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The influence of transannular interactions on the redox properties of the tricarbonylchromium complexes of ortho-, meta- and para-[2.2]cyclophane

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The redox behaviour of the [2.2]cyclophane complexes, $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ [*ortho* (1,2), *meta* (1,3) and *para* (1,4) isomers], has been examined by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][PF_6]$–CH_2Cl_2. The complexes display a one-electron oxidation in the region +0.7–+1.0 V (*vs.* Ag–AgCl), with the reversible half-wave potential varying in the order *ortho* > *meta* > *para*. The variation in reversible potential for the oxidation process indicates that the three cyclophane isomers impart different degrees of stabilisation on the $\{Cr(CO)_3\}$ moiety, in accord with the anticipated variation in the inter-ring π–π interaction within ortho-, meta- and para-cyclophane. The IR spectra of the $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]^{+\bullet}$ radical cations have been collected by *in situ* spectroelectrochemical electrogeneration. Despite the different reversible potentials for the oxidation of the three $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]^z$ complexes, their IR spectra, both in the neutral and cationic states, are all quite similar, with the A_1 and E bands occurring in the region 1961–1956 and 1887–1876 cm^{-1} ($z = 0$) and 2071–2068 and 2006–2003 cm^{-1} ($z = 1+$) respectively. The stability of the one-electron oxidised products, as judged by cyclic voltammetry, IR and EPR spectroelectrochemistry, also varies with cyclophane isomer, in the order *para* > *meta* > *ortho*. The stability of the $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)]^{+\bullet}$ cation is such that it has also been characterised by EPR spectroscopy. The EPR spectrum consists of a rhombic pattern of three lines at $g = 2.0860$, 2.0374 and 1.9940 G corresponding to g_1, g_2 and g_3.

Introduction

The systematic chemistry of cyclic compounds that contain at least one aromatic benzene molecule and an aliphatic bridge, now commonly referred to as 'cyclophanes', developed in the 1950's as a consequence of pioneering studies by Cram and co-workers.[1] Since then this field of research has grown enormously. In particular the complexation of transition metals to cyclophane ligands has attracted considerable interest,[2] with the main focus being on synthetic studies aimed at the development of one-dimensional polymers consisting of alternating cyclophane and metal complex units, as it is considered that compounds of this type may have interesting physical properties.[3]

The simplest class of cyclophanes are those containing just two benzene rings that are joined by two ethanediyl linkages. These are termed the [2.2]cyclophanes,[2] of which there are five possible symmetrical isomers depending upon the location of the $–CH_2CH_2–$ linkages (*ortho*, *meta* or *para*) and the orientation of the benzene rings (*syn* or *anti* in the case of [2.2]orthocyclophane and [2.2]metacyclophane). The isomers are depicted in Fig. 1. The first cyclophane to be prepared was *anti*-[2.2]metacyclophane in 1899,[4] and then some fifty years later, in 1951, [2.2]paracyclophane was isolated.[5] The remaining isomers have since been characterised, including *syn*-[2.2]metacyclophane which can be prepared at low temperature,[6] and [2.2]orthocyclophane which exists in solution as a 1 : 1 equilibrium mixture of the *syn*- and *anti*-conformations.[7]

Whilst some of the chemistry of the [2.2]cyclophanes is similar to that of classical arenes, significant differences arise as a consequence of the close proximity of the two arene rings. For instance, the first order rate constant for the reaction of [2.2]paracyclophane with chromium hexacarbonyl is *ca.* 25% greater than that for the analogous reaction of *p*-xylene ($C_6H_4Me_2$-1,4).[8] The enhanced reactivity of [2.2]paracyclophane is a consequence of the closeness of the two rings which gives rise to a through space π–π (transannular) interaction that increases the π-electron density on the outer faces of the ligand. In addition the two rings are distorted from planarity on account of the internal ring strain, which is relieved to some extent by the co-ordination of an electron withdrawing $\{Cr(CO)_3\}$ fragment.

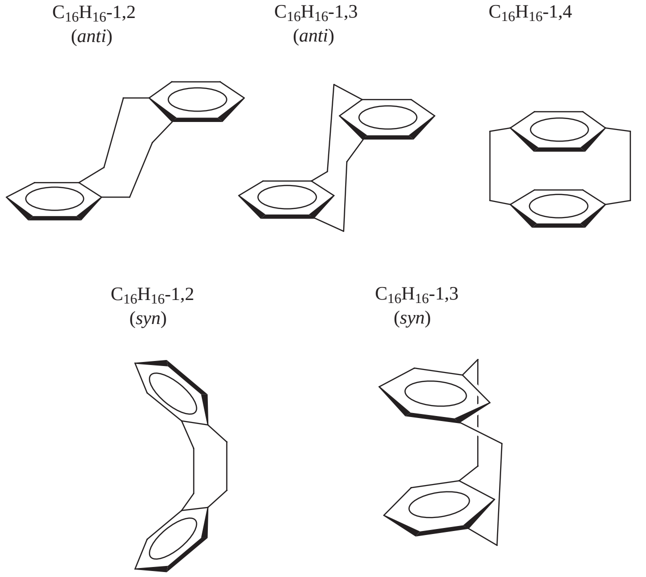

Fig. 1 [2.2]cyclophane ligands.

Both the transannular interaction and the intramolecular strain energy associated with the [2.2]cyclophane molecules

Table 1 Voltammetric data for the oxidation of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})$] complexes[a]

Complex	E_{pa}/mV	E_{pc}/mV	ΔE_p/mV	I_{pc}/I_{pa}	$E_{1/2}$/V
[$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$]	962	858	104	≈0.9	≈+0.91[b]
[$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,3)$]	872	800	72	1.0	+0.84[c]
[$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)$]	782	698	84	1.0	+0.74

[a] Measured in 0.2 mol dm^{-3} [NBu_4][PF_6]–CH_2Cl_2 at ≈213 K. Potentials are quoted *vs.* the Ag–AgCl reference electrode, against which the $Fc^{0/+}$ couple has an $E_{1/2}$ value of +0.55 V. $\Delta E_p = E_{pa} - E_{pc}$, $E_{1/2} = (E_{pa} + E_{pc})/2$, all data taken from cyclic voltammograms recorded at a platinum macrodisc working electrode and at a scan rate of 100 mV s^{-1}. [b] Chemically irreversible at ≈290 K. [c] Partially reversible at ≈290 K, *i.e.* $I_{pc}/I_{pa} < 1.0$ at a scan rate of 100 mV s^{-1}.

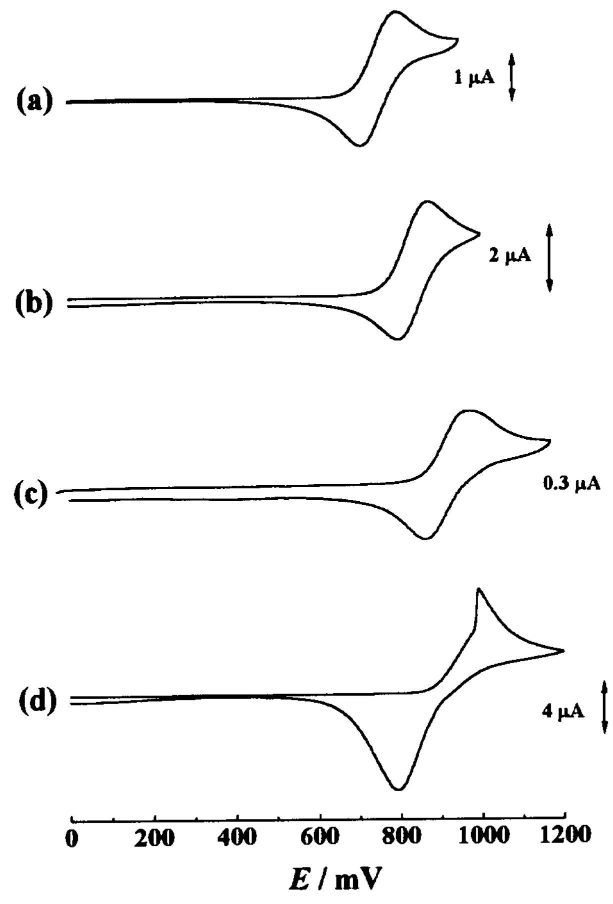

Fig. 2 Cyclic voltammetry of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})$] complexes in 0.2 mol dm^{-3} [NBu_4][PF_6]–CH_2Cl_2 at a platinum macrodisc working electrode *vs.* a Ag–AgCl reference electrode. (a) 1.0 mmol dm^{-3} solution of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)$] at ≈290 K. (b) 1.4 mmol dm^{-3} solution of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,3)$] at ≈290 K. (c) 0.5 mmol dm^{-3} solution of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$] at ≈213 K. (d) 4.6 mmol dm^{-3} solution of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$] at ≈213 K. Scan-rate = 100 mV s^{-1} in all cases.

are anticipated to vary, depending upon the identity of the isomer. However what remains uncertain is how this variation in inter-ring π–π interaction influences various physicochemical properties of transition metal complexes of these ligands. In an effort to address this issue, the tricarbonylchromium complexes of the *ortho*-, *meta*- (*anti*) and *para*-isomers of [2.2]cyclophane have been synthesised, and examined by a variety of electrochemical and spectroelectrochemical techniques. The results from these studies provide a fundamental insight into the way in which the cyclophane rings communicate with one another upon complexation to a metal fragment.

Results and discussion

Previous electrochemical investigations of arenetricarbonylchromium complexes, [$Cr(CO)_3(\eta^6\text{-arene})$], have established that by using solvent–electrolyte combinations of low nucleophilicity these complexes frequently display a one-electron oxidation to yield the 17-electron radical cation, [$Cr(CO)_3(\eta^6\text{-arene})]^{+\bullet}$, that is often stable on the timescale of a conventional cyclic voltammetric experiment (seconds), but decomposes over a longer time span.[9,10] The redox behaviour of the [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})$] complexes has been investigated in a readily available, poorly nucleophilic electrolyte–solvent combination, *viz.* [NBu_4][PF_6]–CH_2Cl_2.

A cyclic voltammogram of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)$] at a conventional macrodisc platinum working electrode ($r = 1.0$ mm) is shown in Fig. 2(a). Over the scan rate range of 20–5000 mV s^{-1} this complex displays a chemically reversible oxidation having a reversible half-wave potential ($E_{1/2}$) of +0.74 V, with the shape of the current–potential response being consistent with a one-electron charge-transfer process (Table 1). Comparing the limiting current value from a steady state voltammogram obtained at a platinum microdisc working electrode ($r = 7$ μm) for this complex with that from an equimolar solution of [$Cr(CO)_3(\eta^6\text{-}C_6H_6)$], which is known to exhibit a one-electron oxidation,[10] confirms that the oxidation is a one-electron process. The voltammetric oxidation of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,3)$], as shown in Fig. 2(b), is qualitatively similar, except that it is only partially reversible at room temperature ($I_{pc}/I_{pa} < 1.0$) at a scan rate of 100 mV s^{-1}. However the process becomes fully reversible in the chemical sense upon cooling the solution to 213 K. The reversible potential for the [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,3)]^{0/+}$ couple is also shifted significantly from that of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)]^{+/0}$, with $E_{1/2}$ being +0.84 V in the former and +0.74 V in the latter case.

The cyclic voltammetry of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$] is considerably more complicated than that of the other complexes, in that the appearance of the oxidation process is markedly dependent upon the concentration of the complex. For dichloromethane solutions less than 1.0 mM in complex, cyclic voltammetry at a platinum macrodisc working electrode at 290 K reveals only an irreversible wave with an oxidation peak at $E_{pa} = +0.97$ V, using a scan rate of 100 mV s^{-1}. However, lowering the temperature of the solution to 213 K results in the appearance of a reduction peak, E_{pc}. The cyclic voltammogram of a 0.5 mM solution of [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$] in 0.2 mol dm^{-3} [NBu_4][PF_6]–CH_2Cl_2 at 213 K is shown in Fig. 2(c). At a scan-rate of 100 mV s^{-1}, the presence of a small post wave, seen as a broadening of the oxidation process, is apparent and indicative of weak adsorption of the neutral [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$] complex to the working electrode.[11] In accord with this proposition, the magnitude of the current for the forward wave (I_{pa}) is slightly enhanced over that for the return wave (I_{pc}). The separation of the solution and post waves is clearly small, which implies that [$Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)$] adsorbs only weakly to the electrode. Upon increasing the concentration of the complex in solution, the appearance of the oxidation process changes markedly. The cyclic voltammogram of a solution 4.6 mmol dm^{-3} in complex at 213 K is shown in Fig. 2(d). As the potential is swept in the positive direction, the current begins to increase slowly until a potential of ≈+0.99 V is reached whereupon the current increases very rapidly before decaying away in a manner which at sufficiently

Table 2 $E_{1/2}$ values for the oxidation of selected $[Cr(CO)_3(\eta^6\text{-arene})]$ complexes

Complex	$E_{1/2}$/V [a]
$[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$	+0.97 [b,c,d]
$[Cr(CO)_3(\eta^6\text{-}C_6H_4Me_2\text{-}1,2)]$	+0.89 [b,c]
$[Cr(CO)_3(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)]$	+0.90 [b,c]
$[Cr(CO)_3(\eta^6\text{-}C_6H_4Me_2\text{-}1,4)]$	+0.88 [b,c]

[a] *vs.* Ag–AgCl reference electrode, against which $Fc^{0/+}$ is measured at +0.55 V. [b] Ref. 15. [c] To convert potentials from ref. 15 to the reference electrode used in this study 0.08 V was added to each couple. As a cross check, a complex common to both studies, *viz.* $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$, was measured under the experimental conditions used in this work. [d] This work.

Table 3 Infrared data for $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]^z$ complexes, $z = 0, 1+$

	$\nu(CO)^a/cm^{-1}$	
Complex	$z = 0$	$z = 1+$ [b]
$[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]$	1961, 1887	2071, ≈2003 (br)
$[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,3)]$	1959, 1880	2069, ≈2006 (br)
$[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)]$	1956, 1876	2068, ≈2006 (br)

[a] Measured in 0.2 mol dm^{-3} $[NBu_4][PF_6]\text{–}CH_2Cl_2$, in an IRRAS cell at low temperature. [b] br = broad.

positive potentials is consistent with a diffusion controlled process. On the return scan, a more typical wave is observed, which has a significant component of both diffusion and adsorption. The overall response is highly reproducible and the sharp rise in oxidative current is observed on a variety of working electrode materials (*i.e.* platinum, gold and glassy carbon), and the current spike persists over the range of scan rates used in this study (20–5000 mV s^{-1}). This behaviour at high complex concentrations is consistent with formation of a thick film of $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]$ on the working electrode, followed by rapid removal of excess surface attached material over a very narrow potential range. For example if the solubility of the oxidised product, $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]^{+\bullet}$, is greater than that of the reactant, the sharp increase in current may be associated with the sudden removal by dissolution of the surface attached species. After removal of the surface attached material the current may rise sharply to a maximum value before decaying in a fashion that is typical of a diffusion controlled process.[12] Electrocrystallisation processes frequently give rise to sharp increases in current,[13] however switching the potential at different values on the forward scan does not lead to current crossover, a characteristic of such processes.[14] Thus it appears that the current spike is associated with almost complete removal of a surface attached material formed at high solution concentrations. The results from the voltammetric studies are summarised in Table 1.

Although the surface attachment of $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]$ on to the working electrode precludes an accurate determination of the reversible potential for oxidation of this complex, it is still apparent from Fig. 2 and the data in Table 1 that the [2.2]cyclophane complexes are oxidised at progessively more positive potentials, in the order *para* < *meta* < *ortho*. In order to fully appreciate the significant differences in the $E_{1/2}$ values for these complexes, it is useful to compare the values obtained in this study with those of some other arenetricarbonylchromium complexes. Hunter *et al.* have prepared and characterised a large number of $[Cr(CO)_3(\eta^6\text{-arene})]$ complexes and investigated their spectroscopic and electrochemical properties.[15] The potentials for oxidation of some relevant compounds are listed in Table 2. The potentials have been converted to a common reference electrode scale. It is notable that the potentials for oxidation of the dimethylbenzene complexes are all very similar, regardless of the isomer. On this basis it is reasonable to assume that the ethanediyl bridges linking the two aromatic rings in the $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ complexes have essentially the same through bond inductive influence, regardless of isomeric disposition. This assumption gains further merit by noting that the $E_{1/2}$ value for the $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]^{0/+}$ couple is essentially the same as that for the dimethylbenzene complexes. This is not unexpected when it is noted that only in the case of the aromatic rings in coordinated [2.2]orthocyclophane are significant deformities thought to be absent,[16] and as such no transannular electronic and steric effects occur in this compound since there is no significant overlap of the π-orbitals due to the spatial arrangement of the two rings.

The relatively large differences in the reversible potentials for the oxidation of the three isomeric [2.2]cyclophane complexes can therefore be attributed to the varying degrees to which the uncomplexed ring donates π-electron density through space to the aromatic ring which carries the $\{Cr(CO)_3\}$ group. As noted above, in $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]$ no interactions of this type are present hence the $E_{1/2}$ value for the oxidation of this complex is essentially identical to that of $[Cr(CO)_3(\eta^6\text{-}C_6H_4Me_2\text{-}1,2)]$. The [2.2]metacyclophane ligand in $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,3)]$ adopts an *anti*-conformation, as opposed to a *syn*-conformation, and it has been shown previously that interconversion does not occur over a wide temperature range.[6] Consequently there is some degree of through space π-overlap between the two rings in coordinated [2.2]metacyclophane, culminating in increased electron donation from the ring bearing the $\{Cr(CO)_3\}$ moiety. Previous studies of uncomplexed *anti*-[2.2]metacyclophane led to the conclusion that the transannular interaction was confined to the inner carbon atoms of the arene rings, *i.e.* the single aromatic carbon atoms that lie between those bearing the $\text{–}CH_2CH_2\text{–}$ linkages.[16] In the case of $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)]$ the arene rings lie almost directly above each other, which leads to the transannular interaction being maximised. Consequently, for this complex, the full effect of the through space π–π interaction results in the $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)]$ complex being easier to oxidise, compared with $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,2)]$, by some 200 mV.

Hunter *et al.* noted that the stability of the $[Cr(CO)_3(\eta^6\text{-arene})]^{+\bullet}$ radical cation, as judged by the ratio of peak currents (I_{pc}/I_{pa}) obtained from the cyclic voltammograms, was related to the electron richness at the metal centre.[15] Electron-donating substituents on the arene ring had the effect of increasing the stability of $[Cr(CO)_3(\eta^6\text{-arene})]^{+\bullet}$ (I_{pc}/I_{pa} tending towards unity for a given scan rate), whilst electron withdrawing substituents had the converse effect. A similar pattern is observed for the [2.2]cyclophane complexes using data obtained at a scan rate of 100 mV s^{-1}.

The $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ complexes have also been examined by IR spectroelectrochemistry using an infrared reflection–absorption spectroscopy (IRRAS) cell in an effort to characterise the oxidised products more fully. The 1800–2100 cm^{-1} region of the IR spectra of the neutral $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ complexes contains two bands corresponding to the carbonyl stretching vibrations [$\nu(CO)$] of A_1 and E symmetry, as are typically observed for $[Cr(CO)_3(\eta^6\text{-arene})]$ complexes.[17] Upon oxidation these bands shift by some 110–120 cm^{-1} to higher wavenumber, as is typically observed upon oxidation of transition metal complexes for which the HOMO has a considerable amount of metal character and no significant structural change is associated with the charge transfer process.[18] The $\nu(CO)$ band positions for the $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ and $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]^{+\bullet}$ complexes are listed in Table 3, and the spectral changes accompanying the oxidation of $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16}\text{-}1,4)]$ in an IRRAS cell are shown in Fig. 3.

The IR spectroelectrochemical studies have also confirmed

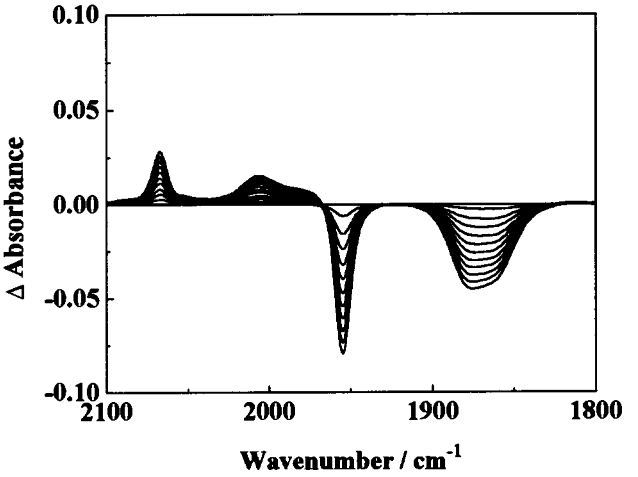

Fig. 3 The changes in the IR difference spectrum upon oxidation of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)] in 0.2 mol dm^{-3} [NBu$_4$][PF$_6$]–CH$_2$Cl$_2$ in an IRRAS cell at ≈213 K. The horizontal line at zero absorbance corresponds to the initial spectrum of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)] prior to oxidation (*i.e.* the sample spectrum ratioed by itself). Upon oxidation consumption of the parent complex is indicated by increasing negative absorbance at 1956 and 1876 cm^{-1}, whilst increasing positive absorbance at 2068 and ≈2006 cm^{-1} corresponds to the formation of the radical cation, [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$.

the trend in radical cation stability established by cyclic voltammetry. The oxidised product [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$ is quite persistent at 290 K, with the electrolysis proceeding to ≈50% completion before some decomposition is observed, as shown by the loss of isosbestic points and the failure to quantitatively regenerate the starting spectrum upon re-reduction. At 213 K the oxidation of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)] becomes fully reversible on the timescale and conditions of the IR spectroelectrochemical experiment. The [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,3)]$^{+\bullet}$ radical cation is notably more reactive in that at ≈290 K the electrolysis only proceeds to ≈10% before decomposition is observed, whilst in the case of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,2)] the oxidation is not fully reversible in the chemical sense even at 210 K. At low temperature the electrolysis proceeds to ≈60% completion before the [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,2)]$^{+\bullet}$ spectrum ceases to gain intensity. Continuation of the electrolysis past this point results in the growth of a weak band at 2138 cm^{-1} signifying the evolution of free carbon monoxide. Within a short time the bands due to [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,2)]$^{+\bullet}$ also collapse indicating decomposition of this radical cation *via* loss of carbon monoxide.

All previous attempts to obtain EPR spectra of [Cr(CO)$_3$(η^6-arene)]$^{+\bullet}$ complexes have been unsuccessful, however by using an EPR spectroelectrochemical cell which permits electrolyses to be performed at low temperature *in situ*,[19] [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$ has been characterised by EPR spectroscopy. However attempts to collect the EPR spectra of the [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,3)]$^{+\bullet}$ and [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,2)]$^{+\bullet}$ radical cations were unsuccessful, highlighting the differences in stability invoked by the three [2.2]cyclophane isomers.

The EPR spectrum of electrogenerated [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$ in frozen (≈90 K) 0.2 mol dm^{-3} [NBu$_4$][PF$_6$]–CH$_2$Cl$_2$ is shown in Fig. 4(a). The spectrum consists of three components corresponding to $g_1 = 2.0860$, $g_2 = 2.0374$ and $g_3 = 1.9940$ G, each of which has a different line width. The simulated spectrum is shown in Fig. 4(b), with line widths of $\Delta_1 = 33$, $\Delta_2 = 20$ and $\Delta_3 = 11$ G for g_1, g_2 and g_3 respectively. The g values are similar to those obtained for [Cr(CO)$_2$(PR$_3$)(η^6-C$_6$Me$_6$)]$^{+\bullet}$ [PR$_3$ = PEt$_3$, PPh$_3$, P(OEt)$_3$ or P(OPh)$_3$], although the overall appearance of the spectrum is quite different due to the absence of hyperfine coupling to ^{31}P atom.[20] Room temperature solution phase spectra of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$ could not be obtained, as the complex decomposed upon warming. Over the time span of the electrolysis in the EPR spectroelectrochemical cell† the [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,2)]$^{+\bullet}$ and [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,3)]$^{+\bullet}$ complexes were confirmed to be unstable, since spectra of frozen solutions contained more than the three expected resonances and were not entirely reproducible.

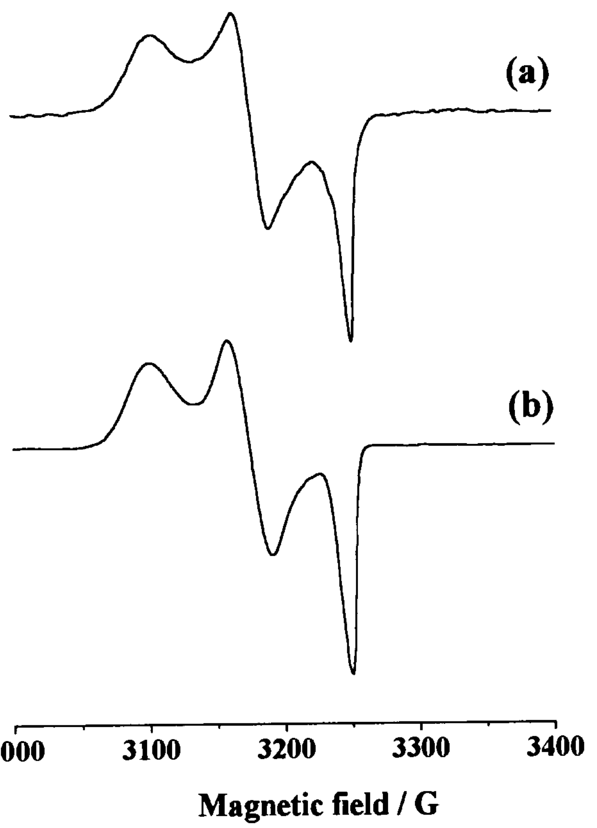

Fig. 4 (a) EPR spectrum of a frozen solution at ≈90 K of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$, electrogenerated in 0.2 mol dm^{-3} [NBu$_4$][PF$_6$]–CH$_2$Cl$_2$. (b) Simulated EPR spectrum, $g_1 = 2.0860$, $g_2 = 2.0374$ and $g_3 = 1.9940$, $\Delta_1 = 33$ G, $\Delta_2 = 20$ G, $\Delta_3 = 11$ G.

Conclusion

Cyclic voltammetry of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,2)], [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,3)] and [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)] in 0.2 mol dm^{-3} [NBu$_4$][PF$_6$]–CH$_2$Cl$_2$ has shown that under specified conditions each of these complexes undergoes a chemically reversible one-electron oxidation to the corresponding radical cation, [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$)]$^{+\bullet}$. The highly reactive radical cations have been characterised by IR spectroscopy and, in the case of [Cr(CO)$_3$(η^6-C$_{16}$H$_{16}$-1,4)]$^{+\bullet}$, by EPR spectroscopy. The reversible potential for oxidation of these complexes varies in the order *para* < *meta* < *ortho*. Comparison of these data with those from other related [Cr(CO)$_3$(η^6-arene)] complexes indicates that the variation in potential for oxidation occurs due to differing degrees of through space π-donation from the uncomplexed ring to the ring bearing the {Cr(CO)$_3$} moiety.

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† It is important to note that the timescale for electrolysis in the EPR and IR spectroelectrochemical cells is very different, on account of the different cell volume/working electrode area ratios (V_C/A_{WE}) for the two spectroelectrochemical cells. In the IRRAS cell the V_C/A_{WE} ratio is small such that electrolysis of the thin-layer under spectroscopic interrogation can be complete in 30–60 s. Electrogeneration in the EPR cell takes considerably longer on account of the small surface area of the working electrode, making the V_C/A_{WE} ratio relatively large. Using the same conditions as those for the IR spectroelectrochemical experiments, electrolysis in the EPR spectroelectrochemical cell typically took 10–15 min.

Experimental

Sample preparation

Chromium hexacarbonyl and [2.2]paracyclophane were purchased from Aldrich Chemicals and were used without further purification. [2.2]Orthocyclophane and [2.2]metacyclophane were prepared according to literature procedures.[21,22] The $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ complexes were prepared by refluxing $[Cr(CO)_6]$ with the appropriate ligand in dry, deoxygenated 1,4-dioxane under a nitrogen atmosphere. The Strohmeier reflux method was used in all reactions in order to ensure that the $[Cr(CO)_6]$ was not lost from the reaction mixture by sublimation.[23] 1,4-Dioxane was distilled from Na wire before use. The $[Cr(CO)_3(\eta^6\text{-}C_{16}H_{16})]$ complexes were characterised by NMR and IR spectroscopy,[15,24,25] and gave satisfactory elemental analysis (C, H).

Electrochemical and spectroelectrochemical measurements

Voltammetric measurements were made using a Cypress Systems computer controlled electroanalysis system (model CS-2000). Measurements were performed in a one compartment cell which supported a platinum, gold or glassy carbon macrodisc or a platinum microdisc working electrode, a platinum coiled wire auxiliary electrode and a Ag–AgCl reference electrode, against which the potential of the ferrocene–ferrocenium ($Fc^{0/+}$) couple was measured at +0.55 V. All measurements were made in 0.2 mol dm^{-3} $[NBu_4][PF_6]$–CH_2Cl_2 electrolyte solution. The solvent was freshly distilled from CaH_2 directly before use, and deoxygenated with dry nitrogen until oxygen was no longer detected electrochemically.

In situ IR spectroelectrochemical measurements were performed in an infrared reflection–absorption spectroscopy (IRRAS) cell,[26,27] mounted in the sample compartment of a Bruker IFS 55 FTIR spectrometer. X-Band EPR spectra were recorded using a Varian E12 spectrometer. The sample was electrogenerated in an EPR spectroelectrochemical cell[19] immersed in an acetone–dry ice cold bath. Electrolyses were performed with a PAR 174A Polargraphic Analyzer. At the completion of the electrolysis, the solution was frozen in liquid N_2, then transferred to the cryostat within the cavity of the spectrometer, and the spectra recorded at ≈90 K. The field was calibrated with external diphenylpicrylhydrazyl. The EPR simulation was performed with the Bruker program Simfonia®, for a three component spectrum, with each component having a different line width. Gaussian lineshapes were assumed.

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References

1 D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 1971, **4**, 204 and refs. therein; F. Vögtle and P. Neumann, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 73; J. Kleinschroth and H. Hopf, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 469.

2 J. Schultz and F. Vögtle, *Top. Curr. Chem.*, 1994, **172**, 41; A. de Meijere and B. König, *Synlett*, 1997, 1221.

3 V. Boekelheide, *Pure Appl. Chem.*, 1986, **58**, 1.

4 M. M. Pellegrin, *Recl. Trav. Chim. Pays-Bas*, 1899, **18**, 458.

5 D. J. Cram and H. J. Steinberg, *J. Am. Chem. Soc.*, 1951, **73**, 5691.

6 R. H. Mitchell, T. K. Vinod, G. J. Bodwell, K. S. Weerawarna, W. Anker, R. V. Williams and G. W. Bushnell, *Pure Appl. Chem.*, 1986, **58**, 15.

7 M. Benedikt and K. Schlögl, *Monatsh. Chem.*, 1978, **109**, 805.

8 P. J. Dyson, D. G. Humphrey, J. E. McGrady, D. M. P. Mingos and D. J. Wilson, *J. Chem. Soc., Dalton Trans.*, 1995, 4039.

9 M. J. Morris, *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 5, ch. 8, p. 494.

10 C. G. Zoski, D. A. Sweigart, N. J. Stone, P. H. Rieger, E. Mocellin, T. F. Mann, D. R. Mann, D. K. Gosser, M. M. Doeff and A. M. Bond, *J. Am. Chem. Soc.*, 1988, **110**, 2109.

11 R. H. Wopschall and I. Shain, *Anal. Chem.*, 1967, **39**, 1514.

12 W. R. Heineman and P. T. Kissinger, *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, New York, 1984, ch. 3, pp. 78–93.

13 Southampton Electrochemistry Group, *Instrumental Methods in Electrochemistry*, ed. T. J. Kemp, Ellis Horwood, Chichester, 1985, ch. 6, pp. 210–212.

14 A. M. Bond, S. Fletcher, F. Marken, S. J. Shaw and P. G. Symons, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3925.

15 A. D. Hunter, V. Mozol and S. D. Tsai, *Organometallics*, 1992, **11**, 2251.

16 T. Sato, K. Torizuka, R. Komaki and H. Atobe, *J. Chem. Soc., Perkin Trans. 2*, 1980, 561.

17 G. Davidson and E. M. Riley, *Spectrochim. Acta, Part A*, 1971, **27**, 1649.

18 C. A. Blaine, J. E. Ellis and K. R. Mann, *Inorg. Chem.*, 1995, **34**, 1552.

19 D. A. Fiedler, M. Koppenol and A. M. Bond, *J. Electrochem. Soc.*, 1995, **142**, 862.

20 M. P. Castellani, N. G. Connelly, R. D. Pike, A. L. Rieger and P. H. Rieger, *Organometallics*, 1997, **16**, 4369.

21 W. Baker, R. J. Banks, D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, 1945, 27.

22 W. Baker, J. McOmie and J. M. Norman, *J. Chem. Soc.*, 1951, 1114.

23 W. Strohmeier, *Chem. Ber.*, 1961, **94**, 2490.

24 E. Langer and H. Lehner, *Tetrahedron*, 1973, **29**, 375.

25 D. J. Cram and D. I. Wilkinson, *J. Am. Chem. Soc.*, 1969, **82**, 5721.

26 S. P. Best, R. J. H. Clark, R. P. Cooney and R. C. S. McQueen, *Rev. Sci. Instrum.*, 1987, **58**, 2071.

27 S. P. Best, S. A. Ciniawsky and D. G. Humphrey, *J. Chem. Soc., Dalton Trans.*, 1996, 2945.

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