

Electrochemical Detection of the $\text{Cr}(\text{CO})_3(\text{MeCN})_3^+$ Intermediate in the One-electron Oxidation of Arene- and Thiophene-chromiumtricarbonyl Complexes

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Oxidation of $\text{LCr}(\text{CO})_3$, ($\text{L} = \text{C}_6\text{H}_6$, $\text{C}_6\text{H}_5\text{Cl}$, dimethylaniline, thiophene, 3-methylthiophene) in acetonitrile leads to a rapid follow-up reaction in which the intermediate $\text{Cr}(\text{CO})_3(\text{MeCN})_3^+$ is detected by cyclic voltammetry.

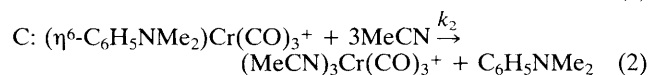
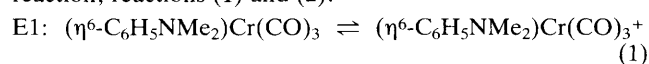
The electrochemistry^{1–3} of arenechromiumtricarbonyl compounds is of importance considering the synthetic utility of these organometallics. For example, they can be used as intermediates in the synthesis of steroids.^{4,5} The arene ligand of interest can be readily removed from the $\text{Cr}(\text{CO})_3$ moiety by I_2 oxidation. Our results below show that this oxidation may also be accomplished electrochemically, while providing new insight into the fate of the chromium species. In addition to the arene complexes (**1a–d**) we report the electrochemistry of thiophene–chromium complexes (**2a, b**).†

We have found that the electrochemistry of these complexes is exemplified by the dimethylaniline complex, (**1a**), which undergoes a partially chemically reversible oxidation in CH_2Cl_2 at $E_{1/2} = +0.27 \text{ V vs. Ag/Ag}^+$. The anodic peak height corresponds to a one-electron electron transfer, as observed previously.^{6,7} The CH_2Cl_2 used was h.p.l.c. grade, rigorously dried using activated neutral alumina in order to ensure reversibility, otherwise the peak current ratio, $i_{p,c}/i_{p,a}$ was markedly reduced. Presumably the cation radical (**1a**)⁺, $(\eta^6\text{-C}_6\text{H}_5\text{NMe}_2)\text{Cr}(\text{CO})_3^+$ is prone to nucleophilic attack from water impurities.

Figure 1(a) shows the cyclic voltammogram (c.v.) of (**1**) recorded using the more nucleophilic solvent, MeCN. Here the oxidation (peak at $+0.27 \text{ V vs. Ag/Ag}^+$) is irreversible as shown by the complete absence of a cathodic peak. Like many other organometallic cations the radical is attacked by strongly co-ordinating solvents such as MeCN. Our observations have, for the first time, revealed direct evidence for one of the initial

products of this reaction. On the reverse sweep a new reversible wave, absent on the initial scan in this region, appears with $E^{0'} = -0.33 \text{ V vs. Ag/Ag}^+$. The observed redox potential corresponds closely to that previously observed for $(\text{MeCN})_3\text{Cr}(\text{CO})_3^{+/0}$.⁸ Attempts to isolate this product were unsuccessful; prolonged electrolysis resulting in a green solution of Cr^{III} . We did, however, succeed in verifying the assignment by generating $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ independently as a product of the photochemically-induced stepwise replacement of CO in $\text{Cr}(\text{CO})_6$. The peak corresponding to reversible oxidation of photogenerated $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ has a potential which is identical to that observed in the electrochemical experiments, thus confirming our assignment.

Returning to the electrochemical reactions, the $(\text{MeCN})_3\text{Cr}(\text{CO})_3^+$ product clearly arises from the attack of MeCN on the cation (**1**)⁺, $(\eta^6\text{-C}_6\text{H}_5\text{NMe}_2)\text{Cr}(\text{CO})_3^+$, with displacement of the arene ligand. Electrochemically speaking, this amounts to an EC reaction, *i.e.* electron transfer followed by a chemical reaction, reactions (1) and (2).



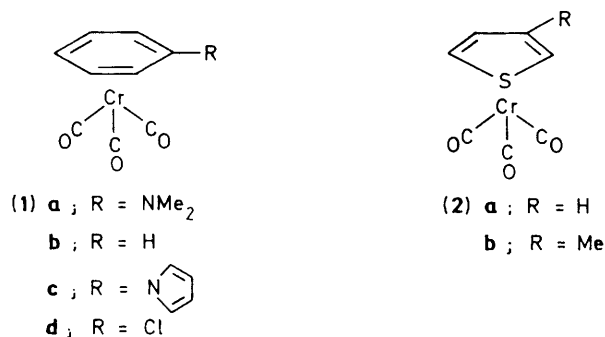
The $(\text{MeCN})_3\text{Cr}(\text{CO})_3^+$ intermediate is then detected on the reverse sweep. According to the theory of EC reactions, the anodic peak potential, $E_{p,a}$, should be scan-rate (v) dependent and $I_{p,a} v^{-1/2}$ should be independent of v . Thus a plot of the observed $E_{p,a}$ of reaction (1) against $\ln v$ is linear with slope 64 mV , close to the theoretical value, 60 mV .⁹ The very rapid follow-up chemical step shifts the peak position to

† All complexes were characterized by n.m.r., mass spectroscopy and elemental analysis.

Table 1. C.v. data for irreversible oxidation of $\text{LCr}(\text{CO})_3$ complexes.^a

Ligand, L	$E_{p,a}$ V	$E_{p,a}(\text{L})$ V	$E^0(\text{prod})$ V	$i_{p,c}(\text{prod})/i_{p,a}$
<i>N,N'</i> -Dimethyl aniline	0.27	0.57	-0.35	0.16
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
<i>N</i> -Phenyl pyrrole	0.49	1.27	-0.32	0.08
Chlorobenzene	0.58	0.90	-0.35	0.01

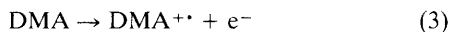
^a Peak potentials (as measured at a uniform scan rate of 200 mV s^{-1}) in V vs. Ag/Ag^+ ($E^0 \text{Fc}/\text{Fc}^+ = +0.12 \text{ V}$).



less positive potentials where the driving force (and hence rate) of electron transfer is slower.

Alternative products of the displacement reaction (2) might be $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ and $\text{C}_6\text{H}_5\text{NMe}_2^+$. However, this is unlikely, given that the potential for oxidation of $\text{C}_6\text{H}_5\text{NMe}_2$ is much higher than that of $(\text{MeCN})_3\text{Cr}(\text{CO})_3$. Also, this requires a second electron transfer step [oxidation of $(\text{MeCN})_3\text{Cr}(\text{CO})_3$] at the redox potential and our results do not support such an ECE scheme.

Figure 1(b) is identical to 1(a) except that it shows the effect of increasing the anodic potential limit of the c.v. scan. A further peak at $+0.57 \text{ V}$ is observed which corresponds closely to the oxidation of the free $\text{C}_6\text{H}_5\text{NMe}_2$ ligand. This particular oxidation is itself known¹⁰ to be a complex ECE reaction involving dimerisation of the electrogenerated cation (DMA^{++}) to tetramethylbenzidine (TMB); reactions (3) and (4). The waves marked with an asterisk in Figure 1(b) denote the two one-electron reductions of the TMB product.



We have examined several other arene complexes, (**1a–d**), and some thiophene complexes, (**2a, b**). These $\text{LCr}(\text{CO})_3$ complexes, while having quite different anodic peak potentials, $E_{p,a}$, exhibit similar behaviour, and the same product redox wave [$E^0(\text{prod})$] regardless of L (see Table 1). Table 1 also gives the ratio of the current for the reduction of the product acetonitrile complex and the oxidation of the arene complex. This ratio is always less than unity, as predicted by our own computer simulations.¹¹ The ratio also decreases as the oxidation potential of the arene complex increases. 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 $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex.

An attempt was made to measure the pseudo-first-order rate constant for reaction (2), k_2' ($= k_2[\text{MeCN}]$), by fast-scan c.v. 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

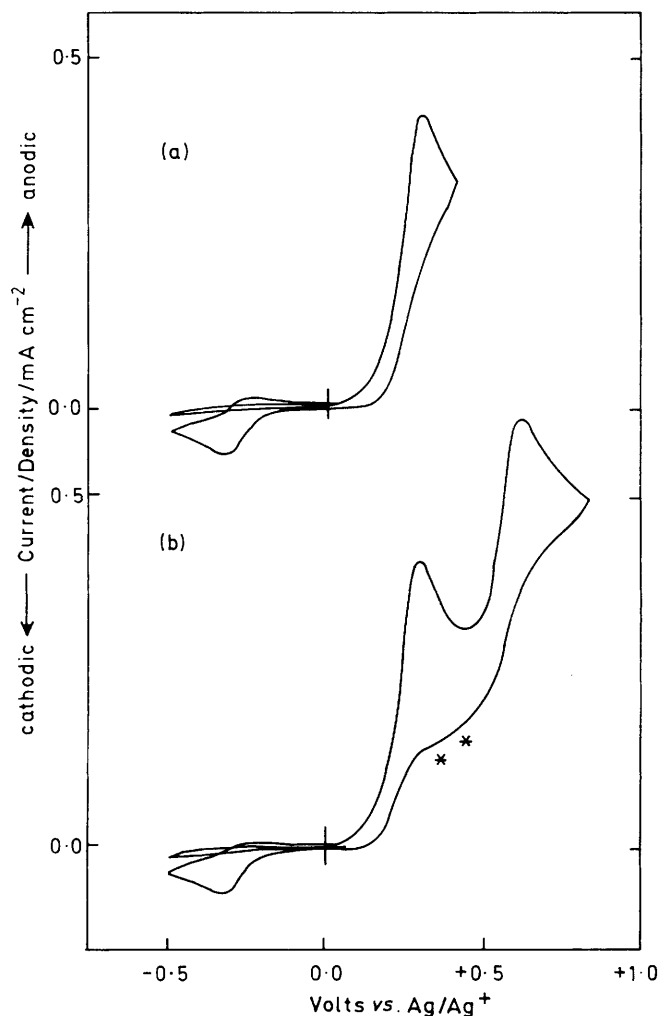


Figure 1. Cyclic voltammetry (75 mV s^{-1}) of the oxidation of 5 mM (**1**) ($\eta^6\text{-C}_6\text{H}_5\text{NMe}_2$) $\text{Cr}(\text{CO})_3$ in MeCN, supporting electrolyte 0.1 M TBAT (tetra-*n*-butylammonium tetrafluoroborate). (a) Anodic limit $+0.5 \text{ V}$; (b) anodic limit $+0.8 \text{ V}$. Asterisks denote the reduction of tetramethylbenzidine.

peak was observed. This places a lower limit of *ca.* 10^2 s^{-1} on k_2' . Use of convolution techniques does, however, reveal a cathodic peak when the scan rate is $0.4\text{--}10 \text{ V s}^{-1}$; detailed analysis is in progress.

In conclusion, our proposed mechanism has the unique advantage of incorporating a directly observed intermediate, $(\text{MeCN})_3\text{Cr}(\text{CO})_3^+$, which we observe for the first time, demonstrating that one-electron oxidation leaves the $\text{Cr}(\text{CO})_3$ unit intact, but renders the arene ligand extremely labile in the 17-electron intermediate. Previous workers have shown that

when the arene ligand is mesitylene (1,3,5- $\text{C}_6\text{Me}_3\text{H}_3$) or hexamethylbenzene the oxidation in acetonitrile becomes more reversible.¹² Presumably the cation is sterically hindered from acetonitrile attack, which we have shown to be the first step in the decomposition. As far as Mo and W are concerned, only the mesitylene and hexamethylbenzene tricarbonyl complexes have been examined in acetonitrile by cyclic voltammetry. The oxidation of these compounds is irreversible, but for the tungsten complexes an intermediate is observed as a product of the electrochemical oxidation, proposed to be $\text{L}'\text{W}(\text{CO})_3(\text{MeCN})^+$ ($\text{L}' = \text{C}_6\text{Me}_3\text{H}_3$ or C_6Me_6),^{12‡} or alternatively a W^{II} species, $\text{L}'\text{W}(\text{CO})_3\text{X}^+$ ($\text{X} = \text{ClO}_4^-$ from the supporting electrolyte).¹³ Thus the various arene complexes would appear to have quite different electrochemistry, 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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‡ We have shown that this species is *not* $\text{W}(\text{CO})_3(\text{MeCN})_3^{+/0}$, as would be expected if an analogous EC reaction mechanism to the arene Cr complexes was being followed.

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