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CHARACTERISATION AND OXIDATION OF PENTAKIS(ISOCYANIDE)-NITROSYLCHROMIUM(0) COMPLEXES

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SUMMARY

Denitrosylation of $[Cr(NO)_2(NCMe)_4][PF_6]_2$ by CNR (R = Me, t-Bu or p-ClC_6H_4) afforded diamagnetic $[Cr(NO)(CNR)_5][PF_6]$, which could be oxidised, chemically or voltammetrically, to paramagnetic $[Cr(NO)(CNR)_5][PF_6]_2$ ($S=\frac{1}{2}$). Voltammetric evidence for $[Cr(NO)(CNR)_5]^{3+}$, and for $\{Cr[CN(p\text{-}MeC_6H_4)]_6\}^{1+,2}$ as oxidation products of $\{Cr[CN(p\text{-}MeC_6H_4)]_6\}^0$, was also obtained.

INTRODUCTION

In our previous voltammetric examination of mixed carbonyl isocyanide complexes of chromium(0)[1] we discovered that the half-wave potential for the reaction:

$$[Cr(CO)_{6-n}(CNR)_n]^0 \rightleftharpoons [Cr(CO)_{6-n}(CNR)_n]^+ + e^- \; (0 < n < 3)$$

was surprisingly insensitive to the nature of R when the substituent was an alkyl group. In an attempt to corroborate these findings we decided to investigate the (anodic) voltammetric properties of other chromium(0) isocyanide complexes, including those of $[Cr(CNR)_6]^0$.

The species $[Cr(CNR)_6]^0$ (R = aryl) are well known[2] but, with the exception of the carbonyl compounds already mentioned, few other chromium(0) isocyanide complexes have been characterised. However, displacement of MeCN from $[Cr(NO)_2(NCMe)_4]^{2+}$ [3] by CNR would appear to provide a viable route to nitrosyl isocyanide complexes formally containing Cr^0. Such a method has already been employed in the syntheses of sulphur ligand complexes *cis*-$[Cr(NO)_2(S_2CNMe_2)_2]$ and *cis*-$\{Cr(NO)_2[S_2C_2(CN)_2]_2\}^{2-}$ [3].

RESULTS AND DISCUSSION

Synthetic studies

Treatment of the golden-yellow *trans*-$[Cr(NO)_2(NCMe)_4][PF_6]_2$ with CNR (R = Me, t-Bu or p-ClC_6H_4) in acetonitrile afforded the purple-red mononitrosyl

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TABLE 1

ANALYTICAL, CONDUCTIVITY AND M.P. DATA OBTAINED FROM $[Cr(NO)(CNR)_5][PF_6]$

RNC	*Analytical data, found (calcd.)(%)*			Λ[a]	*M.p. (°C)*
	C	*H*	*N*		
MeNC	28.0 (27.8)	3.7 (3.5)	19.0 (19.4)	85	120 dec.
t-BuNC	46.7 (46.7)	7.0 (7.0)	13.1 (13.1)	64	142 dec.
p-ClC_6H_4NC[b]	46.1 (45.9)	2.4 (2.2)	9.1 (9.2)	70	157 dec.[c]

[a] In $ohm \cdot cm^{-1} \cdot mole^{-1}$ in $MeNO_2$; for a 1/1 electrolyte Λ ca. 80. [b] Cl analysis 19.2 (19.4). [c] Turns red at 127°.

$[Cr(NO)(CNR)_5][PF_6]$ (analytical data, Table 1). These complexes were diamagnetic, are formally isoelectronic with $[Cr(CO)_6]$ and $[Cr(CNR)_6]$, and are related to $[Cr(NO)(CN)_5]^{4-}$ [4]. Our attempts to obtain isocyanide complexes by direct alkylation of $[Cr(NO)(CN)_5]^{3-}$ in Me_2SO afforded only $[Cr(NO)(OSMe_2)_5]^{2+}$ [5]. The addition of four mole equivalents of CNR to one equivalent of $[Cr(NO)_2(NCMe)_4]^{2+}$, in an attempt to prepare $[Cr(NO)_2(CNR)_4]^{2+}$, led only to the formation of tars from which only small amounts of $[Cr(NO)(CNR)_5][PF_6]$ could be isolated.

Reaction of $[Cr(NO)(CNR)_5][PF_6]$ with $AgPF_6$ in dichloromethane gave a bright red solution and a precipitate of metallic Ag. From the solution red crystals were obtained ($R = p\text{-}ClC_6H_4$) and, although elemental analyses were unsatisfactory, probably because of contamination by the starting material, it seems very likely that these consisted mainly of $[Cr(NO)(CNR)_5][PF_6]_2$. This dication is paramagnetic ($S = \frac{1}{2}$) and isoelectronic with $[Cr(NO)(CN)_5]^{3-}$.

Spectral studies

The IR spectra of the complexes were recorded in KBr discs [ν(CN) and ν(NO), Table 2]. The number of CN stretching frequencies were consistent with idealised C_{4v} symmetry. The absorption of moderate intensity at ca. 2200 cm^{-1} can be assigned to the A_1' mode and the strong band, with accompanying shoulder, at ca. 2160 cm^{-1}, may be assigned to the A_1'' and E modes. The value of ν(NO) in the monocations is dependent on R in RNC, increasing in the order $R = Me <$ t-Bu $< p\text{-}ClC_6H_4$.

TABLE 2

IR AND ^1H NMR DATA OBTAINED FROM $[Cr(NO)(CNR)_5][PF_6]$

RNX	*IR Spectral data*[a] *ν(CN)*	*ν(NO)*	*^1H NMR data τ*[b]
MeNC	2162 s, 2194 s, 2230 (sh)	1675	6.40
t-BuNC	2120 s, 2200 s, 2070 (sh)	1685	8.46
p-ClC_6H_4NC	2190 s, 2170 s, 2110 (sh)	1710	2.58
p-ClC_6H_4NC[c]	2260 (br), 2130 (sh), 2110 (sh)	1820 s, 1710 w	

[a] In KBr disc (cm^{-1}). [b] In $(CD_3)_2CO$. [c] Oxidised species obtained using Ag^+ with monocation.

That the red species believed to be mainly $[Cr(NO)(CNR)_5]^{2+}$ was contaminated by the monocation was initially established by IR spectroscopy. The values of $\nu(CN)$ and $\nu(NO)$ in the dication had increased by ca. 100 and 110 cm^{-1}, respectively ($R = p\text{-}ClC_6H_4$), relative to those obtained from $[Cr(NO)(CNR)_5]^+$.

The dicationic species are paramagnetic, exhibiting, at room temperature in dichloromethane, broad singlet ESR spectral signals. The spectral parameters, $\langle g \rangle =$ 1.9968 (R = Me) and 1.9938 ($R = p\text{-}ClC_6H_4$) compare favourably with those obtained from the isoelectronic $[Cr(NO)(CN)_5]^{3-}$ [6]. The line widths of the signals obtained from the dications exceeded 21 G, and ^{14}N ($I = 1$) and ^{53} Cr ($I = \frac{3}{2}$) hyperfine splittings were not resolved.

The ^1H NMR spectra of the monocationic species afforded no useful information.

Voltammetric studies

The three nitrosyls complexes, and $Cr[CN(p\text{-}MeC_6H_4)]_6$, were investigated voltammetrically in dichloromethane using a rotating platinum electrode (Table 3).

TABLE 3

VOLTAMMETRIC DATA OBTAINED FROM CHROMIUM ISOCYANIDE COMPLEXES

Complex	*Voltammetry*			*Cyclic Voltam.*[d]		*Process*
	$E_{\frac{1}{2}}$[a]	$E_{\frac{3}{4}}-E_{\frac{1}{4}}$[b]	i_d/C[c]	E_{pa}	E_{pc}	
$[Cr(NO)(CNMe)_5]^+$	+0.21	50	5.3	0.30	0.10	+1→+2
	+0.79	75	4.5	0.88	0.64	+2→+3
$\{Cr(NO)[CN(t\text{-}Bu)]_5\}^+$	+0.31	69	4.9	0.40	0.20	+1→+2
	+1.04	61	4.9	1.18	0.99	+2→+3
$\{Cr(NO)[CN(p\text{-}ClC_6H_4)]_5\}^+$	+0.59	59	5.2	0.69	0.50	+1→+2
	+1.38	62	4.8	1.47	1.28	+2→+3
$\{Cr[CN(p\text{-}MeC_6H_4)]_6\}^0$	+0.18	93	5.4	0.23	−0.01	0→+1
	+0.84	83	5.0	0.90		+1→+2

[a] In V. [b] In mV, reversibility criterion; for a reversible wave value is 59 mV for one electron process. [c] In μA/mm; for one electron process, $\{Ni[S_2C_2(CN)_2]_2\}^- + e^- \rightleftharpoons \{Ni[S_2C_2(CN)_2]_2\}^{2-}$, value 5.0. [d] Anodic and cathodic peaks in cyclic voltammograms; for a reversible wave separation between peaks ca. 200 mV.

All of the compounds underwent *two* reversible one-electron oxidation processes. The half-wave potentials for the process

$$[Cr(NO)(CNR)_5]^{+1} \rightleftharpoons [Cr(NO)(CNR)_5]^{+2} + e^-$$

were in the range +0.2→+0.6 V, accounting for the comparative ease of oxidation of the mono- to the di-cations. The primary oxidation potential for $\{Cr[CN(p\text{-}MeC_6H_4)_6]\}^0$ was more cathodic than those of the nitrosyls, but our attempts to prepare the monocation by Ag^+ oxidation were unsuccessful; reaction with iodine has, however, afforded[7] oxidised species *viz.* $[Cr(CNR)_5I]$*. The observation of second oxidation process in the hexakis-isocyanide is at variance with previously reported data[8].

The $E_{\frac{1}{2}}$-values for the oxidation of $[Cr(NO)(CNR)_5]^+$ were dependent on R in RNC, becoming more anodic in the order R = Me < t-Bu < $p\text{-}ClC_6H_4$, and there

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* This may contain either $[Cr(CNR)_5]^+$ or $[Cr_2(CNR)_{10}]^{2+}$.

was a linear correlation between the $E_{\frac{1}{2}}$-values of both waves and ν(NO). This was surprising in view of our previous observations[1] that $E_{\frac{1}{2}}$ for the oxidation of $[Cr(CO)_{6-n}(CNR)_n]^0$ was insensitive to the nature of R when the species contained alkyl isocyanides used in the nitrosyl complexes. Having recognised that here there is an alkyl group substituent effect, we expected that the order of $E_{\frac{1}{2}}$-values would be R = t-Bu < Me < p-ClC_6H_4. That the alkyl substituent order is reversed would appear to suggest that t-BuNC is a better π-acceptor and/or poorer σ-donor than MeNC, a suggestion not immediately rationalised in terms of inductive $(+I)$ electronic effects. Studies of Pt^{II} complexes, $[Pt(QR'_3)_2(CNR)Me]^+$ (Q = P or As)[9] have led to the proposal that, in these compounds at least, the σ-donor capacity of RNC is not influenced by the inductive properties of R, and is essentially constant. If this proposal is also valid in the Cr^0 complexes, then we must conclude that t-BuNC is a better π-acceptor than MeNC. However, our studies of the redox behaviour of $[M(CO)_{6-n}(CNR)_n]^0$ led us to the conclusion[1] that the contribution of RNC to $(d \rightarrow \pi)$ π-bonding was negligible and that variations in the σ-donor strength of the isonitrile was primarily responsible for the changes observed in oxidation potential. Adopting this view, we are forced to admit that in the nitrosyl complexes, t-BuNC is a *poorer* σ-donor than MeNC. Although the latter view seems intuitively unreasonable, we are presently unable to resolve this ambiguity.

It is usual, however, to explain unresolved anomalies in the behaviour of compounds containing t-Bu groups by invoking steric effects. Molecular models of the $[Cr(NO)(CNR)_5]^+$ species indicate that there are no geometrical or configurational differences between the compounds when R = Me or t-Bu which can be ascribed to steric hindrance. It is possible, however, that the geometry of the complex may change at or near the electrode surface and that the relative sizes of the R groups could then become important. It is also possible that the t-Bu group is a more effective "insulator" than the Me group, thereby hindering the electron-transfer reaction.

EXPERIMENTAL

The complex $[Cr(NO)_2(NCMe)_4][PF_6]_2$ was prepared by the literature method[3]. Elemental analyses were determined by the Microanalytical Laboratory of this Department. Conductivity measurements were made with a Phillips conductivity meter.

IR spectra were measured using Infracord 457 and Perkin–Elmer 180 spectrophotometers. ^1H NMR and ESR spectra were obtained using Varian HA100 and E3 spectrometers, respectively.

Voltammetric data were obtained using a Beckmann Electroscan 30 polarograph. The solvent was dichloromethane (complex 10^{-3} M) and the base electrolyte was $[Et_4N][ClO_4]$ (0.05 M). Results are quoted relative to the SCE (1 M in LiCl) and are corrected, where appropriate for iR drop; the estimated error in data is ±10 mV. Voltammograms were recorded using a rotating Pt electrode (620 rev·min^{-1}) and cyclic voltammograms were obtained with a stationary Pt electrode.

Pentakis(isocyanide)nitrosylchromium hexafluorophosphate, $[Cr(NO)(CNR)_5][PF_6]$, *R = Me, t-Bu or p-*ClC_6H_4

To an acetonitrile solution (30 ml) of $[Cr(NO)_2(NCMe)_4][PF_6]_2$ (1.0 g) was added an excess of RNC. The mixture, initially golden-yellow, was shaken for 30 min during which time it became deep purple. The solvent was removed *in vacuo* and the residue, dissolved in chloroform, chromatographed on alumina using chloroform as eluant. The first, minor, yellow band, a mixture of products, was discarded, and the second, major, purple band was collected. The solvent was slowly removed *in vacuo* affording purple crystals (yields 41%, R = Me, 38%, R = t-Bu, or 57%, R = *p*-ClC_6H_4).

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