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SYNTHESIS OF TETRAKIS(ALKYLISOCYANIDE)BIS(TRIARYLARSINE) COBALT(II) COMPLEXES. LIGAND SUBSTITUTION WITHOUT REDUCTION IN PENTAKIS(ALKYLISOCYANIDE)COBALT(II) Clifford A. L. Becker^a

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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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(Received September 28, 1993)

Reactions of excess triarylarsine with *pentakis*(alkylisocyanide)cobalt(II) in EtOH or CH₂Cl₂ have produced complexes of the form $[Co(CNR)_4(AsR_3)_2]X_2$, where $X = C1O_4$, BF₄; AsR₃ = AsPh₃, As(C₆H₄Me- ρ)₃; CNR = CNC₆H₁₁, CNCHMe₂, CNCH₂Ph, CNC₄H₉-*n*. Magnetic susceptibilities ($\mu_{eff} = 1.8 \cdot 2.3$ BM), v(-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, v(-N=C), and molar conductivity data are compatible with tetragonal structures in CH₂Cl₂ and CH₃CN solutions, but may suggest *cis*-isomerization in CF₃CH₂OH solution. Reactions with Ph₂AsCH₂CH₂AsPh₂ have produced $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, CNR = CNCHMe₂, CNC₆H₁₁, CNCH₂Ph; which appear to be six-coordinate, in which Ph₂AsCH₂CH₂AsPh₂ is monodentate. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2$, R = C₆H₁₁, CH₂Ph; may be the *cis*-isomers. Solution leads to formation of the tetrahedral complexes, $[Co(OAsR_3)_4]X_2$, R = Ph, C₆H₄Me-p; X = C1O₄, BF₄.

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 $[Co(CNPh)_5](C1O_4)_2.H_2O$ produced $[Co(CNPh)_3(AsPh_3)_2]C1O_4$,¹ in a reduction/ligand-substitution reaction analogous to that for PPh₃.² Reaction with $[Co(CNC_6H_3Me_2-2,6)_5](C1O_4)_2.0.5H_2O$ produced $[Co(CNC_6H_3Me_2-2,6)_4(C1O_4)_2]$, while reaction with $[Co(CNC_6H_3Me_2-2,6)_5](BF_4)_2 \cdot 0.5H_2O$ afforded only $[Co(CNC_6H_3Me_2-2,6)_5]BF_4$.³ AsPh₃ failed to react with $[Co(CNCMe_3)_4H_2O](C1O_4)_2$,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 - ρ)_3, Ph_2AsCH_2CH_2AsPh_2 (Strem Chemicals), were used without further purification. $[Co_2(CNCHMe_2)_{10}](C1O_4)_4 \cdot 5H_2O$ 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.

$[Co(CNC_6H_{11})_4(AsPh_3)_2](C1O_4)_2$

A solution of 670 mg Co(C1O₄)₂·6H₂O dissolved in 3.0 cm³ of EtOH and filtered through cotton was chilled in ice. Then 1.000 g C₆H₁₁NC (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 AsPh₃ (5:1 As:Co mole ratio), dissolved in 1.5 cm³ of CH₂Cl₂ 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 cm³ 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 cm³ of CH₂Cl₂, filtered through cotton with a 1.0 ml CH₂Cl₂ rinse, and precipitated by dropwise addition of 15.0 cm³ 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 cm³ of CH₂Cl₂, filtered through cotton, and chilled in ice. Then 925 mg AsPh₃ (5:1 As:Co mole ratio) dissolved in 1.0 cm³ of CH₂Cl₂ was added dropwise while the reaction mixture was stirred. The dark yellow-brown solution became dark red-brown in colour while AsPh₃ 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 cm³ of ether had been added. A total volume of 5.0 cm³ of ether was added, and the

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dark green microcrystalline product was filtered at room temperature and washed with 2.0 cm³ of ether (345 mg). Addition of 1.0 cm³ 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 cm³ of CH₂Cl₂, filtered through cotton, and precipitated by dropwise addition of 4.0 cm³ of ether. The dark green microcrystals were filtered without prior chilling in ice and washed twice with 2.0 cm³ 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 v(-N=C) IR patterns are illustrated in Figure 1.

Synthesis of the Complexes

Complexes involving the CNCHMe₂ and CNCH₂Ph ligands were synthesized starting from the previously-isolated Co(II)-alkylisocyanide complexes, $[Co_2(CNCHMe_2)_{10}](C1O_4)_4 \cdot 5H_2O$ and $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$, reacted CH₂Cl₂, as in the synthesis of $[Co(CNCH_2Ph)_4(AsPh_3)_2](BF_4)_2$. in $[Co_2(CNC_6H_{11})_{10}](C1O_4)_4 \cdot xH_2O$ has never been successfully isolated, and handling $[Co_2(CNC_4H_9-n)_{10}](C1O_4)_4 \times H_2O$ is very undesirable,⁶ so triarylarsinecomplexes involving CNC_6H_{11} and CNC_4H_9 -n are best prepared by reaction $[Co(CNR)_5](C1O_4)_2$ in situ in EtOH, as in the synthesis of $[Co(CNC_6H_{11})_4(AsPh_3)_2](C1O_4)_2$. 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 CH₂Cl₂/ether.

Reactions with Ph2AsCH2CH2AsPh2 are surprisingly similar to reactions with the simple triarylarsines, leading to complexes of the form $[Co(CNR)_4(Ph_2AsCH_2CH_2AsPh_2)_2]X_2, X = C1O_4, BF_4.$ A mole ratio of 5:1 As:Co was maintained by using only 2.5 moles of Ph₂AsCH₂CH₂AsPh₂ in these reactions, but two Ph₂AsCH₂CH₂AsPh₂ 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 Ph₂AsCH₂CH₂AsPh₂ 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 $[Co(CNC_4H_9-n)_5](C1O_4)_2$ decomposed upon attempted filtration and washing with ether. A blue-green product from the reaction of $As(C_6H_4Me-\rho)_3$ with $[Co(CNCHMe_2)_5]C1O_4)_2$ appeared to be a mixture of $[Co(CNR)_4(AsR_3)_2](C1O_4)_2$ and $[Co(OAsR_3)_4](C1O_4)_2$, already initially prepared, so attempted characterization would have been meaningless. Complete conversion to the intense azure-coloured compound $[Co(OAsR_3)_4](C1O_4)_2$ eventually took place in the solid state. $[Co(CNCHMe_2)_4(AsPh_3)_2](C1O_4)_2$, which could be characterized except for magnetic susceptibility (the material would not pack in a Gouy tube), slowly converted to $[Co(OAsPh_3)_4](C1O_4)_2$ in the solid state over weeks to

TAUR I DOUD STATE PROPERTIES OF ICHTANIS(AIN/ITSOC) ATTIN	Anterna in the second	formation (III) manage				
Complex/Colour/M.pt.	_v (-N≡C)	Electronic spectra	$\chi_{g} \times 10^{9/\mu_{eff}}$	Elemental a	inalysis, foun	d/calc.
				U	Н	z
[Co(CNC ₆ H ₁₁)4(AsPh ₃) ₂](C1O 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)	1090 ± 20 2.25 ± 0.01 BM	58.75 58.81	5.69 5.71	4.16 4.29
[Co(CNC ₆ H ₁₁) ₄ (AsPh ₃) ₂](BF ₄) ₂ Dark green 140-155°C (dcc)	2213 vs ~2181 w(sh)	\sim 2/00r (1.04) \approx 720sh (0.67) \sim 630 (0.85) \sim 570sh (0.76) \sim 320br (1.01) \sim 320br (1.03)	828 ± 5 2.06 ± 0.01 BM	60.12 59.98	6.28 5.82	3.96 4.37
[Co(CNC ₆ H ₁₁) ₄ {As(C ₆ H ₄ Me-p) ₃ }](C1O ₄) ₂ Dark green 165-183*C (dec)	2210 vs ~2182 vw(sh)	~270 (1.02) ~620br (0.86) 400br (0.99) ~320br (1.00)	567 ± 8 1.92 ± 0.01 BM	59.80 60.44	5.90 6.23	4.23 4.03
[Co(CNC ₆ H ₁₁)4(Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ ·0.5CH ₂ Cl ₂ Pale green 173-180°C (dec)	2220 m 2205 vs	$\sim 2/0$ (0.97) -625br (0.38) 3855h (0.91) 335 (1.01)	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](C1O ₄) ₂ Dark green	2215 vs ~2180 w(sh)	~250 (0.97) ~650br (0.94) ~410br (1.02)	*	53.70 54.46	5.10 5.10	4.89 4.89
155-150°C (acc) [Co(CNCHMe ₂)4(Ph ₂ AsCH ₂ CH ₂ AsPh ₂)2](C1O ₄)2 Medium green 161-166°C (acc)	2215 vs ~2182 w(sh)	~310br (1.02) ~630br (0.77) ~370br (1.07) ~330br (1.08)	870 ± 40 2.19 ± 0.03 BM	53.86 54.20	5.05 5.08	3.59 3.72
[Co(CNC4H9-1)4(AsPh3)2](ClO4)2 Dark green 113 - (2550 - (352)	2226 vs ~2193 vw(sh)	~280br (1.07) ~620br (0.87) ~400br (1.00)	635±5 1.83±0.01 BM	55.83 55.92	5.52 5.53	4.63 4.66
143-133 C (acc) [Co(CNC4H9-1)4 {As(C ₆ H4Me-p) ₃ }2](C1O ₄)2·0.5CH2Cl ₂ Dark green	2225 vs ~2191 w(sh)	~ 5100f (1.02) ~630br (0.60) ~400sh (1.01)	*	56.43 56.47	6.07 6.00	4.03 4.21
Corror C (dec) [Co(CH2Ph)4(AsPh ₃) ₂](BF ₄) ₂ Dark green 147-150°C (dec)	2229 vs ~2195 w(sh)	$\sim 4001 (1.06)$ $\sim 630br (0.88)$ $\sim 330br (1.01)$ $\sim 330 (1.03)$	1160 ± 23 2.31 ± 0.02 BM	61.76 62.18	4.39 4.45	3.98 4.27
[Co(CNCH ₂ Ph) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](BF ₄) ₂ ·0.5CH ₂ Cl ₂ Medium gren 119-129 °C (dec)	2234 s ~2215 vs	~2900f (1.01) ~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

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

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*Satisfactory magnetic susceptibility measurement could not be obtained.

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$\frac{\text{CH}_2\text{CI}_2}{[\text{Co}(\text{CNC}_6\text{H}_{11})_4(\text{AsPh}_3)_2](\text{CIO}_4)_2} - \frac{\text{CH}_2\text{CI}_2}{-2202} \text{ w}(\text{sh})} - \frac{2228}{2202} \text{ w}(\text{sh})} - \frac{2203}{2188} \text{ m}} \\ \frac{(\text{Co}(\text{CNC}_6\text{H}_{11})_4(\text{AsPh}_3)_2](\text{EIO}_4)_2}{2189} - \frac{2228}{2200} \text{ w}(\text{sh})} - \frac{2215}{2189} \text{ w}} \\ \frac{(\text{Co}(\text{CNC}_6\text{H}_{11})_4(\text{AsPh}_3)_2](\text{CIO}_4)_2}{2122} - \frac{2222}{2200} \text{ w}(\text{sh})} - \frac{2216}{2189} \text{ w}} \\ \frac{(\text{Co}(\text{CNC}_6\text{H}_{11})_4(\text{Ph}_3\text{AsCH}_3\text{CH}_3\text{Ph}_3)_2](\text{CIO}_4)_2}{2124} - \frac{2228}{2124} \text{ w}} - \frac{2205}{2166} \text{ s}} \\ \frac{(\text{Co}(\text{CNC}_6\text{H}_{11})_4(\text{Ph}_3\text{AsCH}_3\text{CH}_3\text{Ph}_3)_2](\text{CIO}_4)_2}{2124} - \frac{2228}{2124} \text{ w}} - \frac{2205}{2164} \text{ m}} \\ \frac{(\text{Co}(\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2(\text{CO}\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2} - \frac{2226}{2124} \text{ w}} - \frac{2213}{2164} \text{ m}} \\ \frac{(\text{Co}(\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2(\text{CO}\text{A})_2} - \frac{2226}{212} \text{ vs}} - \frac{2233}{218} \text{ w}} \\ \frac{(\text{Co}(\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2220} - \frac{2223}{223} \text{ vs}} - \frac{2233}{2164} \text{ m}} \\ \frac{(\text{Co}(\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2220} - \frac{2223}{223} \text{ vs}} + \frac{2223}{2164} \text{ m}} \\ \frac{(\text{Co}(\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2220} - \frac{2223}{223} \text{ vs}} + \frac{2223}{2164} \text{ m}} \\ \frac{(\text{Co}(\text{CNC}\text{HMe}_3)_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2220} - \frac{2223}{223} \text{ vs}} + \frac{2223}{223} \text{ w}} \\ \frac{(\text{Co}(\text{CNC}\text{HM}_9\text{-P})_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{222} - \frac{2223}{223} \text{ vs}} + \frac{2223}{223} \text{ vs}} + \frac{2223}{223} \text{ vs}} \\ \frac{(\text{Co}(\text{CNC}\text{HM}_9\text{-P})_4(\text{AsPh}_3)_3](\text{CIO}_4)_2}{2239} \text{ vs}} + \frac{2233}{223} \text{ vs}} + \frac{2223}{223} \text{ vs}} \\ \frac{(\text{Co}(\text{CNC}\text{HM}_9\text{-P})_3)_3](\text{CIO}_4)_2} - \frac{2239}{223} \text{ vs}} + \frac{2223}{23} \text{ vs}} + \frac{2223}{23} \text{ vs}} \\ \frac{(\text{Co}(\text{CNC}\text{HM}_9\text{-P})_3)_3](\text{CIO}_4)_2} - \frac{2239}{23} \text{ vs}} + \frac{2223}{23} \text{ vs}} + \frac{2222}{23} \text{ vs}} + \frac{2223}{23} \text{ vs}} + \frac{2223}{23$	CF ₃ CH ₂ OH 2213 s(sh) 2207 s(sh) 2208 m 2215 s ~ 2208 w(sh) 2189 m 2206 s 2189 w 2164 m 2164 m	$\begin{array}{c} CH_2 Cl_2 \\ 760 br (125) \\ -675 sh (105) \\ -575 sh (105) \\ -372 sh (510) \\ 319 (1100) \\ -250 (12,000) \\ -805 br (1900) \\ -805 br (1900) \\ -675 sh (100) \\ 305 sh (810) \\ -575 sh (100) \\ 790 br (150) \\ 720 sh (1300) \\ -245 (16,000) \\ 762 br (155) \\ -310 sh (1300) \\ -245 (16,000) \\ -760 br (100) \\ 657 sh (93) \end{array}$	CH ₃ CN 720br (92) ~315sh (640)	
[Co(CNC ₆ H ₁₁) ₄ (AsPh ₃) ₂](C1O ₄) ₂ -2202 w(sh) 2207 s(sh) 2188 m (Co(CNC ₆ H ₁₁) ₄ (AsPh ₃) ₂](BF ₄) ₂ 2228 vs 2215 s (Co(CNC ₆ H ₁₁) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2222 vs 2218 w (Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₃) ₂](C1O ₄) ₂ 2222 vs 2206 s (Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₃) ₂](C1O ₄) ₂ 2222 vs 2206 s (Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₃) ₂](C1O ₄) ₂ 2222 vs 2206 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2228 vs 2206 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2227 vs 2205 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2227 vs 2205 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2229 vs 2205 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s (Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2232 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2232 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2230 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2230 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2220 vs 2230 vs 2223 s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2220 vs 2230 vs 2223 vs 2220 s s(sh) (Co(CNCH9-r)) ₄ (AsPh ₃)	2213 s(sh) 2207 s(sh) 2188 m 2215 s ~2208 w(sh) 2189 m 2206 s 2187 w 2164 m 2164 m	760br (125) ~675sh (105) ~372sh (510) 319 (1100) ~250 (12,000) ~805br (190) ~675sh (100) 305sh (810) ~250 (12,000) 790br (130) ~230sh (130) ~230sh (130) ~230sh (150) ~230sh (150) ~230sh (150) ~230sh (1300) ~245 (16,000) 762br (155) ~260r (100) 657sh (93)	720br (92) ~315sh (640)	
$ [Co(CNC_6H_{11})_4(AsPh_3)_2](BF_4)_2 \qquad -2200 w(sh) \qquad 2201 s(sh) \qquad 2188 m \qquad -2200 w(sh) \qquad 2188 m \qquad -2200 w(sh) \qquad 2188 m \qquad -2200 w(sh) \qquad 2189 m \qquad 2189 w \qquad 2180 m \qquad 2201 s(sh) \qquad 2166 w \qquad 2166 w \qquad 2166 w \qquad 2164 m \qquad 2166 w \qquad 2100 c(CNCHMe_2)_4(AsPh_3)_2](CIO_4)_2 \qquad 2221 v(sh) \qquad 2220 s \qquad 2220 s \qquad 2201 s(sh) \qquad 2202 m $	220/ stsn) 2188 m 2215 s ~2208 w(sh) 2189 m 2189 w 2189 w 2164 m 2164 m	~70.558 (100) ~7758 (510) 319 (1100) ~250 (12,000) ~6758 (100) ~6758 (100) ~790br (12,000) 790br (150) ~226 (16,000) ~245 (16,000) ~245 (16,000) ~760br (130) ~760br (130) ~760br (100) ~760br (100) 6575h (93)	(040) USC 16~	305
[Co(CNC ₆ H ₁₁) ₄ (AsPh ₃) ₂](BF ₄) ₂ -2200 w(sh) -2208 w ₅ -2208 w ₅ (sh) -2189 m [Co(CNC ₆ H ₁₁) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2222 v ₅ 2232 w ₅ 2189 w [Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2222 v ₅ 2124 w 2166 w [Co(CNC(HMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2227 v ₅ 2124 w 2165 w [Co(CNC(HMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2227 v ₅ 2220 s [Co(CNC(HMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 v ₅ 2213 s [Co(CNC(HMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 v ₅ 2213 s [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2233 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2233 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2233 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2233 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 v ₅ -2232 w(sh)	2215 s ~2208 w(sh) 2189 m 2232 w 2206 s 2189 w 2164 m 2164 m	319 (1100) ~250 (12,000) ~250 (12,000) ~6758h (100) 3055h (810) ~250 (12,000) 790br (150) ~2320sh (1300) ~245 (16,000) ~245 (16,000) ~250sh (1300) ~265 (100) ~760br (100) ~760br (100) ~760br (100) ~750sh (1300) ~760br (100) ~760br (100) ~760br (100) ~760br (100)	246 (11 000)	561 85
[Co(CNC ₆ H ₁₁) ₄ (AsPh ₃) ₂](BF ₄) ₂ -2200 w(sh) -2208 w(sh) -2208 w(sh) 2189 m [Co(CNC ₆ H ₁₁) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2222 vs 2232 w 2232 w 2177 w [Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2222 vs 2205 s 2166 w [Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2228 vs 2177 w 2166 w [Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2123 s 2164 m [Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s 2164 m [Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s 2163 w [Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2213 s 2223 w(sh) 2220 s 213 s 2223 w(sh) 2220 s 2233 w(sh) 2220 m	2215 s ~2208 w(sh) 2189 m 2232 w 2206 s 2189 w 2186 w 2164 m	~250 (12,000) ~675h (100) ~675h (100) 3055h (810) ~250 (12,000) 790br (150) ~226h (1300) ~2320h (1800) ~245 (16,000) 762br (155) ~320sh (1800) ~265h (1300) ~760br (100) 657sh (93)	223 (11,000)	23
[Co(CNC ₆ H ₁)) ₄ (AsPh ₃) ₂](BF ₄) ₂ 2228 vs 2238 vs -2200 w(sh) 2159 m [Co(CNC ₆ H ₁)) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2222 vs 2235 206 s 2206 s 2206 s 2206 s 2166 w [Co(CNC ₆ H ₁)) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2228 vs 2105 2157 w 2166 w 2166 w [Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2227 vs 2200 s 2166 w 2166 w 2166 w 2166 w 2166 w 2166 m 200 (CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2227 vs 2220 s 213 s 2166 w 2166 w 2166 w 2160 m 200 (CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s 2163 m 2164 m 200 (CNCHMe ₂) ₄ (Ph ₃ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2220 vs 22230 w(sh) 2220 s 213 s 2223 w(sh) 2160 (CNC ₄ H ₉ -m) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2223 vs -2233 w(sh) 2220 s 2223 w(sh) 2220 s 2233 w(sh) 2202 m 2233 w(sh) 2202 m	2215 s ~2208 w(sh) 2189 m 2206 s 2189 w 2189 w 2164 m 2164 m	~805br (190) ~675sh (100) 305sh (810) ~250 (12,000) 790br (150) ~226sh (1300) ~2320sh (1800) ~320sh (1800) ~325sh (500) ~375sh (500) ~760br (100) 657sh (93)		
$ [Co(CNC_6H_{11})_4(As(C_6H_4Me-p)_3)_2](C1O_4)_2 2222 vs 2232 v 2232 v 2208 w(sf)) 2189 w 2189 w 2189 w 2189 w 2189 w 2166 w 2124 w 2166 w 2166 w 2164 m 2167 w 2164 m 2167 w 2164 m 2167 w 2164 m 2160(CNCHMe_2)_4(AsPh_3)_2](C1O_4)_2 2221 v 2220 s 2164 m 200(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_3)_2](C1O_4)_2 2226 vs 2213 s 2164 m 200(CNCHMe_2)_4(Ph_3h_3)_2](C1O_4)_2 2226 vs 2221 s 2213 s 2205 w(sh) 2220 w(sh) 2220 w(sh) 2220 w(sh) 2220 w(sh) 2220 w(sh) 2220 v 2220 w(sh) 2220 s 213 w(sh) 2220 v 2220 22220 v 2220 v 22220 v 222$	~2208 w(sn) 2189 m 2232 w 2206 s 2189 w 2186 w 2164 m 2164 m	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	720br (81)	320
$ [Co(CNC_6H_{11})_4 (As(C_6H_4Me-p)_3)_2] (C1O_4)_2 2222 v_5 2232 v_5 2206 s_2 2189 w_2 2166 w_2 2124 w_2 2164 w_2 2166 w_2 2166 w_2 2164 w_2 2164 w_2 2164 w_2 2164 w_2 2164 m_2 2164 m_2 2164 m_2 2220 s_2 2230 s_2 2230 s_2 2230 v_5 22230 w(sh) 2223 v_5 2223 s_2 2233 w(sh) 22230 v(sh) 22230 v$	2107 m 2232 w 2206 s 2189 w 2187 w 2166 w 2164 m	~2504 (12,00) 790br (150) 720br (150) ~2205h (1300) ~2305h (1800) ~245 (16,000) 762br (155) ~3205h (155) ~3205h (155) ~245 (16,000) ~760br (100) 6575h (93)	$\approx 3155h (/00)$	125
[Co(CNC ₆ H ₁₁) ₄ (As(C ₆ H ₄ Me-p) ₃] ₂](C1O ₄) ₂ 2222 vs 2232 w 2206 s 2189 w 2166 w 2164 m 2177 w 2164 w 2166 w 2166 w 2167 w 2166 w 2166 w 2177 w 2166 w 2164 m 2185 w 2164 m 2227 vs 2220 s 2213 s 2205 s 2213 s 2205 w sh) ₂ [Co(CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2227 vs 2223 v 2223 vs 2223 s 2185 w 2164 m 200 CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2223 vs 2223 w sh) ₂ [Co(CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s 2213 s 2223 w sh) ₂ [Co(CNC4H9-η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2223 vs 2223 vs 2223 w sh) ₂ [Co(CNC4H9-η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs -2233 vs -2233 w sh) ₂ [Co(CNC4H9-η) ₄ (AsCG ₄ H ₄ Me-p) ₃] ₂](C1O ₄) ₂ 2233 vs 2223 w sh) ₂ 2220 s 213 w sh) ₂ [Co(CNC4H9-η) ₄ (AsCG ₄ H ₄ Me-p) ₃] ₂](C1O ₄) ₂ 2223 vs 2223 w sh) ₂ 2223 w sh) ₂ 2220 s 2233 w sh) ₂ 2220 s 2232 w sh) ₂ 2220 s 2232 w sh) ₂ 2220 s 2232 w sh) ₂ 2220 s 2202 m 2232 w sh) ₂ 2220 s 2202 m 2232 w sh) ₂ 2220 s 2202 m 2233 w sh) ₂ 2220 s 2202 m 223 w sh) ₂ 223 w sh)	2232 w 2206 s 2189 w 2177 w 2166 w 2164 m	790br (150) 420sh (130) ~230sh (1800) ~245 (16,000) 762br (155) ~385sh (500) ~320sh (155) ~245 (16,000) ~760br (100) 657sh (93)	219 (12.000)	31
[Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2228 vs 2205 s 2177 w 2166 w 2166 w 2167 w 2166 w 2168 w 2185 w 2223 w 22	2206 s 2189 w 2205 s 2177 w 2166 w 2164 m	420sh (1300) ~320sh (1800) ~245 (16,000) 762br (155) ~385sh (500) ~320sh (1300) ~245 (16,000) ~760br (100) 657sh (93)	726br (90)	300
$ [Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2 2228 vs 2177 w 2166 w 2177 w 2166 w 2167 w 2166 w 2166 w 2160 CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2 2227 vs 2164 m 2164 m 2185 w 2168 w 2168 w 2168 w 2168 w 2185 w 2223 v 22230 w(sh) 22230 w(sh) 22230 w(sh) 22230 w(sh) 22230 v 22230 w(sh) 22230 v 22230 w(sh) 22230 v 22230 w(sh) 22220 v 2230 w(sh) 22220 w(sh) 2222$	2189 w 2205 s 2177 w 2166 w 2164 m	~ 320sh (1800) ~ 245 (16.000) 762br (155) ~ 385sh (500) ~ 320sh (1300) ~ 245 (16.000) ~ 760br (100) 657sh (93)	~315sh (1100)	200
[Co(CNC ₆ H ₁₁) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2228 vs 2177 w 2166 w 2168 w 2185 w 2223 vs 2223 vs 2223 w (sh) 2220 (CNC4H9-t) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2226 vs 2223 vs 2223 w (sh) 2220 (CNC4H9-t) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2223 vs 2223 w (sh) 2220 w (sh) 2223 vs 2223 w (sh) 2220 v (sh) 2223 w (sh) 2220 v (sh) 2220	2205 s 2177 w 2166 w 2220 s 2164 m	762br (155) 762br (155) ~385sh (500) ~320sh (1300) ~245 (16,000) ~760br (100) 657sh (93)	248 (29,000)	185
[Co(CNCHMe ₂)4(AsPh ₃) ₂](C1O ₄) ₂ 2227 vs 2166 w 2164 m 2177 w 2164 m 2164 m 2168 m 2164 m 2168 w 2168 vs 22230 s 2185 w 2133 vs 22232 w(sh) 22205 w(sh) 22232 vs 22232 w(sh) 22205 w(sh	2177 w 2166 w 2220 s 2164 m	~3854 (500) ~3856 (500) ~245 (16.000) ~760br (100) 657sh (93)	728hr (105)	t č
[Co(CNCHMe ₂)₄(AsPh ₃) ₂](C1O ₄) ₂ 2227 vs 2220 s [Co(CNCHMe ₂)₄(Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s [Co(CNC4H ₉ -η)₄(AsPh ₃) ₂](C1O ₄) ₂ 2229 vs -2230 w(sh) [Co(CNC4H ₉ -η)₄(As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs -2243 w(sh) [Co(CNC4H ₉ -η)₄(As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs -2232 w(sh) 2213 v 2205 m	2166 w 2220 s 2164 m	~320sh (1300) ~245 (16.000) ~760br (100) 657sh (93)	≈315 (1100)	205
[Co(CNCHMe ₂) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2227 vs 2220 s [Co(CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s [Co(CNC4H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 22239 vs 22230 w(sh) [Co(CNC4H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2223 v(sh) [Co(CNC4H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs 2223 v(sh) [Co(CNC4H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs 2223 v(sh) [Co(CNC4H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs 2223 v(sh) [Co(CNC4H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2230 vv(sh) 2220 s	2220 s 2164 m	~245 (16,000) ~760br (100) 657sh (93)	245sh (40,000)	175
[Co(CNCHMe ₂)₄(AsPh ₃) ₂](C1O ₄) ₂ 2221 vs 2220 s [Co(CNCHMe ₂)₄(Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs 2239 vs 2220 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs -2233 vs -2232 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2220 vw(sh) 2220 vw(sh) 2220 s 2133 w 2202 m	2220 s 2164 m	~760br (100) 657sh (93)		28
[Co(CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](CIO ₄) ₂ 2226 vs 2213 s [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](CIO ₄) ₂ 2239 vs ~2230 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](CIO ₄) ₂ 2239 vs ~2223 v(sh) [Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](CIO ₄) ₂ 2239 vs ~2223 v(sh) 2220 vw(sh) 2220 s 2133 w 2202 m	2164 m	657sh (93)	740br (68)	320
[Co(CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s 2185 w 2185 w 2200 w(sh) (Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs ~2230 w(sh) (Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs ~2233 vs ~2232 w(sh) (Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2220 vw(sh) 2220 s 2133 w 2202 m			≈315sh (/00) 247 /02 /02	210
[Co(CNCHMe ₂) ₄ (Ph ₂ AsCH ₂ CH ₂ AsPh ₂) ₂](C1O ₄) ₂ 2226 vs 2213 s 2185 w 2185 w [Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](C1O ₄) ₂ 2239 vs ~2230 w(sh) 2221 s ~2205 w(sh) 2220 vw(sh) ~2223 w(sh) ~2170 vw(sh) 2220 s 2133 w 2202 m		~250 (0000)	(nnc.12) 147	C01 00
[Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](CIO ₄) ₂ 2239 vs 2230 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](CIO ₄) ₂ 2239 vs -2243 w(sh) [Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](CIO ₄) ₂ 2220 vw(sh) 2220 s w(sh) 2220 x 2170 vw(sh) 2220 s 2133 w 2202 m	2713 s	768hr (140)	746hr (87)	320
[Co(CNC₄H9-η)₄(AsPh ₃) ₂](CIO₄) ₂ 2239 vs ~2230 w(sh) 2221 s ~2205 w(sh) 2205 w(sh) ~2205 w(sh) ~2203 vs ~2232 w(sh) ~2170 vw(sh) 2220 s 133 w 2202 m	2185 W	405 (1200)	≈315sh (1100)	516
[Co(CNC₄H9-η)₄(AsPh ₃) ₂](CIO₄) ₂ 2239 vs ~2230 w(sh) 2221 s ~2205 w(sh) ~2205 w(sh) ~2205 w(sh) ~2205 w(sh) ~2232 vs ~2232 w(sh) ~2170 vw(sh) 2220 s 2133 w 2202 m		~315sh (1400)	246 (14.000)	185
[Co(CNC ₄ H ₉ -η) ₄ (AsPh ₃) ₂](CIO ₄) ₂ 2239 vs ~2230 w(sh) 2221 s ~2205 w(sh) ~2205 w(sh) ~2205 w(sh) ~2204 w(sh) ~2232 w(sh) ~2170 vw(sh) 2220 s s 2133 w 2202 m		245 (14,000)	-222 (14,000)	25
2221 s ~2205 w(sh) ~2205 w(sh) ~2239 vs ~2234 w(sh) ~2232 w(sh) ~2232 w(sh) ~2170 vw(sh) 2220 s 2133 w 2202 m	~2230 w(sh)	765br (160)	728br (86)	305
-2205 w(sh) -2205 w(sh) -2243 w(sh) -2243 w(sh) -2232 w(sh) -2232 w(sh) -2232 w(sh) -22220 s -2133 w 2133 w 2202 m	2221 s	≈410sh (220)	~310sh (570)	185
[Co(CNC ₄ H ₉ -η) ₄ (As(C ₆ H ₄ Me-p) ₃) ₂](C1O ₄) ₂ 2239 vs ~22243 w(sh) ~2232 w(sh) ~2232 w(sh) ~2232 w(sh) ~2170 vw(sh) 2220 s 2133 w 2202 m	\sim 2205 w(sh)	~315sh (930)	246 (10,000)	175
[co(cNC₄Hg-η)₄(As(C ₆ H₄Me-p) ₃) ₂](c1U₄)2 2239 vs ~2243 w(sh) ≈2220 vw(sh) ~2232 w(sh) ~2170 vw(sh) 2220 s 2133 w 2202 m		250 (12,000)	224 (10,000)	11
\approx 2170 vW(sh) \sim 2220 s \sim 213 w (sh) 2220 s 2133 w 2202 m	$\sim 2243 \text{ w(sh)}$	790br (145)	716br (120)	305
2133 w (SII) 2202 m	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	~ 0.051	~21 USU (/UU)	1001
	20272 2010 m	432 (1300) ~330eb (1500)	241 (22,000)	<u> </u>
	III 7077	249 (16.000)		707
[Co(CNCH ₂ Ph) ₄ (AsPh ₃) ₂](BF ₄) ₂ 224 vs 2224 vs	2224 vs	820br (195)	702br (56)	315
≈2230 w(sh) ~2220 w(sh)	\sim 2220 w(sh)	413 (635)	=390sh (580)	210
$\sim 2170 \text{ w(sh)}$ 2200 w	2200 w	~290sh (6000)	246 (14,000)	180
2134 m		248 (12,000)		19
[Co(CNCH ₂ Ph) ₄ (Ph ₂ AsCH ₂ CH ₂ CH ₂ AsPh ₂) ₂](BF ₄) ₂ 2250 s 2224 s	2224 s	-825br (85)	~700br (50)	315
$(\text{us})_{\text{M}} \leq 617$ $(\text{us})_{\text{M}} > 7272$	(us)m C617	412 (4500)	≈400sn (350)	C 77
. W 101 (10 m(sn) 2135 vs	2160 W	~240ch (2000) ~240ch (44.000)	~2905h (5000) 739ch (30 000)	1/0
02 0113		(000'++) 1150+7	(000,10) 118162	Ç.7

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Figure 1 Representative ν (-N=C) IR patterns for [Co(CNR)₄(AsR₃)₂]X₂ complexes; top to bottom: [Co(CNC₆H₁₁)₄(AsPh₃)₂](C1O₄)₂ (Nujol), [Co(CNC₆H₁₁)₄(As(C₆H₄Me- ρ)₃)₂](C1O₄)₂ (Nujol), [Co (CNC₆H₁₁)₄(AsCH₂AsCH₂CH₂AsPh₂)₂](C1O₄)₂ (Nujol), [Co(CNC₆H₁₁)₄(AsPh₃)₂](C1O₄)₂ (CH₂Cl₂).

months. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ 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). $[Co(CNC_6H_{11})_4(AsPh_3)_2](C1O_4)_2$, $[Co(CNC_6H_{11})_4(As(C_6H_4Me-p)_3)_2](C1O_4)_2$ and $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ 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 ; $X = C1O_4$, BF_4 , to be discussed more thoroughly in a subsequent paper.

Reaction of As($C_6H_4Me-\rho$)₃ with $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ (in CH_2Cl_2) produced the cobalt(III) complex, $[Co(CNCH_2Ph)_4 \{OAs(C_6H_4Me-\rho)_3\}_2](BF_4)_3$, as previously reported.⁷ This reaction may be solvent-dependent; faster recovery allowed isolation from EtOH may have of а 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($C_6H_4Me-\rho$)₃ with [Co(CNC₄H₉-n)₅](C1O₄)₂ (in EtOH), however, dark yellow the microcrystalline recovered with dark crystals were green $[Co(CNR)_4(AsR_3)_2](C1O_4)_2$. From the v(-N=C) IR pattern and frequency (2249s cm⁻¹ (Nujol)), this new compound could be $[Co(CNC_4H_9-n)_4]OAs(C_6H_4Me \rho_{3}_{2}(C1O_{4})_{3}$. 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 $A_{s}(C_{6}H_{4}Me-\rho)_{3} > A_{s}Ph_{3} >$ Ph₂AsCH₂CH₂AsPh₂. This reaction pattern is quite remarkable. In so many ligand substitution reactions AsPh₃ behaves analogously to PPh₃, 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 PR₃, AsR₃ and SbR₃. Preliminary results⁹ indicate that reactions with SbPh₃ 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 literature¹⁰ 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, $[Co(CNCMe_3)_4L_2](C1O_4)_2 \cdot xH_2O$, 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

Formula	$\chi_g \times 10^9$	$\chi_{M} \times 10^{6}$
CNC ₆ H ₁₁	-637 ± 8	-69.5 ± 0.9
CNCHMe ₂	-664 ± 9	-45.9 ± 0.6
$CNC_{A}H_{S}-\eta$	-618 ± 4	-51.4 ± 0.3
CNCH ₂ Ph	-579 ± 4	-67.8 ± 0.4
As $(C_6 \tilde{H}_5)_3$	-572 ± 14	-175 ± 4
As $(C_6H_4Me-p)_3$	-562 ± 24	-196 ± 8
Ph ₂ AsCH ₂ CH ₂ AsPh ₂	-482 ± 25	-234 ± 12

 Table 3 Measured diamagnetic susceptibilities.

Co(II) complexes, 1.7-2.0 BM, however, according to values suggested by Figgis and Nyholm¹³. Tetragonal structures for *trans*-[Co(CNR)₄(AsR₃)₂]X₂ would clearly be compatible with this magnetic data.

The v(-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 $[Co(CNR)_4(AsR_3)_2]X_2$, $AsR_3 = AsPh_3$, $As(C_6H_4Me-p)_3$, complexes in the solid state, is analogous to known or presumed tetragonal complexes, *e.g.*, $[Co(CNR)_4(C1O_4)_2]$, $R = 2,6-Me_2C_6H_3$,³ 2,6-Et₂C₆H₃;¹⁴ $[Co(CNCMe_3)_4L_2](C1O_4)_2$.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 v(-N=C) IR pattern therefore also supports a tetragonal structure for the $[Co(CNR)_4(AsR_3)_2](C1O_4)_2$ complexes in the solid state. The diffuse reflectance electronic spectra for the $[Co(CNR)_4(AsR_3)_2]X_2$, $AsR_3 = AsPh_3$, $As(C_6H_4Me-p)_3$, complexes (see Table 1) are approximately the same, and similar to most of the spectra for the $[Co(CNCMe_3)_4L_2](C1O_4)_2$ 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 $[Co(CNC_6H_3Et_2-2,6)_4L-L]BF_4$ complexes with bidentate tertiary phosphine ligands.¹⁷ Interestingly, the structure of $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ appears to be different from that of $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ and $[Co(CNCH_2Ph)_4$ ($Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ and $[Co(CNCH_2Ph)_4$ ($Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ and $[Co(CNCH_2Ph)_4$ ($Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$. $[Co(CNCHMe_2)_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ has the same v(-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} , CH₂Ph, complexes, however, have different diffuse reflectance spectra in which the first broad band(s) is(are) noticeably weaker, and drastically different v(-N=C) IR patterns (see Figure 1). Crude $[Co(CNCH_2Ph)_4(Ph_2AsCH_2CH_2AsPh_2)_2](BF_4)_2$ showed the typical v(-N=C) IR pattern (2220vs, ~2190w(sh) cm⁻¹), but reverted to the reported spectrum upon routine recrystallization from CH₂Cl₂/ether, while $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$ 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 v(-N=C) value observed in a Co(III) complex, *e.g.*, 2258 cm⁻¹ for $[Co(CNCH_2Ph)_4[OAs(C_6H_4Me-\rho)_3]_2](BF_4)_3$.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 ($\Lambda_{\rm M}$) for the [Co(CNR)₄(AsR₃)₂]X₂ complexes (see Table 2) in CH₃CN (305–320 Ω^{-1} cm²mol⁻¹), acetone (180–220), and CH₃NO₂ (175–185) are slightly high, but still reasonably close to the expected ranges for 2:1 electrolytes.¹⁸ $\Lambda_{\rm M}$ values in CH₂Cl₂ (17-34 Ω^{-1} cm²mol⁻¹) show considerable ion-pairing; this is customary behaviour for Co(II)-organoisocyanide complexes.^{6,7} $\Lambda_{\rm M}$ values for the [Co(CNR)₄(Ph₂AsCH₂CH₂AsPh₂)₂]X₂ 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 v(-N=C) IR patterns for all of the $[Co(CNR)_4(AsR_3)_2]X_2$ complexes with the triarylarsine ligands and for [Co(CNCHMe₂)₄(Ph₂AsCH₂CH₂AsPh₂)₂](C1O₄)₂, in CH₂Cl₂, 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(CNC₄ H_9-n_4 {As(C₆H₄Me- ρ)₃}₂](C1O₄)₂ and [Co(CNCH₂Ph)₄(AsPh₃)₂](BF₄)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 concentrations so only small are present in these spectra). $[Co(CNC_6H_{11})_4(Ph_2AsCH_2CH_2AsPh_2)_2](C1O_4)_2$, in CH_2Cl_2 , shows a v(-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 CF₃CH₂OH solution, the v(-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 $(C_{2\nu})$ should theoretically show four symmetry-allowed v(-N=C), *i.e.*, $2A_1 + B_1 + B_2$, but these bands could be only partially resolved. This v(-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 v(-N=C) IR pattern observed for [Co(CNR)₄(Ph₂AsCH₂CH₂AsPh₂)₂]X₂, R = C₆H₁₁, CH₂Ph, 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, $\varepsilon \simeq 50$ -200), with higher energy shoulders, culminating in one or more intense charge transfer bands (starting at 245-250 nm, $\varepsilon \simeq 10,000$ -40,000).

Several spectra in CH₂Cl₂ only, especially $[Co(CNCH_2Ph)_4(Ph_2AsCH_2 CH_2AsPh_2)_2](C1O_4)_2$, also exhibit a well-resolved band ~405-430 nm. In general, spectra for the complexes with Ph₂AsCH₂CH₂AsPh₂ appear very similar to spectra for complexes of the AsR₃ ligands with the same RNC, suggesting analogous solution structures. Both λ_{max} and ε of the crystal field band are higher in CH₂Cl₂ than in CH₃CN.

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 $AsR_3 = AsPh_3$, $As(C_6H_4Me-p)_3$; 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_4 Me-p)_3> AsPh_3, and the RNC, CNCHMe₂ > CNC_4H_9-n CNCH_2Ph > CNC_6H_{11}.

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