Journal of Organometallic Chemistry, 104 (1976) 89—98

TRIALKYLPHOSPHITE SUBSTITUTION IN PENTAKIS(AROMATIC ISOCYANIDE)COBALT(I)*

C.A.L. BECKER

Department of Chemistry, Kentucky State University, Frankfort, Kentucky, 40601 (U.S.A.)

(Received June 12th, 1975)

Summary

Trialkylphosphites readily replace aromatic isocyanide ligands in [Co(CNR)$_5$]X (X = ClO$_4$, BF$_4$) to yield [Co(CNR)$_3${P(OR')$_3$}$_2$]X. The isocyanides R = —C$_6$H$_5$, —C$_6$H$_4$F-*p*, —C$_6$H$_4$Cl-*p*, —C$_6$H$_4$Br-*p*, —C$_6$H$_4$I-*p*, —C$_6$H$_4$CH$_3$-*p*, and —C$_6$H$_3$(CH$_3$)$_2$-2,6; and trialkylphosphites R' = —CH$_3$, —CH$_2$CH$_3$, and —CH(CH$_3$)$_2$ have been investigated. Reactions and products show no sensitivity toward oxygen or water. The —N≡C infrared, ^{1}H-NMR, and ^{59}Co-NQR seem compatible with regular trigonal bipyramidal structure in solution and distorted trigonal bipyramidal structure in the solid state.

Introduction

Growing research interest has developed for trialkylphosphite substitution in cobalt(I) complexes. A number of five-coordinate Co^I complexes containing carbonyls and trialkylphosphites have been reported. Substitution of Co$_2$(CO)$_8$ with excess P(OR')$_3$ has resulted in [Co(CO)$_2${P(OMe)$_3$}$_3$] BPh$_4$, [Co(CO){P(OMe)$_3$}$_4$] BPh$_4$ [1] and [Co(CO)$_2${P(OCH$_2$)$_3$CEt}$_3$] BPh$_4$, [Co(CO){P(OCH$_2$)$_3$CEt}$_4$] BPh$_4$ [2,1], while using stoichiometric amounts of P(OCH$_3$)$_3$ resulted in the dimeric (i.e., cobalt(0)) complexes: [Co$_2$(CO)$_{8-n}${P(OCH$_3$)$_3$}$_n$], n = 1,2,3 [3]. An acyl derivative, [CH$_3$COCo(CO)$_2${P(OMe)$_3$}$_2$], was obtained with large excess (i.e., 10/1 mole ratio) of P(OCH$_3$)$_3$ [1]. Hydride derivatives are also known; as e.g., [HCo(CO)$_2${P(OCH$_2$)$_3$CEt}$_2$] [4,2] and [HCo(CO){P(OCH$_2$)$_3$CEt}$_3$] [2]. The complexes [Co(CO)$_2${PhP(OEt)$_2$}$_3$] BPh$_4$ and [CoI(CO)$_2${PhP(OEt)$_2$}$_2$] have been prepared [5] by substitution of CO into the atmosphere-sensitive [CoI{PhP(OEt)$_2$}$_4$] BPh$_4$.

---

* Presented in part at the 29th Southwest Regional Meeting of the American Chemical Society, December 1973, Abstract No. 183 (Inorg. Div.); and the 169th National Meeting of the American Chemical Society, April 1975, Abstract No. 59 (Inorg. Div.).

The complexes, $[Co(CNR)_3\{PhP(OEt)_2\}_2]ClO_4$; R = $-C_6H_5$, $-C_6H_4CH_3$-*p*, $-C_6H_4OCH_3$-*p*, $-C_6H_4CH_3$-*o*, $-C_6H_{11}$, $-C_6H_3(CH_3)_2$-2,6; and $[Co(CNR)_3\{P(OCH_3)_3\}_2]ClO_4$; R = $-C_6H_5$, $-C_6H_4NO_2$-*p*, $-C_6H_3(CH_3)_2$-2,6; have recently been prepared and characterized [5]. Preparation was by isocyanide reaction with $[CoX\{PhP(OEt)_2\}_4]ClO_4$, X = Cl, Br, I; or, reaction of anhydrous cobalt(II) chloride, $PhP(OEt)_2$ or $P(OCH_3)_3$, and the isocyanide in ethanol in 1/3.5/2.5 mole ratio, respectively. The exceptional compound, $[Co(CNC_6H_4NO_2\text{-}p)_2\{PhP(OEt)_2\}_3]ClO_4$, was prepared under reaction conditions producing 3/2 isocyanide-phosphonite complexes with the other aromatic isocyanides [5]. This present study reports trialkylphosphite, i.e., $P(OCH_3)_3$, $P(OCH_2CH_3)_3$, and $P\{OCH(CH_3)_2\}_3$, substitution in pentakis(aromatic isocyanide)cobalt(I), in excess amount (10/1 molar ratio) and very short reaction time. The synthesis and initial characterization of $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OCH_3\}_2]BF_4$ has already been reported by the author [6].

Pentakis(trialkylphosphite)cobalt(I) is also well-established, being characterized by $[Co\{P(OCH_2)_3CCH_3\}_5]^+$ [7], $[Co\{P(OCH)_3(CH_2)_3\}_5]^+$ [8,9], $[Co\{P(OCH_3)_3\}_5]^+$ [1,8,9,10], $[Co\{P(OCH_3)_3\}_2\{P(OCH_2)_3CC_2H_5\}_3]^+$ [1] and $[Co\{P(OC_2H_5)_3\}_5]^+$ [11]. Reaction of $[Co\{P(OCH_3)_3\}_5]BF_4$ with aromatic isocyanide is an alternate method of preparation for $[Co(CNR)_3\{P(OCH_3)_3\}_2]BF_4$ [10]. Five-coordinate cobalt(I) complexes with trialkylphosphite ligands have already been partially investigated, therefore, though not as extensively as cobalt(I) complexes with trialkyl- and triaryl-phosphine ligands.

Experimental

Pentakis(aromatic isocyanide)cobalt(I) perchlorate and tetrafluoroborate were prepared as previously described [12,13,6]. Commercial trialkylphosphites were vacuum distilled under vigorous stirring. Anhydrous diethyl ether was filtered through an alumina column immediately before use; nujol was dried over $CaCl_2$. Proton-NMR spectra were recorded on a Varian A-60 or HA-100 at ambient temperature in 99.8% $CDCl_3$ using CH_2Cl_2 as secondary internal reference (δ 5.28). Infrared spectra were recorded on a Beckman IR-7 in nujol mull or CH_2Cl_2 solution (4-5%) using 0.1 mm pathlength NaCl cells. Electronic spectra were measured in CH_2Cl_2 solution ($\sim 10^{-5}$ *M*) using a Cary Model 14 spectrophotometer. The ^{59}Co-NQR signals were measured on room-temperature polycrystalline samples (0.8-2.0 g) using a coherency-controlled superregenerative spectrometer following the design of Peterson and Bridenbaugh [14] but modified to operate with maximum sensitivity over the range 3-50 MHz. This instrument in Professor M.J.S. Dewar's research laboratory is described elsewhere [15]. Elemental analyses were performed commercially.

Preparation of $[Co(CNR)_3\{P(OR')_3\}_2]X$

General preparation of the $[Co(CNR)_3\{P(OR')_3\}_2]X$ complexes followed the procedure described for $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OCH_3)_3\}_2]BF_4$ [6]. A 0.50-2.0 g sample of $[Co(CNR)_5]X$ was dissolved in 1.5-5.0 ml CH_2Cl_2 and filtered through cotton. Trialkylphosphite in 10/1 molar ratio was added rapidly dropwise, immediately followed by dropwise addition of diethyl ether to effect precipitation (5.0-15.0 ml). The light yellow crystals were thoroughly cooled in ice, filtered, and dried under suction/air. A second crop could often be obtained upon adding more ether. Crude product was recrystallized from CH_2Cl_2/ether. Yield: 55-70%.

Alternate preparation of $[Co(CNC_6H_5)_3\{P(OCH_3)_3\}_2]ClO_4$

A 0.30 g sample of $[Co(CNC_6H_5)_5]ClO_4$ was dissolved in 7.0 ml CH_3OH and filtered. Then 0.55 g $P(OCH_3)_3$(l) was added rapidly dropwise while the solution was being stirred. Approximately 1.0 ml distilled water added slowly dropwise effected precipitation. Recrystallization from CH_2Cl_2/ether was preferable to CH_3OH/water. Yield: 60%.

Alternate preparation of $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OCH_2CH_3)_3\}_2]BF_4$

A 0.50 g sample of $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ was dissolved in 2.0 ml CH_2Cl_2, filtered, and treated with 1.00 g $P(OCH_2CH_3)_3$(l) added dropwise. This solution was stirred 8.0 h at 25°C before precipitation by dropwise addition of 12.0 ml diethyl ether. Crude product was recrystallized from CH_2Cl_2/ether. Yield 65%.

Results and discussion

The complexes prepared in this study are summarized in Table 1. All are pale-yellow crystalline solids with faint odor of trialkylphosphite. No significant difference for ClO_4^- or BF_4^- salts could be observed. Melting points, which are approximate due to gradual discoloration over a temperature range before well-defined decomposition, indicate reasonable thermal stability. Pyrolysis of the free isocyanides would take place at lower temperatures.

The —N≡C infrared frequencies (nujol, 25°C) for these complexes are summarized in Table 2. The pattern of one very strong, broad band (2065-2095 cm^{-1}) with a higher and lower energy shoulder is maintained for all complexes, in solution as well as solid state, although in solution the two weak bands are less pronounced. The CH_2Cl_2-solution IR spectra for $[Co(CNR)_3\{P(OR')_3\}_2]^+$ can probably be viewed as containing single —N≡C fundamental stretches, and thereby compatible to D_{3h} symmetry. Treating extra but weak IR bands commonly seen for five-coordinate cobalt(I) complexes as nonfundamental absorptions seems to be standard practice [5,16]. In solid state $[Co(CNR)_3\{P(OR')_3\}_2]X$ are probably distorted trigonal bipyramidal structures. Besides the —N≡C IR being in apparent conflict with D_{3h} symmetry, the ^{59}Co-NQR asymmetry parameters (η) are too large for regular trigonal bipyramidal coordination [17]. Since almost any distortion will lower the symmetry of a trigonal bipyramid, it should be expected that the bulky ligands in $[Co(CNR)_3\{P(OR')_3\}_2]^+$ show some deviation from D_{3h} behavior. Drastic distortions of bond lengths and angles from idealized trigonal bipyramidal structure — including significant non-linearity of Co—C≡N and C≡N—C bonds — have been observed in all pentakis(aromatic isocyanide)cobalt(I) complexes investigated: $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ [18] (square pyramidal), $[Co(CNC_6H_5)_5]ClO_4$ [19,17], $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ [20] and $[Co(CNC_6H_2\{CH_3\}_3\text{-}2,4,6)_5]ClO_4$ [21]. An X-ray structure is being performed on a single crystal of $[Co(CNC_6H_4F\text{-}p)_3\{P(OCH_3)_3\}_2]BF_4$ [19], but results are not yet available.

The dominant ν(CN) in $[Co(CNR)_3\{P(OR')_3\}_2]X$ is at lower energy than

(continued on p. 94)

TABLE 1

AROMATIC ISOCYANIDE-TRIALKYLPHOSPHITE COBALT(I) COMPLEXES

Compound	M.P. (°C)	Analyses found (calcd.) (%)			
		C	H	N	Halogen
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	211-213, Dec.	40.06 (40.21)	3.87 (3.75)	5.19 (5.21)	Cl, 13.32 (13.19)
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH_2CH_3)_3\}_2]BF_4$	210-214, Dec.	44.53 (44.50)	4.76 (4.75)	4.69 (4.72)	Cl, 12.04 (11.94)
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH\{CH_3\}_2)_3\}_2]ClO_4$	183-184, Dec.	47.23 (47.43)	5.40 (5.51)		Cl, 14.52 (14.36)
$[Co(CNC_6H_4F\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	202-204, Dec.	42.80 (42.83)	4.00 (3.99)	5.50 (5.55)	
$[Co(CNC_6H_4Br\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	206-208, Dec.	34.36 (34.50)	3.20 (3.22)		Br, 25.60 (25.50)
$[Co(CNC_6H_4I\text{-}4)_3\{P(OCH_3)_3\}_2]ClO_4$	180-183, Dec.	29.90 (29.65)	2.68 (2.76)		I, 35.10 (34.81)
$[Co(CNC_6H_5)_3\{P(OCH_3)_3\}_2]BF_4$	194-197, Dec.	45.80 (46.11)	4.57 (4.73)	5.83 (5.97)	
$[Co(CNC_6H_4CH_3\text{-}4)_3\{P(OCH_3)_3\}_2]ClO_4$	184-187, Dec.	47.30 (47.54)	5.26 (5.19)		Cl, 4.88 (4.68)
$[Co(CNC_6H_3\{CH_3\}_2\text{-}2,6)_3\{P(OCH_3)_3\}_2]ClO_4$	169-171, Dec.	49.46 (49.54)	6.06 (5.67)	5.17 (5.25)	Cl, 4.38 (4.43)

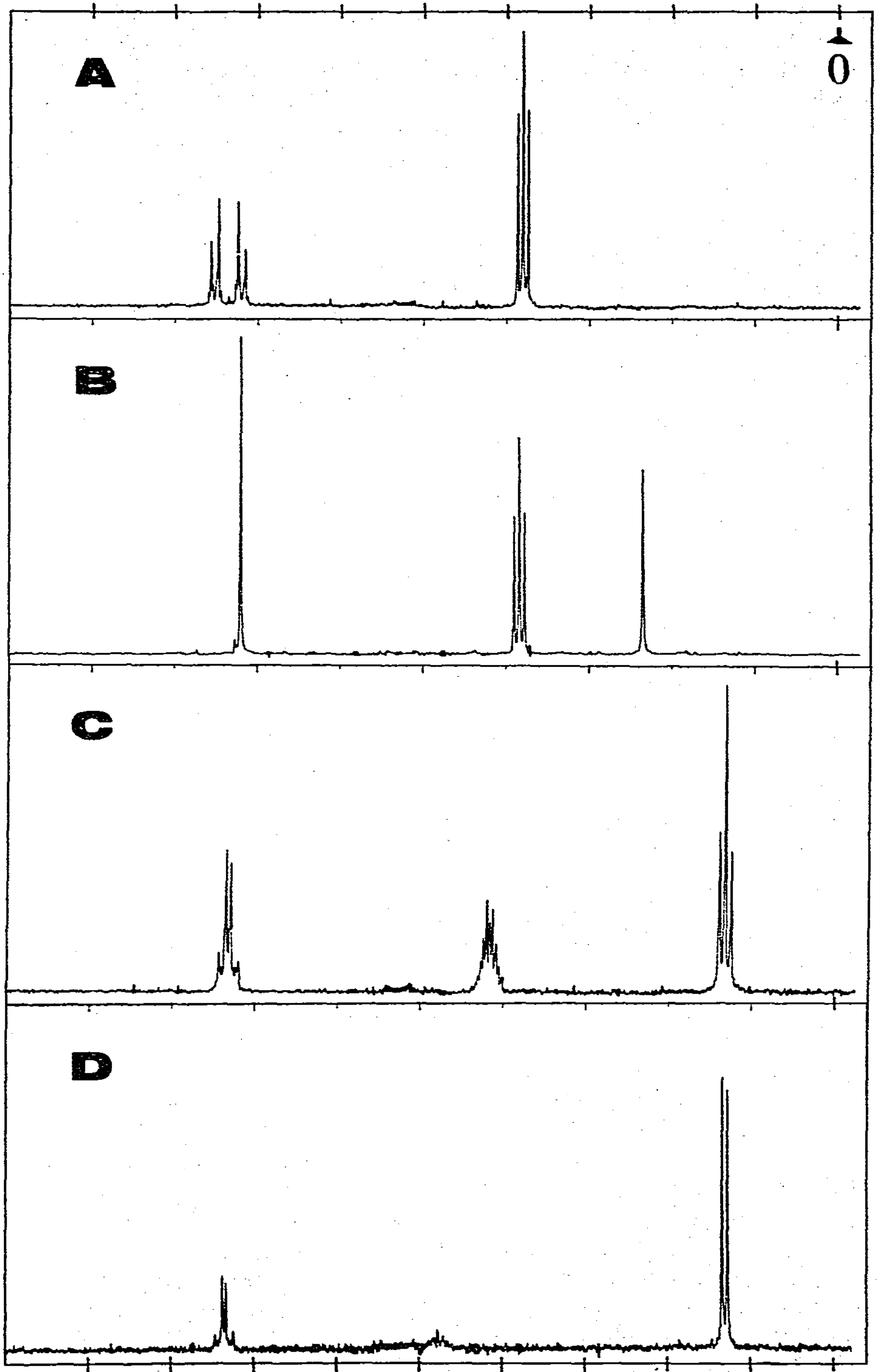

Fig. 1. The ^{1}H-NMR spectra (100 MHz; right to left, δ 0.00-δ10.00) for selected $[\mathrm{Co(CNR)_3\{P(OR')_3\}_2}]\mathrm{X}$ complexes, in $\mathrm{DCCl_3}$ at ambient temperature with $\mathrm{CH_2Cl_2}$ as secondary internal reference (δ5.28). (A) $[\mathrm{Co(CNC_6H_4Br}$-$p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{BF_4}$; (B) $[\mathrm{Co(CNC_6H_4CH_3}$-$p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{ClO_4}$; (C) $[\mathrm{Co(CNC_6H_4}$-Cl-$p)_3\{\mathrm{P(OCH_2CH_3)_3}\}_2]\mathrm{BF_4}$; (D) $[\mathrm{Co(CNC_6H_4Cl}$-$p)_3\{\mathrm{P(OCH\{CH_3\}_2)_3}\}_2]\mathrm{ClO_4}$.

TABLE 2

INFRARED AND PROTON NMR VALUES FOR AROMATIC ISOCYANIDE-TRIALKYLPHOSPHITE COBALT(I) COMPLEXES

Compound	Isocyanide infrared (cm^{-1})[a]
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	2018 w(sh), 2092 s(br), 2154 w(sh)
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH_2CH_3)_3\}_2]BF_4$	2016 m(sh), 2080 s, 2145 w(sh)
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH\{CH_3\}_2)_3\}_2]ClO_4$	2018 w(sh), 2065 s(br), 2134 m(sh)
$[Co(CNC_6H_4F\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	2055 w(sh), 2095 s(br), 2157 w(sh)
$[Co(CNC_6H_4Br\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	2015 w(sh), 2090 s, 2150 vw(sh)
$[Co(CNC_6H_4I\text{-}4)_3\{P(OCH_3)_3\}_2]ClO_4$	2010 w(sh), 2083 s, 2188 m
$[Co(CNC_6H_5)_3\{P(OCH_3)_3\}_2]BF_4$	2002 m, 2093 s, 2152 vw(sh)
$[Co(CNC_6H_4CH_3\text{-}4)_3\{P(OCH_3)_3\}_2]ClO_4$	2044 m(sh), 2094 s(br), 2152 vw(sh)
$[Co(CNC_6H_3\{CH_3\}_2\text{-}2,6)_3\{P(OCH_3)_3\}_2]ClO_4$	2005 w(sh), 2072 s(br), 2140 w(sh)

[a] Symbols used: w, weak; vw, very weak; m, medium; s, strong; sh, shoulder; br, broad. [b] Symbols used: s, singlet; d, doublet; t, triplet; δ_1, δ_2, components of AB pattern; (n), number of apparent peaks in partially-resolved multiplet.

in the corresponding $[Co(CNR)_5]X$ [13] (e.g., 2065-2092 cm^{-1} vs. 2110-2120 cm^{-1}, for R = $-C_6H_4Cl\text{-}p$), suggesting increased π^*-electron acceptance and/or decreased σ-electron donation by the remaining $C\equiv NR$ when two isocyanides are replaced by trialkylphosphites. This is in agreement with the general contention that trialkylphosphites are stronger σ-donating and weaker π^*-accepting ligands than aromatic isocyanides. Decrease in ν(CN) is observed upon substituting $R' = -CH_3$, to $-CH_2CH_3$, to $-CH(CH_3)_2$ in $[Co(CNC_6H_4Cl\text{-}p)_3\{P(OR')_3\}_2]X$ (i.e., ν(CN) = 2092, 2080, 2065 cm^{-1}, respectively). This is in good accord with increasing electron releasing ability (based on induction) $-CH_3 < -CH_2CH_3 < -CH(CH_3)_2$, which renders the phosphorus more σ-donating and less π^*-accepting. Decrease in ν(CN) for $CNC_6H_3\{CH_3\}_2$-2,6 relative to CNC_6H_5 (i.e., 2072 vs. 2093 cm^{-1}) was also observed; this has been explained as steric effect [5].

Proton-NMR data for $[Co(CNR)_3\{P(OR')_3\}_2]^+$ are summarized in Table 2 and some important spectra are pictured in Fig. 1. The ^1H-integrations give excellent confirmation of the elemental analyses. The aromatic protons for the most part give an *AB* pattern despite the real *AA'BB'* nature. Aromatic proton frequencies in $[Co(CNR)_3\{P(OR')_3\}_2]X$ tend to be shifted upfield relative to CNR and to $[Co(CNR)_5]X$ [13] or are approximately the same as the free ligand [13]. In $[Co(CNR)_3\{P(OCH_3)_3\}_2]^+$ a single aromatic frequency is observed with $CNC_6H_4CH_3\text{-}p$, while in $[Co(CNR)_5]^+$ the *para*-substituent electronically equivalent to coordinated $-N\equiv C$ was bromine [13]. This again indicates increased electron density about the $-N\equiv C-$ i.e., decreased σ-donation and increased π^*-acceptance — in $[Co(CNR)_3\{P(OR')_3\}_2]X$ over $[Co(CNR)_5]X$. Coordinated $P(OCH_3)_3$ is virtually coupled into 1/2/1 triplets in the same manner for all $[Co(CNR)_3\{P(OCH_3)_3\}_2]^+$ complexes and shows little variation in frequency (i.e., δ 3.81-3.87). Coordinated $P(OCH_2CH_3)_3$ is also best explained in terms of virtual coupling, but the lone proton in coordinated $P(OCH\{CH_3\}_2)_3$ is insufficiently resolved to confirm virtual coupling. The coordinated trialkyl-

Proton NMR spectrum^b		
CNC_6H_4X	$P(OR')_3$	^{1}H-Ratio: $CNR/P(OR')_3$
δ_1 7.38, δ_2 7.32	δ 3.85 (t; J, 6.0 Hz)	3.00/1.98
δ_1 7.38, δ_2 7.27	δ 4.18 (9) δ 1.33 (t; J, 7.0 Hz)	3.00/1.98
δ_1 7.41, δ_2 7.31	δ 4.80 (5) δ 1.30 (d; J, 6.0 Hz)	3.00/2.06
δ_1 7.30, δ_2 7.06 (8:5,3)	δ 3.81 (t; J, 6.0 Hz)	3.00/2.00
δ_1 7.54, δ_2 7.23	δ 3.82 (t; J, 6.0 Hz)	3.00/1.96
δ_1 7.76, δ_2 7.10	δ 3.84 (t; J, 6.0 Hz)	3.00/1.93
δ 7.38 (s)	δ 3.87 (t; J, 6.0 Hz)	3.00/2.02
δ 7.20 (s) δ 2.36 (s)	δ 3.84 (t; J, 6.0 Hz)	3.00/2.04
δ 7.15 (s) δ 2.44 (s)	δ 3.82 (t; J, 6.0 Hz)	3.00/1.98

phosphites exhibit downfield shifts relative to free ligand values. The NMR behavior (i.e., virtual coupling) suggests *trans* position for the phosphite ligands [22] and isocyanide ligands equivalent on the NMR time scale.

Cobalt-59 nuclear quadrupole resonance measurements for selected $[Co(CNR)_3\{P(OR')_3\}_2]X$ complexes are tabulated in Table 3. Signal and coupling constant values are intermediate to those for type I [12,13] (typical signal: 30.827, 20.531, 10.445 MHz; coupling constants, 143.8-144.7 MHz; η, 0.048-0.066) and types III [12,13] (36.692, 24.193, 13.284 MHz; 171.3-171.7 MHz; 0.155-0.162) and IV [23] (37.432, 24.742, 13.349 MHz; 174.6-175.3 MHz; 0.128-0.144) $[Co(CNR)_5]X$ complexes [17]. These coupling constants are higher than those for $[Co(CO)_3\{P(OCH_3)_3\}_2]BPh_4$ (136.1 MHz) and $[Co\{P(OCH_3)_3\}_5]BPh_4$ (153.7 MHz), and rank with the highest values observed for $[Co(CO)_4X]$, 97-162 MHz; X = $SnCl_3$ (161.45 MHz), $SnBr_3$ (159.88 MHz), SnI_3 (153.04 MHz), and $GeCl_3$ (161.48 MHz) [24]. At least some of the asymmetry parameters (η) are too large to be compatible with D_{3h} symmetry about the

TABLE 3

COBALT NQR MEASUREMENTS FOR AROMATIC ISOCYANIDE-TRIALKYLPHOSPHITE COBALT(I) COMPLEXES

Complex	Signals (MHz)	η	Coupling Constant (MHz)
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	34.33, 22.88, 11.51	0.038	160.29
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH_2CH_3)_3\}_2]BF_4$	34.42, 22.935, 11.525	0.034	163.25
$[Co(CNC_6H_4Cl\text{-}4)_3\{P(OCH\{CH_3\}_2)_3\}_2]ClO_4$	34.114, 22.692, 11.740	0.0925	159.40
$[Co(CNC_6H_4F\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	34.97, 23.225, 12.025	0.0925	163.35
$[Co(CNC_6H_4Br\text{-}4)_3\{P(OCH_3)_3\}_2]BF_4$	34.073, 22.630, 11.565	0.0721	159.04
$[Co(CNC_6H_5)_3\{P(OCH_3)_3\}_2]BF_4$	35.509, 23.666, 11.917	0.0418	165.759
$[Co(CNC_6H_3\{CH_3\}_2\text{-}2,6)_3\{P(OCH_3\}_2]ClO_4$	34.298, 22.210, 14.686	0.303	161.503

cobalt, for which experimental η values should approach zero indicating equivalent x and y axes. A value of $\eta = 0.057$ was measured for $[\mathrm{Co(CNC_6H_5)_5}]\mathrm{ClO_4} \cdot \mathrm{HCCl_3}$ [17], in which bonding along the x and y axes is similar but not identical [18], so experimental values for which η should theoretically be zero should be smaller than 0.06. (Experimental values of $\eta \equiv 0$ would probably not be measured.) No explanation can be offered for the anomalous values obtained for $[\mathrm{Co(CNC_6H_3\{CH_3\}_2\text{-}2,6)_3\{P(OCH_3)_3\}_2}]\mathrm{ClO_4}$, other than obvious steric considerations. In other respects this complex is analogous to other compounds in this series. Correlation of increasing η values with greater pronouncement of the —N≡C IR side bands, both suggesting departure from regular trigonal bipyramidal structure, could not be observed.

Dichloromethane solution electronic spectra (25°C) in the region 5000-2250 Å: $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{BF_4}$ (1.55×10^{-5} *M*); maxima, 3350 Å (ϵ = 25,800), 2600 Å (~45,000), 2350 Å (~45,000); $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$ (1.25×10^{-4} *M*); 3780 Å (810), 2980 Å (3380), 2530 Å (~6800), 2250 Å (~6500); and $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{BF_4}$ (1.24×10^{-5} *M*); 3400 Å (36,000), ~2550 Å (Gaussian resolution, $\epsilon \approx 33{,}000$), ~2300 Å ($\approx$37,000); are shown in Fig. 2. The 3780 Å absorption in $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$ should be a crystal field band, probably the first spin-allowed transition $^1A'_1\,[(e'')^4(e')^4] \rightarrow {}^1E'$-$[(e'')^4(e')^3(a'_1)]$, while the other absorptions are probably metal-to-ligand charge transfer bands. The $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$ transitions are significantly less intense than those for $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{BF_4}$ and $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{BF_4}$. Similarity in general appearance of the charge-transfer spectra suggests the same electronic transitions, possibly the three one-electron, symmetry-allowed transitions from the highest energy filled MO, $e'\{d_{\sigma,\pi}\}$ — arising principally from metal orbitals — into three of the four empty MO's from equatorial group-ligand π^* orbitals, A'_2, E', E''. (The fourth group-ligand orbital

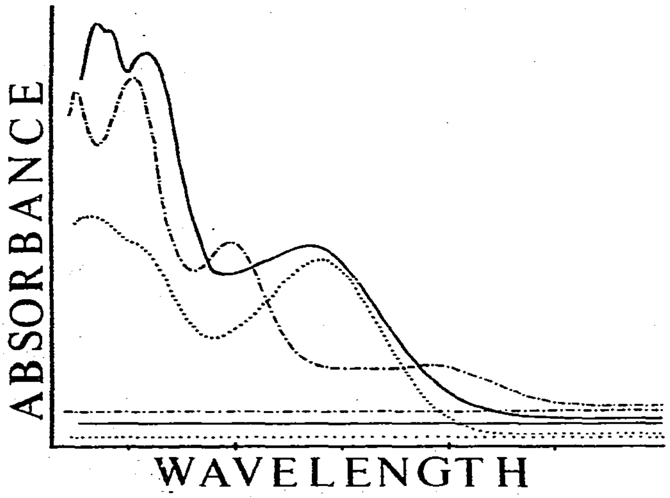

Fig. 2. Solution electronic spectra ($\mathrm{CH_2Cl_2}$, 25°C; right to left, wavelength 5000-2250 Å) for selected aromatic isocyanide-trialkylphosphite cobalt(I) complexes: $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{BF_4}$, 1.55×10^{-5} M (———); $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$, 1.25×10^{-4} M (— · — ·); and $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{BF_4}$, 1.24×10^{-5} M (·········).

$(\Gamma_\pi\{\mathrm{eq}\})$, A_2'', does not involve a symmetry-allowed one-electron transition from $e'\{d_{\sigma,\pi}\}$.)

$$\begin{aligned}{}^1A_1'[(e''\{d_\pi\})^4(e'\{d_{\sigma,\pi}\})^4] &\rightarrow {}^1E'[(e''\{d_\pi\})^4(e'\{d_{\sigma,\pi}\})^3(E'\{\mathrm{eq},\pi^\star\})^1]\\ &\rightarrow {}^1E'[(e''\{d_\pi\})^4(e'\{d_{\sigma,\pi}\})^3(A_2'\{\mathrm{eq},\pi^\star\})^1]\\ &\rightarrow {}^1A_2''[(e''\{d_\pi\})^4(e'\{d_{\sigma,\pi}\})^3(E''\{\mathrm{eq},\pi^\star\})^1]\end{aligned}$$

These $d_\pi \rightarrow \pi^\star$ transitions may be expected to be very intense and quite similar for trigonal bipyramidal $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{BF_4}$ and $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{BF_4}$, but different in $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$ since the excited state would involve $\pi^\star$-orbitals of only the equatorial ligands. Other charge-transfer transitions would also be possible.

Electronic spectra for $[\mathrm{Co(CNCH_3)_5}]\mathrm{ClO_4}$ (i.e. 35,600 cm^{-1} (2810 Å), $\epsilon = 7{,}000$ and 43,700 cm^{-1} (2290 Å), $\epsilon = 10{,}500$) have been assigned [25] as a *d—d* and $d \rightarrow \pi^\star$ transition, respectively, and this interpretation extended to spectra of selected $[\mathrm{Co(CNR')_3\{P(C_6H_5)_3\}_2}]\mathrm{PF_6}$ and $[\mathrm{Co(CNR)_3\{P(C_6H_5)_3\}_2}]\mathrm{PF_6}$ complexes [26] (representative spectra: ~2700 Å ($\epsilon \simeq 30{,}000$), ~2300 Å (~50,000); and ~3500 Å ($\epsilon \simeq 35{,}000$), ~2800 Å (~40,000), ~2400 Å (~74,000), respectively). While spectra of low-spin trigonal bipyramidal d^8 Ni(II) complexes are characterized by an intense (e.g., $\epsilon \simeq 600$ - 2300 [27] (aliphatic ligands), $\epsilon \simeq 900$ - 6,000 [28] (aromatic ligands)) crystal field band, ${}^1A_1'[(e'')^4(e')^4] \rightarrow {}^1E'[(e'')^4(e')^3(a_1')]$, and a weaker, higher energy CF band, ${}^1A_1'[(e'')^4(e')^4] \rightarrow {}^1E''[(e'')^3(e')^4(a_1')]$, which may be obscured by very intense charge transfer bands; data for $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{BF_4}$, $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$ and $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_3\{\mathrm{P(OCH_3)_3}\}_2]\mathrm{BF_4}$ does not support assigning any of the three intense transitions as crystal field *d—d* bands. Room-temperature solution electronic spectra for $[\mathrm{Co(CNR)_5}]^+$ and $[\mathrm{Co(CNR)_3\{P(OR')_3\}_2}]^+$ complexes, the three higher energy transitions in $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4}$, and possibly also the spectra for $[\mathrm{Co(CNR)_3\{P(C_6H_5)_3\}_2}]\mathrm{PF_6}$, all seem to be of the same electronic nature: $d \rightarrow \pi^\star$ charge-transfer bands. Not only does $[\mathrm{Co\{P(OCH_3)_3\}_5}]\mathrm{BF_4(CH_2Cl_2)}$ exhibit a lower energy, less intense absorption (i.e., 3780 Å ($\epsilon = 810$)), which is probably the sought-after *d—d* band, but the reflectance [29] and $\mathrm{N_2}$(l)-temperature mull [30] spectra for $[\mathrm{Co(CNC_6H_5)_5}]\mathrm{ClO_4}$ exhibit a similar band albeit poorly resolved. Assignment of these three intense absorptions as charge-transfer bands, with crystal field spectra obscured, seems reasonable.

Reaction in $\mathrm{CH_3OH}$/water - which is more or less restricted to $[\mathrm{Co(CNC_6H_5)_5}]\mathrm{X}$ due to solubility - is less satisfactory than $\mathrm{CH_2Cl_2}$/ether because the crystals are not as well formed, but no oxidation or other decomposition due to the direct presence of water can be detected. Extended reaction time appears to have no effect on the reaction of $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{BF_4}$ with $\mathrm{P(OCH_2CH_3)_3}$. Dialkylphosphites do not readily replace aromatic isocyanides in $[\mathrm{Co(CNR)_5}]\mathrm{X}$; only unreacted starting material was recovered when $\mathrm{HP(OCH_3)_2}$ and $\mathrm{HP(OCH_2CH_3)_2}$ were reacted with $[\mathrm{Co(CNC_6H_4Cl}\text{-}p)_5]\mathrm{ClO_4}$ under conditions analogous to trialkylphosphite substitution. Substitution reactions of $[\mathrm{Co(CNR)_5}]\mathrm{X}$ with triarylphosphites; i.e., $\mathrm{P(OC_6H_5)_3}$ and $\mathrm{P(OC_6H_4Cl}\text{-}p)_3$ are dissimilar to trialkylphosphite substitution, and lead in general to complexes of the form, $[\mathrm{Co(CNR)_4P(OR)_3}]\mathrm{X}$ [31].

Acknowledgement

The Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged for partial support of this research and for a research scholarship to the undergraduate laboratory assistant, William Jackson.

References

1 S. Attali and R. Poilblanc, Inorg. Chim. Acta, 6 (1972) 475.
2 B.L. Booth, M. Gardner, and R.N. Haszeldine, Chem. Commun., (1969) 1388.
3 G. Capron-Cotigny, These 3ème cycle, Paris (1967).
4 R.F. Heck, J. Amer. Chem. Soc., 85 (1963) 1220; 87 (1965) 2572.
5 E. Bordignon, U. Coatto, U. Mazzi, and A.A. Orio, Inorg. Chem., 13 (1974) 935.
6 C.A.L. Becker, Syn. React. Inorg. Metal-org. Chem., 4 (1974) 213.
7 J.G. Verkade and T.S. Piper, Inorg. Chem., 2 (1963) 944.
8 T. Huttemann, Jr., B. Foxman, C. Sperati, and J. Verkade, Inorg. Chem., 4 (1965) 951.
9 K.J. Coskran, T.J. Huttemann, and J.G. Verkade, in R.F. Gould, (Ed.), Advances in Chemistry Series, American Chemical Society, Washington, D.C. 62 (1967) p. 598.
10 G.W. Bachman and C.A.L. Becker, Syn. React. Inorg. Metal-org. Chem., 5 (1975) 151.
11 L.W. Gosser and G.W. Parshall, Inorg. Chem., 13 (1974) 1947.
12 C.A.L. Becker, J. Inorg. Nucl. Chem., 35 (1973) 1375.
13 C.A.L. Becker, J. Inorg. Nucl. Chem., 37 (1975) 703.
14 G.E. Peterson and P.M. Bridenbaugh, Rev. Sci. Instr., 35 (1964) 698; 36 (1965) 702.
15 W.I. Simpson, M.A. Thesis, University of Texas at Austin, 1971; see also, M.J.S. Dewar, D.B. Patterson, and W.I. Simpson, J. Chem. Soc., Dalton Trans., (1973) 2381.
16 F.A. Cotton and R.V. Parish, J. Chem. Soc., (1960) 1440.
17 C.A.L. Becker, M. McKee, W.I. Simpson, and M.J.S. Dewar, data reported in part at the 169th National Meeting of the American Chemical Society, April 1975, Abstract No. 117 (Inorg. Div.).
18 L.D. Brown, D.R. Greig, and K.N. Raymond, Inorg. Chem., 14 (1975) 645.
19 S.H. Simonsen, personal communication.
20 S.H. Simonsen and W.C. Bryson, personal communication, data reported in part at the 29th Southwest Regional Meeting of the American Chemical Society, December 1973, Abstract No. 184 (Inorg. Div.).
21 W.C. Bryson and S.H. Simonsen, personal communication, data reported in part at the 30th Southwest Regional Meeting of the American Chemical Society, December 1974, Abstract No. 240 (Inorg. Div.).
22 J.M. Jenkins and B.L. Shaw, Proc. Chem. Soc., London, (1963) 279.
23 C.A.L. Becker, Inorg. Nucl. Chem. Lett., 11 (1975) 295.
24 T.L. Brown, Accounts Chem. Res., 7 (1974) 408.
25 Y. Dartiguenave, M. Dartiguenave, and H.B. Gray, Bull. Soc. Chim. Fr., (1969) 4225.
26 J.W. Dart, M.K. Lloyd, R. Mason, J.A. McCleverty, and J. Williams, J. Chem. Soc., Dalton Trans., (1973) 1747.
27 G.S. Benner, W.E. Hatfield, and D.W. Meek, Inorg. Chem., 3 (1964) 1544; G.S. Benner and D.W. Meek, Inorg. Chem., 6 (1967) 1399.
28 C.M. Harris, R.S. Nyholm, and D.J. Phillips, J. Chem. Soc., (1960) 4379; G. Dyer, J.G. Hartley, and L.M. Venanzi, J. Chem. Soc., (1965) 1293; G. Dyer and D.W. Meek, Inorg. Chem., 4 (1965) 1398; 6 (1967) 149.
29 J.M. Pratt and P.R. Silverman, J. Chem. Soc. (A), (1967) 1286.
30 C.A.L. Becker, unpublished data, reported in part at the 161st National Meeting of the American Chemical Society, March 1971, Abstract No. 85 (Inorg. Div.).
31 C.A.L. Becker, data reported in part at the 167th National Meeting of the American Chemical Society, April 1974, Abstract No. 114 (Inorg. Div.); and the 169th National Meeting of the American Chemical Society, April 1975, Abstract No. 59 (Inorg. Div.).