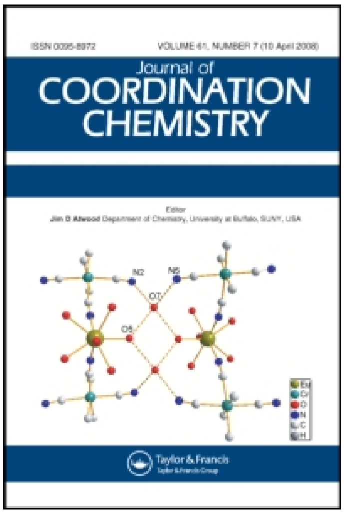

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SYNTHESIS AND CHARACTERIZATION OF *TRIS*(ALKYLISOCYANIDE) *BIS*(TRIARYL-PHOSPHINE)COBALT(II) COMPLEXES

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SYNTHESIS AND CHARACTERIZATION OF *TRIS*(ALKYLISOCYANIDE)*BIS*(TRIARYLPHOSPHINE)COBALT(II) COMPLEXES

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A series of complexes having the general formula, $[Co(CNR)_3(PR_3)_2]X_2$, $X = ClO_4$, BF_4 with $CNR = CNCMe_3$, $CNCHMe_2$, CNC_6H_{11}, $CNCH_2Ph$ and $PR_3 = PPh_3$, $P(C_6H_4Me\text{-}p)_3$, $P(C_6H_4OMe\text{-}p)_3$ has been synthesized and characterized. Synthesis can be achieved by reaction of $[Co(CNR)_4(AsPh_3)_2]X_2$ complexes with controlled excess of PR_3 ligands, and by $AgClO_4$/$AgBF_4$ oxidation of the $[Co(CNR)_3(PR_3)_2]X$ complexes. The latter procedure is preferable. Alternate syntheses of the $[Co(CNR)_3(PR_3)_2]X$ complexes have also been employed. Five-coordinate Co(II) complexes have not been obtained using $CNCMe_3$ with $P(C_6H_4Me\text{-}p)_3$ ligands, $CNCH_2Ph$ with $P(C_6H_4OMe\text{-}p)_3$ ligands, or $CNC_4H_9\text{-}n$ with PPh_3 ligands. $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ produced only $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ upon forced oxidation with excess $AgClO_4$. $[Co(CNR)_3(PR_3)_2]X_2$ complexes appear to undergo varying degrees of distortion from regular (*i.e.*, D_{3h} symmetry) axially-disubstituted trigonal bipyramidal coordination in the solid state, as evidenced by $\nu(-N{\equiv}C)$ IR patterns, but to assume regular trigonal bipyramidal coordination in solution. Effective magnetic moments indicate one-electron paramagnetism, and solution electronic spectra are compatible with trigonal bipyramidal coordination.

Keywords: Alkylisocyanide; triarylphosphine; cobalt(II) complexes; low-spin complexes

INTRODUCTION

Reactions of triarylphosphines and trialkylphosphines with Co(II)-alkylisocyanide complexes are well-established as reduction/ligand substitution in which the disubstituted five-coordinate Co(I) complexes, $[Co(CNR)_3(PR_3)_2]ClO_4$, are recovered usually in good yields.[1–7] Reactions with $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ and $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ have been extensively investigated in this laboratory.[5,6] In one instance, however, a Co(II) complex, $[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$, was also recovered, but only as a minor product.[8] Cyclic voltammograms in CH_3CN for $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes with both triarylphosphine and trialkylphosphine ligands often exhibit *quasi*-reversible behaviour ($\Delta E_p = 60-250\,mV$),[9] suggesting a finite existence of the $[Co(CNR)_3(PR_3)_2]^{2+}$ species. A stable, five-coordinate Co(II) complex with alkylisocyanide and triarylphosphine ligands, $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$, has recently been synthesized, both by reaction of excess PPh_3 with $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ and by oxidation of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$ with $AgClO_4$.[10]

This paper reports the synthesis and characterization of a series of $[Co(CNR)_3(PR_3)_2](ClO_4)_2$ complexes, systematically prepared with the alkylisocyanides, $CNCMe_3$, CNC_6H_{11}, $CNCHMe_2$, and $CNCH_2Ph$, and the triarylphosphines, PPh_3, $P(C_6H_4Me\text{-}p)_3$, and $P(C_6H_4OMe\text{-}p)_3$. Limits to the range of stability for the Co(II) oxidation state with regard to the triarylphosphine ligand are also investigated.

EXPERIMENTAL

Reagents

Commercially available alkylisocyanides, $CNCMe_3$, CNC_6H_{11}, $CNCHMe_2$, $CNCH_2Ph$, and $CNC_4H_9\text{-}n$ (Strem Chemicals, Fluka, and Aldrich) were used without redistillation. $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$, $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$, and $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ were synthesized as previously reported.[5,6,11,12] Commercially available triarylphosphines, PPh_3, $P(C_6H_4Me\text{-}p)_3$, $P(C_6H_4OMe\text{-}p)_3$, and $P(C_6H_4Cl\text{-}p)_3$ (Strem Chemicals) were used without recrystallization. Anhydrous $AgClO_4$ and $AgBF_4$ were supplied by Strem Chemicals. Solvents used for IR and electronic spectra, CH_2Cl_2, CF_3CH_2OH, and CH_3NO_2, were of the purest grade commercially available. Anhydrous diethylether was filtered through an alumina column immediately before use.

Instrumentation

IR spectra were recorded on a Perkin Elmer 2000 FT-IR spectrophotometer. Solution electronic spectra were recorded on a Shimadzu UV-2101 spectrometer, over the range 900–200 nm, and on a Perkin Elmer Lambda 12 spectrometer, over the range 1100–600 nm. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey Alfa magnetic susceptibility balance. C, H, and N elemental analyses were obtained commercially and performed using a Carlo Erba CHN-O/S elemental analyzer, model 1106. Co was analysed for samples dissolved in BDH HiperSolv methanol for HPLC using a Varian SpectrAA.10 atomic absorption spectrometer operating at 304.4 nm with 0.5 nm slit width. Standards were prepared from $(CH_3COO)_2Co \cdot 4H_2O$ analysed reagent in HPLC-grade methanol over the range 25–45 ppm Co.

$[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$

A 500 mg sample of $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ was dissolved in 3.5 cm^3 of CH_2Cl_2, filtered through cotton using 0.5 cm^3 of CH_2Cl_2 as rinse, and chilled in ice. Then 291 mg of $P(C_6H_4Me\text{-}p)_3$ (1 : 2.5 Co : P mol ratio) dissolved in 1.0 cm^3 of CH_2Cl_2 was added dropwise while the solution was stirred. The solution colour changed from dark green, through yellow-brown, to dark red-brown as the ligand was added. The solution was allowed to stand for 3 min at room temperature, after which ether was added dropwise. Initial precipitation of a rust-red coloured product was observed after 16.0 cm^3 of ether had been added. A total of 22.0 cm^3 of ether was added, and the mixture was chilled in ice for 45 min. The brick-red microcrystalline product was filtered from an orange-coloured solution, and washed twice with 2.0 cm^3 portions of ether. The crude product (265 mg, 58% yield) was dissolved in 1.5 cm^3 of CH_2Cl_2, filtered through cotton, and precipitated by dropwise addition of 3.5 cm^3 of ether. After chilling in ice (45 min), the bright red-brown microcrystals were filtered and washed twice with 2.0 cm^3 portions of ether. Yield: 220 mg (83% recovery; 48% overall yield).

Addition of 2.5 cm^3 of ether to the original filtrate, and overnight refrigeration, afforded a second crop of mixed red-brown and dark green microcrystals (118 mg). Nujol IR spectra confirmed the presence of $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ and unreacted $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$, but the absence of any $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2]ClO_4$, thus increasing the apparent yield of crude product by 24–26%.

$[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$

A 500 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 4.0 cm^3 of CH_3CN, filtered through cotton using 0.5 cm^3 of CH_3CN as rinse, and chilled in ice. Then, 1.078 g of PPh_3 (1 : 5 Co : P mol ratio) dissolved in

1.0 cm^3 of CH_2Cl_2 was added dropwise while the solution was stirred. The dark blue solution rapidly became red-orange during ligand addition. As soon as ligand addition was completed, diethylether was added dropwise at room temperature. Initial precipitation of a golden-yellow product was observed after 5.0 cm^3 of ether had been added. A total of 15.0 cm^3 of ether was added, and the reaction mixture was chilled in ice for 45 min. The golden-yellow microcrystalline product was filtered from a dark orange coloured solution, and washed twice with 2.0 cm^3 portions of ether. Yield: 261 mg; Nujol IR spectra indicated that this first crop was a mixture of $[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$ and $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$.

The original filtrate was partially evaporated at room temperature under a fume hood, re-dissolved in 1.0 cm^3 of CH_2Cl_2, and filtered through cotton. Dropwise addition of 12.5 cm^3 of ether induced precipitation of an orange solid. After thorough chilling in ice (1 h), the pale orange microcrystals were filtered from the orange solution and washed twice with 2.0 cm^3 portions of ether. Yield: 401 mg (52%); Nujol IR spectra indicated that this crop was only $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$.

The first crop was dissolved in 2.0 cm^3 of CH_2Cl_2, three drops of $N_2H_4 \cdot H_2O$ were added, and the resulting mixture was vigorously agitated for several minutes before decantation of the CH_2Cl_2 phase from a small aqueous phase (mostly adhering to the walls of the flask) and filtration through cotton. Dropwise addition of 10.0 cm^3 of ether and chilling in ice (45 min) afforded a crop of golden-yellow microcrystalline product (209 mg), which was combined with the original second (crude) crop. Combined Co(I) product (*i.e.*, 610 mg; 80% yield) was then dissolved in 2.0 cm^3 of CH_2Cl_2, filtered through cotton, precipitated by dropwise addition of 6.0 cm^3 of ether, chilled in ice (45 min), filtered and washed twice with 2.0 cm^3 portions of ether. Yield: 596 mg (98% recovery; 78% overall yield).

$[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$

A 500 mg sample of $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$ was dissolved in 1.5 cm^3 of CH_2Cl_2 and filtered through cotton using 0.5 cm^3 of CH_2Cl_2 as rinse. Then 110 mg of crushed $AgClO_4$ (1 : 1.10 Co : Ag mol ratio) was added, and the heterogeneous reaction mixture was stirred vigourously for 15 min. The white $AgClO_4$ blackened upon contact with the solution, and an Ag mirror formed on the bottom and walls of the flask. The solution was decanted from the residual solid and filtered through cotton twice using 0.5 cm^3 of CH_2Cl_2 rinse each time. Dropwise addition of ether to this clear, dark yellow solution caused an almost immediate precipitation of bright yellow solid. A total of 5.0 cm^3 of ether was added, and the reaction mixture was chilled in ice for 45 min. The yellow product was filtered from a yellow-brown solution, and washed twice with 1.5 cm^3 portions of ether. The crude product (395 mg; 72% yield) was dissolved in 3.0 cm^3 of CH_2Cl_2, filtered through cotton, and precipitated by dropwise addition of 5.0 cm^3 of ether. After chilling in ice (45 min), the canary-yellow microcrystals were filtered from the pale orange filtrate and washed twice with 1.5 cm^3 portions of ether. Yield: 296 mg (75% recovery; 54% overall yield). Upon overnight refrigeration, a second crop of darker yellow compound (71 mg) was recovered, but Nujol IR indicated a mixed Co(II)–Co(I) composition so this small sample was discarded.

$[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$

A 1.000 g sample of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ was dissolved in 3.0 cm^3 of CH_2Cl_2, filtered through cotton using additional 0.5 cm^3 of CH_2Cl_2 as rinse, and chilled in ice. Next, 1.875 g of $P(C_6H_4OMe\text{-}p)_3$ (1 : 3.5 Co : P mol ratio) dissolved in 5.0 cm^3 of CH_2Cl_2 was added dropwise while the solution was stirred. The dark blue solution took on a blood-red colour as the ligand was added. Then, six drops of $N_2H_4 \cdot H_2O$ were added, and the mixture was stirred vigourously for 1.5 min, while the colour changed to the red-orange (bromine-colour) characteristic of Co(I) solutions. The CH_2Cl_2 phase was decanted and twice filtered through cotton. Dropwise addition of ether effected precipitation after addition of 15.0 cm^3 of ether. A total of 18.0 cm^3 of ether was added, and the reaction mixture was chilled in ice for 1.5 h. The golden-yellow microcrystalline product was filtered from a bright orange-coloured filtrate, and washed twice with 2.0 cm^3 portions of ether. Yield: 1.475 g (86%). The crude product was dissolved in 2.5 cm^3 of CH_2Cl_2, filtered through cotton, and precipitated by dropwise addition of 6.0 cm^3 of ether. After chilling in ice (45 min), the golden-yellow microcrystals were filtered from a pale orange solution and washed twice with 2.0 cm^3 portions of ether. Yield: 1.410 g (96% recovery; 82.5% overall yield).

RESULTS AND DISCUSSION

Physical properties of the $[Co(CNR)_3(PR_3)_2]X_2$, $X = ClO_4$, BF_4 complexes in the solid state are summarized in Table I; some physical properties in the solution state are listed in Table II; typical $\nu(-N{\equiv}C)$ IR patterns in Nujol mull and in solution are illustrated in Figure 1; diamagnetic

TABLE I Solid state properties of *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(II) complexes

Complex/Colour/m.p.	$\nu(-N{\equiv}C)$[a]	$\chi_g \times 10^6/\mu_{eff}$	*Elemental analysis, found/calc.*			
			C	*H*	*N*	*Co*
$[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$ Canary yellow 178–182°C (dec)	2178 vs ≈2205 vw(sh) ≈2150 vw(sh)	1.76 ± 0.03 2.45 ± 0.02 BM	58.84 59.37	5.63 5.57	3.98 4.07	5.10 5.71
$[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ Golden yellow 195–200°C (dec)	2190 vs 2208 w(sh) ≈2155 vw(sh)	0.850 ± 0.018 1.92 ± 0.01 BM	61.70 61.69	5.73 5.72	3.76 3.70	5.00 5.31
$[Co(CNCHMe_2)_3(PPh_3)_2](ClO_4)_2 \cdot 0.5CH_2Cl_2$ Golden yellow 192–200°C (dec)	2190 vs ≈2157 vw(sh)	2.92 ± 0.04 2.89 ± 0.02 BM	56.52 56.44	5.11 5.08	4.05 4.07	5.78 5.71
$[Co(CNCH_2Ph)_3(PPh_3)_2](BF_4)_2 \cdot 0.3CH_2Cl_2$ Yellow-brown 188–192°C (dec)	2193 vs 2209 s	1.053 ± 0.007 2.07 ± 0.01 BM	64.23 63.87	4.76 4.59	3.65 3.71	I[b] 5.20
$[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2 \cdot 0.8CH_2Cl_2$ Brick red 196–198°C (dec)	2195 vs ~2178 sh	2.05 ± 0.08 2.77 ± 0.04 BM	60.52 60.72	6.21 6.12	3.29 3.33	4.53 4.67
$[Co(CNCHMe_2)_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2 \cdot 0.7CH_2Cl_2$ Yellow-brown 180–186°C (dec)	2197 vs	1.77 ± 0.06 2.47 ± 0.03 BM	57.80 57.97	5.70 5.73	3.71 3.71	4.71 5.20
$[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2 \cdot 0.6CH_2Cl_2$ Rust red 152–155°C (dec)	2177 vs	1.54 ± 0.04 2.49 ± 0.02 BM	54.76 54.78	5.70 5.60	3.19 3.33	4.31 4.67
$[Co(CNC_6H_{11})_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2 \cdot 0.5CH_2Cl_2$ Flesh pink 88–95°C (dec)	2187 vs ≈2208 w(sh)	2.44 ± 0.12 3.08 ± 0.06 BM	57.15 57.23	5.79 5.75	3.10 3.15	4.30 4.42
$[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$ Rust red 198–206°C (dec)	2199 vs ≈2168 w(sh)	1.51 ± 0.05 2.40 ± 0.03 BM	55.05 55.43	5.46 5.43	3.33 3.59	5.11 5.04

[a] Values for $\nu(-N{\equiv}C)$ are given in cm^{-1}; s = strong, w = weak, v = very, sh = shoulder; [b] Insufficient solubility in CH_3OH for accurate analysis.

TABLE II Solution properties of *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(II) complexes

Complex	$\nu(-N\equiv C)$ *infrared*[a]			*Electronic spectra*[b]	
	CH_2Cl_2	CF_3CH_2OH	CH_3NO_2	CH_2Cl_2	CF_3CH_2OH
$[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$	2181 vs	2179 vs	2181 vs	925 br (263)	~922 br (152)
	[~2147 w(sh)]	[~2128 w]	[~2138 w]	457 sp (694)	462 sp (670)
	~2110 w	[~2088 w]	2094 m	352 sh (11,600)	~353 sh (13,700)
	~2075 w	[~2055 w]	~2070 w	331 (12,600)	330 (15,200)
				~276 sh (12,900)	~277 sh (13,800)
				229 (46,500)	~229 sh (51,000)
$[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$	2192 vs	2187 vs	2190 vs	928 br (195)	932 br (175)
	[~2154 vw]		[~2137 w]	455 (925)	463 (780)
	~2105 vw		~2098 m	~351 (9750)	~356 (12,500)
	~2076 vw		~2073 m	327 (10,500)	329 (13,500)
				~265 br (22,000)	~282 sh (13,000)
					~273 sh (13,500)
					229.5 sh (44,500)
$[Co(CNCHMe_2)_3(PPh_3)_2](ClO_4)_2$	2194 vs	2190 vs	2193 vs	932 br (305)	932 br (275)
	[~2157 w]	[~2159 vw]	[~2166 vw(sh)]	456 sp (963)	464 sp (800)
	[~2143 w]	[~2115 w]	[~2136 w]	353 (11,800)	358 (13,300)
		[~2082 w]	~2096 w	329 (12,500)	330 (13,800)
		[~2050 w]	~2074 w	~275 sh (13,900)	279 sh (13,200)
				230 (53,600)	229 sh (46,700)
$[Co(CNCH_2Ph)_3(PPh_3)_2](BF_4)_2$	~2196 w	2197 vs	2201 s	≈914 br (195)	≈920 br (172)
	2090 vs[c]	[~2163 w]	[~2170 w]	462 sp (1140)	471 sp (1020)
		[~2126 w]	[~2134 w(sh)]	358 (11,200)	362 (12,100)
		[~2087 w]	2099 m	330 (11,000)	332 (11,300)
		[~2053 w]	~2075 w(sh)	~270 sh (18,100)	~283 sh (12,200)
					≈230 sh (50,000)
$[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$	2189 vs	2185 vs	2188 vs	931 br (324)	933 br (195)
	[~2160 vw(sh)]	[~2129 w]	~2083 w	475 sp (1000)	482 sp (890)
	~2085 vw	[~2089 w]		368 (12,900)	370 (19,400)
		[~2055 w]		344 (12,100)	339 (18,300)
				~288 sh (13,000)	288.5 (21,600)
				236 (60,900)	235 sh (104,000)

TABLE II (*Continued*)

Complex	$\nu(-N{\equiv}C)$ *infrared*[a]			*Electronic spectra*[b]	
	CH_2Cl_2	CF_3CH_2OH	CH_3NO_2	CH_2Cl_2	CF_3CH_2OH
$[Co(CNCHMe_2)_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$	2191 vs	2188 vs	2191 vs	928 br (327)	929 br (294)
	[$\sim$2155 vw]	[$\sim$2158 w]	[$\sim$2137 w]	475 sp (1090)	482 sp (901)
		[$\sim$2122 w]	$\sim$2100 w	368 (13,400)	370 (14,500)
		[$\sim$2083 w]	$\sim$2070 w	344 sh (12,700)	343 sh (13,100)
		[$\sim$2050 w]		$\sim$288 sh (13,300)	290 sp (13,100)
				235 (61,400)	236 sh (64,400)
$[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$	2177 vs	2177 vs	2177 vs	926 br (322)	$\sim$928 br (197)
	[$\sim$2144 w]	[$\sim$2124 vw]	[$\sim$2145 vw]	$\approx$545 sh (570)	$\approx$530 sh (750)
		[$\sim$2083 w]	$\sim$2090 vw	$\approx$490 sh (1030)	$\approx$480 sh (1200)
		[$\sim$2049 w]	$\sim$2060 vw	390 sp (16,100)	389 sp (18,600)
				350 sh (10,900)	349 sp (11,900)
				305 sh (12,500)	305 (13,400)
				251 (89,700)	$\approx$283 sh (17,800)
					251 sp (91,000)
$[Co(CNC_6H_{11})_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$	2186 vs	2183 vs	2186 vs	927 br (367)	932 br (349)
		[$\sim$2159 w(sh)]		$\approx$520 sh (1020)	$\approx$535 sh (770)
		[$\sim$2124 w]		389 sp (14,900)	391 sp (14,400)
		[$\sim$2083 w]		351 sh (10,500)	350 sh (9600)
		[$\sim$2049 w]		302 sh (11,900)	305 (10,400)
				251 (82,500)	250 (71,900)
$[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$	2189 vs	2186 vs	2189 vs	922 br (275)	930 br (302)
	[$\sim$2153 vw]	[$\sim$2158 w]	[$\sim$2137 w]	$\approx$660 sh (70)	$\approx$540 sh (830)
		[$\sim$2123 w]	$\sim$2100 w	$\approx$510 sh (760)	390 sp (15,300)
		[$\sim$2083 w]	$\sim$2073 w	389 (6700)	351 sh (10,200)
		[$\sim$2049 w]		343 (6200)	305 sh (10,900)
				$\approx$280 sh (23,000)	250 (69,000)
				250 (66,000)	

[a] Values for $\nu(-N{\equiv}C)$ are given in cm^{-1}; s = strong, w = weak, v = very, sh = shoulder, sp = sharp; probable solvent bands are shown in brackets; [b] The $\lambda_{max}(\epsilon)$ values are given in nm ($M^{-1}\,cm^{-1}$); [c] Probable Co(I) complex due to reduction in this solvent.

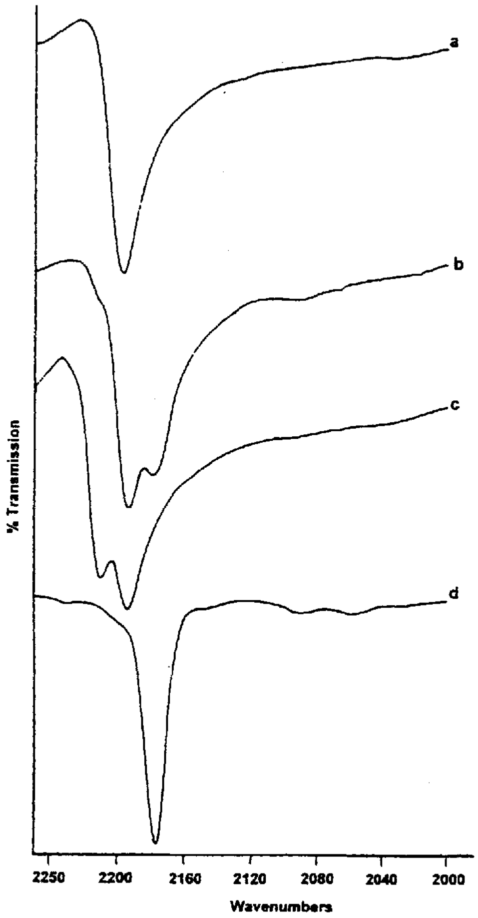

FIGURE 1 Representative $\nu(-N{\equiv}C)$ IR patterns for the $[Co(CNR)_3(PR_3)_2]X_2$ complexes, a: $[Co(CNCHMe_2)_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ (in Nujol); b: $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ (in Nujol); c: $[Co(CNCH_2Ph)_3(PPh_3)_2](BF_4)_2$ (in Nujol); d: $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$ (in CH_3NO_2).

values for the alkylisocyanide and triarylphosphine ligands are listed in Table III.

Synthesis of the Complexes

Although the five-coordinate *tris*(alkylisocyanide)*bis*(triarylphosphine)-cobalt(II) complexes can be synthesized by either reaction of triarylphosphines with the appropriate $[Co(CNR)_4(AsPh_3)_2]X_2$ complexes, or by

TABLE III Measured diamagnetic susceptibilities

Formula	$\chi_g \times 10^9$	$\chi_M \times 10^6$
$CNCMe_3$	-647 ± 11	-53.8 ± 0.9
CNC_6H_{11}	-637 ± 8	-69.5 ± 0.9
$CNCHMe_2$	-664 ± 9	-45.9 ± 0.6
$CNCH_2Ph$	-579 ± 4	-67.8 [illegible] 0.4
$P(C_6H_4Me\text{-}p)_3$	-655 ± 12	-199 ± 4
$P(C_6H_4OMe\text{-}p)_3$	-571 ± 5	-201 ± 2

$AgClO_4/AgBF_4$ oxidation of the appropriate $[Co(CNR)_3(PR_3)_2]X$, $X = ClO_4$, BF_4 complexes,[10] the latter procedure is superior as a general method, and therefore was employed for most of the syntheses in this investigation. Synthesizing the $[Co(CNR)_3(PR_3)_2]X_2$ complexes from $[Co(CNR)_4(AsPh_3)_2]X_2$, while keeping both the formation of $[Co(CNR)_3(PR_3)_2]X$ and the amount of unreacted $[Co(CNR)_4(AsPh_3)_2]X_2$ to a minimum, requires different, experimentally-established, individual reaction conditions for each PR_3 and CNR ligand used, rendering this procedure tedious. This method was used to synthesize $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$, however, and the reaction conditions were adjusted to leave unreacted $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ starting material in preference to the formation of $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2]ClO_4$, which would have occurred for longer reaction periods and/or a higher mol ratio of PR_3 to Co(II). Unreacted $[Co(CNR)_4(AsPh_3)_2](ClO_4)_2$ is, in general, more easily removed from $[Co(CNR)_3(PPh_3)_2](ClO_4)_2$ than is $[Co(CNR)_3(PPh_3)_2]ClO_4$.

The reported preparation of $[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$ by $AgClO_4$ oxidation of $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$, in 1 : 1.10 Co : Ag mol ratio, is typical of this method of synthesis. Slight excess of Ag^+ and sufficient reaction times are necessary for total (or near total) oxidation of the Co(I), but large excesses of Ag^+ especially, and prolonged reaction times to a lesser extent, tend to decrease yield of the Co(II) complex. It is possible that some oxidation of the alkylisocyanide and/or triarylphosphine ligands takes place during this reaction, increasingly so with excess Ag^+ and/or prolonged reaction time. In the case of the attempted oxidation of $[Co(CNC_4H_9\text{-}n)_3(PPh_3)_2]ClO_4$ (see later section), formation of $[Co(OPPh_3)_4](ClO_4)_2$ is clear evidence for the oxidation of the PR_3 ligands. Competing oxidation of PR_3 and/or CNR could account for the rather modest yields of the Co(II) complexes.

The $[Co(CNR)_3(PR_3)_2]X$, $X = ClO_4$, BF_4 complexes are readily prepared through reaction of excess triarylphosphine ligand with the pure alkylisocyanide-Co(II) complexes, either previously isolated in the solid state as

$[Co(CNCMe_3)_4H_2O](ClO_4)_2$,[5] $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$,[6] and $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$,[11] or reacted *in situ* for $[Co(CNC_6H_{11})_5](ClO_4)_2$ and $[Co(CNC_4H_9\text{-}n)_5](ClO_4)_2$. Incomplete reduction of Co(II) to Co(I) is achieved in many instances, so a minor product of $[Co(CNR)_3(PR_3)_2]X_2$ may be obtained with the crude $[Co(CNR)_3(PR_3)_2]X$ product. The Co(II) complex remaining unreduced in the sample can be reduced to $[Co(CNR)_3(PR_3)_2]X$ with $N_2H_4 \cdot H_2O$, however, either by treating the isolated crude product with a small amount of $N_2H_4 \cdot H_2O$, as in the reported synthesis of $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$, or by adding several drops of $N_2H_4 \cdot H_2O$ to the initial reaction mixture, as in the reported synthesis of $[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$. The latter procedure is shorter, and tends to produce better yield.

Attempts to oxidize $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ to $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2](ClO_4)_2$ have thus far been unsuccessful. Upon reaction with $AgClO_4$ using the usual 1 : 1.1 Co : Ag mol ratio, only unreacted Co(I) starting material was recovered. Increasing the Ag : Co mol ratio to 1.25 : 1 and changing the first solvent from CH_3CN to CF_3CH_2OH produced a small amount of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ along with unreacted Co(I) starting material, and reaction with $AgClO_4$ in 1 : 2 Co : Ag mol ratio only increased the still mediocre yield of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$. Driving the Co(I) oxidation with excess Ag^+ and longer reaction times still apparently cannot produce the desired $[Co(CNR)_3(PR_3)_2]^{2+}$ complex, or that complex once formed is insufficiently stable to allow isolation, decomposing instead to the pure alkylisocyanide complex of Co(II). The irreversibility of the oxidative cycle for $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$[9] actually forecasts this problem in the synthesis. Reaction of $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ with excess $P(C_6H_4Cl\text{-}p)_3$ also produced only unreacted starting material in good yield (52%). Thus, it appears that the stability of the $[Co(CNR)_3(PR_3)_2]^{2+}$ complexes becomes limited for triarylphosphine ligands with electron-withdrawing substituents, as well as the corresponding Co(I) complexes simply becoming increasingly difficult to oxidize, as evidenced by their increasing oxidation potentials.[9]

Five-coordinate $[Co(CNR)_3(PR_3)_2]^{2+}$ complexes with $CNCMe_3$ and $P(C_6H_4Me\text{-}p)_3$, and with $CNCH_2Ph$ and $P(C_6H_4Me\text{-}p)_3$ or $P(C_6H_4OMe\text{-}p)_3$ ligands are absent in Tables I and II; the chemistry in these instances is different and still under investigation. The $[Co(CNCMe_3)_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ complex may exist, but the six-coordinate Co(II) species, $[Co(CNCMe_3)_4\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$, is more stable in solution and appears to be the major product in $AgClO_4$ oxidation of $[Co(CNCMe_3)_3\{P(C_6H_4Me\text{-}p)_3\}_2]ClO_4$. At present there is no explanation for this apparently anomalous behaviour. With $CNCH_2Ph$ and $P(C_6H_4OMe\text{-}p)_3$ ligands, an unexpected apparent disproportionation of Co(II) leads to the products $[Co(CNCH_2Ph)_3\{P(C_6H_4OMe\text{-}p)_3\}_3]BF_4$ and $[Co(CNCH_2Ph)_4\{P(C_6H_4OMe\text{-}p)_3\}_2](BF_4)_3$, which are currently under investigation. The high solubility of $[Co(CNCH_2Ph)_3\{P(C_6H_4Me\text{-}p)_3\}_2]BF_4$ has restricted study, but it appears that a $[Co(CNCH_2Ph)_3\{P(C_6H_4Me\text{-}p)_3\}_2](BF_4)_2$ complex is formed.

Attempts to synthesize $[Co(CNC_4H_9\text{-}n)_3(PR_3)_2](ClO_4)_2$ complexes has been limited to unsuccessful cases using the PPh_3 ligand. After apparent oxidation of $[Co(CNC_4H_9\text{-}n)_3(PPh_3)_2]ClO_4$ with $AgClO_4$, a dark blue product, identified as $[Co(OPPh_3)_4](ClO_4)_2$ by IR and electronic spectra,[10] was isolated after extensive refrigeration and recrystallization. The tendency for $[Co(CNR)_3(PR_3)_2]^{2+}$ complexes to decompose into $[Co(OPR_3)_4]^{2+}$ in solution has been investigated for $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$[10] and $[Co(CNCMe_3)_3\{P(C_6H_4NMe_2\text{-}p)_3\}_2](ClO_4)_2$,[13] so the reaction observed here is not unexpected for a Co(II) product that remains in solution or in contact with the solution for a prolonged period. Relatively rapid isolation of the $[Co(CNR)_3(PR_3)_2]X_2$ complexes is essential.

Characterization of the Complexes

Characterization of the $[Co(CNR)_3(PR_3)_2]X_2$ complexes in the solid state is primarily through Nujol mull $\nu(\text{-N}{\equiv}C)$ IR patterns and magnetic susceptibility measurements, since the poorly-defined decomposition ranges are not very diagnostic. The typical IR pattern of one strong band with an unresolved but distinct lower-energy shoulder, illustrated by $[Co(CNCHMe_2)_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ (see Figure 1(a)), can be interpreted as supporting trigonal bipyramidal coordination, with the slight distortion that is common in the solid state. A rigorously D_{3h} trigonal bipyramid with equatorial CNR ligands requires only one $\nu(\text{-N}{\equiv}C)$ of course (*i.e.*, E'), but some slight distortion in the solid state is usually present. For $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$ even a single $\nu(\text{-N}{\equiv}C)$ is observed, but for $[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$ and $[Co(CNC_6H_{11})(PPh_3)_2](ClO_4)_2$ both higher-energy, as well as lower-energy, shoulders are observed, *albeit* weak to very weak shoulders. These patterns are all compatible with trigonal bipyramidal coordination.

Two complexes, notably $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ (see Figure 1(b)) and $[Co(CNCH_2Ph)_3(PPh_3)_2](BF_4)_2$ (see Figure 1(c)), have $\nu(\text{-N}{\equiv}C)$ IR patterns with two dominant bands. This is not compatible with non-distorted or slightly distorted, axially disubstituted, trigonal bipyramidal coordination. This pattern, especially as shown in Figure 1(b), is reminiscent of the $\nu(\text{-N}{\equiv}\text{C})$ IR patterns often seen for $[\text{Co(CNR)}_3(\text{PR}_3)_2]\text{ClO}_4$ complexes with arylisocyanides as well as alkylisocyanides, and with triarylphosphine and trialkylphosphine ligands.[5,6,9,14–16] These five-coordinate Co(I) complexes have been interpreted[17] as having C_{2v}-distorted, axially disubstituted, trigonal bipyramidal structures in which equatorial bond angles deviate from 120°. An equatorially disubstituted, trigonal bipyramid (C_{2v} symmetry), an axial-equatorial disubstituted, trigonal bipyramid (C_s), or any disubstituted square pyramidal coordination (C_{2v} or C_s) would also account for this IR pattern by having three allowed $\nu(\text{-N}{\equiv}\text{C})$ modes. Adduction of CH_2Cl_2 molecules in the crystal lattice, common for Co(II) as well as Co(I) complexes with organoisocyanide ligands, could be a reason for this apparent deviation from idealized D_{3h} trigonal bipyramidal coordination.

Effective magnetic moments (μ_{eff}) for the $[\text{Co(CNR)}_3(\text{PR}_3)_2]\text{X}_2$ complexes (see Table I) were calculated from room-temperature magnetic susceptibility measurements necessarily assuming Curie Law behaviour and using diamagnetic corrections for the ions taken from the literature[18] and directly measured for the ligands (see Table III). Magnetic moments are primarily within the range normally observed for low-spin Co(II) complexes in general, *i.e.*, 1.8–2.7 BM,[18,19] although the value for $[\text{Co(CNC}_6\text{H}_{11})_3\{\text{P(C}_6\text{H}_4\text{OMe-}p)_3\}_2](\text{ClO}_4)_2\cdot 0.5\text{CH}_2\text{Cl}_2$ (3.08 BM) is abnormally high. Because of the strong similarities within this series of complexes, however, it would be expected that all of these complexes exhibit one-electron paramagnetism, which is typical for five-coordinate Co(II) complexes with strong field ligands. The value of 3.08 BM is still well below the normal range for high-spin Co(II) complexes, *i.e.*, 4.3–5.2 BM.[18,19]

Observed $\nu(\text{-N}{\equiv}\text{C})$ infrared frequencies for the $[\text{Co(CNR)}_3(\text{PR}_3)_2]\text{X}_2$ complexes in CH_2Cl_2, $\text{CF}_3\text{CH}_2\text{OH}$, and CH_3NO_2 are summarized in Table II, and a representative spectrum is illustrated in Figure 1(d). The basic pattern is a single, strong band at 2177–2201 cm^{-1}, and this is compatible with an axially-disubstituted, trigonal bipyramidal coordination of rigorously D_{3h} symmetry. In many of the spectra, however, especially those in $\text{CF}_3\text{CH}_2\text{OH}$, several weak to very weak bands are observed, which are probably solvent bands that have not been completely erased by using the pure solvent in the background scans. In some spectra there is also evidence for apparent partial reduction to a Co(I) species, presumably $[\text{Co(CNR)}_3(\text{PR}_3)_2]^+$. For $[\text{Co(CNCH}_2\text{Ph)}_3(\text{PPh}_3)_2](\text{BF}_4)_2$ in CH_2Cl_2, but not in $\text{CF}_3\text{CH}_2\text{OH}$ or CH_3NO_2, this apparent reduction is extensive. The $\nu(\text{-N}{\equiv}\text{C})$ stretch for the Co(I) species occur in the range 2070–2090 cm^{-1}

and there may also be a second, lower-energy, weaker band. The two complexes $[Co(CNC_6H_{11})_3\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ and $[Co(CNCH_2Ph)_3(PPh_3)_2](BF_4)_2$, that exhibited unusual IR patterns in the solid state, show a regular pattern in solution, except that the latter complex shows extensive reduction in CH_2Cl_2. It appears then, that these complexes show distortion from regular trigonal bipyramidal coordination only in the solid state, reverting to rigorous D_{3h} symmetry in solution.

Electronic spectra for the $[Co(CNR)_3(PR_3)_2]X_2$ complexes, in CH_2Cl_2 and CF_3CH_2OH (see Table II), are not very diagnostic. They exhibit a very broad, apparently crystal field band at ~915–935 nm, a sharp, apparently crystal field band at ~455–485 nm, and a number of charge transfer bands in the UV region. These electronic spectra are also compatible with trigonal bipyramidal coordination. Acetonitrile could not be used as a solvent due to reduction of some of the complexes. Spectra in CH_2Cl_2 and CF_3CH_2OH appear to be analogous, although solutions in CF_3CH_2OH can be measured to shorter wavelength. These appear to be non-coordinating solvents.

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