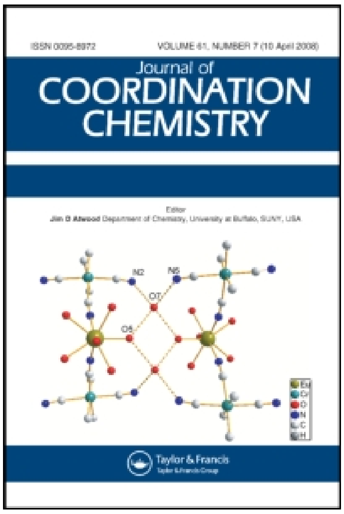

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SYNTHESIS OF MONOSUBSTITUTED *PENTAKIS*(2,6-DIETHYLPHENYLISO CYANIDE)-COBALT(I) COMPLEXES WITH BIDENTATE TERTIARY PHOSPHINE LIGANDS.
I. MONOMETALLIC COMPLEXES

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Reaction of $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ with bidentate phosphines leads to monosubstituted Co(I) complexes, $[Co(CNC_6H_3Et_2\text{-}2,6)_4(L\text{-}L)]BF_4$, where L-L = $Ph_2P(CH_2)_nPPh_2$, n = 1-4,6; $Ph_2PCH_2CH_2AsPh_2$, $Ph_2PC_6H_4PPh_2$-*p*, $Ph_2PCH{=}CHPPh_2$-*trans*. Reaction conditions are such that disubstitution would be possible, but bidentate bridging to form bimetallic complexes is not favoured. Comparison of $\nu(-N{\equiv}C)$ IR, electronic spectra, and molar conductivities with values for $[Co(CNC_6H_3Et_2\text{-}2,6)_4L]X$, where X = ClO_4, BF_4; L = monodentate triarylphosphine; indicates that these new complexes must also be five-coordinate Co(I) complexes, in which the potentially bidentate phosphine ligands are coordinated through only one P atom. Structures are approximately trigonal bipyramidal in solution and the solid state, with the phosphine ligand occupying an axial position.

KEY WORDS: 2,6-diethylphenylisocyanide, arylisocyanide, tertiary phosphine, cobalt(I), bidentate ligand

INTRODUCTION

Chelating abilities of polydentate tertiary phosphine ligands are well-established with many transition metal cations. With $[Co(CNCMe_3)_5]^+$, for example, two, three, and four coordination sites can be substituted by P atoms of the appropriate polydentate phosphine.[1] *Pentakis*(arylisocyanide)cobalt(I) complexes, in general, tend to disubstitute in reaction with monodentate triarylphosphines,[2-4] but ease of monosubstitution clearly parallels steric bulk in the RNC: $C_6H_5NC \sim p\text{-}MeC_6H_4NC < o\text{-}MeC_6H_4NC \ll 2,6\text{-}Me_2C_6H_3NC \sim 2,4,6\text{-}Me_3C_6H_2NC \ll 2,6\text{-}Et_2C_6H_3NC$.[3] $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$, with X = ClO_4, BF_4, is monosubstituted in all reactions with monodentate triarylphosphines investigated,[2-4] as well as with monodentate trialkylphosphines.[5] $[Co(CNC_6H_3Et_2\text{-}2,6)_3(PPh_3)_2]ClO_4$ could not even be detected in ^1H-NMR studies of solution-phase disproportionations of the monosubstituted complexes, as follows.[6]

$$2[Co(CNR)_4PR_3]^+ \rightleftharpoons [Co(CNR)_3(PR_3)_2]^+ + [Co(CNR)_5]^+$$

Disubstituted *pentakis*(2,6-diethylphenylisocyanide)cobalt(I) complexes, $[Co(CNR)_3(PR_3)_2]X$, with $X = ClO_4$, BF_4, are however readily obtained in reduction/ligand substitution reactions on $[Co(CNR)_4(ClO_4)_2]$ and $[Co(CNR)_5](BF_4)_2 . H_2O$ with triarylphosphines.[7,8] Thus while monosubstitution appears to be the preferred reaction for $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$, $X = ClO_4$, BF_4, with tertiary phosphine ligands, the possibility of disubstitution cannot be excluded. With the additional driving force of the chelate effect, disubstitution by such bidentate phosphine ligands as $Ph_2PCH_2CH_2PPh_2$ or $Ph_2P(CH_2)_3PPh_2$ could be expected. Results observed in this study, however, show otherwise.

EXPERIMENTAL

Reagents

RNHCHO, $R = 2,6\text{-}Et_2C_6H_3$ hereafter, was prepared from commercial RNH_2 (Aldrich) and formic acid[9] and converted to RNC by published procedure.[2,10] $[Co(CNR)_5](BF_4)_2 . H_2O$ was prepared as reported.[8] Commercial bidentate phosphines (Strem Chemicals) were used without further purification. Anhydrous diethyl ether was filtered through an alumina column immediately before use.

Instrumentation

IR spectra were recorded on a Perkin-Elmer 1710 FT-IR instrument. Solution electronic spectra were recorded on a Shimadzu UV-365 spectrophotometer. Molar conductivities were measured on ~0.001M samples at 25.0°C using a Crison model 525 conductimeter. The C, H, N and P elemental analyses were performed commercially.

$[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$

A 1.50 g sample of $[Co(CNC_6H_3Et_2\text{-}2,6)_5](BF_4)_2 . H_2O$ was dissolved in 7.5 cm^3 of pyridine, the dark blue solid producing an initial dark green solution which became yellow-brown in colour within 10-15 min at 25°C. Filtration through cotton produced a clear red-brown (bromine coloured) solution. Dropwise addition of 3.0 cm^3 of distilled water caused initial precipitation; a total volume of 6.0 cm^3 of distilled water was added, and the mixture was chilled in ice for 1 h. The bright yellow crystals (890 mg) were filtered, an additional 1.5 cm^3 of distilled water was added dropwise to the filtrate, and upon lengthy refrigeration a second crop (300 mg) was obtained. Crude product was dissolved in $CHCl_3$, filtered through cotton, and precipitated by dropwise addition of ether. Yield: 820 mg (61%). *Anal.* Calcd. for $CoC_{55}H_{65}BF_4N_5$: C, 70.14; H, 6.96; N, 7.44%. Found: C, 70.52; H, 7.10; N, 7.36%. IR $\nu(\text{—N}\equiv\text{C})$: 2103 vs, 2149 s ($cm^{-1}$; nujol); 2103 vs, 2146 s (CH_2Cl_2); Λ_M: 145 (acetone), 145 (CH_3CN), 90 (CH_3OH), 85 (CH_3NO_2), 70 (CH_2Cl_2) $\Omega^{-1}\ cm^2\ mol^{-1}$.

[Co($CNC_6H_3Et_2$-2,6)$_4Ph_2PCH_2CH_2PPh_2$]BF_4

A 750 mg sample of [Co($CNC_6H_3Et_2$-2,6)$_5$]BF_4 was dissolved in 2.0 cm^3 of CH_2Cl_2, filtered through cotton, and treated with a filtered solution of 793 mg $Ph_2PCH_2CH_2PPh_2$ (*i.e.*, 1:2.5 Co:ligand mole ratio) dissolved in 3.0 cm^3 of CH_2Cl_2, added dropwise with stirring at room temperature. The reaction mixture was allowed to stand 30 min at 25°C; an odour of free RNC was noted. Initial precipitation of fine yellow crystals occured after addition of 20.0 cm^3 of ether. A total volume of 42.5 cm^3 of ether was added, and the solution chilled for 45 min before filtration. Addition of excess ether to the filtrate and overnight refrigeration afforded a second crop of yellow crystals. The first crop (670 mg) was recrystallized from 2.0 cm^3 of CH_2Cl_2 and 13.0 cm^3 of ether; the second crop (145 mg) was separately recrystallized from CH_2Cl_2/ether. Total yield: 650 mg (69%).

[Co($CNC_6H_3Et_2$-2,6)$_4Ph_2PC_6H_4PPh_2$-p]BF_4

A solution of 890 mg of *p*-$Ph_2PC_6H_4PPh_2$ in 10.0 cm^3 of CH_2Cl_2 was filtered through cotton. Then, 750 mg [Co($CNC_6H_3Et_2$-2,6)$_5$]BF_4 (1:2.5 Co:ligand mole ratio) was added as solid, with 0.5 cm^3 of CH_2Cl_2 rinse. The odour of liberated RNC was immediately evident. The reaction mixture was allowed to stand for 45 min at room temperature, after which ether was added slowly. Slight precipitation was noted after addition of 14.0 cm^3 of ether, but a total volume of 30.0 cm^3 of ether was added, and the solution was chilled for 1.5 h. A pale yellow solid (290 mg) was filtered from the dark orange solution; addition of 60.0 cm^3 of ether to the filtrate and overnight refrigeration produced a second crop (110 mg) of dark yellow microcrystals. Successive additions of more ether, prolonged chilling, and slight evaporation afforded three more crops of dark yellow product (490 mg total); a sixth crop was recovered in the form of a very pale, yellow powder. The second to fifth crops (600 mg) were combined and recrystallized from 3.5 cm^3 of CH_2Cl_2 and 15.0 cm^3 of ether. Yield: 430 mg (72% recovery; 44% overall yield). The first and sixth crops were predominantly unreacted phosphine, and were therefore discarded.

RESULTS AND DISCUSSION

The monosubstituted, monometallic Co(I) complexes formed in the reaction between [Co($CNC_6H_3Et_2$-2,6)$_5$]BF_4 and selected bidentate phosphine ligands are summarized in Table 1, with major physical properties.

Synthesis of the Complexes

Phosphines having relatively high solubilities in CH_2Cl_2, such as $Ph_2P(CH_2)_nPPh_2$, n = 1 – 3; $Ph_2PCH_2CH_3AsPh_2$, and $Ph_2PC{\equiv}CPPH_2$, were reacted according to the synthesis for [Co(CNR)$_4Ph_2PCH_2CH_2PPh_2$]BF_4. Phosphines having more limited solubility in CH_2Cl_2, such as $Ph_2P(CH_2)_nPPh_2$, n = 4 – 6; (*p*-$MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me$-*p*$)_2$, $Ph_2PC_6H_4PPh_2$-*p*, and $Ph_2PCH{=}CHPPh_2$-*trans*, were reacted according to the synthesis for [Co(CNR)$_4Ph_2PC_6H_4PPh_2$-*p*]BF_4.

Table 1 Monometallic complexes of pentakis (2,6-diethylphenylisocyanide)cobalt(I) tetrafluoroborate monosubstituted with bidentate tertiary phosphine ligands.

	ν(—N≡C) Infrared[b]			Electronic spectra[c]			Elemental analysis (%) Found/calcd.			
Compound[a]/M.pt. (°C)	Nujol	CH_2Cl_2	CH_3NO_2	CH_2Cl_2	CH_3CN	Molar conductivity[d]	C	H	N	P
$[Co(CNR)_4Ph_2PCH_2PPh_2]BF_4$	~ 1988 vw(sh)	1991 w	~ 1990 vw	328 (15,100)	324 (12,600)	147	71.02	6.63	4.84	5.54
104-109 (decomp)	2059 vs(br)	2078 vs(br)	2076 vs(br)	261 (55,200)	259 (53,200)	139	71.01	6.39	4.80	5.31
	2099 w	~ 2108 w(sh)	~ 2108 w(sh)			91				
	2150 m	~ 2118 vw(sh)	≈ 2122 vw(sh)			85				
		2160 m	2160 m			63				
$[Co(CNR)_4Ph_2P(CH_2)_2PPh_2]BF_4$	~ 1990 vw(sh)	1996 w	~ 1998 w	329 (20,200)	330 (16,800)	149	70.83	6.80	4.84	5.04
110-114 (decomp)	2062 vs(br)	2074 vs	2076 vs(br)	259 (75,500)	260 (59,400)	142	71.18	6.49	4.74	5.24
	2107 w	2106 w	≈ 2109 vw(sh)		~ 238 sh	93				
	2156 m	≈ 2114 vw(sh)	2127 w			86				
		2159 m	2160 m			65				
$[Co(CNR)_4Ph_2P(CH_2)_3PPh_2]BF_4$	~ 1992 vw(sh)	1992 w	~ 1992 vw(sh)	330 (16,100)	330 (17,400)	148	71.61	6.79	4.67	5.32
154-156 (decomp)	2067 vs(br)	2075 vs	2075 vs	263 (57,000)	263 (61,000)	136	71.36	6.58	4.69	5.18
	2108 w	2107 w	2106 w			88				
	2159 m	2159 m	≈ 2123 vw(sh)			82				
			2160 m			66				
$[Co(CNR)_4Ph_2P(CH_2)_4PPh_2]BF_4$	~ 1992 vw(sh)	1994 w	1994 w	~ 328 (14,100)	~ 326sh (14,100)	145	71.35	6.76	4.54	5.10
111-115 (decomp)	≈ 2035 w(sh)	~ 2049 w(sh)	2049 m(sh)	260 (58,600)	271 (75,000)	136	71.52	6.67	4.63	5.12
	2066 vs	2073 vs(br)	2073 vs(br)		239 (161,000)	93				
	2105 w	~ 2105 w(sh)	~ 2103 w(sh)			90				
	2156 m	≈ 2123 vw(sh)	~ 2125 vw(sh)			47				
		2159 m	2160 m							

$[Co(CNR)_4Ph_2P(CH_2)_6PPh_2]BF_4$	~1995 vw(sh)	1994 w	1993 w	329 (17,300)	324 (14,800)	144	71.25	6.81	4.61	4.95
106-116 (decomp)	2071 vs	≈2046 w(sh)	~2044 w(sh)	268sh (71,400)	263 (61,100)	142	71.84	6.84	4.53	5.01
	2105 w	2073 vs	2072 vs	242 (142,000)		91				
	2156 m	2108 w	~2105 w(sh)			87				
		≈2122 vw(sh)	≈2123 vw(sh)			60				
		2158 m	2159 m							
$[Co(CNR)_4Ph_2P(CH_2)_2AsPh_2]BF_4$	~1995 vw(sh)	1997 w	1997 vw	331 (17,900)	331 (17,800)	148	68.61	6.32	4.61	2.45
122-125 (decomp)	2067 vs(br)	2074 vs(br)	2074 vs(br)	260 (60,000)	261 (60,800)	141	68.63	6.25	4.57	2.53
	2106 w	~2104 w(sh)	2105 w(sh)		~237sh	89				
	2155 m	≈2122 vw(sh)	≈2123 vw(sh)			82				
		2157 m	2160 m			72				
$[Co(CNR)_4Ph_2PCH{=}CHPPh_2\text{-trans}]BF_4$	~1994 vw(sh)	1995 w	1997 w	328 (21,000)	325 (19,300)	150	71.00	6.55	4.64	5.22
88-95 (decomp)	2068 vs	2078 vs	2079 vs	260 (57,300)	257 (53,300)	140	71.31	6.33	4.75	5.25
	2103 w	2106 w	~2108 w(sh)		~238sh	90				
	2152 m	~2123 vw(sh)	~2124 vw(sh)			84				
		2159 m	2160 m			69				
$[Co(CNR)_4Ph_2PC_6H_4PPh_2\text{-p}]BF_4$	~1990 vw(sh)	2080 vs(br)	2080 vs(br)	325 (21,900)	325 (16,200)	175	72.29	6.21	4.23	5.27
218-224 (decomp)	2079 vs(br)	2108 w	2110 w	260 (58,300)	252 (52,200)	175	72.31	6.23	4.56	5.04
	2110 vw(sh)	2122 vw(sh)	2126 vw(sh)	239sh (59,100)	238sh (59,500)	115				
	2162 m	2159 m	2161 m		230sh (62,500)	105				
						56				

[a] $R = C_6H_3Et_2$-2,6. [b] $\nu(—N{\equiv}C)$ in cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [c] $\lambda_{max}(\varepsilon)$ in nm without Gaussian resolution. [d] Molar conductivity, $\Lambda_M = 1000\ L_{correct}\ C_M^{-1}$ in $ohm^{-1}\ cm^2\ mole^{-1}$, first value in $CH_3C(O)CH_3$, second value in CH_3CN, third value in CH_3OH, fourth value in CH_3NO_2, fifth value in CH_2Cl_2.

Table 2 Solution properties for cobalt(I) complexes of 2,6-diethylphenylisocyanide and monodentate triarylphosphine ligands.

	Isocyanide IR[b]		Electronic spectra[c]		
Compound[a]	CH_2Cl_2	Nujol	CH_2Cl_2	CH_3CN	Molar conductivity[d]
$[Co(CNR)_4P(C_6H_5)_3]ClO_4$	~1999 vw	~2000 vw	335 (20,900)	333 (15,700)	146
	2078 s	2069 s(br)	264 (60,000)	261 (51,800)	134
	2108 w	~2083 m(sh)	~234sh (60,000)	≈238sh	89
	~2128 vw(sh)	2109 w		~230sh (57,400)	81
	2160 m	2159 m			68
$[Co(CNR)_4P(C_6H_4OMe\text{-}p)_3]ClO_4$	~2000 vw	~2000 vw	~338sh (20,000)	~336sh (16,800)	131
	2074 s	2070 sh(br)	≈276sh	≈275sh	121
	2105 w	2104 w	254 (73,100)	253 (66,400)	84
	2159 m	2156 m	≈239sh	~243sh (63,900)	75
					63
$[Co(CNR)_4P(C_6H_4Cl\text{-}p)_3]ClO_4$	~1999 vw	~1999 vw	331 (22,700)	328 (14,000)	139
	2082 s	2067 vs(br)	~261sh (62,100)	~256sh (48,700)	129
	~2111 w(sh)	2079 s(br)	244 (71,800)	~236sh (61,000)	85
	~2127 vw(sh)	2110 w			79
	2163 m	2159 m			64
$[Co(CNR)_4P(C_6H_4F\text{-}p)_3]ClO_4$[e]	1995 vw	~1991 vw(sh)	332 (22,700)	332 (15,800)	143
	2079 vs	2068 vs(br)	262 (60,300)	257 (54,000)	137
	2109 w	2108 w	237 (59,400)	≈238sh	89
	~2126 vw(sh)	2158 m		~231sh (57,900)	81
	2160 m				66
$[Co(CNR)_4P(C_6H_4Me\text{-}p)_3]ClO_4$[f]	1994	~1990 vw(sh)	337 (21,500)	334 (19,600)	147
	2074 vs	2045 s	266 (60,200)	264 (52,700)	132
	2104 w	2078 w	242 (67,500)	240 (59,300)	89
	~2122 vw(sh)	2105 w			82
	2157 m	2156 m			70
$[Co(CNR)_4\{2\text{-}Ph_2PC_5H_4N\}]ClO_4$[g]	1998 w	~1998 vw(sh)	333 (19,700)	330 (14,600)	145
	2082 vs(br)	2059 vs(br)	261 (61,600)	257 (51,800)	135
	2109 w	2107 w		~236sh (52,000)	90
	2125 w(sh)	2156 m		~230sh (54,300)	81
	2159 m				67

[a] R = $C_6H_3Et_2$-2,6. [b] $\nu(\text{—N}\equiv\text{C})$ in cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [c] $\lambda_{max}(\varepsilon)$ in nm, without Gaussian resolution. [d] Molar conductivity, $\Lambda_M = 1000\ L_{correct}\ C_M^{-1}$ in $\Omega^{-1}\ cm^2\ mol^{-1}$; first value in acetone, second in CH_3CN, third in CH_3OH, fourth in CH_3NO_2, fifth in CH_2Cl_2. [e] Anal. Calcd. for $CoC_{62}H_{64}ClF_3N_4O_4P$: C, 66.99, H, 5.80; N, 5.04%; found: C, 66.63; H, 5.70; N, 4.76%. [f] Anal. Calcd. for $CoC_{65}H_{73}ClN_4O_4P$: C, 70.99; H, 6.69; N, 5.09%; found: C, 70.76; H, 6.28; N, 4.83%. [g] Anal. Calcd. for $CoC_{61}H_{66}ClN_5O_4P$: C, 69.21; H, 6.28; N, 6.62%; found: C, 68.92; H, 6.22; N, 6.42%.

Several phosphines required a considerable volume of CH_2Cl_2 for solubility, which consequently required large volumes of ether and increased risk of the product separating as an oil. Prolonged chilling (several days) was required in some instances. Reaction appeared to take place with $Ph_2P(CH_2)_5PPh_2$. and (p-$MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me$-$p)_2$, but the resulting oils could not be crystallized. Reaction with $Ph_2PC{\equiv}CPPh_2$ required prolonged refrigeration (several weeks), and the product recovered was the bimetallic complex $[(RNC)_4CoPh_2PC{\equiv}CPPh_2Co(CNR)_4](BF_4)_2$ (to be reported elsewhere).

Results of these syntheses seem to indicate that a reluctance to disubstitute, or alternatively a tendency to monosubstitute, in $[Co(CNC_6H_3Et_2\text{-}2,6)_5]^+$ is a stronger driving force than the chelate effect for ligands such as $Ph_2P(CH_2)_nPPh_2$. This is rather interesting. It should be noted, however, that known disubstituted complexes most probably involve *trans* positioning of the triarylphosphines, but a chelating bidentate phosphine would necessarily occupy an axial and an equatorial position or possibly two equatorial positions. This could be significant in the stabilization of the Co(I) complex. Opportunity for bidentate bridging between two $Co(CNR)_4$ moieties, especially with phosphines such as $Ph_2PC_6H_4PPh_2$-p, $Ph_2PCH{=}CHPPh_2$-*trans*, and $Ph_2PC{\equiv}CPPh_2$, is probably minimized by the excess phosphine in the 2.5:1 phosphine:Co mole ratio. Behaviour of $Ph_2PC{\equiv}CPPh_2$ in forming a bimetallic complex in spite of the reaction conditions is unique. if reaction conditions are favourable for bidentate bridging, such as reacting excess $[Co(CNR)_5]BF_4$ with the phosphine (*e.g.*, 1:3 phosphine:Co mole ratio) or reacting $[Co(CNR)_4(L\text{-}L)]BF_4$ with additional $[Co(CNR)_5]BF_4$, bimetallic complexes are obtained, as will be reported in a subsequent paper.

Characterization of the Complexes

Physical properties, IR (ν(—N≡C)) and solution electronic spectra and molar conductivities (Λ_M) for the new complexes are listed in Table 1. Comparison with these properties for *pentakis*(2,6-diethylphenylisocyanide)cobalt(I) monosubstituted with monodentate triarylphosphines (Table 2) shows such strong similarity that analogous structures must be adopted. The ν(—N≡C) IR patern in particular, previously published,[3,5,11,12] is in effect a "fingerprint" for monosubstituted *pentakis*(arylisocyanide)cobalt(I) complexes in general. Similarity of this pattern in solid and solution states indicates there are no significant structural changes upon dissolution. Electronic spectra consisting of two charge-transfer bands ~325 – 330 nm, ~250 – 270 nm are also typical for these complexes. The inevitable conclusion is that these new complexes must contain five-coordinate Co(I), in which the potentially bidentate phosphine ligands are coordinated through only one P atom. $Ph_2PCH_2CH_2AsPh_2$ is undoubtedly coordinated through P, with free As, since triarylarsine shows no reaction with *pentakis*(arylisocyanide)cobalt(I).[13]

Actual structures of all these monosubstituted Co(I) complexes are most probably slightly distorted trigonal bipyramidal, in solution and solid states, with the phosphine ligand in an axial position. The ν(—N≡C) IR pattern has previously been so interpreted.[5,12,14] Electronic bands are almost certainly charge-transfer in nature, most probably $d_\pi \rightarrow \pi^*$ metal to ligand transitions. Molar conductivity values in acetone, CH_3CN, CH_3OH, and CH_3NO_2 are within the ranges anticipated for 1:1 electrolytes,[15] so the Λ_M values in CH_2Cl_2 (45–70 Ω^{-1} cm^2 mol^{-1}) probably represent fully dissociated 1:1 electrolytes.

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