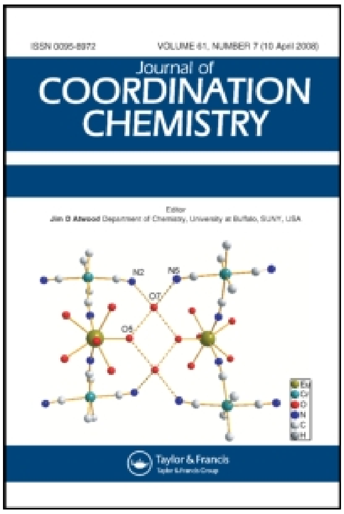

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SYNTHESIS OF TETRAKIS(ALKYLISOCYANIDE)BIS(TRIARYLARSINE) COBALT(II) COMPLEXES. LIGAND SUBSTITUTION WITHOUT REDUCTION IN PENTAKIS(ALKYLISOCYANIDE)COBALT(II)

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SYNTHESIS OF TETRAKIS(ALKYLISOCYANIDE)BIS(TRIARYLARSINE) COBALT(II) COMPLEXES. LIGAND SUBSTITUTION WITHOUT REDUCTION IN PENTAKIS(ALKYLISOCYANIDE)COBALT(II)

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Reactions of excess triarylarsine with *pentakis*(alkylisocyanide)cobalt(II) in EtOH or CH_2Cl_2 have produced complexes of the form $[Co(CNR)_4(AsR_3)_2]X_2$, where X = ClO_4, BF_4; AsR_3 = $AsPh_3$, $As(C_6H_4Me\text{-}p)_3$; CNR = CNC_6H_{11}, $CNCHMe_2$, $CNCH_2Ph$, $CNC_4H_9\text{-}n$. Magnetic susceptibilities (μ_{eff} = 1.8-2.3 BM), ν(-N≡C), and diffuse reflectance electronic spectra suggest a tetragonal structure, *trans*-$[Co(CNR)_4((AsR_3)_2]X_2$, in the solid state. Electronic spectra, ν(-N≡C), and molar conductivity data are compatible with tetragonal structures in CH_2Cl_2 and CH_3CN solutions, but may suggest *cis*-isomerization in CF_3CH_2OH solution. Reactions with $Ph_2AsCH_2CH_2AsPh_2$ have produced $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, CNR = $CNCHMe_2$, CNC_6H_{11}, $CNCH_2Ph$; which appear to be six-coordinate, in which $Ph_2AsCH_2CH_2AsPh_2$ is monodentate. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ appears to be tetragonal in solid and solution states, but $[Co(CNR)_4((Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, R = C_6H_{11}, CH_2Ph; may be the *cis*-isomers. Solution decomposition leads to formation of the tetrahedral complexes, $[Co(OAsR_3)_4]X_2$, R = Ph, $C_6H_4Me\text{-}p$; X = ClO_4, BF_4.

KEYWORDS: Alkylisocyanide, triarylarsine, cobalt(II) complexes, substitution reactions

INTRODUCTION

Reaction of triphenylarsine with *pentakis*(arylisocyanide)cobalt(II) complexes has produced several different products. Reaction with $[Co(CNPh)_5](ClO_4)_2.H_2O$ produced $[Co(CNPh)_3(AsPh_3)_2]ClO_4$,[1] in a reduction/ligand-substitution reaction analogous to that for PPh_3.[2] Reaction with $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2.0.5H_2O$ produced $[Co(CNC_6H_3Me_2\text{-}2,6)_4(ClO_4)_2]$, while reaction with $[Co(CNC_6H_3Me_2\text{-}2,6)_5](BF_4)_2\cdot0.5H_2O$ afforded only $[Co(CNC_6H_3Me_2\text{-}2,6)_5]BF_4$.[3] $AsPh_3$ failed to react with $[Co(CNCMe_3)_4H_2O](ClO_4)_2$,[4] but $[Co(CNCMe_3)_4AsPh_3]PF_6$ has been prepared by ligand substitution into the Co(I) complex.[5]

In the work reported here, triarylarsines simply ligand-substitute one RNC and add a second AsR_3, thereby increasing the Co(II) coordination sphere to six. No evidence for reduction to Co(I) is observed, even in the presence of the liberated RNC, but rather some tendency for oxidation is observed.

EXPERIMENTAL

Reagents

Commercial alkylisocyanides CNC_6H_{11}, $CNCHMe_2$, $CNCH_2Ph$, CNC_4H_9-*n*, and triarylarsines $AsPh_3$, $As(C_6H_4Me\text{-}p)_3$, $Ph_2AsCH_2CH_2AsPh_2$ (Strem Chemicals), were used without further purification. $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ and $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ were prepared as previously reported.[6,7] Anhydrous diethyl ether was filtered through an alumina column immediately before use.

Instrumentation

IR spectra were recorded on a Mattson Polaris FT-IR instrument. Solution electronic spectra were recorded on a Shimadzu UV-365 spectrophotometer; diffuse reflectance spectra were measured using an integrating sphere attachment to the Shimadzu UV-365. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey magnetic susceptibility balance. Effective magnetic moments were calculated assuming Curie Law behaviour. Molar conductivities were measured on ~0.001 M solutions at 25°C using a Crison 525 conductimeter. C,H and N elemental analyses were performed using a Carlo Erba CHN-O/S elemental analyzer, model 1106.

$[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$

A solution of 670 mg $Co(ClO_4)_2 \cdot 6H_2O$ dissolved in 3.0 cm^3 of EtOH and filtered through cotton was chilled in ice. Then 1.000 g $C_6H_{11}NC$ (neat; 5:1 RNC:Co mole ratio) was added dropwise while the Co(II) solution was stirred. The solution turned from pink to dark blue in colour, but no solid precipitated. Next, 2.80 g $AsPh_3$ (5:1 As:Co mole ratio), dissolved in 1.5 cm^3 of CH_2Cl_2 and filtered through cotton, was added dropwise while the reaction mixture was stirred. The colour of the solution changed to yellow-brown while arsine was being added, and a green solid precipitated. Dark green crystals were filtered from the brown solution and washed three times with 2.0 cm^3 portions of ether, which were added to the filtrate. Overnight refrigeration of the filtrate afforded a second crop of grass-green microcrystals. The crude product (2.22 g; 93% yield) was dissolved in 10.0 cm^3 of CH_2Cl_2, filtered through cotton with a 1.0 ml CH_2Cl_2 rinse, and precipitated by dropwise addition of 15.0 cm^3 of ether. Yield: 2.01 g (91% recovery; 84% overall yield).

$[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$

A 500 mg sample of $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ was dissolved in 3.5 cm^3 of CH_2Cl_2, filtered through cotton, and chilled in ice. Then 925 mg $AsPh_3$ (5:1 As:Co mole ratio) dissolved in 1.0 cm^3 of CH_2Cl_2 was added dropwise while the reaction mixture was stirred. The dark yellow-brown solution became dark red-brown in colour while $AsPh_3$ was being added, but no precipitate formed. When ligand addition was complete, the reaction mixture was warmed to room temperature and ether was carefully added dropwise. Initial precipitation was observed after 3.0 cm^3 of ether had been added. A total volume of 5.0 cm^3 of ether was added, and the dark green microcrystalline product was filtered at room temperature and washed with 2.0 cm^3 of ether (345 mg). Addition of 1.0 cm^3 of ether to the filtrate and chilling in ice afforded a second crop of dark green microcrystals. The crude product (450 mg; 57% yield) was dissolved in 2.0 cm^3 of CH_2Cl_2, filtered through cotton, and precipitated by dropwise addition of 4.0 cm^3 of ether. The dark green microcrystals were filtered without prior chilling in ice and washed twice with 2.0 cm^3 portions of ether. Yield: 410 mg (91% recovery; 52% overall yield).

RESULTS AND DISCUSSION

Physical properties of the new $[Co(CNR)_4(AsR_3)_2]X_2$ complexes in the solid state are summarized in Table 1; some physical properties in solution are listed in Table 2. Representative $\nu(\text{-N}{\equiv}C)$ IR patterns are illustrated in Figure 1.

Synthesis of the Complexes

Complexes involving the $CNCHMe_2$ and $CNCH_2Ph$ ligands were synthesized starting from the previously-isolated Co(II)-alkylisocyanide complexes, $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ and $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$, reacted in CH_2Cl_2, as in the synthesis of $[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$. $[Co_2(CNC_6H_{11})_{10}](ClO_4)_4 \cdot xH_2O$ has never been successfully isolated, and handling $[Co_2(CNC_4H_9\text{-}n)_{10}](ClO_4)_4 \cdot xH_2O$ is very undesirable,[6] so triarylarsine-complexes involving CNC_6H_{11} and $CNC_4H_9\text{-}n$ are best prepared by reaction of $[Co(CNR)_5](ClO_4)_2$ *in situ* in EtOH, as in the synthesis of $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$. Either reaction would presumably yield the same product, *i.e.*, $[Co(CNR)_4(AsR_3)_2]X_2$; these reactions are not solvent-controlled. Crude products isolated from EtOH, however, tend to be more pure, possibly due to rapid precipitation with less time for solution decomposition. Recrystallizations are necessarily from CH_2Cl_2/ether.

Reactions with $Ph_2AsCH_2CH_2AsPh_2$ are surprisingly similar to reactions with the simple triarylarsines, leading to complexes of the form $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, X = ClO_4, BF_4. A mole ratio of 5:1 As:Co was maintained by using only 2.5 moles of $Ph_2AsCH_2CH_2AsPh_2$ in these reactions, but two $Ph_2AsCH_2CH_2AsPh_2$ ligands nevertheless substituted in all instances. Crude products required substantially larger volumes of CH_2Cl_2, however, for recrystallization. As will be discussed later, data support monodentate coordination of $Ph_2AsCH_2CH_2AsPh_2$ in these complexes.

Several anticipated products are conspicuously absent from the list of new complexes in Tables 1 and 2. A green product from the reaction of $Ph_2AsCH_2CH_2AsPh_2$ with $[Co(CNC_4H_9\text{-}n)_5](ClO_4)_2$ decomposed upon attempted filtration and washing with ether. A blue-green product from the reaction of $As(C_6H_4Me\text{-}p)_3$ with $[Co(CNCHMe_2)_5]ClO_4)_2$ appeared to be a mixture of $[Co(CNR)_4(AsR_3)_2](ClO_4)_2$ and $[Co(OAsR_3)_4](ClO_4)_2$, already initially prepared, so attempted characterization would have been meaningless. Complete conversion to the intense azure-coloured compound $[Co(OAsR_3)_4](ClO_4)_2$ eventually took place in the solid state. $[Co(CNCHMe_2)_4(AsPh_3)_2](ClO_4)_2$, which could be characterized except for magnetic susceptibility (the material would not pack in a Gouy tube), slowly converted to $[Co(OAsPh_3)_4](ClO_4)_2$ in the solid state over weeks to

Table 1 Solid state properties of tetrakis(alkylisocyanide)bis(triarylarsine)cobalt(II) complexes

Complex/Colour/M.pt.	ν(-N≡C)	Electronic spectra	$\chi_g \times 10^9/\mu_{eff}$	Elemental analysis, found/calc.		
				C	H	N
$[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$ Dark green 160-169°C (dec)	2211 vs ~2178 w(sh)	≈720sh (0.75) ~630 (0.88) ~570sh (0.80) 410br (0.99) ~270br (1.04)	1090 ± 20 2.25 ± 0.01 BM	58.75 58.81	5.69 5.71	4.16 4.29
$[Co(CNC_6H_{11})_4(AsPh_3)_2](BF_4)_2$ Dark green 140-155°C (dec)	2213 vs ~2181 w(sh)	≈720sh (0.67) ~630 (0.85) ~570sh (0.76) ~400 (1.01) ~320br (1.03) ~270 (1.02)	828 ± 5 2.06 ± 0.01 BM	60.12 59.98	6.28 5.82	3.96 4.37
$[Co(CNC_6H_{11})_4\{As(C_6H_4Me\text{-}\rho)_3\}_2](ClO_4)_2$ Dark green 165-183°C (dec)	2210 vs ~2182 vw(sh)	~620br (0.86) 400br (0.99) ~320br (1.00) ~270 (0.97)	567 ± 8 1.92 ± 0.01 BM	59.80 60.44	5.90 6.23	4.23 4.03
$[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2 \cdot 0.5CH_2Cl_2$ Pale green 173-180°C (dec)	2220 m 2205 vs	~625br (0.38) 385sh (0.91) 335 (1.01) ~250 (0.97)	710 ± 30 2.17 ± 0.03 BM	56.62 56.56	5.47 5.48	3.04 3.28
$[Co(CNCHMe_2)_4(AsPh_3)_2](ClO_4)_2$ Dark green 135-150°C (dec)	2215 vs ~2180 w(sh)	~650br (0.94) ~410br (1.02) ~310br (1.02)	*	53.70 54.46	5.10 5.10	4.89 4.89
$[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ Medium green 161-166°C (dec)	2215 vs ~2182 w(sh)	~630br (0.77) ~370br (1.07) ~330br (1.08) ~280br (1.07)	870 ± 40 2.19 ± 0.03 BM	53.86 54.20	5.05 5.08	3.59 3.72
$[Co(CNC_4H_9\text{-}\eta)_4(AsPh_3)_2](ClO_4)_2$ Dark green 143–155°C (dec)	2226 vs ~2193 vw(sh)	~620br (0.87) ~400br (1.00) ~310br (1.02)	635±5 1.83±0.01 BM	55.83 55.92	5.52 5.53	4.63 4.66
$[Co(CNC_4H_9\text{-}\eta)_4\{As(C_6H_4Me\text{-}\rho)_3\}_2](ClO_4)_2 \cdot 0.5CH_2Cl_2$ Dark green 156-165°C (dec)	2225 vs ~2191 w(sh)	~630br (0.60) ~400sh (1.01) 340br (1.08)	*	56.43 56.47	6.07 6.00	4.03 4.21
$[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$ Dark green 147-150°C (dec)	2229 vs ~2195 w(sh)	~630br (0.88) ~390br (1.01) ~330 (1.03) ~290br (1.01)	1160 ± 23 2.31 ± 0.02 BM	61.76 62.18	4.39 4.45	3.98 4.27
$[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2 \cdot 0.5CH_2Cl_2$ Medium green 119-129 °C (dec)	2234 s ~2215 vs	≈680br, sh (0.59) ~600br (0.64) ~400sh (1.04) ~330br (1.06)	650 ± 20 2.13 ± 0.02 BM	58.93 59.13	4.44 4.52	3.07 3.26

*Satisfactory magnetic susceptibility measurement could not be obtained.

Table 2 Solution properties of tetrakis(alkylisocyanide)bis(triarylarsine)cobalt(II) complexes.

Complex	ν(-N≡C) infrared[a]		Electronic spectra[b]		Λ_M[c]
	CH_2Cl_2	CF_3CH_2OH	CH_2Cl_2	CH_3CN	
$[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$	2228 vs	2213 s(sh)	760br (125)	720br (92)	305
	~2202 w(sh)	2207 s(sh)	~675sh (105)	~315sh (640)	195
		2188 m	~372sh (510)	246 (11,000)	185
			319 (1100)	223 (11,000)	23
			~250 (12,000)		
$[Co(CNC_6H_{11})_4(AsPh_3)_2](BF_4)_2$	2228 vs	2215 s	~805br (190)	720br (81)	320
	~2200 w(sh)	~2208 w(sh)	~675sh (100)	≈315sh (700)	220
		2189 m	305sh (810)	246 (12,000)	185
			~250 (12,000)	219 (12,000)	31
$[Co(CNC_6H_{11})_4\{As(C_6H_4Me\text{-}\rho)_3\}_2](ClO_4)_2$	2222 vs	2232 w	790br (150)	726br (90)	300
		2206 s	420sh (1300)	~315sh (1100)	200
		2189 w	~320sh (1800)	248 (29,000)	185
			~245 (16,000)		34
$[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$	2228 vs	2205 s	762br (155)	728br (105)	315
	2124 w	2177 w	~385sh (500)	≈315 (1100)	205
		2166 w	~320sh (1300)	245sh (40,000)	175
			~245 (16,000)		28
$[Co(CNCHMe_2)_4(AsPh_3)_2](ClO_4)_2$	2227 vs	2220 s	~760br (100)	740br (68)	320
		2164 m	657sh (93)	≈315sh (700)	210
			~310sh (1300)	247 (21,500)	185
			250 (9000)		20
$[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$	2226 vs	2213 s	768br (140)	746br (87)	320
		2185 w	405 (1200)	≈315sh (1100)	215
			~315sh (1400)	246 (14,000)	185
			245 (14,000)	~222 (14,000)	25
$[Co(CNC_4H_9\text{-}\eta)_4(AsPh_3)_2](ClO_4)_2$	2239 vs	~2230 w(sh)	765br (160)	728br (86)	305
		2221 s	≈410sh (220)	~310sh (570)	185
		~2205 w(sh)	~315sh (930)	246 (10,000)	175
			250 (12,000)	224 (10,000)	17
$[Co(CNC_4H_9\text{-}\eta)_4\{As(C_6H_4Me\text{-}\rho)_3\}_2](ClO_4)_2$	2239 vs	~2243 w(sh)	790br (145)	716br (120)	305
	≈2220 vw(sh)	~2232 w(sh)	~670sh (115)	~310sh (700)	180
	~2170 vw(sh)	2220 s	432 (1500)	247 (29,000)	175
	2133 w	2202 m	~320sh (1500)		20
			249 (16,000)		
$[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$	2241 vs	2224 vs	820br (195)	702br (56)	315
	≈2230 w(sh)	~2220 w(sh)	413 (635)	≈390sh (580)	210
	~2170 w(sh)	2200 w	~290sh (6000)	246 (14,000)	180
	2134 m		248 (12,000)		19
$[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$	2250 s	2224 s	~825br (85)	~700br (50)	315
	~2230 m(sh)	2195 w(sh)	412 (4500)	≈400sh (350)	235
	2170 m(sh)	2160 w	~290sh (5600)	~290sh (6000)	170
	2135 vs		~240sh (44,000)	239sh (39,000)	25

[a] The ν(-N≡C) in cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder. [b] The $\lambda_{max}(\varepsilon)$ in nm, without Gaussian resolution. [c] Molar conductivity, $\Lambda_M = 1000\ L_{corrected}C^{-1}{}_M$ in $\Omega^{-1}\ cm^2\ mol^{-1}$; first value in CH_3CN, second value in acetone, third value in CH_3NO_2, fourth value in CH_2Cl_2.

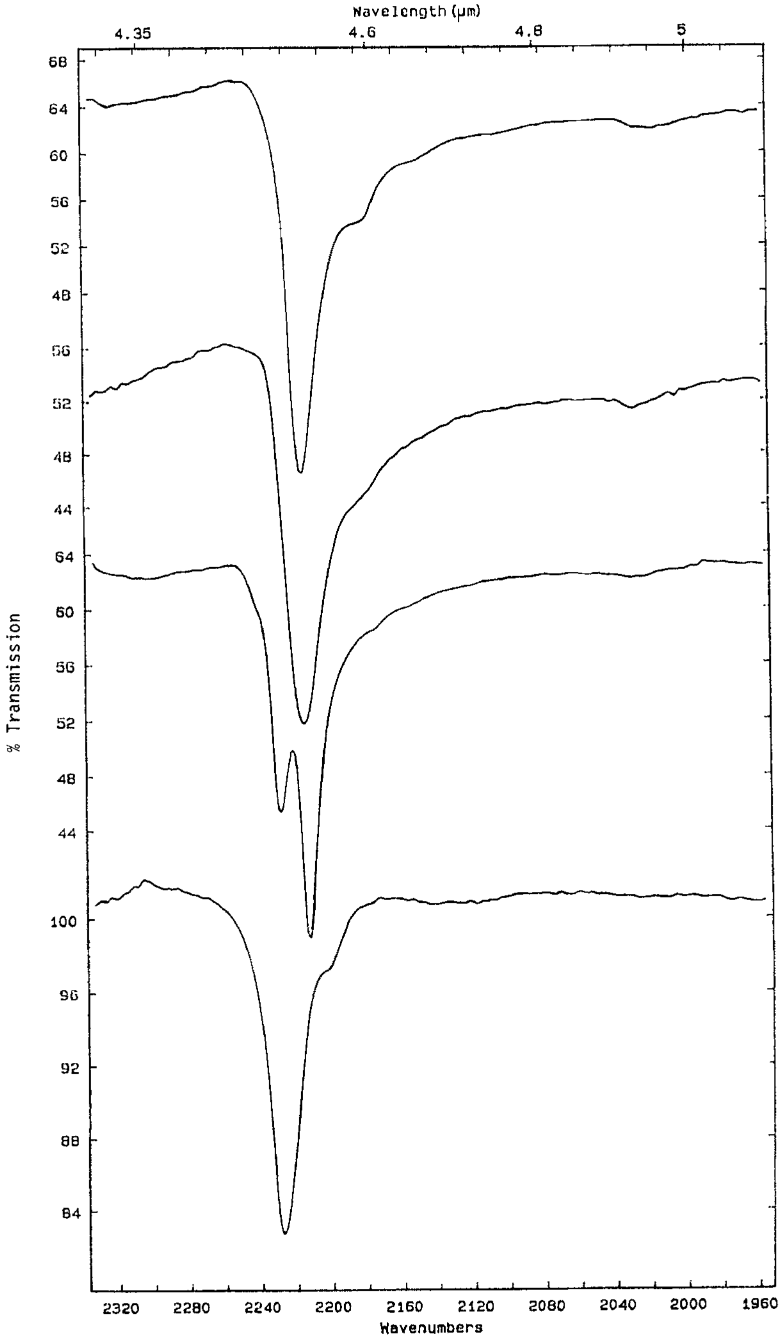

Figure 1 Representative $\nu(\text{-N}{\equiv}\text{C})$ IR patterns for $[\text{Co(CNR)}_4(\text{AsR}_3)_2]\text{X}_2$ complexes; top to bottom: $[\text{Co(CNC}_6\text{H}_{11})_4(\text{AsPh}_3)_2](\text{ClO}_4)_2$ (Nujol), $[\text{Co(CNC}_6\text{H}_{11})_4\{\text{As(C}_6\text{H}_4\text{Me-p)}_3\}_2](\text{ClO}_4)_2$ (Nujol), $[\text{Co(CNC}_6\text{H}_{11})_4(\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2)_2](\text{ClO}_4)_2$ (Nujol), $[\text{Co(CNC}_6\text{H}_{11})_4(\text{AsPh}_3)_2](\text{ClO}_4)_2$ (CH_2Cl_2).

months. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ is stable in the solid state. $[Co(CNC_6H_{11})_4(AsPh_3)_2](BF_4)_2$ also becomes a mixture of blue $[Co(OAsPh_3)_4](BF_4)_2$ and green $[Co(CNC_6H_{11})_4(AsPh_3)_2](BF_4)_2$ over a long period (*ca* one year). $[Co(CNC_6H_{11})_4(AsPh_3)_2](ClO_4)_2$, $[Co(CNC_6H_{11})_4\{As(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ and $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ are stable in the solid state. Multiple recrystallization of the $[Co(CNR)_4(AsR_3)_2]X_2$-$[Co(OAsR_3)_4]X_2$ mixtures from CH_2Cl_2/ether leads to isolation of the pure tetrahedral complexes, $[Co(OAsR_3)_4]X_2$, R = Ph, C_6H_4Me-p; X = ClO_4, BF_4, to be discussed more thoroughly in a subsequent paper.

Reaction of $As(C_6H_4Me\text{-}p)_3$ with $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ (in CH_2Cl_2) produced the cobalt(III) complex, $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$, as previously reported.[7] This reaction may be solvent-dependent; faster recovery from EtOH may have allowed isolation of a Co(II) complex. $[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$ and $[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$ appear to be stable in the solid state. In a second crop from the reaction of $As(C_6H_4Me\text{-}p)_3$ with $[Co(CNC_4H_9\text{-}n)_5](ClO_4)_2$ (in EtOH), however, dark yellow crystals were recovered with the microcrystalline dark green $[Co(CNR)_4(AsR_3)_2](ClO_4)_2$. From the ν(-N≡C) IR pattern and frequency (2249s cm^{-1} (Nujol)), this new compound could be $[Co(CNC_4H_9\text{-}n)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_3$. Further investigation is required.

Whereas triarylphosphines promote immediate reduction/ligand substitution upon reaction with *pentakis*(alkylisocyanide)cobalt(II),[4,8] triarylarsines initially substitute in the Co(II) complexes. These Co(II) complexes, $[Co(CNR)_4(AsR_3)_2]X_2$, are at least somewhat metastable with respect to oxidation, however, as is clearly evidenced by the relative ease of formation of $[Co(OAsR_3)_4]X_2$ and $[Co(CNR)_4(OAsR_3)_2]X_3$ in both solution and solid state. Ability to promote oxidation in their complexes appears to be in the order $As(C_6H_4Me\text{-}p)_3 > AsPh_3 > Ph_2AsCH_2CH_2AsPh_2$. This reaction pattern is quite remarkable. In so many ligand substitution reactions $AsPh_3$ behaves analogously to PPh_3, *albeit* often somewhat less reactive. For triarylphosphines to rapidly reduce *pentakis*(alkylisocyanide)cobalt(II) complexes while triarylarsines substitute in *pentakis*(alkylisocyanide)cobalt(II) with some tendency to spontaneously oxidize to the triarylarsine oxide and even promote Co(II) oxidation to Co(III), is a drastic change from the usual pattern of parallel behaviour for PR_3, AsR_3 and SbR_3. Preliminary results[9] indicate that reactions with $SbPh_3$ are even more prone to oxidation of Co(II) in the formation of $[Co(CNR)_4(OSbPh_3)_2]X_3$ complexes.

Characterization in the Solid State

Effective magnetic moments for the $[Co(CNR)_4(AsR_3)_2]X_2$ complexes were calculated from room-temperature magnetic susceptibility measurements (Table 1) assuming Curie Law behaviour and using diamagnetic corrections for the ions taken from the literature[10] and directly measured for the ligands (Table 3). Magnetic moments (1.8-2.3 BM) are within the range observed for low-spin Co(II) complexes in general, 1.8-2.7 BM[10,11] and within the range previously reported for tetragonally-substituted six-coordinated Co(II) with four alkylisocyanide ligands, $[Co(CNCMe_3)_4L_2](ClO_4)_2 \cdot xH_2O$, L = aromatic and cyclic aliphatic amines (1.8-2.5 BM).[12] These μ_{eff} values are distributed between the ranges appropriate for low-spin square planar Co(II) complexes, 2.1-2.9 BM, and spin-paired octahedral

Table 3 Measured diamagnetic susceptibilities.

Formula	$\chi_g \times 10^9$	$\chi_M \times 10^6$
CNC_6H_{11}	-637 ± 8	-69.5 ± 0.9
$CNCHMe_2$	-664 ± 9	-45.9 ± 0.6
CNC_4H_9-η	-618 ± 4	-51.4 ± 0.3
$CNCH_2Ph$	-579 ± 4	-67.8 ± 0.4
As $(C_6H_5)_3$	-572 ± 14	-175 ± 4
As $(C_6H_4Me\text{-}\rho)_3$	-562 ± 24	-196 ± 8
$Ph_2AsCH_2CH_2AsPh_2$	-482 ± 25	-234 ± 12

Co(II) complexes, 1.7-2.0 BM, however, according to values suggested by Figgis and Nyholm[13]. Tetragonal structures for *trans*-$[Co(CNR)_4(AsR_3)_2]X_2$ would clearly be compatible with this magnetic data.

The ν(-N≡C) IR pattern of one strong band (2210-2230 cm^{-1}, dependent on the particular RNC) with an unresolved lower-energy shoulder (see Figure 1), seen for all of the $[Co(CNR)_4(AsR_3)_2]X_2$, AsR_3 = $AsPh_3$, $As(C_6H_4Me\text{-}\rho)_3$, complexes in the solid state, is analogous to known or presumed tetragonal complexes, *e.g.*, $[Co(CNR)_4(ClO_4)_2]$, R = 2,6-$Me_2C_6H_3$,[3] 2,6-$Et_2C_6H_3$;[14] $[Co(CNCMe_3)_4L_2](ClO_4)_2$.[12] This pattern has been previously interpreted as indicating a slightly distorted square planar arrangement of four organoisocyanide ligands, as confirmed in X-ray structures.[14,15] The ν(-N≡C) IR pattern therefore also supports a tetragonal structure for the $[Co(CNR)_4(AsR_3)_2](ClO_4)_2$ complexes in the solid state. The diffuse reflectance electronic spectra for the $[Co(CNR)_4(AsR_3)_2]X_2$, AsR_3 = $AsPh_3$, $As(C_6H_4Me\text{-}\rho)_3$, complexes (see Table 1) are approximately the same, and similar to most of the spectra for the $[Co(CNCMe_3)_4L_2](ClO_4)_2$ complexes.[12] This further supports a tetragonal structure for the $[Co(CNR)_4(AsR_3)_2]X_2$ complexes.

Structures of the $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$ complexes in the solid state are unclear. While eight coordination is known for Co(II), as in the dodecahedral species $(Ph_4As)_2[Co(NO_3)_4]$,[16] it would be unexpected with ligands as bulky as $Ph_2AsCH_2CH_2AsPh_2$. Characterization data appear to be most consistent with six-coordinate Co(II), in which case $Ph_2AsCH_2CH_2AsPh_2$ must be acting as a monodentate ligand. Having normally-chelating bidentate ligands coordinated through only one site is not unknown in cobalt-organoisocyanide chemistry, as in the recently-reported series of $[Co(CNC_6H_3Et_2\text{-}2,6)_4L\text{-}L]BF_4$ complexes with bidentate tertiary phosphine ligands.[17] Interestingly, the structure of $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ appears to be different from that of $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ and $[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ has the same ν(-N≡C) IR pattern, μ_{eff} value, and diffuse reflectance spectrum characteristic of the $[Co(CNR)_4(AsR_3)_2]X_2$ complexes with monodentate triarylarsines, and has probably the same tetragonal structure.

The $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, R = C_6H_{11}, CH_2Ph, complexes, however, have different diffuse reflectance spectra in which the first broad band(s) is(are) noticeably weaker, and drastically different ν(-N≡C) IR patterns (see Figure 1). Crude $[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$ showed the typical ν(-N≡C) IR pattern (2220vs, ~2190w(sh) cm^{-1}), but reverted to the reported spectrum upon routine recrystallization from CH_2Cl_2/ether, while

$[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$ exhibited the reported spectrum upon initial precipitation. The higher energy band in each spectrum, 2234 and 2220 cm^{-1}, respectively, is slightly higher than the dominant band of the "*trans*-" pattern for these particular RNC ligands (5–10 cm^{-1}), but is still substantially lower than the ν(-N≡C) value observed in a Co(III) complex, *e.g.*, 2258 cm^{-1} for $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$.[7] Thus partial oxidation to Co(III) should be excluded as a possibility. What could be occurring here is *cis*-isomerization of the normally *trans*-configuration of the two $Ph_2AsCH_2CH_2AsPh_2$ ligands. Further investigation would be necessary to elucidate these structures.

Characterization in Solution

Molar conductivity values (Λ_M) for the $[Co(CNR)_4(AsR_3)_2]X_2$ complexes (see Table 2) in CH_3CN (305–320 $\Omega^{-1}cm^2mol^{-1}$), acetone (180–220), and CH_3NO_2 (175–185) are slightly high, but still reasonably close to the expected ranges for 2:1 electrolytes.[18] Λ_M values in CH_2Cl_2 (17-34 $\Omega^{-1}cm^2mol^{-1}$) show considerable ion-pairing; this is customary behaviour for Co(II)-organoisocyanide complexes.[6,7] Λ_M values for the $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$ complexes are comparable to values found for complexes with monodentate triarylarsine ligands. Thus all of the complexes reported here can be considered to be 2:1 electrolytes in solution.

The ν(-N≡C) IR patterns for all of the $[Co(CNR)_4(AsR_3)_2]X_2$ complexes with the triarylarsine ligands and for $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$, in CH_2Cl_2, are basically the same as seen in the solid state (see Figure 1). This suggests that the *trans*-tetragonal geometry is maintained in CH_2Cl_2 solution. $[Co(CNC_4H_9\text{-}n)_4\{As(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_2$ and $[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$, however, also show weak bands at 2133, 2170 cm^{-1}, suggesting a Co(I) species, that may be formed in solution (Co(I) ν(-N≡C) IR bands are extremely intense,[6] so only small concentrations are present in these spectra). $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$, in CH_2Cl_2, shows a ν(-N≡C) IR pattern analogous to the triarylarsine complexes, but with a weak band, possibly due to Co(I), at ~2144 cm^{-1}. $[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$ has a weaker Co(II) pattern, 2250, 2230 cm^{-1}, with a stronger Co(I) pattern, 2135, 2170 cm^{-1}; it is otherwise also analogous to the complexes with the triarylarsines. Thus, in CH_2Cl_2 solution, all of the Co(II) complexes appear to have the same *trans*-tetragonal structure.

In CF_3CH_2OH solution, the ν(-N≡C) IR patterns are more difficult to interpret. Almost all of the complexes show two closely-spaced bands, often unresolved, with a less intense band at lower energy, all within the range appropriate for Co(II) complexes. A *cis*-substituted octahedral geometry (C_{2v}) should theoretically show four symmetry-allowed ν(-N≡C), *i.e.*, $2A_1 + B_1 + B_2$, but these bands could be only partially resolved. This ν(-N≡C) IR pattern is certainly more complex than that observed for the presumably *trans*-tetragonal structure, and could be indicative of a *cis*- geometry. This pattern, however, does not closely resemble the ν(-N≡C) IR pattern observed for $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, R = C_6H_{11}, CH_2Ph, in the solid state.

Solution electronic spectra for almost all of the new complexes in CH_2Cl_2 and CH_3CN (see Table 2) show basically the same pattern of a broad crystal field band (~700-800 nm, ε ≈50-200), with higher energy shoulders, culminating in one or more intense charge transfer bands (starting at 245-250 nm, ε ≈10,000-40,000).

Several spectra in CH_2Cl_2 only, especially $[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](ClO_4)_2$, also exhibit a well-resolved band ~405-430 nm. In general, spectra for the complexes with $Ph_2AsCH_2CH_2AsPh_2$ appear very similar to spectra for complexes of the AsR_3 ligands with the same RNC, suggesting analogous solution structures. Both λ_{max} and ε of the crystal field band are higher in CH_2Cl_2 than in CH_3CN.

All complexes decompose in solution, but decomposition rates and patterns vary depending on the particular RNC, arsine, and solvent. Complexes with $Ph_2AsCH_2CH_2AsPh_2$ ligands decompose into unidentified product(s), but complexes with AsR_3 = $AsPh_3$, $As(C_6H_4Me\text{-}p)_3$; systematically convert over a period of days into intense blue, tetrahedral $[Co(OAsR_3)_4]X_2$ complexes, easily identified by their typical electronic spectra.[19,20] This solution-phase oxidation/decomposition will be further investigated in a subsequent paper, but preliminary observations indicate that the reaction rates are clearly related to both the AsR_3, $As(C_6H_4Me\text{-}p)_3 > AsPh_3$, and the RNC, $CNCHMe_2 > CNC_4H_9\text{-}n$ $CNCH_2Ph > CNC_6H_{11}$.

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