Journal of Organometallic Chemistry, 248 (1983) 321–328
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

NEW ISOCYANIDE COMPLEXES OF CHROMIUM DERIVED FROM ETHANOLIC SOLUTIONS OF CHROMIUM(II)

FREDERICK R. LEMKE, DAVID E. WIGLEY and RICHARD A. WALTON *
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 (U.S.A.)

(Received December 10th, 1982)

Summary

Treatment of ethanolic solutions of chromium(II) (which are derived from the reduction of $CrCl_3 \cdot 6H_2O$ solutions) with excess phenyl isocyanide in the presence of KPF_6 affords the complex $[Cr(CNPh)_5Cl]PF_6$. Under similar conditions, *p*-tolyl isocyanide yields the chromium(I) complex $[Cr(CN\text{-}p\text{-}tol)_6]PF_6$. The paramagnetic, yellow-green compound $[Cr(CNPh)_5Cl]PF_6$ decomposes in dichloromethane solution to yield the chromium(II) species $[Cr(CNPh)_6](PF_6)_2$. Treatment of dichloromethane solutions of $[Cr(CNPh)_5Cl]PF_6$ with tertiary phosphines PR_3 (PR_3 = $P\text{-}n\text{-}Bu_3$, $P\text{-}n\text{-}Pr_3$, PEt_3 or PEt_2Ph) and with 1,2-bis(diphenylphosphino)ethane (dppe) gives paramagnetic *trans*-$[Cr(CNPh)_4(PR_3)Cl]PF_6$ and $[Cr(CNPh)_3(dppe)Cl]PF_6$. However, bis(diphenylphosphino)methane (dppm) reacts with $[Cr(CNPh)_5Cl]PF_6$ to yield the diamagnetic, seven-coordinate complex $[Cr(CNPh)_5(dppm)](PF_6)_2$. In the presence of excess $P(OR)_3$ (R = Me or Et), ethanolic chromium(II) solutions and PhNC react to form $[Cr(CNPh)_5Cl]PF_6$ whereas amines and phosphines lead to the formation of the homoleptic 18-electron compound $Cr(CNPh)_6$.

Introduction

The cleavage of metal–metal bonds by π-acceptor ligands is now a well-established procedure by which the high-yield synthesis of certain mononuclear complexes can be accomplished [1,2]. As a part of our continuing efforts in this area, we recently [3] directed our attention toward the use of this method in the formation of the homoleptic alkyl isocyanide complexes of chromium(II), $[Cr(CNR)_n](PF_6)_2$ ($n = 6$ or 7). Unfortunately, the interaction of the π-acceptor alkyl isocyanide ligands with multiply bonded chromium(II) compounds such as $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ and $Cr_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine), did not provide a route to the desired complexes. However, we were successful subsequently

---

* Address correspondence to this author.

0022-328X/83/$03.00

in isolating both the six- and seven-coordinate alkyl isocyanide complexes of chromium(II), viz. $[Cr(CNR)_6](PF_6)_2$ and $[Cr(CNR)_7](PF_6)_2$, by the alternative strategy of interacting ethanolic chromium(II) solutions with excess RNC ligand, in the presence of KPF_6. From these studies [3] we realized the potential utility of such a direct synthetic method in the formation of various other compounds of chromium. We have now explored the interaction of ethanolic chromium(II) solutions with phenyl isocyanide and find behavior somewhat different from that we experienced with alkyl isocyanides; mixed ligand complexes, rather than homoleptic isocyanide complexes are produced. An account of these investigations is provided herein.

Experimental

Starting materials

The isocyanide ligands, phenyl isocyanide (PhNC), *p*-tolyl isocyanide (*p*-tolNC), and t-butyl isocyanide (Me_3CNC) were prepared by standard literature procedures [4]. All monodentate tertiary phosphines and the bidentate phosphines, 1,2-bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)methane (dppm), were obtained from commercial sources and were used as received. All other reagents and solvents were obtained from commercial sources and were used as received.

Reaction procedure

All reactions were carried out under an atmosphere of dry nitrogen, and all solvents were deoxygenated prior to use by purging with N_2 gas.

A. Reactions of ethanolic solutions of chromium(II)

(i) $[Cr(CNPh)_5Cl]PF_6$. A freshly prepared ethanolic solution of chromium(II) (prepared from 1 g of $CrCl_3 \cdot 6H_2O$ dissolved in 20 ml of ethanol and reduced using a Zn/Hg amalgam) [5] was syringed slowly into a stirred solution of 6 ml of PhNC and 1 g of KPF_6 in 10 ml of ethanol. This mixture was stirred vigorously for 30 min, after which time the yellow-green precipitate was filtered off. This complex was purified by stirring in water for 1–2 h, after which time the product was filtered off, washed with copious amounts of ethanol followed by diethyl ether, and dried in vacuo. Yield, 0.90g (28%). Found: C, 55.20; H, 3.79; Cl, 5.23. $C_{35}H_{25}ClCrF_6N_5P$ calcd.: C, 56.20; H, 3.37; Cl, 4.74%. Attempts to recrystallize this product from dichloromethane/diethyl ether solutions resulted in partial decomposition and formation of the homoleptic complex $[Cr(CNPh)_6](PF_6)_2$.

The same complex was formed when the phosphite ligands $P(OR)_3$ (R = Me or Et) were added to the mixture of PhNC and KPF_6 prior to the addition of the chromium(II) solution.

(ii) $[Cr(CN\text{-}p\text{-}tol)_6]PF_6$. This homoleptic isocyanide complex was prepared by a procedure analogous to that described in section *A(i)* for the phenyl isocyanide-chloride complex, by using 4 ml of *p*-tolNC. Purification as described in section *A(i)* yielded an orange-brown solid. Alternatively, it may be recrystallized from acetone/hexane mixtures. Yield, 0.81 g (21%). This previously reported [6] complex was identified on the basis of its spectroscopic and electrochemical properties.

(iii) $Cr(CNPh)_6$. An ethanolic chromium(II) solution (prepared from 0.50 g of $CrCl_3 \cdot 6H_2O$ in 15 ml of ethanol and reduced using a Zn/Hg amalgam) [5] was

syringed slowly into a vigorously stirred mixture of 2.0 ml of PhNC and 0.90 ml of t-butylamine in 5 ml of ethanol. The red solution which immediately formed was stirred for 30 min at room temperature after which time the red-brown solid which formed was filtered off. The product was extracted from this solid with benzene; reduction in volume of the red benzene filtrate yielded red crystals with a green reflectance. Yield, 0.23 g (16%). A similar procedure but using the tertiary phosphine ligand PEt_2Ph in place of t-butylamine afforded this same product. This known complex [7] was identified on the basis of its electrochemical [6] and spectroscopic [8] properties.

B. Reactions of $[Cr(CNPh)_5Cl]PF_6$ with tertiary phosphines

(i) $[Cr(CNPh)_4(P\text{-}n\text{-}Bu_3)Cl]PF_6$. A quantity of $[Cr(CNPh)_5Cl]PF_6$ (0.15 g) was added to 10 ml of dichloromethane and 0.10 ml of tri-n-butylphosphine were immediately syringed into this solution. This mixture was heated to reflux for 10 min, after which time the darkened solution was reduced in volume and a quantity of diethyl ether was added to precipitate the orange-yellow product. Yield 0.088 g (52%). This complex could be recrystallized from dichloromethane/diethyl ether mixtures. Anal. Found: C, 55.93; H, 5.79. $C_{40}H_{47}ClCrF_6N_4P_2$ calcd.: C, 56.71; H, 5.59%.

(ii) $[Cr(CNPh)_4(P\text{-}n\text{-}Pr_3)Cl]PF_6$. Orange crystals of this complex were obtained by a procedure analogous to that described in *B(i)*; yield 48%. Anal. Found: C, 54.38; H, 5.21; Cl, 4.29. $C_{37}H_{41}ClCrF_6N_4P_2$ calcd.: C, 55.20; H, 5.13; Cl, 4.40%.

(iii) $[Cr(CNPh)_4(PEt_3)Cl]PF_6$. This complex formed as gold crystals by the procedure described in section *B(i)*; yield 46%. This derivative was identified on the basis of its spectroscopic and electrochemical properties which were analogous to those of the other phosphine derivatives.

(iv) $[Cr(CNPh)_4(PEt_2Ph)Cl]PF_6$. This complex was obtained as yellow-orange crystals by an analogous procedure to that described in section *B(i)*; yield, 46%. Anal. Found: C, 55.38; H, 4.58. $C_{38}H_{35}ClCrF_6N_4P_2$ calcd.: C, 56.27; H, 4.35%.

(v) $[Cr(CNPh)_3(dppe)Cl]PF_6$. A solution of 0.15 g of $[Cr(CNPh)_5Cl]PF_6$ and 0.12 g of dppe in 12 ml of dichloromethane was gently refluxed for 30 min. After this period, the reaction solution was reduced in volume, filtered, a quantity of diethyl ether was added and the sample was refrigerated. The orange-red crystals which formed were filtered off, washed with diethyl ether, and dried in vacuo. Yield, 0.13 g (68%). Recrystallization could be effected from dichloromethane/diethyl ether mixtures. Anal. Found: C, 59.11; H, 4.21; Cl, 3.57. $C_{47}H_{39}ClCrF_6N_3P_3$ calcd.: C, 60.04; H, 4.18; Cl, 3.77%.

(vi) $[Cr(CNPh)_5(dppm)](PF_6)_2$. This diamagnetic complex was obtained after recrystallization, as orange crystals from the reaction of 0.16 g of $[Cr(CNPh)_5Cl]PF_6$ and 0.15 g of dppm by procedure similar to that described in section *B(v)*. Yield, 0.066g (24%). Anal. Found: C, 57.67; H, 4.49; Cl, 0.35. $C_{60}H_{47}CrF_{12}P_4N_5$ calcd.: C, 58.03; H, 3.81; Cl, 0.00%. The very small amount of Cl found in the microanalytical determination may be due to a trace of lattice CH_2Cl_2 in the crystalline material.

C. Formation of $[Cr(CNPh)_6]PF_6$ from $[Cr(CNPh)_5Cl]PF_6$

To a solution of 0.16 g of $[Cr(CNPh)_5Cl]PF_6$ in 10 ml of dichloromethane were added 0.21 ml of t-butylamine. This mixture was stirred at room temperature for 30 min, reduced in volume, and a quantity of diethyl ether was added to precipitate a dark solid. This solid was filtered off and the filtrate was further reduced in volume to precipitate the product. Yield: 0.037 g (22%). This compound was identified through its electrochemical and spectroscopic properties [6] which were in full accord with its formulation.

Physical measurements

Infrared spectra of Nujol mulls were recorded in the region 4000–400 cm^{-1} with a Beckman IR-12 spectrophotometer, using KBr plates. Solution infrared spectra were recorded in dichloromethane in the 2300–2000 cm^{-1} region utilizing the Beckman IR-12 spectrophotometer. A PE-R32 spectrometer was used to measure magnetic moments by the Evans Method [9,10] on dichloromethane solutions of the complexes at room temperature. Cyclic voltammetry experiments were performed on dichloromethane solutions of the complexes containing 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. All measurements were made in a single-chambered cell and were taken at a platinum bead electrode. Voltammetric measurements were taken with a Bioanalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett–Packard Model 7035B x-y recorder. $E_{1/2}$ values were referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. Conductivity data were obtained on $\sim 10^{-3}$ M acetonitrile solutions of complexes employing an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. Microanalyses were performed by Dr. H.D. Lee of the Purdue University microanalytical laboratory, and Galbraith Laboratories, Inc., Knoxville, Tennessee.

Results and discussion

Reactivity studies

The reaction of ethanolic solutions of chromium(II) with an excess of phenyl isocyanide, in the presence of KPF_6, leads to the formation of the pentakis(isocyanide) complex $[Cr(CNPh)_5Cl]PF_6$. The coordination of a chloride ligand, clearly originating from the $CrCl_3 \cdot 6H_2O$ starting material, stands in contrast to our previous study [3] involving alkyl isocyanides, in which reactions with RNC (R = CMe_3 or C_6H_{11}) led to the isolation of the homoleptic complexes $[Cr(CNR)_6](PF_6)_2$. It is perhaps surprising that this chloride product is obtained, especially since we observe that recrystallization of this product from dichloromethane/diethyl ether solutions leads to partial decomposition and formation of $[Cr(CNPh)_6](PF_6)_2$. This decomposition suggests the homoleptic complex $[Cr(CNPh)_6](PF_6)_2$ to be the thermodynamically favored product. We can envisage the chloride complex as a kinetic product which, upon its formation, precipitates as a result of its limited solubility in the ethanol reaction solvent. The reaction of chromium(II) solutions with excess *p*-tolyl isocyanide under similar conditions, leads to formation of the previously described [6] homoleptic complex $[Cr(CN\text{-}p\text{-}tol)_6]PF_6$. The isolation of a chromium(I) product from ethanolic chromium(II) solutions is simply a reflection of the reducing propensity of organic isocyanides [11]. Although yields of this latter derivative are rather low, this is a much simpler and more direct route to this product than that previously reported, viz., by the reaction of *p*-tolNC with $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ to generate $Cr(CN\text{-}p\text{-}tol)_6$, followed by oxidation with $AgPF_6$ [6].

In the course of this study, the substitution chemistry of the chromium(II) complex $[Cr(CNPh)_5Cl]PF_6$ was investigated. Reactions of this compound with tertiary phosphines PR_3(P-n-Bu_3, P-n-Pr_3, PEt_3 or PEt_2Ph) in dichloromethane resulted in the formation of the mixed-ligand derivatives $[Cr(CNPh)_4(PR_3)Cl]PF_6$. These paramagnetic orange to yellow compounds, in contrast to their precursor, are stable in dichloromethane solution and may easily be recrystallized from dichloromethane/diethyl ether solutions.

In a similar reaction, $[Cr(CNPh)_5Cl]PF_6$ and 1,2-bis(diphenylphosphino)ethane in refluxing dichloromethane form $[Cr(CNPh)_3(dppe)Cl]PF_6$. Under identical reaction conditions, bis(diphenylphosphino)methane reacts with $[Cr(CNPh)_5Cl]PF_6$ to yield the seven-coordinate complex $[Cr(CNPh)_5(dppm)](PF_6)_2$. This compound's diamagnetism and characteristic electrochemical properties (vide infra) confirm its 18-electron configuration. The dppm derivative is stable in solution (dichloromethane, acetone) and may easily be recrystallized from these solvents by the addition of diethyl ether. This surprising difference in the reactivity of $[Cr(CNPh)_5Cl]PF_6$ with dppe and dppm could result from the somewhat more modest steric requirements of the dppm ligand as compared to dppe [12]. In any event, loss of chloride is preferred and this diamagnetic seven-coordinate complex is isolated. The analogous molybdenum complex $[Mo(CNPh)_5(dppm)](PF_6)_2$ has been isolated previously [11].

In an attempt to generate amine-containing derivatives of $[Cr(CNPh)_5Cl]PF_6$, under reaction conditions similar to those employed in the phosphine reactions, we succeeded in simply reducing the complex and isolating the homoleptic species $[Cr(CNPh)_6]PF_6$ (identified on the basis of its electrochemical properties [6]). This reaction suggested to us that the addition of a limited amount of an amine to the reaction between ethanolic chromium(II) and PhNC might reduce the complex to form $[Cr(CNPh)_6]PF_6$ and block the incorporation of chloride ion. Such a reaction however, in the presence of KPF_6, resulted in the formation of a mixture of the homoleptic complexes $[Cr(CNPh)_6]PF_6$ and $Cr(CNPh)_6$, suggesting that the zerovalent species was the thermodynamically favored product in this reaction. In accord with this, we find that an excess of amine (t-butyl amine or isopropyl amine) and excess PhNC react with ethanolic chromium(II) solutions to generate as the principal product, $Cr(CNPh)_6$. Similar behavior was observed when an excess of PEt_2Ph was used instead of the amine *. As in the case of the *p*-tolyl isocyanide derivative $[Cr(CN\text{-}p\text{-}tol)_6]PF_6$ (vide supra), this synthetic route constitutes a simple and quite direct method of generating this complex. $Cr(CNPh)_6$, and other aryl isocyanide complexes, are usually synthesized by the method of Malatesta and co-workers, viz., the scission of the Cr–Cr quadruple bond of $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ by ArNC [7].

Spectroscopic and electrochemical studies

Infrared spectra of both Nujol mulls and dichloromethane solutions of compounds prepared in this study are summarized in Table 1. The isocyanide $\nu(C{\equiv}N)$ stretching region (2000–2300 cm^{-1}) provides both an indication of oxidation state changes, as well as ligand substitutions. The pentakis(isocyanide) derivative

---

* When the less basic phosphite ligands $P(OR)_3$ (R = Me or Et) are used in place of the amine or phosphine, the reaction between chromium(II), phenyl isocyanide and KPF_6 in ethanol gives unreduced $[Cr(CNPh)_5Cl]PF_6$. However, when t-butyl isocyanide is substituted for PhNC, the seven coordinate complex $[Cr(CNCMe_3)_5(P(OR)_3)_2](PF_6)_2$ (albeit somewhat impure), possessing similar properties to analogous mixed alkyl isocyanide/phosphine derivatives of chromium(II) [3], is produced.

TABLE 1

INFRARED, CONDUCTIVITY AND MAGNETIC MOMENT DATA FOR ISOCYANIDE COMPLEXES OF CHROMIUM

Complex	ν(C≡N) (cm^{-1})[a]		Λ_m[b]	μ_{obs}[c]
	Nujol mull	CH_2Cl_2 solution		
$[Cr(CNPh)_5Cl]PF_6$	2194w, 2178w[d], 2129s	2195w, 2177w[d], 2135s	137	2.68
$[Cr(CNPh)_4(P\text{-}n\text{-}Bu_3)Cl]PF_6$	2175w, 2110s	2118s	129	2.78
$[Cr(CNPh)_4(P\text{-}n\text{-}Pr_3)Cl]PF_6$	2166w, 2111s	2118s	128	2.77
$[Cr(CNPh)_4(PEt_3)Cl]PF_6$	2114s	2119s	153	2.98
$[Cr(CNPh)_4(PEt_2Ph)Cl]PF_6$	2166w, 2115s	2120s	155	2.72
$[Cr(CNPh)_3(dppe)Cl]PF_6$	2144m, 2097s	2154w, 2106s	139	2.59
$[Cr(CNPh)_5(dppm)](PF_6)_2$	2170m, 2121s, 2080s	2167w, 2123m, 2088m	240	0
$[Cr(CN\text{-}p\text{-}tol)_6]PF_6$	2068s, 2031m	2075m, 2036w	121	1.60

[a] Abbreviations are as follows: s, strong; m, medium; w, weak. [b] Values in ohm^{-1} cm^2 mol^{-1}. Measured on ~ 10^{-3} *M* acetonitrile solutions of complexes at room temperature. [c] Values in Bohr magnetons, determined on dichloromethane solutions of complexes at room temperature by the Evans Method. [d] The origin of this weak band is uncertain.

$[Cr(CNPh)_5Cl]PF_6$ is characterized by a weak $\nu(C{\equiv}N)_{axial}$ stretching mode at 2194 cm^{-1}, and a strong $\nu(C{\equiv}N)_{equatorial}$ mode at 2129 cm^{-1}. Upon substitution of an isocyanide ligand by PR_3, the higher energy mode vanishes and the 2129 cm^{-1} mode is shifted to lower energies by about 15–20 cm^{-1}. This is a reflection of axial substitution by a more strongly σ-donating and poorer π-accepting phosphine ligand (as compared to isocyanide ligands) to form *trans*-$[Cr(CNPh)_4(PR_3)Cl]PF_6$. As expected, the enhanced transfer of electron density into the π^* levels of the PhNC ligands induces a weakening of the C≡N bond as evidenced by these infrared measurements.

Also summarized in Table 1 are molar conductivity values measured on acetonitrile solutions of complexes, and magnetic moment values for dichloromethane solutions of the complexes as determined by the Evans Method [9,10]. For the complex $[Cr(CNPh)_5Cl]PF_6$ as well as its phosphine-substituted analogs, Λ_m values are consistent with the assignment of these complexes as 1/1 electrolytes in acetonitrile [13], an observation which confirms the covalently bound nature of the chloride. The conductivity of the dppm derivative $[Cr(CNPh)_5(dppm)](PF_6)_2$, is well within the range of values associated with 2/1 electrolytes in acetonitrile [13]. The values of μ_{obsd} for $[Cr(CNPh)_5Cl]PF_6$, as well as the $[Cr(CNPh)_4(PR_3)Cl]PF_6$ and $[Cr(CNPh)_3(dppe)Cl]PF_6$ derivatives, are in accord with low-spin chromium(II) species, possessing two unpaired electrons. The expected diamagnetism of $[Cr(CNPh)_5(dppm)](PF_6)_2$ was readily verified by the Evans Method, showing that this complex resembled other seven-coordinate chromium(II) derivatives of this type [3]. In the case of the *p*-tolNC derivative $[Cr(CN\text{-}p\text{-}tol)_6]PF_6$, the 17-electron configuration of the complex is borne out in its solution magnetic moment of $\mu_{obsd} = 1.60\ \mu_B$.

The electrochemical properties of complexes prepared in this study are summarized in Table 2. In the parent complex $[Cr(CNPh)_5Cl]PF_6$ (Fig. 1a) and in its phosphine analogs, $[Cr(CNPh)_4(PR_3)Cl]PF_6$ (Fig. 1b), we observe a reversible

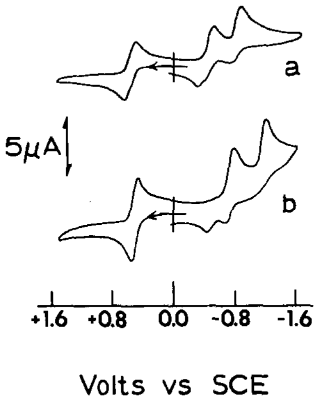
TABLE 2

VOLTAMMETRIC HALF-WAVE AND PEAK POTENTIALS FOR ISOCYANIDE COMPLEXES OF CHROMIUM [a]

Complex	$E_{1/2}$(ox)	$E_{p,c}$(red)(1)	$E_{p,c}$(red)(2)
$[Cr(CNPh)_5Cl]PF_6$	+0.53(95)	−0.44	−0.89
$[Cr(CNPh)_4(P\text{-n-}Bu_3)Cl]PF_6$	+0.50(95)	−0.77	−1.20
$[Cr(CNPh)_4(P\text{-n-}Pr_3)Cl]PF_6$	+0.49(95)	−0.79	−1.20
$[Cr(CNPh)_4(PEt_3)Cl]PF_6$	+0.49(90)	−0.79	−1.20
$[Cr(CNPh)_4(PEt_2Ph)Cl]PF_6$	+0.49(85)	−0.74	−1.17
$[Cr(CNPh)_3(dppe)Cl]PF_6$	+0.41(85)	−0.70(90) [b]	−1.29
$[Cr(CNPh)_5(dppm)](PF_6)_2$	+1.17 [c]	−0.92	
$[Cr(CN\text{-}p\text{-}tol)_6]PF_6$ [d]	+0.96(100)	+0.18(95) [e]	−0.42(100) [f]
$[Cr(CNPh)_6]PF_6$ [d]	+0.97(85)	+0.21(90) [e]	−0.39(90) [f]
$Cr(CNPh)_6$ [d]	+0.99(85)	+0.21(95) [e]	−0.39(100) [e]

[a] Values in volts vs. SCE with a Pt-bead electrode and 0.2 *M* tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte; values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. [b] Reversible; $E_{1/2}$ value reported. [c] $E_{p,a}$ value reported; $i_{p,a}/i_{p,c} \gg 1$. [d] Data for this complex are in very good agreement with that reported by Treichel and Essenmacher [6]. [e] Value of $E_{1/2}$(ox) reported. [f] Value of $E_{1/2}$(red) reported.

[14,15] one-electron oxidation at $E_{1/2} \sim +0.5$V vs SCE, and two irreversible one-electron reductions at the values indicated in Table 2. We are able to observe electrochemically therefore, the sequence of oxidation states $Cr^{III} \rightleftarrows Cr^{II} \rightleftarrows Cr^{I} \rightleftarrows Cr^{0}$, a result which is expected in light of previous electrochemical studies on other chromium isocyanide complexes [3,16,17]. The $E_{1/2}$(ox) values, and in particular, the $E_{p,c}$(red) values of the phosphine-substituted derivatives are shifted to more negative potentials as compared to their parent complex $[Cr(CNPh)_5Cl]PF_6$. The relative ease with which the phosphine derivatives are oxidized, as well as the greater difficulty in



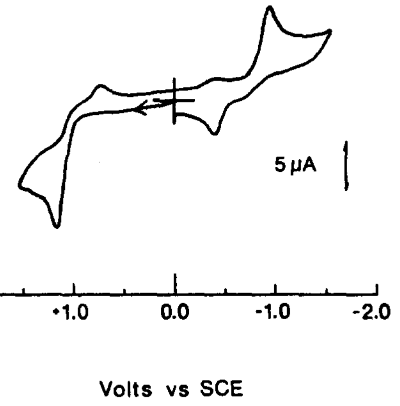


Fig. 1. Cyclic voltammograms in 0.2 *M* tetra-n-butylammonium hexafluorophosphate/dichloromethane of (a) $[Cr(CNPh)_5Cl]PF_6$ and (b) $[Cr(CNPh)_4(P\text{-n-}Bu_3)Cl]PF_6$ recorded at 200 mV/s.

Fig. 2. Cyclic voltammogram in 0.2 *M* tetra-n-butylammonium hexafluorophosphate/dichloromethane of $[Cr(CNPh)_5(dppm)](PF_6)_2$.

reducing the compounds, reflects the more potent σ-donor ability and poorer π-accepting ability of a PR_3 ligand as compared to PhNC. This trend was also observed from the shift in $\nu(C\equiv N)$ frequencies in the infrared spectra of these compounds (vide supra). The only anomaly observed in these data is the apparent reversibility of the first couple (i.e. Cr^{II}/Cr^{I}) in the dppe derivative $[Cr(CNPh)_3(dppe)Cl]PF_6$. Voltammetric data for the homoleptic species $[Cr(CN\text{-}p\text{-}tol)_6]PF_6$, $[Cr(CNPh)_6]PF_6$, and $Cr(CNPh)_6$, are reported in Table 1 for our experimental conditions. The electrochemistry of these three complexes has previously been investigated [6,16,17] and, accordingly, will not be discussed further here.

In the case of the complex $[Cr(CNPh)_5(dppm)](PF_6)_2$ (Fig. 2), we observe an irreversible oxidation at $E_{p,a} = +1.17V$ vs. SCE ($i_{p,a} \gg i_{p,c}$) and an irreversible reduction at $E_{p,c} = -0.92V$ ($i_{p,a} \ll i_{p,c}$). This voltammogram is reminiscent of that for the analogous molybdenum species $[Mo(CNPh)_5(dppm)](PF_6)_2$ [11], although the Mo^{II}/Mo^{III} couple in the molybdenum complex is reversible.

Acknowledgment

We thank the National Science Foundation (Grant CHE82-06117) for research support. D.E.W. wishes to thank Conoco for Fellowship support during 1982–1983.

References

1 R.A. Walton, in M.H. Chisholm (Ed.), Reactivity of Metal–Metal Bonds; ACS Symposium Series, No. 155, (1981) p. 207.

2 See for example, (a) C.A. Hertzer, R.E. Myers, P. Brant and R.A. Walton, Inorg. Chem., 17 (1978) 2383; (b) T. Nimry, M.A. Urbancic and R.A. Walton, Inorg. Chem., 18 (1979) 691; (c) P. Brant, F.A. Cotton, J.C. Sekutowski, T.E. Wood and R.A. Walton, J. Amer. Chem. Soc., 101 (1979) 6588.

3 W.S. Mialki, D.E. Wigley, T.E. Wood and R.A. Walton, Inorg. Chem., 21 (1982) 480.

4 W.D. Weber, G.W. Gokel and I.K. Ugi, Angew. Chem. Int. Ed. Engl., 11 (1972) 530.

5 D.N. Grindly, An Advanced Course in Practical Inorganic Chemistry; Butterworths, London, 1964, p. 53.

6 P.M. Treichel and G.J. Essenmacher, Inorg. Chem., 15 (1976) 146.

7 L. Malatesta, A. Sacco and G. Ghilmi, Gazz. Chim. Ital., 82 (1952) 516.

8 K.R. Mann, M. Cimolino, G.L. Geoffroy, G.S. Hammond, A.A. Orio, G. Albertin and H.B. Gray, Inorg. Chim. Acta, 16 (1976) 97.

9 D.F. Evans, J. Chem. Soc., (1959) 2003.

10 J.L. Deutsch and S.M. Poling, J. Chem. Educ., 46 (1969) 167.

11 D.D. Klendworth, W.W. Welters, III and R.A. Walton, Organometallics, 1 (1982) 336.

12 J.C. Dewan, T.E. Wood, R.A. Walton and S.J. Lippard, Inorg. Chem., 21 (1982) 1854.

13 W.J. Geary, Coord. Chem. Rev., 7 (1971) 81.

14 For sweep rates (ν) between 50 and 400 mV/s, the ratio $i_p/\nu^{1/2}$ was constant and $i_{p,a}/i_{p,c} \approx 1$ in accord with diffusion control. The potential separation between anodic and cathodic peaks, ΔE_p, was in the range 85–100mV for a sweep rate of 200 mV/s. With our electrochemical setup [15] these observations are consistent with this being a reversible electron transfer process.

15 T.C. Zietlow, D.D. Klendworth, T. Nimry, D.J. Salmon and R.A. Walton, Inorg. Chem., 20 (1981) 947.

16 P.M. Treichel, D.W. Firsich and G.P. Essenmacher, Inorg. Chem., 18 (1979) 2405.

17 D.A. Bohling, J.F. Evans and K.R. Mann, Inorg. Chem., 21 (1982) 3546.