes II. The thiophene complexes have the potential to be oxidized to radical cations like the free ligand; these cations could also couple to form polymers, as is found for the free ligand [13]. Our results on complexes I and II show that oxidation proceeds via the Cr^1 intermediate $(MeCN)_3Cr(CO)_3{}^+$ where no loss of CO groups occurs, and that this intermediate is unique to Cr: the corresponding Mo and W arene tricarbonyl cations do not suffer displacement of the arene ligand.



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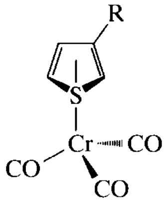

(II)

Experimental

The solvents used were HPLC grade (Aldrich) and before use were thoroughly deoxygenated with dry nitrogen or argon. Unless otherwise stated all the electrochemical experiments were carried out with a 2mM solution of the complex containing 0.1 *M* supporting electrolyte (Bu_4NPF_6). Ag/Ag^+ reference electrodes were used consisting of a Ag wire dipping in a solution of 5 mM $AgNO_3/0.1$ *M* Bu_4NPF_6 in acetonitrile with cracked glass bead junction [14]. The working electrode was a Pt button electrode (1mm diameter) with either a Pt wire or a Pt flag counter electrode.

All measurements were made using a Pine RDE4 potentiostat coupled to a Graphtec WX2300 X-Y recorder or an Amel model 567 function generator and potentiostat unit driven from a BBC microcomputer using software developed at St. Andrews and interfaced via a Datalab DL1200 waveform recorder. After recording each cyclic voltammogram the working electrode was removed from solution and polished using P600 sanding paper in order to ensure reproducibility.

Computer simulations were carried out with software supplied by Prof. A.J. Bard. We made some minor modications to the original program, QUINGEN.

Chemicals

Apart from $(C_6H_5Cl)Cr(CO)_3$ and $(C_6H_5NC_4H_4)Cr(CO)_3$ which were kindly supplied by Dr. T. Miller (MIT), all arene complexes were either from Aldrich and used without further purification or synthesised from the parent arene and $Cr(CO)_6$ (either by refluxing in decalin or the neat arene) [15]. The thiophene complexes were synthesised via $(pyridine)_3Cr(CO)_3$ [16,17] and characterised by ^1H NMR and IR spectroscopy and CHN microanalysis. All complexes were treated as air sensitive until they were obtained as solids, which were stored under nitrogen in a freezer compartment. Solutions of the complexes are particularly susceptible to photo-oxidation under natural light but are much more stable under artificial lighting. In the case of (3-phenylthiophene)$Cr(CO)_3$ both η^6-arene and η^6-thiophene coordinated complexes are possible. Refluxing a mixture of $Cr(CO)_6$ and 3-methylthiophene in decalin gave exclusively the η^6-arene isomer (as indicated by ^1H NMR spectroscopy). Preparation via $(pyridine)_3Cr(CO)_3$ gave a complex mixture which was not separated.

Results and discussion

Cyclic voltammetry of a model complex: $(PhNMe_2)Cr(CO)_3$

Many of the organometallic complexes studied in this work undergo reversible one-electron oxidation in CH_2Cl_2. For example, the $PhNMe_2$ complex Ia is oxidized at $E_1^{0'} = +0.27$ V vs Ag/Ag^+, as shown in Fig. 1, waves 1,1′. By comparison with the wave height of ferrocene, the anodic peak height of wave 1 corresponds to a one-electron transfer, as observed previously [18–20]. The reversibility of the oxidation in the case of the $PhNMe_2$ complex is sensitive to impurities in the solvent or supporting electrolyte; the solvent must be rigorously dried before use. When the reversibility is less, as measured by the deviation from unity of the ratio of peak heights i_{pa}/i_{pc} (where in this case i_{pa} is the peak current of the anodic wave 1, and i_{pc} is the peak current of the cathodic wave 1′) there is a new broad reduction wave 2 at ca. −0.54 V vs Ag/Ag^+, presumably due to $Cr^{II} \rightarrow Cr^0$ reduction. This wave's height increases on scanning through the second oxidation wave 3 at $E_{p,a} = +1.0$ V vs Ag/Ag^+, as shown by the broken line in Fig. 1.

The CV of Ia dissolved in the more nucleophilic solvent, MeCN (Fig. 2), demonstrates that in this case the oxidation at +0.27 V vs Ag/Ag^+ (wave 1 peak potential, $E_{pa}(1)$) is irreversible as evidenced by the complete absence of a cathodic peak. The radical is attacked by strongly coordinating solvents such as MeCN. Our observations provide direct evidence for one of the initial products of this reaction: on the reverse sweep a new reversible wave (2/2′), absent during the initial scan in this region, appears with $E^0(2) = -0.33$ V vs Ag/Ag^+. This observed redox potential corresponds closely to that previously observed for $(MeCN)_3Cr(CO)_3^{+/0}$ [21]. Prolonged electrolysis results in a yellow solution of $(MeCN)_3Cr(CO)_3^0$, readily identified by its IR spectrum (Fig. 3). Substituted metal carbonyls may also be generated by photochemical methods, and so we decided to confirm our assignment of the redox wave at −0.33 V vs Ag/Ag^+ by photochemical generation of this species with simultaneous electrochemical monitoring. A solution of $Cr(CO)_6$ in MeCN/0.1 mol dm^{-3} TBAT was photolyzed using a UV lamp. At the beginning of the experiment a CV scan revealed only one redox wave at +1.2 V, due to reversible one-electron oxidation of $Cr(CO)_6$. After 90 min photolysis, the CV showed that this wave was considerably reduced in height and a series of peaks had grown in due to substituted species $(MeCN)_xCr(CO)_{6-x}$ (Fig. 4). The waves grew in sequentially in the order 1–3 until reaching a photostationary state after ca. 90 min. The waves 0–3 have redox potentials $E^{0'} = 1.02$, 0.42,

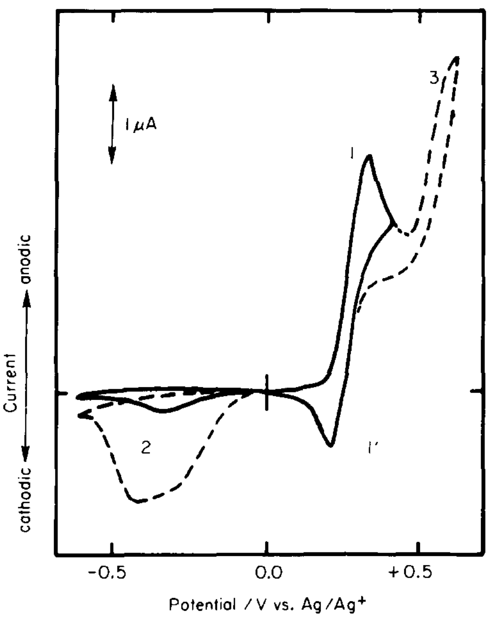

Fig. 1. Cyclic voltammetry (100 mV s^{-1}) of the oxidation of 2 mM I, (η^6-$PhNMe_2$)$Cr(CO)_3$ in CH_2Cl_2, supporting electrolyte 0.1 *M* TBAT. Ref vs Ag/Ag^+.

-0.06, -0.45 V vs $Fc^{0/+}$ (based on $E^0Fc^{0/+} = +0.17\ V_{Ag/Ag+}$), corresponding to the $(MeCN)_xCr(CO)_{6-x}$ species with $x = 0$–4 respectively. Previously reported $E^{0'}$ (vs $Fc^{0/+}$) values [21] are as follows: $Cr(CO)_6$, 1.05V; $(MeCN)Cr(CO)_5$, 0.46V; *cis*-$(MeCN)_2Cr(CO)_4$, -0.07; *fac*-$(MeCN)_3Cr(CO)_3$, -0.45 (based on $E^{0'}$ $Fc^{0/+} = 0.31\ V_{sce}$). In addition we observe an irreversible wave at $+0.69$ V, which we assign to the *trans* isomer of $(MeCN)_2Cr(CO)_4$.

$(MeCN)_3Cr(CO)_3$ was also generated thermally by refluxing $Cr(CO)_6$ in MeCN for 24 h, and again the CV (Fig. 5) revealed a one-electron oxidation at the same potential, -0.47 V vs $Fc^{+/0}$.

Returning to the electrochemical reactions, the $(MeCN)_3Cr(CO)_3{}^+$ product clearly arises from the attack of MeCN on the cation Ia^+, $(PhNMe_2)Cr(CO)_3{}^+$, with displacement of the arene ligand. Electrochemically speaking, this amounts to an EC reaction, i.e. electron transfer followed by a chemical reaction:

$$\text{E1: } (PhNMe_2)Cr(CO)_3 \rightleftharpoons (PhNMe_2)Cr(CO)_3{}^+ + e^- \qquad (1)$$

$$\text{C: } (PhNMe_2)Cr(CO)_3{}^+ + 3MeCN \xrightarrow{k_2} (MeCN)_3Cr(CO)_3{}^+ + PhNMe_2 \qquad (2)$$

The $(MeCN)_3Cr(CO)_3{}^+$ intermediate is then detected on the reverse sweep. According to the theory of EC reactions, the anodic peak potential, E_{pa}, should be scan-rate (ν) dependent and the product $I_{pa} \cdot \nu^{-1/2}$ should be independent of ν. Thus a plot of the observed E_{pa} of reaction 1 against $\log_{10}(\nu/\nu^*)$ is linear with intercept $E_{pa}{}^*$ (i.e. the peak potential at the lowest scan rate $\nu^* = 10$ mV s^{-1}) and slope 64.9 mV, close to the theoretical value, $59/n$ mV, for a 1-electron oxidation where the electron transfer step is irreversible [22]. The very rapid follow-up

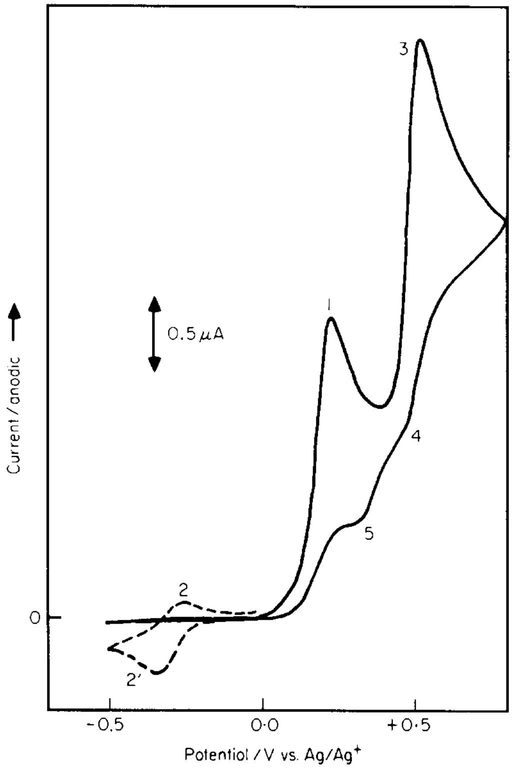

Fig. 2. Cyclic voltammetry (200 mV s^{-1}) of the oxidation of 2 mM I, (η^6-$PhNMe_2$)$Cr(CO)_3$ in MeCN, 0.1 *M* TBAT.

chemical step shifts the peak position to less positive potentials where the driving force (and hence rate) of electron transfer is slower. Thus the peak position shifts with scan rate in much the same way as does that of a slow electron transfer reaction. The value of *n*, the number of electrons transferred in the reaction, has been the subject of some controversy. Thus Bond et al. [5] believe that for the benzene complexes *n* is closer to 2, since they assume that the electrogenerated Cr^I species is oxidized further to Cr^{II}. In our own experiments, however, the electrode is not at a sufficiently high potential to carry out this reaction during the sweep through the first oxidation wave of Ia.

Fig. 2 also shows the effect of increasing the anodic potential limit of the CV scan. A further peak (3) at +0.57 V is observed which corresponds closely to the oxidation of the free $PhNMe_2$ ligand. This particular oxidation is itself known [23] to be a complex ECE reaction involving dimerisation of the electrogenerated cation ($PhNMe_2^{+\cdot}$) to tetramethylbenzidene (TMB):

$$PhNME_2 \rightarrow PhNMe_2^{+\cdot} + e^- \qquad (3)$$

$$2PhNMe_2^{+\cdot} \rightarrow TMB + 2H^+ + 2e^- \qquad (4)$$

This scheme predicts that the second oxidation wave 3 (due to the free ligand) is a 2-electron process. However, the height of the second wave is not observed to be twice that of the first wave. The reason is that there is time after the first oxidation

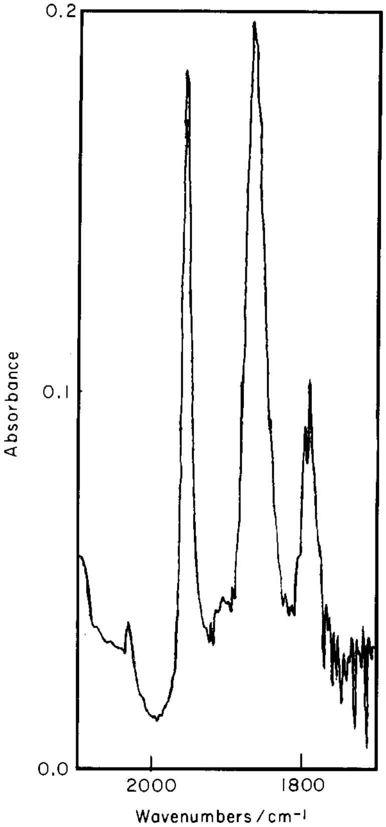

Fig. 3. FTIR spectrum of the CO stretching region obtained after 1 h bulk electrolysis of 2 mM dm^{-3} I in MeCN/0.1 *M* TBAT. Besides the strong peaks due to starting material (1951, 1863 cm^{-1}) a new peak at 1789 cm^{-1} has appeared due to $(MeCN)_3Cr(CO)_3$.

for diffusion of the decomplexed ligand away from the electrode. Finally, the waves marked 4 and 5 in Fig. 2 are probably due to the two one-electron reductions of the TMB product, and are only observed after scanning through wave 3.

Other arene Cr complexes

We have examined the electrochemical oxidation of several other arene and thiophene chromium complexes in MeCN (Table 1). The $LCr(CO)_3$ complexes, while having quite different anodic peak potentials, $E_{pa}(1)$, exhibit similar behaviour, and the same reversible product redox wave $E_2^{0'}$) regardless of L. This is important evidence confirming our assignment of this species as one which does not contain complexed arene ligand, and illustrates that the mechanism of oxidation of each complex proceeds via the same intermediate. Table 1 also gives the ratio of the currents for the reduction of the product acetonitrile complex and the oxidation of the arene complex, $R = i_{pc}(2)/i_{pa}(1)$ (numbering of peaks as in Fig. 2). This ratio is a function of the nature of the supporting electrolyte anion. Thus the amount of MeCN-containing product is greater when using PF_6^- rather than BF_4^-. Bond et al. [4] also found that this anion was preferable in achieving reversible

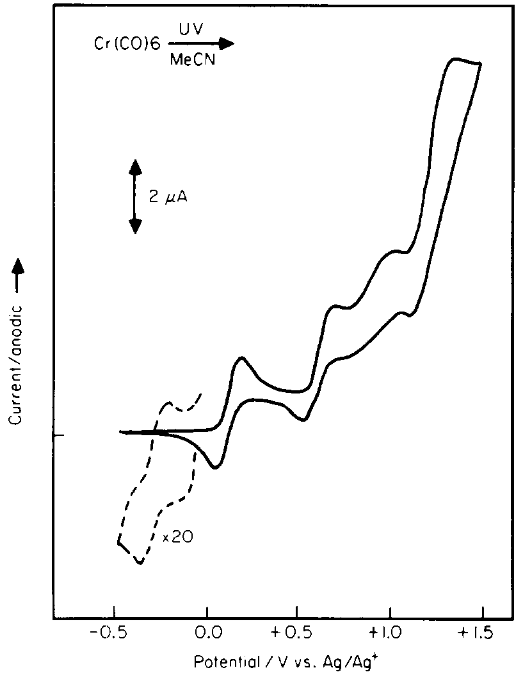

Fig. 4. CV obtained after 90 mins photolysis of a pyrex cell containing 5 mM $Cr(CO)_6$/0.1 *M* TBAT in MeCN. Area of electrode 2×10^{-3} cm^2. Scan rate 200 mV s^{-1}. The dashed line shows the CV trace due to $(MeCN)_3Cr(CO)_3{}^{+/0}$, after a 20 times scale expansion.

oxidation of the benzene complex in CH_2Cl_2; the reason appears to be the greater reactivity of $BF_4{}^-$ with organometallic cations (leading to BF_3 and coordinated F^-). Even for $PF_6{}^-$, increasing the concentration of supporting electrolyte had an effect on the ratio. We cannot rule out the possibility that an impurity in the electrolyte (such as water) is competing with MeCN for the cation.

Steady-state current microelectrode voltammetry

In CH_2Cl_2 it is not possible to observe stable steady-state voltammetry of these complexes with a 25μm Pt microelectrode. On oxidation a plateau begins to form corresponding to a one-electron process; however, this soon collapses when the scan positive is continued. This behaviour is probably caused by the coating of the electrode with an insulating layer, since the response is restored by repolishing the microelectrode. The effect is somewhat dependent on the particular complex; the C_6Me_6 complex gave rise to less of a coating problem.

When the solvent is MeCN, the coating problem is considerably reduced, but only in the absence of supporting electrolyte. Thus stable, steady-state currents are observed as shown in Fig. 6. The steady-state current plateaux are equivalent to one-electron oxidations (Table 2) if a diffusion coefficient, D, is assumed to be close to that of ferrocene (2×10^{-5} cm^2 s^{-1}). The equation for a planar disk microelectrode is assumed, with the effective (electrochemical) electrode radius determined to be 9.2 μm:

$$i = 4n\mathrm{FrDc} \qquad (5)$$

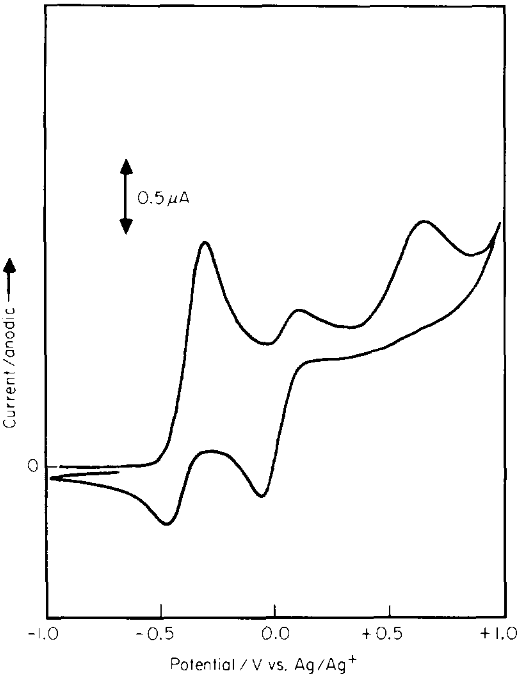

Fig. 5. CV of thermally-produced $(MeCN)_3Cr(CO)_3{}^0$ (5 mmol dm^{-3} solution of $Cr(CO)_6$ in MeCN refluxed for 30 h, followed by addition of TBAT electrolyte). The solution contains a mixture of $(MeCN)_3Cr(CO)_3{}^0$ ($E^{0\prime} = -0.41$ V_{Ag}) and $(MeCN)_2Cr(CO)_4{}^0$ ($E^{0\prime} = 0.01$ V_{Ag}). In addition an irreversible oxidation is observed at +0.64 V which we assign to the second one-electron oxidation of $(MeCN)_3Cr(CO)_3{}^+$.

The values of i are subject to errors arising from partial coating of the electrode, leading to lower currents than expected. Greater accuracy is obtained by determining the current due to ferrocene in the same solution or directly after the test solution, and measuring the i/i(Fc) ratio (Table 2). Addition of supporting

Table 1

CV data for irreversible oxidation of $LCr(CO)_3$ complexes in MeCN [a]

Ligand, L	$E_{p,a}$ (V)	$E_{p,a}$ (L) (V)	E^0 (prod) (V)	R $i_{p,c}$ (prod)/$i_{p,a}$
N,*N*-dimethyl-aniline	0.27	0.57	−0.35	0.16 [b]
Aniline	0.28	0.90	−0.33	0.29 [c]
Thiophene	0.24	0.59	−0.33	0.27
3-Methylthiophene	0.18	0.60	−0.32	0.45
Benzene	0.67	1.93	−0.33	< 0.01
N-Phenyl pyrrole	0.49	1.27	−0.32	0.08
Chlorobenzene	0.58	0.90	−0.35	0.01
3-Phenyl-thiophene	0.49	–	−0.30	0.18 [c]
C_6Me_6	0.45	–	–	0.00
$C_6H_3Me_3$	0.52	–	−0.30	0.02

[a] Peak potentials (as measured at a uniform scan rate of 200 mV s^{-1}) in V vs Ag/Ag+ (E^0 Fc/Fc+ = +0.12 V). [b] Ratio 0.25 using $TBAPF_6$. [c] 0.1 *M* $TBAPF_6$, 100 mV s^{-1}.

Table 2

Microelectrode voltammetry of $LCr(CO)_3$ complexes in MeCN in the absence of supporting electrolyte

L	C (mM)	$E_{1/2}$ (vs Fc)	i/i (Fc)
C_6H_6	9.75	0.60	0.92
mesitylene	3.47	0.56	0.95
C_6Me_6	5.16	0.46	0.92
$PhNMe_2$	2.40	0.23	0.82

electrolytes (TBAT, $TBAPF_6$) rapidly reduces the currents to zero. Water addition (ca. 2%) does not reduce the plateau current, so moisture in the electrolyte can be ruled out as the cause of its deleterious effect. For L = Ph, $C_6Me_3H_3$ and C_6Me_6 further oxidation gives non steady-state currents as shown in Fig. 6. Two plateaux of approximately equal height with $E_{1/2}$ at 0.54 V (L = Ph) and 1.15 V (independent of L) respectively are consistent with an overall 2-electron oxidation to $(MeCN)_3Cr(CO)_3^{2+}$. For L = $PhNMe_2$, further oxidation gives a second, smaller plateau. This is consistent with the CV: the small plateau corresponding to oxidation of released $PhNMe_2$. From the plateau current a lower limit to the rate constant k' can be obtained from the microelectrode equation for an ECE reaction [24]:

$$1/\Delta n = \left[\left(D/\left(n_2^2k'\right)\right)^{1/2}(\pi/2r) + 1/n_2\right] \tag{6}$$

where Δn is the apparent number of electrons involved, taken in this case to be i(2nd plateau)/i(1st plateau); n_2 is the number of electrons involved in the

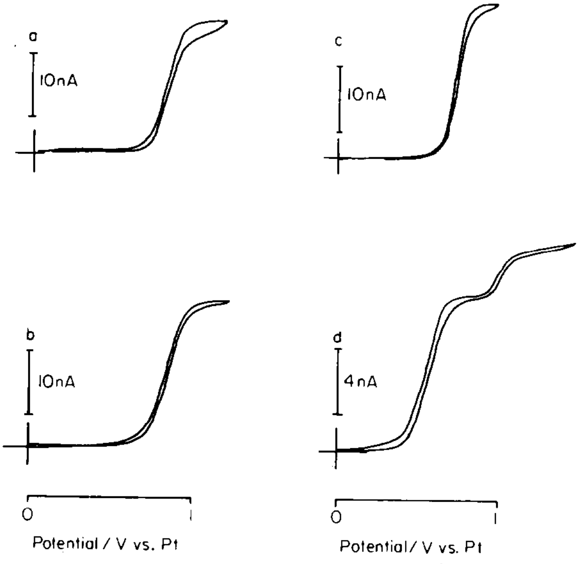

Fig. 6. Cyclic microvoltammetry (100 mV s^{-1}, 25 μm dia electrode) in MeCN in the absence of supporting electrolyte of (a) 3.59 mM $(C_6H_6)Cr(CO)_3$; (b) 3.47 mM $(1,3,5\text{-}C_6H_3Me_3)Cr(CO)_3$; (c) 5.16 mM $(C_6Me_6)Cr(CO)_3$; (d) 2.40 mM $(PhNMe_2)Cr(CO)_3$.

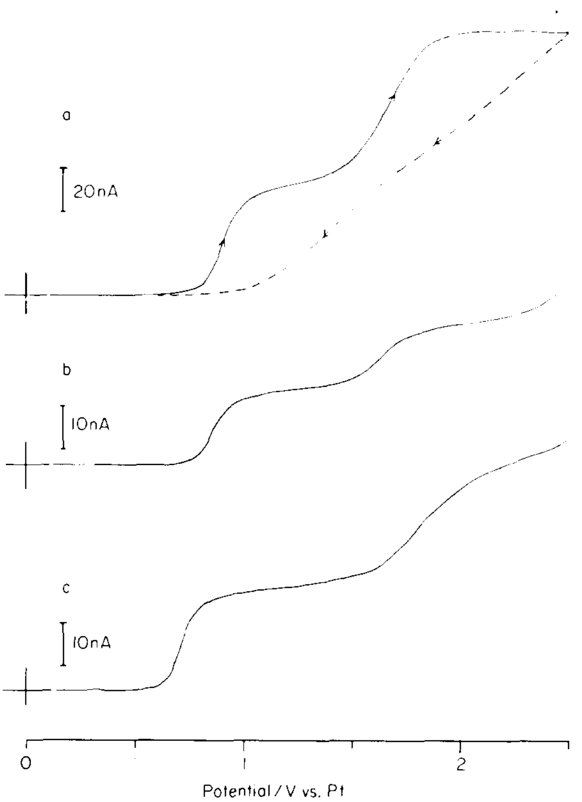

Fig. 7. Extended anodic range cyclic microvoltammetry (100 mV s^{-1}, 25 μm dia electrode) in MeCN in the absence of supporting electrolyte of (a) 3.59 mM $(C_6H_6)Cr(CO)_3$; (b) 3.47 mM $(1,3,5\text{-}C_6H_3Me_3)Cr(CO)_3$; (c) 5.16 mM $(C_6Me_6)Cr(CO)_3$.

oxidation of $PhNMe_2$ ($n = 1.2e^-$ from a separate microelectrode experiment on free $PhNMe_2$). The derived value of k', 12 s^{-1}, is rather lower than indicated above by CV with larger electrodes, and this could reflect the role of supporting electrolyte in speeding up the release of the arene ligand.

If the voltage sweep is continued, a second plateau of equal height to the first one is observed, but the return sweep no longer retraces the forward sweep (as for the benzene complex, Fig. 7(a)). This indicates that electrode coating is occurring; a brief excursion to +3 V or, better, re-polishing the microelectrode restores the original response. Similar traces are observed for the mesitylene and C_6Me_6 complexes (Figs. 7(b) and (c)), with the second oxidation at ca. +1.7 V. Note that this second oxidation must correspond to an oxidation of the starting complex. It cannot be due to a product of the first oxidation, as these rapidly diffuse away from the microelectrode. Preliminary experiments using fast CV and low temperatures were plagued by the electrode fouling problem and the resistance of the solvent.

Alternative mechanisms

Alternative products of the reaction of Ia^+ with MeCN might be $(MeCN)_3Cr(CO)_3$ and $PhNMe_2{}^+$. However, these are unlikely, given that the

Table 3

Results of the digital simulation of the irreversible oxidation of $LCr(CO)_3$ complexes in MeCN [a]

$E_{p,a}$ (V)	k (s^{-1})	R
+0.58	10^3	0.30 [b]
	10^2	0.38
	10	–
	1	0.28
+0.27	10^3	–
	10^2	0.43
	10	–
		–
+0.18	10^3	0.45 [b]
	10^2	0.44
	10	–
	1	0.35

[a] Unless stated otherwise all data are for a scan rate of 0.2 V s^{-1} and program resolution parameter of 1. [b] Scan rate 2.0 V s^{-1}; resolution parameter = 1.

potential for oxidation of $PhNMe_2$ is much higher than that of $(MeCN)_3Cr(CO)_3$. Also, this requires a second electron transfer step (ECE) since oxidation of both $PhNMe_2$ and $(MeCN)_3Cr(CO)_3$ are favourable at this potential.

Digital simulation of the electrochemical response: effect of scan rate, rate constant and $E^{0'}(1)$ of complex

The ratio R is always less than unity, as predicted by our own computer simulations, Table 3, Figs. 8 and 9. The main reason for this is diffusion: some of the $(MeCN)_3Cr(CO)_3{}^+$ diffuses away from the electrode before it is reduced on the return sweep. The rate of the reaction with acetonitrile can be expressed in terms of a pseudo-first order rate constant k' rather than the second-order rate constant k_2, since the concentration of neat MeCN is 19.15 mol dm^{-3}, i.e. $k' = 19.15\ k_2$. For a rate constant $k' = 10^3\ s^{-1}$, the predicted scan rate dependence is shown in Fig. 8. It should be noted that the peak height for $(MeCN)_3Cr(CO)_3$ varies very little until the very highest scan rate (900 V s^{-1}) is reached. Our experimental data also shows little variation in this current, confirming that the follow-up reaction is extremely fast. Scan-rate and rate-constant are clearly related by the kinetic parameter $\lambda = (k'/\nu)(RT/nF)$. The effect of changing the rate constant k' over the range 1, 10 and 100 s^{-1} is depicted in Fig. 9. The predicted CV for $k_2 = 10^3\ s^{-1}$ is identical to that for $k_2 = 10^2\ s^{-1}$. That for $k_2 = 10\ s^{-1}$ shows a small degree of reversibility, hence a lower bound on the rate constant is ca. 50 s^{-1}. This compares with a value of $10^3\ s^{-1}$ for the disappearance of $(C_6H_6)Cr(CO)_3$ in MeCN obtained by Parker et al. [4]. An attempt was made to measure the pseudo-first-order rate constant for reaction 2, $k_2' = (k_2[MeCN])$, by fast-scan CV using microelectrodes. Microelectrodes are useful in minimising the effects of solution resistance. Even at the highest scan rates employed (50 V s^{-1}), no cathodic current peak was observed. This places a lower limit of ca. $10^2\ s^{-1}$ on k_2'. The calculated value of R also decreases as the oxidation potential of the

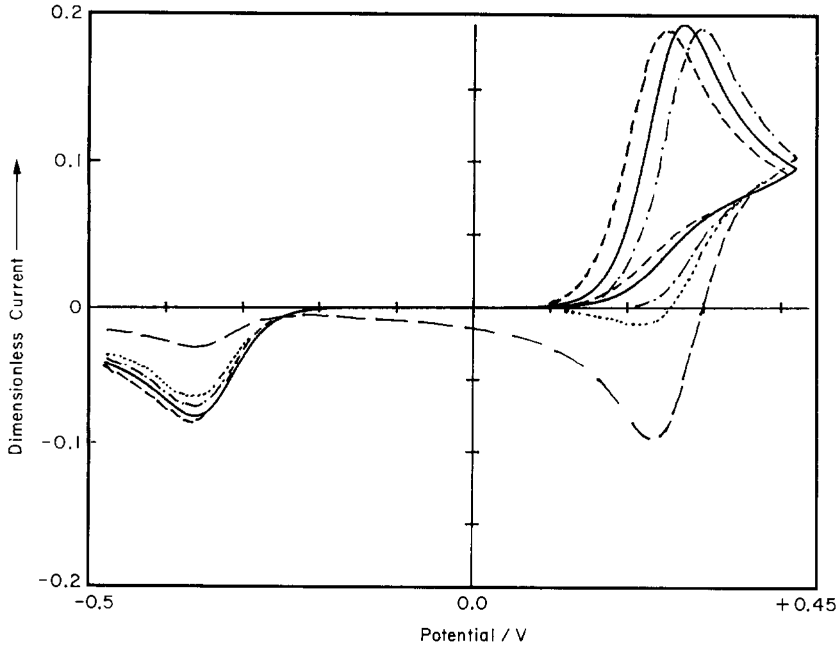

Fig. 8. Simulated scan-rate dependence for the oxidation of $(PhNMe_2)Cr(CO)_3$ ($E^{0'} = 0.27$ V vs Ag/Ag$^+$) assuming the simple mechanism represented by eqns (1) and (2) in the text and a pseudo first order rate constant $k = 10^3$ s^{-1}. Scan rates (Vs^{-1}): ------ 1; ——— 4; -.-.-.-. 49; ······ 100; – – – 900.

arene complex increases, from $R_{calc} = 0.47$ for $E_1^{0'} = +0.18$ to $R_{calc} = 0.38$ for $E_1^{0'} = +0.27$ and 0.58 V (Fig. 10, Table 3). However, the observed ratio decreases markedly more with increasing electrode potential than predicted by our computer simulations. For example, the chlorobenzene complex has $R_{obs} = 0.01$, compared to the predicted value 0.39. This may reflect a depletion of the acetonitrile complex due to further irreversible oxidation and decomposition, indeed bubbles of CO were observed during oxidation of the $(C_6H_6)Cr(CO)_3$ and $(C_6H_5Cl)Cr(CO)_3$ complexes. This would then be consistent with Bond's observation of multi-electron oxidation of the Cr in these complexes [5]. To further substantiate this we measured the second oxidation potential of $(MeCN)_3Cr(CO)_3^0$ to be +0.65 V vs SCE. Indeed our simulations show that R is dramatically decreased when the oxidation of $(MeCN)_3Cr(CO)_3^+$ to $(MeCN)_3Cr(CO)_3^{2+}$ is included in the simulations. Another explanation is that the radicals at higher oxidation potential are more reactive towards electrolyte or impurities. Alternatively, the greater amount of acetonitrile substituted product may simply mean that those complexes with a low oxidation potential have more stable cations. The low oxidation state complexes all contain heteroatoms which may be involved in binding to the cation, preventing it from total breakup.

The simulations also help to explain some qualitative findings of our experiments. The amount of MeCN complex, as measured by R, depends on the anodic limit: a higher limit yields slightly less current due to the MeCN complex–this arises from the diffusion of this species out of the diffusion layer. For the same reason, the second CV sweep always gives higher currents for $(MeCN)_3Cr(CO)_3^+$.

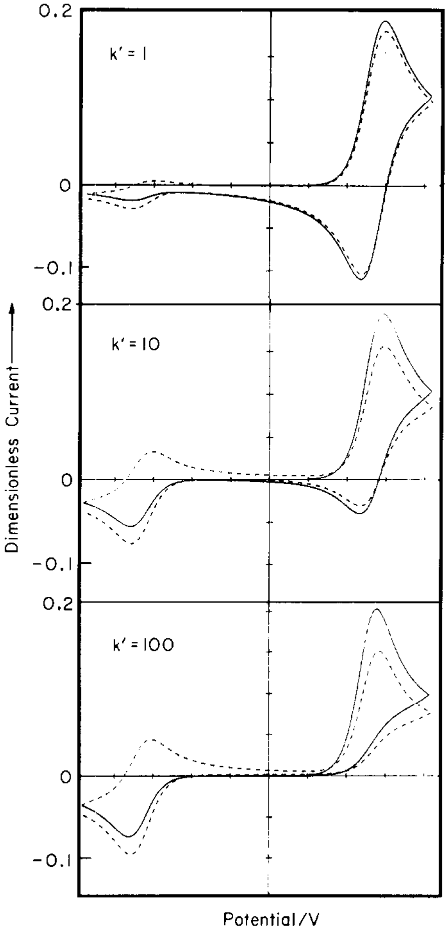

Fig. 9. Calculated rate-constant dependence for the oxidation of $(PhNMe_2)Cr(CO)_3$ ($E^{0'} = 0.27$ V vs Ag/Ag^+) assuming the simple mechanism represented by equationed 1 and 2 and a scan rate of 2 V s^{-1}.

Homogeneous electron transfer

We have not up to now considered the possibility that electron transfer reactions may be occurring in homogeneous solution, for example:

$$LCr(CO)_3{}^+ + (MeCN)_3Cr(CO)_3{}^0 \rightarrow LCr(CO)_3 + (MeCN)_3Cr(CO)_3{}^+ \qquad (7)$$

If reaction 7 were rate determining then raising the concentration would lead to a relative increase in both the current due to $(MeCN)_3Cr(CO)_3{}^+$ reduction and the value of *R*. Experimentally, increasing the concentration of complex (subject to the limits of solubility of the complex in acetonitrile) has no effect on the relative amount of $(MeCN)_3Cr(CO)_3{}^+$ produced. This then rules out a thermodynamically possible bimolecular pathway for homogeneous electron *transfer* reactions of the cation Ia^+ with unreacted $(MeCN)_3Cr(CO)_3$ [4–7,25*]:

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* Reference number with asterisk indicates a note in the list of references.

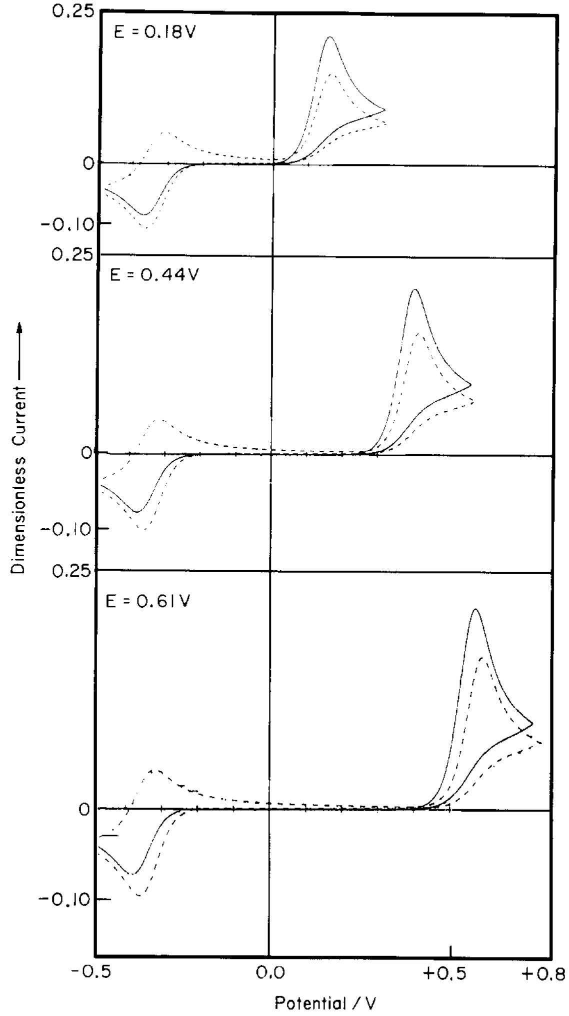

Fig. 10. Calculated dependence of the CV on the oxidation potential of the complex. (Top) +0.18 V; (centre) +0.44 V; (bottom) +0.61 V (all vs Ag/Ag^+). Solid line: 1st scan; broken line: 2nd scan. Scan rate 2 V s^{-1}; $k_1 = 10^3\ s^{-1}$.

Again the lack of a concentration dependence suggests that the homogeneous oxidation to the dications (equation 8) is not rate determining.

$$LCr(CO)_3{}^+ + (MeCN)_3Cr(CO)_3{}^+ \rightarrow LCr(CO)_3 + (MeCN)_3Cr(CO)_3{}^{2+} \qquad (8)$$

All of the data accord with the proposition that the initial electron transfer step (equation 1) is rate determining.

Different behaviour is observed when the solvent is N,N-dimethylformamide (DMF). Degrand et al. [6], have reported a concentration effect on the electrochemistry of these complexes in DMF. We have confirmed this result, and we explain this on the basis of the lesser stability of the intermediate $(DMF)_3Cr(CO)_3{}^+$ complex and its greater readiness to undergo oxidation to the Cr^{II} and Cr^{III} levels.

Table 4

Electrochemical data for oxidation of Mo and W complexes in MeCN

	E_{pa}	E_{pc}	E^0	R
Molybdenum				
1,3,5-$C_6H_3Me_3$	0.50	0.37	0.44	–
C_6Me_6	0.49	0.40	0.45	–
Tungsten				
1,3,5-$C_6H_3Me_3$	0.18	−0.14	–	0.30
C_6Me_6	0.34	−0.14	–	0.48

Comparison with Mo and W arene complexes

Mo and W complexes either show stability to oxidation in MeCN or in the case of tungsten form the stable $LW(CO)_3(MeCN)^+$ cation which on reduction reverts to $LW(CO)_3$. The results are summarized in Table 4. Only Cr complexes can form $(MeCN)_3M(CO)_3{}^+$, while only W can form $LW(CO)_3(MeCN)^+$. The differences are highlighted in the mesitylene complexes where completely different behaviour is seen for all three metals: Cr – L displacement by MeCN; Mo – reversible oxidation; W – reversible formation of MeCN adduct. Only for hexamethylbenzene is uniformity observed—the ligand is so bulky that they are all reversibly oxidized.

Discussion

Both arene- and thiophene-$Cr(CO)_3$ complex monocations are vulnerable to rapid attack by nucleophilic solvents such as MeCN. This is well-known for the arene complexes, but is now established as a reaction pathway for the thiophene complexes also. Dietrich et al. have recently reported electrochemistry of bithiophene complexes in liquid SO_2 [26]. The complexes were oxidised reversibly at ca +0.6 V, but a second one-electron oxidation led to irreversible decomposition.

Our microelectrode data confirm in all cases an initial one-electron oxidation in MeCN in the absence of supporting electrolyte. It has been previously proposed that, at least for the mesitylene Cr complex the initial oxidation was of two-electrons [5]. This means that there is an ECE reaction which is detectable at macroelectrodes, and particularly for the complexes with relatively high oxidation potentials. On the basis of our digital simulation results we propose that $(MeCN)_3Cr(CO)_3{}^+$ is initially formed in the rapid follow-up reaction, and it may be further irreversibly oxidised to the dication. The electrochemical term for the reaction process is an EC reaction. An example of this type of follow-up reaction is that reported by Kochi et al. [27] in which oxidation of $MeCpMn(CO)_2(CN^tBu)^+$ leads in the presence of ^tBuNC to a rapid bimolecular reaction is acetone to give $MeCpMn(CO)(CN^tBu)_2{}^+$ and CO. The product was identified by a reversible wave at $E^{0'} = -0.03$ V vs SCE. The bimolecular rate constant was estimated to be $2 \times 10^3\ M^{-1}\ s^{-1}$ by digital simulation techniques.

The breakup of the electrogenerated cation $ArM(CO)_3{}^+$ may well proceed via an associative pathway, i.e. via the 19e intermediate $ArM(CO)_3(MeCN)^+$. Previous workers have shown that when the arene ligand is mesitylene (1,3,5-$C_6Me_3H_3$) or hexamethylbenzene the oxidation in acetonitrile becomes more reversible [13]. Presumably the cation is sterically hindered from acetonitrile attack, which we have shown to be the first step in the decomposition. The decomposition seems to be promoted by supporting electrolyte anion. We also noticed from the microelectrode work that the presence of supporting electrolyte leads to rapid coating. One possible explanation is that the electrogenerated cation is combining with the large anion to form an insoluble ionic precipitate on the electrode. This would explain the dominance of the coating problem in the least polar solvent used, CH_2Cl_2.

Tyler et al. [28] have shown 19e complexes are very good reducing agents, yet we see no evidence for $ArM(CO)_3(MeCN)^{2+}$, M = Cr and Mo; the oxidation involves only one electron. While the oxidation of the chromium complexes is irreversible, for Mo and W complexes the the oxidation is reversible. This may reflect the M–arene bond energies which increase in the order $Cr < Mo < W$: 191, 280, 362 kJ mol^{-1}. For the tungsten complexes an intermediate is observed as a product of the electrochemical oxidation, proposed to be $L'W(CO)_3(MeCN)^+$ ($L' = C_6Me_3H_3$ or C_6Me_6), [29,30*], or a W^{II} species, $L'W(CO)_3X^+$ ($X = ClO_4^-$ from the supporting electrolyte [24]. Bond et al. [5] have shown that for the W^I cation this oxidation is feasible; thus the difference between metals may well be explained by the difference in $M^{II/I}$ redox potentials.

We have demonstrated conclusively that displacement of the arene ligand and retention of the $Cr(CO)_3$ group is a dominant pathway. Our results show that addition of PR_3 reduces R but we do not know whether this represents substitution of the acetonitrile product or some other process.

Conclusions

Our proposed mechanism has the unique advantage of incorporating a directly observed intermediate, $(MeCN)_3Cr(CO)_3{}^+$, which we have observed for the first time, demonstrating that one-electron oxidation leaves the $Cr(CO)_3$ unit intact but renders the arene ligand extremely labile in the 17-electron intermediate. Arene complexes of the Group VIB metals appear to have quite different electrochemistries, related to factors such as: (i) the steric crowding of the metal centre; (ii) the ability of the cation to form a stable adduct with either solvent or anion; and (iii) the metal–arene bond energy in the cation.

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