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CYCLIC VOLTAMMETRIC STUDIES OF *TRIS*(ALKYLISOCYANIDE)*BIS*(TERTIARY PHOSPHINE)COBALT(I) COMPLEXES

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CYCLIC VOLTAMMETRIC STUDIES OF *TRIS*(ALKYLISOCYANIDE)*BIS*(TERTIARY PHOSPHINE)COBALT(I) COMPLEXES

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Synthesis and characterization of *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(I) complexes, $[Co(CNR)_3(PR_3)_2]ClO_4$, has been extended to include $CNR = CNCMe_3$, $PR_3 = P(C_6H_4CF_3-p)_3$, $P(C_6H_4F-p)_3$, $P(C_6H_4Me-p)_3$; $PR_3 = PPh_3$, $CNR = CNC_6H_{11}$, $CNCH_2Ph$, CNC_4H_9-n. Reduction of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ did not occur with $PR_3 = P(C_6H_4NMe_2-p)_3$ and $P(C_6F_5)_3$. Solution and solid state structures of the new $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes appear to be distorted disubstituted trigonal bipyramidal examples with the phosphine ligands in axial positions, but the extent of distortion from rigorous D_{3h} symmetry in solution appears to vary for different complexes. Oxidation potentials, $E_{1/2}$, measured in CH_3CN, for the oxidation of Co(I) to Co(II), are essentially independent of the RNC ligands, remaining within the narrow range of $+0.20$ to $+0.25V$ for $[Co(CNR)_3(PPh_3)_2]ClO_4$, $R = CMe_3$, $CHMe_2$, C_6H_{11}, CH_2Ph, C_4H_9-n. Variation of the tertiary phosphine ligands has a pronounced effect on the $E_{1/2}$ values, which range from $+0.03$ to $+0.75V$, increasing steadily as PR_3 (in $[Co(CNCMe_3)_3(PR_3)_2]ClO_4$) is varied: $P(NMe_2)_3 < P(C_4H_9-n)_3 \approx P(C_6H_{13}-n)_3 < P(C_6H_4OMe-p)_3 < P(C_6H_4Me-p)_3 < PPh_3 < P(CH_2Ph)_3 < P(C_6H_4Cl-p)_3 \approx P(C_6H_4F-p)_3 < P(CH_2CH_2CN)_3 < P(C_6H_4CF_3-p)_3$. Trends in $E_{1/2}$ values are better explained in terms of σ-donation than π*-acceptance. The voltammograms are in general *quasi*-reversible, but the highest $E_{1/2}$ values show irreversible behaviour. It is proposed that the Co(I) complex, with approximately trigonal bipyramidal structure in solution, is oxidized to the Co(II) complex, $[Co(CNR)_3(PR_3)_2]^{2+}$, with a regular trigonal bipyramidal structure.

KEYWORDS: cyclic voltammetry, alkylisocyanides, cobalt(I) complexes, tertiary phosphines

INTRODUCTION

Numerous *pentakis*(alkylisocyanide)cobalt(I) complexes disubstituted with tertiary phosphine ligands have been synthesized and characterized in recent years.[1-5] Relatively little cyclic voltammetric data, however, appears to have been reported. Half-wave potentials, $E_{1/2}$(oxidation), in CH_2Cl_2 solution, have been reported for a number of Co(I)-alkylisocyanide and arylisocyanide complexes substituted with PPh_3, $PMePh_2$, and $Ph_2PCH_2CH_2PPh_2$ ligands.[2] Cyclic voltammetric data have also been reported in CH_2Cl_2 for some $[Co(CNR)_3L_2]^+$ complexes with selected arylisocyanides and $L = P(OCH_3)_3$ and $P(C_6H_5)(OC_2H_5)_2$.[6]

This present work investigates cyclic voltammetric measurements on various *tris*(alkylisocyanide)*bis*(tertiary phosphine)cobalt(I) complexes in acetonitrile. New *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(I) complexes have been synthesized and characterized to further extend the range of reported[4,5] complexes. The tertiary phosphine ligands now include a wide range of triarylphosphines and trialkylphosphines with both electron-donating and electron-withdrawing substituents, investigated primarily in the $[Co(CNCMe_3)_3(PR_3)_2]ClO_4$ complexes. The alkylisocyanide ligands now span the range $R = CMe_3$, C_4H_9-n, $CHMe_2$, C_6H_{11}, and CH_2Ph; investigated in the $[Co(CNR)_3(PPh_3)_2]ClO_4$ complexes. In this way a fairly wide range of electron environment about the Co(I) could be studied.

EXPERIMENTAL

Reagents

$[Co(CNCMe_3)_4H_2O](ClO_4)_2$, $[Co_2(CNCHMe_2)_{10}](ClO_4)_4.5H_2O$, and $[Co_2(CNCH_2Ph)_{10}](BF_4)_4.H_2O$ were prepared from commercial $CNCHMe_2$, $CNCH_2Ph$ (Strem), and $CNCMe_3$ (Fluka) as previously reported.[4,7,8] Commercial CNC_4H_9-n, CNC_6H_{11}, $P(C_6H_4CF_3$-$p)_3$, $P(C_6H_4F$-$p)_3$, $P(C_6H_4Me$-$p)_3$, $P(C_6F_5)_3$, and $P(C_6H_4NMe_2$-$p)_3$ (Strem) were used without further purification. $[Co(CNR)_3(PR_3)_2]ClO_4$, $CNR = CNCMe_3$, $CNCHMe_2$; $PR_3 = PPh_3$, $P(C_6H_4Cl$-$p)_3$, $P(C_6H_4OMe$-$p)_3$, $P(CH_2Ph)_3$, $P(C_4H_9$-$n)_3$, $P(C_6H_{13}$-$n)_3$, $P(CH_2CH_2CN)_3$, $P(NMe_2)_3$; were prepared as previously reported.[4,5] Anhydrous diethyl ether was filtered through an alumina column immediately before use. For cyclic voltammetry 5 mM solutions of the compounds were freshly prepared in chromatographic-grade acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte.

Instrumentation

IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrophotometer. Solution electronic spectra were recorded on a Shimadzu UV-365 spectrophotometer. Molar conductivities were measured on 0.001 M solutions at 25°C using a Crison model 525 conductimeter. C, H and N elemental analyses were performed using a Carlo Erba CHN-O/S elemental analyzer, model 1106. Cyclic voltammetric measurements were performed using a Metrohm VA Scanner E612 and a Metrohm Polarecord E506 with a three electrode compartment cell. The working and auxiliary electrodes were glassy carbon and platinum wire, respectively; the reference electrode employed was a saturated calomel electrode (SCE). The voltammograms were recorded in the potential range -0.2 V to $+0.8$ V vs (SCE) on a JJ Instruments X–Y recorder, using a sweep rate of 0.1 V/s. Nitrogen gas was bubbled through each solution for 10 min prior to runs.

[Co(CNCMe₃)₃{P(C₆H₄CF₃-p)₃}₂]ClO₄

A 200 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 2.0 cm³ of CH_3CN and filtered through cotton. This solution was maintained at 0°C in an ice bath while 766 mg $P(C_6H_4CF_3$-$p)_3$ (1:5 Co:P mole ratio) dissolved in 1.0 cm³ of

CH_2Cl_2 was added dropwise. Solution colour changed from blue through green to yellow-brown during ligand addition, becoming dark red-orange only as the solution warmed to room temperature. Ether was carefully added dropwise, initial precipitation being observed after addition of 22.5 cm^3. A total volume of 35.0 cm^3 of ether was added, and the reaction mixture was chilled in ice for 40 min. Pale orange microcrystals were filtered and washed with 1.5 cm^3 of ether. Crude product (325 mg; 74% yield) was dissolved in 6.0 cm^3 of CH_2Cl_2, filtered through cotton, and precipitated by dropwise addition of 20.0 cm^3 of ether. Yield: 285 mg (88% recovery; 65% overall yield). Melting range: 200–208°C (dec.); v(-N≡C): 2140w(sh), 2095vs, 2060m(sh) cm^{-1} (Nujol). *Anal.* Calc. for $CoC_{57}H_{51}ClF_{18}N_3O_4P_2$: C, 51.08; H, 3.84; N, 3.14%. Found: C, 51.05; H, 3.84; N, 2.71%.

Analogous syntheses produced the following complexes.

$[Co(CNCMe_3)_3\{P(C_6H_4F-p)_3\}_2]ClO_4.nCH_2Cl_2$: melting range: 165–177°C (dec.); v(-N≡C): 2138w(sh), 2092vs, 2065m(sh,br) cm^{-1} (Nujol). *Anal.* Calc. for $CoC_{51}H_{51}ClF_6N_3O_4P_2.0.2CH_2Cl_2$: C, 58.16; H, 4.90; N, 3.97%. Found: C, 58.44; H, 5.22; N, 3.63%.

$[Co(CNCMe_3)_3\{P(C_6H_4Me-p)_3\}_2]ClO_4.nCH_2Cl_2$: melting range: 170–179°C (dec.); v(-N≡C): 2090s, 2057vs cm^{-1} (Nujol). *Anal.* Calc. for $CoC_{57}H_{69}ClN_3O_4P_2.1.5CH_2Cl_2$: C, 61.43; H, 6.34; N, 3.67%. Found: C, 61.32; H, 6.43; N, 3.45%.

$[Co(CNCH_2Ph)_3(PPh_3)_2]BF_4.nCH_2Cl_2$: melting range: 138–150°C (dec.); v(-N≡C): 2142w, 2082vs(br) cm^{-1} (Nujol). *Anal.* Calc. for $CoC_{60}H_{51}BF_4N_3P_2.0.3CH_2Cl_2$: C, 69.16; H, 4.97; N, 4.01%. Found: C, 69.07; H, 5.04; N, 4.20%.

[Co(CNC_4H_9-n)_3(PPh_3)_2]ClO_4

A solution of 308 mg $Co(ClO_4)_2.6H_2O$ dissolved in 2.0 cm^3 of EtOH was filtered through cotton and chilled in ice. Then 350 mg CNC_4H_9-n (neat; 5:1 RNC:Co mole ratio) was added dropwise while the Co(II) solution was stirred at 0°C. Solution colour changed from pink to dark blue, but no precipitate formed. Then 1.104 g PPh$_3$ (5:1 PPh$_3$:Co mole ratio) dissolved in 1.5 cm^3 of CH_2Cl_2 was added dropwise while the reaction mixture was stirred. Solution colour changed to yellow-green at 0°C, becoming dark red-brown as the solution was allowed to warm to room temperature. Ether was added carefully, dropwise. Initial precipitation was observed after addition of 25.0 cm^3 of ether; a total volume of 35.0 cm^3 of ether was added and the solution was chilled in ice for 45 min. Dark orange microcrystals were filtered and washed with 2.0 cm^3 of ether (660 mg; 84% yield). Crude product was dissolved in 1.5 cm^3 of CH_2Cl_2, filtered through cotton, and precipitated with dropwise addition of 10.0 cm^3 of ether. Yield: 625 mg (95% recovery; 80% overall yield). Melting range: 143–155°C (dec.); v(-N≡C): 2138m, 2092vs, 2088sh, 2048vs cm^{-1} (Nujol). *Anal.* Calc. for $CoC_{51}H_{57}ClN_3O_4P_2$: C, 65.70; H, 6.16; N, 4.51%. Found: C, 66.06; H, 6.34; N, 4.52%.

$[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$: melting range: 165–180°C (dec.); v(-N≡C): 2137w, 2091sh, 2071vs(br), 2044sh cm^{-1} (Nujol). *Anal.* Calc. for $CoC_{57}H_{63}ClN_3O_4P_2$: C, 67.75; H, 6.28; N, 4.16%. Found: C, 67.29; H, 6.20; N, 3.94%.

RESULTS AND DISCUSSION

Solution properties of the currently reported *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(I) complexes are summarized in Table 1; the oxidation potentials in CH_3CN for all of the Co(I) complexes studied are reported in Table 2.

Synthesis and Characterization

$[Co(CNR)_3(PR_3)_2]ClO_4$ complexes for which the Co(II) starting material is easily isolable were prepared according to the synthesis for $[Co(CNCMe_3)_3\{P(C_6H_4CF_3\text{-}p)_3\}_2]ClO_4$; $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was initially dissolved in CH_3CN, $[Co_2(CNCH_2Ph)_{10}](BF_4)_4.H_2O$ in CH_2Cl_2, and the triarylphosphine was added dropwise in CH_2Cl_2 solution. Addition of $P(C_6F_5)_3$ to $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ failed to show reaction; unreacted starting materials were recovered in good yields. The exceedingly large cone angle for this triarylphosphine (*i.e.*, 184°)[9] may be more effective in preventing reaction than the electron-withdrawing effect of the $-C_6F_5$ substituents. $P(C_6F_5)_3$ may simply be too bulky to react with the Co(II) species before reduction can take place. $P(NEt_2)_3$, which also has a large cone angle but has strongly electron-donating substituents, did not yield crystalline product in reaction with $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, while $P(NMe_2)_3$ readily formed $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$.[4] Addition of $P(C_6H_4NMe_2\text{-}p)_3$ to $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ produced $[Co(CNCMe_3)_3\{P(C_6H_4NMe_2\text{-}p)_3\}_2](ClO_4)_2$, which will be discussed in a subsequent paper. This Co(II) complex, rather surprisingly, did not show a reduction potential within the voltage range investigated.

$[Co(CNR)_3(PR_3)_2]ClO_4$ complexes for which the Co(II) starting material is not easily isolable, i.e. with CNC_6H_{11} and $CNC_4H_9\text{-}n$;[7] were prepared according to the synthesis for $[Co(CNC_4H_9\text{-}n)_3(PPh_3)_2]ClO_4$. $[Co(CNR)_5](ClO_4)_2$ complexes were prepared in EtOH and reacted *in situ* with excess triarylphosphine dissolved in CH_2Cl_2. If a 2:1 PPh_3:Co(II) mole ratio was used and filtration was rapidly achieved, a minor product of $[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_2$ could be isolated as well as the more soluble $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ major product. This Co(II) complex, with limited solution stability, will be discussed in a subsequent paper.

Solution and solid state structures of the $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes appear to be distorted disubstituted trigonal bipyramidal with the phosphine ligands in axial positions. Molar conductivity values in CH_3CN, acetone, and CH_3NO_2 (see Table 1) are within the ranges expected for 1:1 electrolytes,[10] and Λ_M values in CH_2Cl_2 are similar to those previously obtained for Co(I) complexes assumed to be dissociated.[5,11] Most of the electronic spectra (see Table 1) show three, presumably charge transfer, bands. Three, one-electron, symmetry-allowed, $d_\pi \rightarrow \pi^*$ transitions involving equatorial CNR ligands are expected for trigonal bipyramidal coordination.[12] Extra bands in the UV region may reflect reduced symmetry; five $d_\pi \rightarrow \pi^*$ (equatorial) charge-transfer bands become allowed under C_{2v} symmetry.

The $\nu(-N\equiv C)$ IR pattern observed in these $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes has been well characterized in disubstituted arylisocyanide[13] and alkylisocyanide[4,5] five-coordinate complexes of Co(I). Only one $\nu(-N\equiv C)$ IR band (E') should be observed for D_{3h} trigonal bipyramidal coordination. Three $\nu(-N\equiv C)$ IR bands $(2A_1 + B_2)$ are expected for the C_{2v} equatorially-distorted, axially-disubstituted trigonal bipyramidal structure suggested for disubstituted *pentakis*(arylisocyanide)-cobalt(I) complexes.[14] Resolution of at least the lower-energy side band in almost

Table 1 Solution properties of new *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(I) complexes.

Compound	ν(-N≡C) infrared[a]		Electronic spectra[b]		$\Lambda_M^{25°C}$ [c]
	CH_2Cl_2	CH_3NO_2	CH_2Cl_2	CH_3CN	
[Co(CNCMe₃)₃{P(C₆H₄CF₃-*p*)₃}₂]ClO₄	2091vs ~2050w (sh)	2093vs ~2050w (sh)	≈340sh (2700) ≈278sh 269 (45,400) ~233 (53,500)	≈340sh (2600) ≈276sh 266 (42,700) 231sh (50,200)	135 127 81 54
[Co(CNCMe₃)₃{P(C₆H₄F-*p*)₃}₂]ClO₄	~2135vw (sh) 2092vs ~2065br (sh)	~2135vw (sh) 2092vs ~2060br (sh)	≈340sh (3500) ~279sh (32,200) 271 (35,800) 266 (35,300) ~233 (47,900)	≈340sh (3400) ~277sh ~270sh (35,100) 265 (35,500) 231 (45,600)	134 132 82 61
[Co(CNCMe₃)₃{P(C₆H₄Me-*p*)₃}₂]ClO₄	2091vs ~2065br,s	2090vs ~2065br,s	≈340sh (3400) ~280sh (37,700) 275 (38,100) ~268sh 239 (58,200)	≈340sh (3700) ≈280sh 275 (37,400) ~269sh 239sh (57,200)	149 138 85 71
[Co(CNC₆H₁₁)₃(PPh₃)₂]ClO₄	~2150w (sh) 2088vs,br ~2065vw(sh) ~2025vw (sh)	~2135vw (sh) 2086vs,br ~2050vw (sh)	≈460sh (160) ≈340sh (2600) 272 (35,500) 229 (44,500)	≈470sh (120) ≈350sh (2600) 271 (34,700) 229sh (42,600)	150 130 75 65
[Co(CNC₄H₉-*n*)₃(PPh₃)₂]ClO₄	2096vs	~2145vw (sh) 2098vs	≈340sh (3900) 274 (37,600)	≈350sh (3000) 271 (33,400) ~224sh (42,300)	142 135 82 67
[Co(CNCH₂Ph)₃(PPh₃)₂]BF₄	~2135vw (sh) 2093vs	~2140vw (sh) 2093vs	279 (29,600)	≈340sh (4000) 275 (29,500) ≈228sh (42,200)	164 145 85 60

[a]The values ν(-N≡C) are in cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [b]The λ_{max} (ε) value is in nm, without Gaussian resolution. [c]Molar conductivity, $\Lambda_M = 1000\ L_{correct}\ C_M^{-1}$ in ohm^{-1} cm^2 mol^{-1}, $L_{correct} = L_{solution} - L_{solvent}$; first value in acetone, second value in CH_3CN, third value in CH_3NO_2, fourth value in CH_2Cl_2.

Table 2 Oxidation potentials in volts for *tris*(alkylisocyanide)*bis*(tertiaryphosphine)cobalt(I) complexes in acetonitrile solution. Reversible oxidation potentials are designated as $E_{1/2}$ and calculated from $(E_{forward} + E_{reverse})/2$.

Compound		$E_{oxidation}$ (V vs SCE)	E_p (forward) − E_p (reverse) (in mV)
I	$[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$	$E_{1/2} = 0.03V$	(170)
II	$[Co(CNCMe_3)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$	$E_{1/2} = 0.07V$	(170)
III	$[Co(CNCMe_3)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$	$E_{1/2} = 0.08V$	(230)
IV	$[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$	$E_{1/2} = 0.18V$	(250)
V	$[Co(CNCMe_3)_3\{P(C_6H_4Me\text{-}p)_3\}_2]ClO_4$	$E_{1/2} = 0.20V$	(220)
VI	$[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$	$E_{1/2} = 0.24V$	(170)
VII	$[Co(CNCMe_3)_3\{P(CH_2Ph)_3\}_2]ClO_4$	$E_{1/2} = 0.33V$	(100)
VIII	$[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$	0.48V	(Irrev)
IX	$[Co(CNCMe_3)_3\{P(C_6H_4F\text{-}p)_3\}_2]ClO_4$	0.49V	(Irrev)
X	$[Co(CNCMe_3)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$	0.68V	(Irrev)
XI	$[Co(CNCMe_3)_3\{P(C_6H_4CF_3\text{-}p)_3\}_2]ClO_4$	0.75V	(Irrev)
XII	$[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$	$E_{1/2} = 0.12V$	(320)
XIII	$[Co(CNCHMe_2)_3(PPh_3)_2]ClO_4$	$E_{1/2} = 0.20V$	(200)
XIV	$[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]ClO_4$	$E_{1/2} = 0.30V$	(60)
XV	$[Co(CNCHMe_2)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$	0.46V	(Irrev)
XVI	$[Co(CNC_4H_9\text{-}n)_3(PPh_3)_2]ClO_4$	$E_{1/2} = 0.20V$	(155)
XVII	$[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$	$E_{1/2} = 0.22V$	(135)
XVIII	$[Co(CNCH_2Ph)_3(PPh_3)_2]ClO_4$	$E_{1/2} = 0.25V$	(100)

all of the IR spectra supports postulation of deviation from strict D_{3h} trigonal bipyramidal structure in solution, as well as the expected deviation in the solid state. One consideration that may become significant in later discussion is the following. Although all $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes are assumed to be distorted from rigorous D_{3h} symmetry, in solution as well as in the solid state, the extent of distortion undoubtedly varies from one complex to another. Again the $v(-N\equiv C)$ IR pattern may be a gauge of the degree of distortion. As the $[Co(CNR)_3(PR_3)_2]ClO_4$ more closely approximates regular trigonal bipyramidal structure, the $v(-N\equiv C)$ IR pattern approaches a single band. Thus, $[Co(CNCMe_3)_3\{P(C_6H_4F\text{-}p)_3\}_2]ClO_4$, for example, having two relatively strong $v(-N\equiv C)$, would be expected to be more distorted than $[Co(CNC_4H_9\text{-}n)_3(PPh_3)_2]ClO_4$, which shows effectively a single $v(-N\equiv C)$.

Cyclic Voltammetry

Oxidation potential values reported in Table 2 are undoubtedly due to the oxidation of Co(I) to Co(II), the variation in values and reversibility depending on the electron density around the Co, which in turn is governed by the nature of the surrounding ligands and by the structure and geometry of the complexes. Complexes of the type $[Co(CNR)_3(PR_3)_2]^+$, as previously discussed, have at least a distorted trigonal bipyramidal structure, with the three alkylisocyanide ligands in equatorial positions and the two tertiary phosphines in axial positions. Regardless of the precise symmetry notations, the actual orbital occupany for the diamagnetic Co(I) must be $(d_{xz}, d_{yz})^4(d_{xy}, d_{x2\text{-}y2})^4$; $i.e.$, totally filled $3d_{xz}$, $3d_{yz}$, $3d_{xy}$, $3d_{x2\text{-}y2}$ orbitals and empty $3d_{3z2\text{-}r2}$. All of the ligands have σ-donating and π*-accepting bonding ability, but the generally accepted[15,16] order of decreasing $d_\pi \rightarrow \pi^*$ electron-accepting ability is

RNC > PR_3(aryl) > PR_3(alkyl). The strong electron-withdrawing effect of the -CN substituent has been observed[13] to displace $P(CH_2CH_2CN)_3$ into the range of triarylphosphine ligands.

Perhaps the most striking observation that can be made from the list of oxidation potentials (Table 2) is that $E_{1/2}$ is essentially independent of variation of the RNC ligands as long as constant PR_3 is maintained. E_{12} values for the complexes VI, XIII, XVI, XVII, XVIII; spanning the range $[Co(CNR)_3(PPh_3)_2]ClO_4$, R = CMe_3, $CHMe_2$, C_4H_9-n, C_6H_{11}, CH_2Ph, respectively, are all within the narrow range of 0.20 to 0.25V; individual differences may well be within the limits of experimental error. Pairs of $E_{1/2}$ values, for IV, XII; 0.18, 0.12V; VI, XIII; 0.24, 0.20V; VII, XIV; 0.33, 0.30V; and VIII, XV; 0.48, 0.46V; comparing analogous complexes of $CNCMe_3$ and $CNCHMe_2$, are again very similar, although $E_{1/2}$ values for the $CNCMe_3$ complexes do always appear slightly higher than values for the corresponding $CNCHMe_2$ complex.

Previous work is not definitive in assessing $E_{1/2}$ sensitivity to variation in alkylisocyanide ligands. Dart et al.[12] concluded that a significant variation of $E_{1/2}$ exists in relation to the alkylisocyanides in $[Co(CNR)_3(PPh_3)_2]PF_6$ complexes (in CH_2Cl_2), $E_{1/2}$ increasing in the order R = Me (0.12) < Pr^i (0.20) < Bu^t (0.29V). This is in contrast to their own previous work,[17] however, and to $E_{1/2}$ values reported[18] for $[M(CO)_4L_2]$, M = Cr, Mo, W; L = $CNCHMe_2$, $CNCMe_3$; showing very small differences. For $[PtL_2(CNR)Me]^+$ (L = $PMePh_2$, PMe_2Ph) it has been suggested[19] that the σ-donar strength of CNR is essentially independent of the inductive properties of R; so variation in $E_{1/2}$ may therefore depend only on the relatively slight differences in π*-accepting ability of the various alkylisocyanides. Alternately, σ-donation from equatorial trigonal bipyramidal positions to paramagnetic Co(I) may be ineffective in general because the $3d_{xy}$, $3d_{x2-y2}$ orbitals are filled. In simple Valence Bond theory, empty orbitals on the metal must be available to accommodate σ-donation from the equatorial ligands; $3d_{3z2-r2}$ has the right symmetry, but insufficient projection in the xy-plane to be used effectively, and $3d_{xy}$, $3d_{x2-y2}$ are filled, so only 4s and $4p_x$, $4p_y$ are effectively available. Interactions of these high-energy virtual orbitals on Co(I) may stabilize the σ-bonding (ligand) MO's, but should have little effect on the electron density around Co. However, $3d_{3z2-r2}$ will bond effectively with σ-donation from axial ligands. Considering the several interpretations, it may not be surprising that the $E_{1/2}$ values reported do not show definite correlation, or even significant sensitivity, to the alkylisocyanide ligands.

Variation of the tertiary phosphine ligands in the axial positions of $[Co(CNR)_3(PR_3)_2]ClO_4$ has pronounced effect on the $E_{1/2}$ values. Oxidation potentials range from + 0.03V, for PR_3 = $P(NMe_2)_3$, to + 0.75V (irreversible), for PR_3 = $P(C_6H_4CF_3$-$p)_3$, and increase steadily as PR_3 (in $[Co(CNCMe_3)_3(PR_3)_2]ClO_4$, cpds I–XI) is varied: $P(NMe_2)_3$< $P(C_4H_9$-$n)_3 \approx$ $P(C_6H_{13}$-$n)_3$ < $P(C_6H_4OMe$-$p)_3$ < $P(C_6H_4Me$-$p)_3$ < PPh_3 < $P(CH_2Ph)_3$ < $P(C_6H_4Cl$-$p)_3$ ≈ $P(C_6H_4F$-$p)_3$ < $P(CH_2CH_2CN)_3$ < $P(C_6H_4CF_3$-$p)_3$. The same trend for $E_{1/2}$, PR_3 = $P(C_6H_4OMe$-$p)_3$ < PPh_3 < $P(CH_2Ph)_3$ < $P(C_6H_4Cl$-$p)_3$ is seen in $[Co(CNCHMe_2)_3(PR_3)_2]ClO_4$ (cpds XII–XV). As the electron-donating ability of the P atom decreases, the oxidation potential of Co(I) increases. The ν(-N≡C) IR data have been used[4,5,13] to establish relative decreasing $d_\pi \rightarrow \pi^*$ accepting ability as $P(C_6H_4Cl$-$p)_3$ < PPh_3 ≥ $P(CH_2CH_2CN)_3$ > $P(C_6H_4OMe$-$p)_3$ > $P(CH_2Ph)_3$ > $P(NMe_2)_3$ > $P(C_4H_9$-$n)_3$ ≈ $P(C_6H_{13}$-$n)_3$. Poor quality IR data somewhat equivocally rank $P(C_6H_4CF_3$-$p)_3$ >

$P(C_6H_4F-p)_3 \approx P(C_6H_4Cl-p)_3 > PPh_3 > P(C_6H_4Me-p)_3 > P(C_6H_4OMe-p)_3$ in this present work, which is the intuitively expected order.

The $E_{1/2}$ values (Table 2) and $v(-N\equiv C)$ IR data are somewhat in contradiction regarding $P(CH_2CH_2CN)_3$, $P(CH_2Ph)_3$, and $P(NMe_2)_3$. $E_{1/2}$ values suggest that $P(CH_2Ph)_3$ and $P(CH_2CH_2CN)_3$ are even stronger π^*-accepting (weaker σ-donating) and $P(NMe_2)_3$, weaker, than indicated by $v(-N\equiv C)$ IR data. $P(NMe_2)_3$ should be very sterically hindered, due to large cone angle,[9] and may be out of place for this reason; electronic spectra[4] suggest π^*-accepting ability $P(C_6H_{13}-n)_3$ > $P(NMe_2)_3$, more in accord with $E_{1/2}$ values. Although increased π^*-accepting ability/decreased σ-donating ability are usually considered together as one trend, possibly $v(-N\equiv C)$ IR data are more sensitive to the π^*-accepting aspect and $E_{1/2}$ more dependent on σ-donation. Changes in $v(-N\equiv C)$ should directly reflect increased/decreased electron population in π^* orbitals of the $R-N\equiv C$ (i.e. changes in $d_\pi \rightarrow \pi^*$ acceptance), but only indirectly respond to changes in σ-donation by RNC, where increased σ-donation should cause a "tightening" of the $C\equiv N$ (i.e. increased frequency). In approximately trigonal bipyramidal $[Co(CNR)_3(PR_3)_2]^+$ both PR_3 and CNR should be capable of effective $d_\pi \rightarrow \pi^*$ acceptance (through filled $3d_{xz}$, $3d_{yz}$) but only the PR_3, in axial positions, should be able to effectively σ-donate electron density to the Co, through the empty $3d_{3z^2-r^2}$ orbital. Thus the $E_{1/2}$ values are highly sensitive to changes in the σ-donating ability of the PR_3 ligands, the oxidation potential increasing sharply as the electron-donating ability of P decreases.

Voltammograms representing the oxidation of Co(I) to Co(II) were generally reversible or at least *quasi*-reversible, the separation between forward and reverse peaks being shown in Table 2. Compounds VIII, IX, X, XI, and XV (containing $PR_3 = P(C_6H_4Cl-p)_3$, $P(C_6H_4F-p)_3$, $P(CH_2CH_2CN)_3$, $P(C_6H_4CF_3-p)_3$), having the strongest electron-withdrawing substituents on P and consequently the highest $E_{1/2}$ values, are definitely irreversible. Representative voltammograms for reversible behaviour ($[Co(CNCMe_3)_3\{P(CH_2Ph)_3\}_2]ClO_4$) and irreversible behaviour ($[Co(CNCMe_3)_3\{P(C_6H_4Cl-p)_3\}_2]ClO_4$) are shown in Figure 1. There appears to be a definite correlation between *quasi*-reversible/irreversible behaviour and the appearance (shape) of the $v(-N\equiv C)$ IR pattern. Compounds with irreversible voltammograms tend to show at least two reasonably-strong $v(-N\equiv C)$ IR bands, suggesting significant deviation from regular trigonal bipyramidal structure, while compounds showing *quasi*-reversible behaviour tend to have $v(-N\equiv C)$ IR patterns more closely approximating a single band (expected for rigorous D_{3h} symmetry). The only $[Co(CNR)_3(PR_3)_2]^{2+}$ complex of this type to be previously characterized,[20] $[Co(CNCHMe_2)_3\{P(C_6H_4OMe-p)_3\}_2](ClO_4)_2$, appears to be regular trigonal bipyramidal in solution. A possible explanation for the *quasi*-reversible/irreversible behaviour of the voltammograms, then, is that the Co(I) complex, with a distorted trigonal bipyramidal structure, is oxidized to a Co(II) complex with a regular trigonal bipyramidal structure in solution. As the solution structure of the Co(I) complex more closely approximates D_{3h} symmetry, the voltammogram more closely approaches reversible behaviour. This is an alternative explanation to that of Hanzlik *et al.*,[6] who suggested that Co(I), in a regular trigonal bipyramidal structure, is oxidized to Co(II), in a regular trigonal bipyramidal structure that rapidly undergoes chemical change to a square pyramidal (C_{2v}) solution structure.
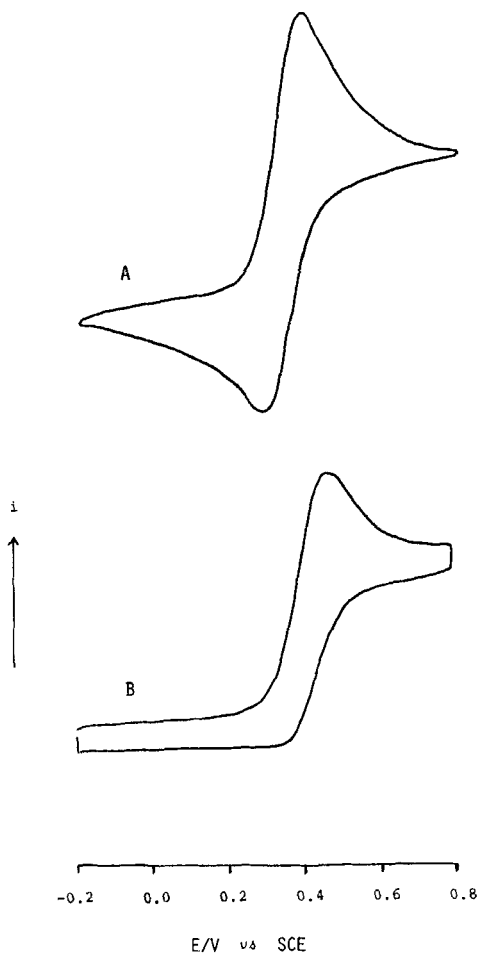
Figure 1   Cyclic voltammograms of (a) $[Co(CNCMe_3)_3\{P(CH_2Ph)_3\}_2]ClO_4$, Compound VII, and (b) $[Co(CNCMe_3)_3\{P(C_6H_4Cl-p)_3\}_2]ClO_4$, Compound VIII. Solutions are in acetonitrile containing 0.1 M (TBAH) supporting electrolyte, run at 0.1 V/s scan rate.

Acknowledgements

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