Inorganica Chimica Acta, 89 (1984) 95–104

Trialkylphosphine Substitution in Pentakis(arylisocyanide)cobalt(I)*

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Received February 10, 1984

Trialkylphosphines, $P(NEt_2)_3$, $P(C_6H_{13}\text{-}n)_3$, and $P(C_2H_4CN)_3$; were investigated in ligand-substitution reactions with $[Co(CNR)_5]X$, $X = ClO_4$, BF_4; $R = C_6H_5$, $o\text{-}MeC_6H_4$, $p\text{-}ClC_6H_4$, $2,6\text{-}Et_2C_6H_3$. The $P(NEt_2)_3$ monosubstituted in all instances, including reduction/ligand substitution reaction with $[Co(CNR)_5](ClO_4)_2$. The $P(C_6H_{13}\text{-}n)_3$ disubstituted, except with the sterically-hindered $R = 2,6\text{-}Et_2C_6H_3$, which monosubstituted. The $P(C_2H_4CN)_3$, whose limited solubility forced departure from the usual CH_2Cl_2 solvent, mono- and disubstituted depending on the arylisocyanide: $[Co(CNR)_3\{P(C_2H_4CN)_3\}_2]X$, $R = C_6H_5$, $C_6H_4Me\text{-}o$, $C_6H_4Cl\text{-}p$; $[Co(CNR)_4P(C_2H_4CN)_3]X$, $R = C_6H_4Cl\text{-}p$, $C_6H_3Et_2\text{-}2,6$. The $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_2H_4CN)_3]ClO_4$ was obtained even in Co(II) reaction, while $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ was obtained in reaction of $P(C_6H_{13}\text{-}n)_3$ with $[Co(CNC_6H_3Et_2\text{-}2,6)_5](ClO_4)_2$. Relative $d_\pi \rightarrow \pi^*$ accepting ability for P-ligands was established from $\nu(\text{-}N{\equiv}C)$ IR data: $RNC \gg P(OMe)_3 > P(C_6H_4Cl\text{-}p)_3 > P(C_6H_5)_3 > P(C_2H_4CN)_3 > P(C_6H_4OMe\text{-}p)_3 > P(C_6H_{13}\text{-}n)_3 > P(NEt_2)_3$. Electronic spectra can be interpreted as $d_\pi \rightarrow \pi^*(eq)$ charge-transfer transitions, with λ_{max} of the first band for $[Co(CNR)_3L_2]X$ in increasing order: $L = P(OMe)_3 < P(C_2H_4CN)_3 < P(C_6H_{13}\text{-}n)_3 < P(NEt_2)_3 < P(C_6H_4Cl\text{-}p)_3 < P(C_6H_5)_3 < P(C_6H_4OMe\text{-}p)_3$. Correlation of phosphine ligand-substitution patterns with π^*-accepting/σ-donating ability was considered.

Introduction

Trialkylphosphite, triarylphosphite, and triarylphosphine ligand-substitution reactions in pentakis(arylisocyanide)cobalt(I), $[Co(CNR)_5]X$, $X = ClO_4$, BF_4; have been extensively investigated. Trialkylphosphites, $P(OR)_3$, $R = Me$, Et, i-Pr; showed disubstitution with all arylisocyanides investigated [1], except the sterically-hindered $2,4,6\text{-}Me_3C_6H_2NC$ [2] and $2,6\text{-}Et_2C_6H_3NC$ [3] which both mono- and disubstitute. Triarylphosphites, $P(OR)_3$, $R = C_6H_5$, $p\text{-}ClC_6H_4$; produced only monosubstituted products, except for the anomalous $[Co(CNC_6H_5)_3\{P(OC_6H_5)_3\}_2]ClO_4$ [4]. The analogous $[Co(CNC_6H_5)_3\{P(OC_6H_4Cl\text{-}p)_3\}_2]ClO_4$ was prepared by ligand substitution in $[Co(CNC_6H_5)_3\{As(C_6H_5)_3\}_2]ClO_4$ [5, 6]. Triarylphosphines, PR_3, $R = C_6H_5$, $p\text{-}ClC_6H_4$, $p\text{-}MeOC_6H_4$; produced mono- and/or disubstituted products depending on RNC, PR_3, and reaction conditions [7, 8]; sterically-hindered RNC and the less-reactive $P(C_6H_4Cl\text{-}p)_3$ favored monosubstitution. Direct reduction/ligand substitution on $[Co(CNR)_5]X_2 \cdot xH_2O$, $X = ClO_4$, BF_4; has been performed using trialkylphosphites, triarylphosphites, and triarylphosphines [9]. Disubstitution is favored here, even with sterically-hindered RNC showing monosubstitution in Co(I) reaction. Some $[Co(CNR)_3(PPh_3)_2]X$ and $[Co(CNR)_4PPh_3]X$ have been prepared by reaction of RNC with $Co(PPh_3)_2X_2$ [10, 11], and several $[Co(CNR)_3L_2]Y$, $L = P(OMe)_3$, $PhP(OEt)_2$; $Y = ClO_4$, BF_4; were prepared by reaction of RNC with $[CoXL_4]Y$, $X = Cl$, Br, I; or with $CoCl_2$–phosphite mixture [12]. Substitution of tertiary phosphines (PPh_3 and polydentate diphenylphosphines) in $[Co(CNBu\text{-}t)_5]PF_6$ has also been investigated [13]. Preparation of $[Co(CNR)_3(PBu_3)_2][Co(CO)_4]$, R = alkyl; by RNC substitution in $[Co(CO)_3PBu_3{}^n]_2$ is reported [14], but a systematic investigation of trialkylphosphine substitution in pentakis(arylisocyanide)cobalt(I) has hitherto not been undertaken.

Trialkylphosphine chemistry of Co(I) is too extensive to survey here, but observation of characteristic substitution patterns is relevant to this study. Ligand substitution in $[Co(CO)_4]_2$ gave $[Co(CO)_3(PR_3)_2]X$, R = Et, C_6H_{13}; $X = [Co(CO)_4]$, BPh_4, $[Cr(SCN)_4(NH_3)_2]$ [15]; $[Co(CO)_3(PR_3)_2]BPh_4$ and $[Co(CO)_2(PR_3)_3]BPh_4$, R = Me, Et [16]; and $[Co(CO)_3\{P(CH_2SiMe_3)_3\}_2][Co(CO)_4]$ [17]. The compounds $[Co(CO)_3(PR_3)_2]ClO_4$, R = Et, Pr, Bu; and

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*Presented in part at the 182nd National Meeting of the American Chemical Society, August 1981, Abst. No. 217 (Inorg. Div.).

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0020-1693/84/$3.00

$[Co(CO)_2(PR_3)_3]ClO_4$, $PR_3 = PEt_3$, PMe_2Ph, $PMePh_2$, PEt_2Ph; are also prepared by reaction of CO with $Co(ClO_4)_2 \cdot 6H_2O$ and PR_3 [18]. Reaction of $[CoL_3]ClO_4$, L = 2,2′-dipyridyl, 1,10-phenanthroline; with CO and PR_3 also produces $[Co(CO)_3(PR_3)_2]ClO_4$, R = Et, Pr, Bu; or $[CoL(PR_3)diene]ClO_4$, $PR_3 = PEt_3$, PPr_3, PBu_3, PEt_2Ph; diene = butadiene, isoprene; with diene and PR_3 [19]. The compounds, $[Co(diene)(PMe_2Ph)_3]ClO_4$, diene = C_4H_6, C_5H_8; are also reported [20]. Halides (X^-) react with $[Co(CO)_3(PR_3)_2]^+$ and $[Co(CO)_2(PR_3)_3]^+$ to produce $[Co(CO)_2(PR_3)_2X]$, X = I, R = Me, Et; X = Cl, R = Et [16]. Four-coordinate $[CoX(PR_3)_3]$, X = Cl, R = Me [21]; X = Cl, $PR_3 = PMe_2Ph$, $PMePh_2$ [22]; X = Cl, Br, I; R = Me [23]; can be used to prepare $[Co(CO)_2(PMe_3)_2X]$, $[Co(CO)(PMe_3)_3X]$, $[Co(CO)(PMe_3)_4]X$, $[Co(PMe_3)_4]BPh_4$, and $[Co(PMe_3)_4(Me_2PH)]X$, X = Cl, Br [23]. The hydride, $[HCo(CO)_3PBu_3]$, was prepared from $[Co(CO)_3PBu_3]_2$ and Et_3SiH [24]. Tributylphosphine substitution in $Me_3SnCo(CO)_4$ gave $Me_3SnCo(CO)_3P(CMe_3)_3$ [25]. Mono- and disubstituted trimethylphosphine complexes of Co(I) are well-established with cyclopentadienyls; *e.g.*; $[CpCo(PMe_3)CO]$ [26], $[(C_5H_4R)Co(CO)PMe_3]$, R = aryl [27]; $[CpCo(PMe_3)_2]$ [22]; $[(C_5H_4R)Co(PMe_3)_2]$, R = alkyl [28]; and $[(C_5H_3RR')Co(PMe_3)_2]$, R, R′ = Me_2CH, Me_3C [29]. Other five-coordinate trimethylphosphine complexes include $[Co(C_2H_4)L(PMe_3)_3]$, L = H, Me, Ph [30]; $Co(PMe_3)_4Me]$, $[Co(PMe_3)_4C{\equiv}CPh]$, $[CoMe(CO)(PMe_3)_3]$ [21]; $[Co(CO)_2(PMe_3)_2COMe]$ [21, 31]; and $[CoL(PMe_3)_3]BPh_4$, L = C_4H_6, C_5H_8 [32]. Mono-, di-, tri-, and tetrasubstituted trialkylphosphine complexes of Co(I) are known, but di- and trisubstituted, pentacoordination seems most prevalent.

Three trialkylphosphines were selected for this investigation: $P(C_6H_{13}\text{-}n)_3$ (unsubstituted trialkylphosphine), $P(NEt_2)_3$ (phosphine with electron-donating substituent), and $P(CH_2CH_2CN)_3$ (phosphine with electron-withdrawing substituent). Arylisocyanides considered were: CNC_6H_5 (unsubstituted arylisocyanide), CNC_6H_4Cl-*p* (isocyanide with electron-withdrawing substituent), CNC_6H_4Me-*o* (isocyanide with electron-donating substituent), and $CNC_6H_3Et_2$-2,6 (sterically-hindered isocyanide). With this selection of PR_3 and RNC, a range of inductive and steric effects could be investigated.

Experimental

Commercial anilines, $C_6H_5NH_2$, *p*-$ClC_6H_4NH_2$, *o*-$MeC_6H_4NH_2$, and 2,6-$Et_2C_6H_3NH_2$; were converted first to N-arylformamides [33], then to arylisocyanides by modification [34] of the synthesis by Hertler and Corey [35]. The Co(II) complexes were prepared as described [36, 37], and reduced to Co(I) as previously described [34, 37, 38]. Commercial tris(2-cyanoethyl)phosphine, $P(C_2H_4CN)_3$ (Strem), tri-n-hexylphosphine, $P(C_6H_{13}\text{-}n)_3$ (Alfa), and tris(diethylamino)phosphine, $P(NEt_2)_3$ (Fluka); were initially used without purification, but $P(NEt_2)_3$ was later vacuum re-distilled. Spectro-grade CH_3NO_2 and CH_3CN were used without purification, but CH_2Cl_2 was distilled over $CaCl_2$. Anhydrous diethyl ether was filtered through an alumina column immediately before use. IR spectra were recorded on a Perkin-Elmer 398 spectrophotometer in Nujol mull and CH_2Cl_2 or CH_3NO_2 (~1%) using 0.106 mm pathlength matched NaCl cells. Electronic spectra were measured in CH_2Cl_2 or CH_3CN ($\sim 1.5 \times 10^{-5}$ *M*) using a Pye Unicam SP 8-250 or Perkin-Elmer 552 UV/VIS spectrophotometer. Elemental analyses were performed commercially.

Preparation of $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(NEt_2)_3]ClO_4$ *(Method A)*

A 350 mg sample of $[Co(CNC_6H_3Et_2\text{-}2,6)_5]ClO_4$ was dissolved in 1.0 ml CH_2Cl_2 and filtered through cotton. Then 453 mg $P(NEt_2)_3$ (5:1 molar ratio) was added dropwise with swirling. Orange color of the solution darkened immediately and odor of RNC was detected. After 80 min, the solution was treated with 6.0 ml ether dropwise to effect precipitation, cooled, and filtered. Two crops of crude product were collected and dried under suction/air. The pale yellow microcrystals were re-crystallized from CH_2Cl_2/Et_2O. Yield: 358 mg, crude (94%); 201 mg, re-crystallized (53%).

Preparation of $[Co(CNC_6H_5)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ *(Method B)*

A solution of 305 mg $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ in 1.1 ml CH_2Cl_2 was filtered through cotton and cooled in ice. Then 554 mg cold $P(C_6H_{13}\text{-}n)_3$ (5:1 molar ratio) was added dropwise. After 60 min, the solution was treated with 45.6 ml cold ether and chilled in ice 90 min. No crystallization occurred, so another 13.3 ml ether was added, and the solution left overnight in a cold room at 7 °C. The bright greenish-yellow crystals which precipitated were re-crystallized from 1.1 ml CH_2Cl_2 and 6.4 ml ether, and dried under suction/air, all manipulations performed at 7 °C. Yield: 205 mg, crude (51%); 135 mg, re-crystallized (34%).

Preparation of $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_2H_4CN)_3\}_2]BF_4$ *and* $[Co(CNC_6H_4Cl\text{-}p)_4P(C_2H_4CN)_3]BF_4$ *(Method C)*

A 514 mg sample of $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ was dissolved in 7.2 ml CH_3CN, filtered through cotton, and treated with 595 mg $P(C_2H_4CN)_3$ (5:1 molar ratio) in 8.1 ml CH_3CN filtered through cotton and added dropwise with swirling. Odor of RNC was detected immediately. After 60 min, 21.9 ml ether was added dropwise to precipitate a first crop, which was collected after cooling in ice. The filtrate evaporated slightly under suction, then 39.9 ml ether was added to precipitate a second crop, which was collected after 10 min cooling in ice. After overnight evaporation under atmospheric pressure, 21.2 ml ether was added dropwise to the filtrate and a third crop was collected after 15 min cooling. Addition of 15.8 ml ether to this filtrate precipitated a fourth crop which was collected after thorough cooling (2 hr).

The first crop (white, mostly $P(C_2H_4CN)_3$) was discarded. IR showed the second crop (yellow) was predominantly disubstituted complex, the fourth crop (orange) monosubstituted, and the third crop (pale orange) a mixture. The third crop was separated by re-crystallization into two fractions, which were added to the initial second and fourth crops, respectively. The crude products, disubstituted (144 mg, 25% yield) and monosubstituted (249 mg, 45%), were re-crystallized from CH_3CN/ether: 4.4 ml CH_3CN, 14.9 ml ether, yield: 100 mg (17%); 1.4 ml CH_3CN, 5.3 ml ether (first crop, discarded); 10.4 ml ether (second crop, retained), yield: 136 mg (25%); second re-crystallization: 2.8 ml CH_3CN, 15.6 ml ether, yield: 95 mg (17%).

Preparation of $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ *(Method D)*

A 500 mg sample of $[Co(CNC_6H_3Et_2\text{-}2,6)_5](ClO_4)_2$ was dissolved in 1.5 ml CH_2Cl_2 by stepwise addition of the solid to the solvent. The solution was filtered through cotton, cooled in ice, and treated with 680 mg $P(C_6H_{13}\text{-}n)_3$ (5:1 molar ratio) added dropwise to the reaction mixture in ice. The green solution turned dark orange during ligand addition, and odor of RNC was detected. The mixture was left 5 min at 25 °C, filtered through cotton, and treated with 30.0 ml ether to precipitate fine crystals. The solution was cooled in ice (45 min), and the pale-yellow microneedles collected on a sintered-glass frit. Crude product, 171 mg (30% yield), was re-crystallized from 0.7 ml CH_2Cl_2 and 2.3 ml ether; yield: 117 mg (20%).

Results and Discussion

New Co(I) complexes with arylisocyanide and trialkylphosphine ligands are listed in Table I with elemental analyses, melting (decomposition) ranges, -N≡C IR frequencies, and electronic spectral values (λ_{max}, ϵ). The complexes are yellow crystals or microcrystals, the disubstituted products being lighter (pale yellow) than the monosubstituted (dark yellow to orange). This color trend is analogous to that in trialkylphosphite [1, 2] and triarylphosphite [4] substitution, but reversed from that seen in triarylphosphine substitution [7].

Methods of Preparation/Ligand Substitution Preference

Preparation of $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(NEt_2)_3]ClO_4$ (Method A) typifies preparation of $P(NEt_2)_3$ complexes: $[Co(CNR)_4P(NEt_2)_3]X$, $R = C_6H_4Me\text{-}o$, $C_6H_4Cl\text{-}p$, $C_6H_3Et_2\text{-}2,6$; and the $P(C_6H_{13}\text{-}n)_3$ complexes: $[Co(CNC_6H_4Me\text{-}o)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$, $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_{13}\text{-}n)_3]ClO_4$. Here starting materials are highly soluble (ligands added neat) and products are stable in solution. Reaction of $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ and $P(NEt_2)_3$ was difficult. For reaction at 25 °C in 1:5 molar ratio, the solution darkened and only tar was recovered, suggesting decomposition. For reaction at 0 °C in 1:2 molar ratio, only starting material was recovered, suggesting no reaction. Attempts with freshly-distilled $P(NEt_2)_3$ for 1:5 molar ratio reacted at 0 °C did yield orange crystals, whose IR showed some product, but mainly starting material. The $[Co(CNC_6H_5)_4P(NEt_2)_3]ClO_4$ was prepared by reaction of $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot H_2O$ and $P(NEt_2)_3$ (Method D), all steps performed at 7 °C. Reaction of $P(NEt_2)_3$ and $[Co(CNR)_5]X$, therefore, shows only monosubstitution.

Whereas reaction of $P(C_6H_{13}\text{-}n)_3$ to produce $[Co(CNC_6H_4Me\text{-}o)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ and $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_{13}\text{-}n)_3]ClO_4$ was easy, reaction with $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$ and $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ (Method B) was difficult. When $[Co(CNC_6H_5)_5]ClO_4 \cdot HCCl_3$ was reacted at 25 °C, no RNC odor was detected and solution dark color suggested decomposition. In this and reactions with $[Co(CNC_6H_4Cl\text{-}p)_5]X$, the RNC ligand, as well as $[Co(CNR)_3\{P(C_6H_{13}\text{-}n)_3\}_2]X$, appears to be decomposed. Satisfactory product was not isolated from reaction of $[Co(CNC_6H_4Cl\text{-}p)_5]X$· ($X = BF_4$, ClO_4) and $P(C_6H_{13}\text{-}n)_3$. Several reactions were performed at 0 °C (1:5 molar ratio), and yellow solid formed after addition of $P(C_6H_{13}\text{-}n)_3$, but the solid darkened into tar before it was collected. Unsuccessful reactions (1:5 molar ratio) were also attempted at 25 °C. Solution color darkened upon ligand addition, but no RNC odor was detected. Small amount of unpurified product isolated by solvent evaporation confirms disubstitution by ν(-N≡C) pattern: 2169vw(sh), 2115w(sh), 2048s, 2009m(sh) (CH_2Cl_2); 2173vw(sh), 2111w(sh), 2047s(br), 2007m(sh) (nujol); but quantity/quality did not justify further characterization. Reaction of $P(C_6H_{13}\text{-}n)_3$ and $[Co(CNR)_5]X$, therefore, shows disubstitution, except with the sterically-hindered $R = C_6H_3Et_2\text{-}2,6$.

Limited solubility of $P(C_2H_4CN)_3$ and its complexes introduced purification difficulty in all reactions, but preparation of $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_2H_4CN)_3\}_2]BF_4$ and $[Co(CNC_6H_4Cl\text{-}p)_4P(C_2H_4CN)_3]BF_4$ (Method C) was the most challenging since this reaction produced both mono- and disubstituted complex. Monosubstituted complex is the more

TABLE I. Trialkylphosphine Complexes of Pentakis(arylisocyanide)cobalt(I).

Compound[a]	M. pt.[b] (°C)	Isocyanide IR[c]		Electronic spectra[d]	Elemental analysis Found (calcd) (%)			
		CH_2Cl_2	Nujol		C	H	N	Cl
$[Co(CNR_1)_3L_2{}^a]ClO_4$	140–143m	2254w[e] 2127w(sh) 2068s 1998w(sh)	2248w 2127w(sh) 2063s(br) 1998w(sh)	333(14,200)[i] 263(45,000) 235(38,700) 213(33,200)	54.76 (54.83)	4.73 (4.57)	14.79 (14.76)	4.03 (4.16)
$[Co(CNR_2)_3L_2{}^a]BF_4$	186–192d	2254w[e] 2124w(sh) 2068s 2006w(sh)	2244w 2118w(sh) 2058s(br) 2001w(sh)	339(16,000)[j] 268(55,000) 243(44,400) 212(35,800)	49.76 (49.56)	3.83 (3.81)	13.30 (13.34)	11.38 (11.28)
$[Co(CNR_2)_4L^a]BF_4$	116–118d	2253w[f] 2180m 2130m(sh) 2090s 2007w(sh)	2248w 2177m 2123w(sh) 2078s(br) 1986vw(sh)	335(20,100)[k] 265(46,900) 241(50,800) 234(50,700) 212(39,600)	50.17 (49.98)	3.31 (3.17)	11.32 (11.03)	15.78 (15.95)
$[Co(CNR_3)_3L_2{}^a]ClO_4$	183–189m/d	2255w[e] 2116w(sh) 2064s 2054m(sh) 2019w(sh)	2247w 2120vw(sh) 2053s(br) 2014vw(sh)	322(12,000)[h] ~289sh(31,100) 266(67,300) ~243sh(42,400) 214(52,900)	56.20 (56.28)	5.05 (5.03)	14.17 (14.07)	3.86 (3.96)
$[Co(CNR_4)_4L^a]ClO_4$	88–95m	2253w[g] 2167m 2118m(sh) 2082s 1996w(sh)	2247w 2158m 2108m(sh) 2087m(sh) 2068s(br) 1992vw(sh)	324(15,500) ~288sh(18,100) 259(44,300) 252(44,300)	64.53 (64.41)	6.60 (6.48)	9.89 (9.92)	3.77 (3.59)
$[Co(CNR_1)_3L_2{}^b]ClO_4$	175–180m/d	2106w(sh) 2045s 2020w(sh) 1998m(sh)	2098vw(sh) 2038s(br) 2016w(sh) 1992m(sh) 1967vw(sh)	341(15,500) ~270sh(33,300) ~255sh(38,700) 234(43,300)	66.23 (65.80)	9.45 (8.95)	4.05 (4.04)	3.24 (3.42)
$[Co(CNR_3)_3L_2{}^b]ClO_4$	200–205m/d	2100w(sh) 2059w(sh) 2036s 2017s(sh) 1967w(sh)	2092w(sh) 2059w(sh) 2034w(sh) 2010s(br) 1967w(sh)	338(10,400) ~288sh(43,700) ~280sh(54,900) 268(59,800) 249sh(49,100)	66.78 (66.57)	9.35 (9.15)	3.95 (3.88)	3.46 (3.28)

$[Co(CNR_4)_3L_2{}^b]ClO_4$	142–150m/d	2096vw(sh) 2035s 1998w(sh)	2096vw(sh) 2029s(br) 1994w(sh)	~334(7,200) 273(75,100) ~249sh(48,100) 228(45,800)	68.86 (68.57)	9.89 (9.69)	3.62 (3.47)	2.88 (2.94)
$[Co(CNR_4)_4L^b]ClO_4$	105–109m	2159m 2103m(sh) 2068s 2000w(sh)	2155m 2100m(sh) 2064s 2000w(sh)	324(14,000) 265(56,000) 240(47,000)	68.94 (68.86)	8.49 (8.42)	5.30 (5.18)	3.46 (3.29)
$[Co(CNR_1)_4L^c]ClO_4$	131–132m/d	2165m 2110w(sh) 2077s 1999vw(sh)	2165m 2111m(sh) 2074s(br) 1999w(sh)	329(15,800) 249(30,300) 233sh(40,600)	58.78 (58.72)	6.19 (6.12)	12.04 (11.99)	4.40 (4.34)
$[Co(CNR_2)_4L^c]BF_4$	150–160d	2165m 2109w(sh) 2076s 2014w(sh)	2164m 2109w(sh) 2070s(br) ~2008vw(sh)	345(12,400) 266(26,100) 243sh(53,800) 235(60,700)	50.35 (50.91)	4.97 (4.88)	10.25 (10.39)	14.85 (15.06)
$[Co(CNR_3)_4L^c]ClO_4$	125–130d	2160m 2105m(sh) 2074s 2056w(sh) 2025w(sh)	2153m 2098m(sh) 2076w(sh) 2067s 2052m(sh) 2026w(sh)	325(10,400) 280sh(45,200) 274(49,500)	60.60 (60.45)	6.62 (6.64)	11.29 (11.22)	4.18 (4.06)
$[Co(CNR_4)_4L^c]ClO_4$	118–122m/d	2152m 2097w(sh) 2061s 1998w(sh)	2149m 2093w(sh) 2060s 1998w(sh)	320(11,400) 262(33,500) 239sh(37,000) 232(39,700)	64.31 (64.52)	7.94 (7.87)	9.51 (9.41)	3.52 (3.41)

[a] $R_1 = C_6H_5$, $R_2 = C_6H_4Cl$-*p*, $R_3 = C_6H_4Me$-*o*, $R_4 = C_6H_3Et_2$-2,6; $L^a = P(CH_2CH_2CN)_3$, $L^b = P(C_6H_{13}$-n), $L^c = P(NEt_2)_3$. [b] Melting (decomposition) range, uncorrected; m = melting without apparent decomposition, d = decomposition without apparent liquefaction, m/d = melting with apparent decomposition. [c] The $\nu(\text{-N}{\equiv}\text{C})$ in cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [d] The $\lambda_{max}(\epsilon)$ in mμ (nm), ϵ without Gaussian resolution. [e] Spectrum in CH_3NO_2. [f] Values in CH_2Cl_2: 2253w, 2176m, 2127m(sh), 2090s, ~2012w(sh). [g] Values in CH_2Cl_2: 2253w, 2165m, 2114w(sh), 2083s. [h] Spectrum in CH_3CN. [i] Values in CH_2Cl_2 (relative ϵ): 326 ($\epsilon \equiv 1$), 272sh(4.88), 265(5.45), 237sh(3.90). [j] Values in CH_2Cl_2 (relative ϵ): 333 ($\epsilon \equiv 1$), 281sh(4.94), 270(5.43), 244(3.90). [k] Values in CH_2Cl_2 (absolute ϵ): 332(14,500), 267(48,100), 244(46,700), 239sh(42,200).

soluble product (solubility: $P(C_2H_4CN)_3 < [Co(CNR)_3\{P(C_2H_4CN)_3\}_2]X < [Co(CNR)_4P(C_2H_4CN)_3]X < [Co(CNR)_5]X$), so purification is more difficult. Multiple re-crystallization and discard of first and sometimes second crops characterized preparation of $[Co(CNC_6H_5)_3\{P(C_2H_4CN)_3\}_2]ClO_4$, $[Co(CNC_6H_4Me\text{-}o)_3\{P(C_2H_4CN)_3\}_2]ClO_4$, $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_2H_4CN)_3]ClO_4$, and $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_2H_4CN)_3\}_2]BF_4$, $[Co(CNC_6H_4Cl\text{-}p)_4P(C_2H_4CN)_3]BF_4$. Acetonitrile, and to a lesser extent nitromethane, is a better solvent for $P(C_2H_4CN)_3$ than dichloromethane, so CH_3CN was used in these reactions. Reaction of $P(C_2H_4CN)_3$ and $[Co(CNR)_5]X$ shows both mono- and disubstitution.

Reaction of the appropriate Co(II) complex with ligand in 1:5 molar ratio (Method D) was used to prepare Co(I) complexes having limited stability in direct Co(I) ligand substitution (*e.g.*, $[Co(CNC_6H_5)_4P(NEt_2)_3]ClO_4$) or disubstituted complexes when the monosubstituted complex is obtained in Co(I) reaction (*e.g.*, $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_{13}\text{-n})_3\}_2ClO_4$). The $[Co(CNC_6H_5)_4P(NEt_2)_3]ClO_4$, $[Co(CNC_6H_4Me\text{-}o)_4P(NEt_2)_3]ClO_4$, $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_2H_4CN)_3]ClO_4$, and $[Co(CNC_6H_3Et_2\text{-}2,6)_3\{P(C_6H_{13}\text{-n})_3\}_2]ClO_4$ were prepared by this method, the CNC_6H_5 complex being handled at 7 °C. The $[Co(CNC_6H_4Cl\text{-}p)_5](BF_4)_2$ has not been prepared [37], so this method could not be used for $[Co(CNC_6H_4Cl\text{-}p)_3\{P(C_6H_{13}\text{-n})_3\}_2]BF_4$. Since Co(II) reaction favors disubstitution [9], appearance of monosubstituted products indicates very strong monosubstitution preference by $P(NEt_2)_3$ and relatively strong preference by $P(C_2H_4CN)_3$.

Decomposition Temperatures

The complexes exhibited different types of melting (decomposition) behavior as well as different temperature ranges (Table I). Some complexes melted without apparent decomposition, others melted with obvious decomposition, and others seemed to decompose without liquefaction. Actual melting would not be expected for these complexes. Disubstituted complexes generally have significantly higher melting (decomposition) ranges than corresponding monosubstituted. This probably indicates greater (thermodynamic) stability for disubstituted complexes. Comparison of these temperature ranges with those of corresponding triarylphosphine complexes [6–8] indicates slightly higher temperatures/greater stability for triarylphosphine complexes. Perchlorate salts crystallize better than tetrafluoroborate, so ClO_4^- was used with all RNC except $p\text{-}ClC_6H_4NC$, with which BF_4^- was used to avoid dual chlorine contribution.

Infrared Spectra

The -N≡C IR pattern identifies mono- or disubstituted complex. Figure 1A shows the typical pattern for monosubstituted complexes: a medium-intensity, high-energy band and a strong, broad band with lower and higher energy shoulders. In Fig. 1B the strong band has additional shoulders, typical of $o\text{-}MeC_6H_4NC$ complexes. Figure 1C is a typical spectrum for a $P(C_2H_4CN)_3$-monosubstituted complex, including the weak cyanide band (~2250 cm^{-1}). The $P(C_2H_4CN)_3$-monosubstituted complexes were measured in CH_2Cl_2 and CH_3NO_2 (because of satisfactory solubility), but disubstituted complexes could be measured only in CH_3NO_2. Spectra in CH_3CN were unsatisfactory because the CH_3CN cyanide band obscured the $P(C_2H_4CN)_3$ cyanide band (despite an apparently satisfactory baseline). For disubstituted complexes typical IR pattern is one strong band with higher and lower energy shoulders. Figure 2C shows a typical pattern, with the relatively weak cyanide band from $P(C_2H_4CN)_3$. In Fig. 2A the lower energy shoulder is pronounced (especially in mull). Figure 2B is for a $o\text{-}MeC_6H_4NC$ complex, characteristically showing resolution of the lower energy shoulder and additional shoulders. From IR patterns contamination of disubstituted complex with monosubstituted can be detected, but purity of monosubstituted complex cannot be similarly judged.

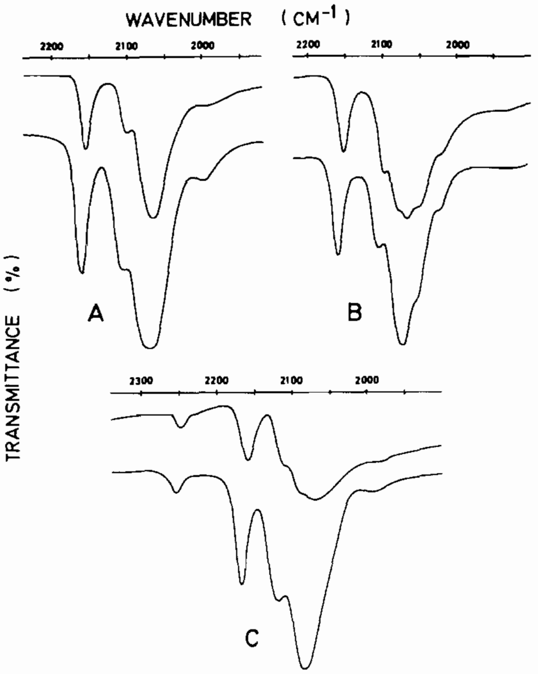

Fig. 1. Selected IR spectra (1950–2350 cm^{-1}) for monosubstituted arylisocyanidecobalt(I) complexes. A. $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_6H_{13}\text{-n})_3]ClO_4$ (top, nujol; bottom, CH_2Cl_2); B. $[Co(CNC_6H_4Me\text{-}o)_4P(NEt_2)_3]ClO_4$ (top, nujol; bottom, CH_2Cl_2); C. $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_2H_4CN)_3]ClO_4$ (top, nujol; bottom, CH_3NO_2).

Solution and mull spectra are very similar in pattern (although mull spectra tend to be broader

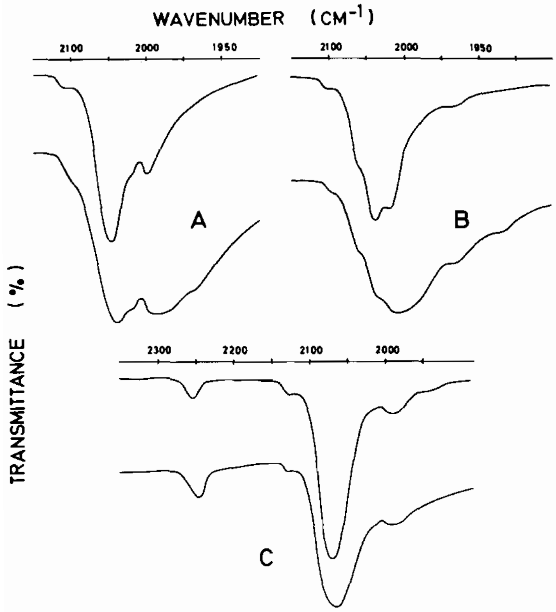

Fig. 2. Selected IR spectra (1950–2350 cm^{-1}) for disubstituted arylisocyanidecobalt(I) complexes. A. [Co(CNC$_6$H$_5$)$_3${P(C$_6$H$_{13}$-n)$_3$}$_2$]ClO$_4$ (top, CH$_2$Cl$_2$; bottom, nujol); B. [Co(CNC$_6$H$_4$Me-*o*)$_3${P(C$_6$H$_{13}$-n)$_3$}$_2$]ClO$_4$ (top, CH$_2$Cl$_2$; bottom, nujol); C. [Co(CNC$_6$H$_5$)$_3${P(C$_2$H$_4$CN)$_3$}$_2$]ClO$_4$ (top, CH$_3$NO$_2$; bottom, nujol).

and may have extra weak shoulders), suggesting similar structure in solution and solid state. Previously [1, 7, 9–13] solution-structures for mono- and disubstituted pentakis(organoisocyanide)cobalt(I) complexes were assumed to be axially-substituted trigonal bipyramids (C_{3v} and D_{3h}, respectively), the extra weak IR bands treated as nonfundamental absorptions [39] and the crystallographic C_{2v} site-symmetry for [Co(CNC$_6$H$_4$F-*p*)$_3${P(OMe)$_3$}$_2$]BF$_4$ [40] notwithstanding. Recently solution IR-Raman investigation suggests C_s symmetry for triarylphosphine-monosubstituted complexes, C_{2v} for trialkylphosphite- and triarylphosphine-disubstituted complexes, and C_{3v} for triarylphosphite-monosubstituted complexes [41]. Coincident Raman and IR bands exclude the possibility that the IR shoulders are nonfundamental absorptions. Similarity between the -N≡C IR patterns for these trialkylphosphine complexes and the triarylphosphine and trialkylphosphite complexes suggests analogous structures. The C_s and C_{2v} equatorially-distorted, axially-substituted trigonal bipyramidal structures should have four (2A′ + 2A″) and three (2A$_1$ + B$_2$) fundamental IR bands, respectively (as experimentally observed), instead of three (2A$_1$ + E) and one (E′), for C_{3v} and D_{3h} substituted trigonal bipyramids, respectively. Raman investigation is intended for these complexes.

IR bands in the region 2300–1950 cm^{-1} (including cyanide bands from P(C$_2$H$_4$CN)$_3$) for the new complexes are listed in Table I. All ν(-N≡C) show the same trends with systematic change of RNC and/or PR$_3$, but for accurate comparison the strongest band in solution-spectra is considered (re-tabulated in Table II). In mono- and disubstituted pentakis(arylisocyanide)cobalt(I) complexes with tertiary P-ligands (Table II: P(NEt$_2$)$_3$, P(C$_6$H$_{13}$-n)$_3$, P(C$_2$H$_4$CN)$_3$; P(C$_6$H$_4$OMe-*p*)$_3$, P(C$_6$H$_5$)$_3$, P(C$_6$H$_4$Cl-*p*)$_3$; P(OMe)$_3$) the ν(-N≡C) follow the trend: CNC$_6$H$_4$Cl-*p* ≳ CNC$_6$H$_5$ > CNC$_6$H$_4$Me-*o* > CNC$_6$H$_3$Et$_2$-2,6. This could be purely inductive effect within the arylisocyanide molecule, since the *p*-chloro substituent behavior as an electron-withdrawing group has been noted in Co(II) complexes [37] and alkyl substituents are electron-releasing groups. The inductive behavior can stabilize or destabilize, respectively, the polar character of the isocyanide bond, R–$\bar{\text{N}}$≡$\bar{\text{C}}$ [42, 43].

Changes in ν(-N≡C) can be used to assess relative π*-accepting abilities of the substituting P-ligands. The ν(-N≡C) increases for σ-donation of electron density to Co(I) and decreases for π*-acceptance ($d_\pi \rightarrow \pi^*$ backbonding) from Co(I). When one or two RNC are substituted, the remaining RNC exhibit more or less π*-acceptance depending on whether the substituting ligands are weaker or stronger π*-acceptors, respectively. Increased or decreased π*-acceptance by RNC is reflected through decreased or increased ν(-N≡C) relative to [Co(CNR)$_5$]X. In accord with decreasing $d_\pi \rightarrow \pi^*$ electron-accepting ability [44]: RNC > PR$_3$; the ν(-N≡C) for trialkylphosphine mono- and disubstituted complexes are significantly lower than values for corresponding [Co(CNR)$_5$]X [45]. With the same RNC and in both mono- and disubstituted complexes, the ν(-N≡C) shows dependency on trialkylphosphine: P(C$_2$H$_4$CN)$_3$ > P(C$_6$H$_{13}$-n)$_3$ > P(NEt$_2$)$_3$. This is expected behavior since P(C$_2$H$_4$CN)$_3$ has an electron-withdrawing substituent which decreases σ-donating ability and enhances π*-accepting ability of the P-atom, whereas P(NEt$_2$)$_3$ has an electron-donating substituent which increases σ-donation and decreases π*-acceptance, relative to the unsubstituted trialkylphosphine, P(C$_6$H$_{13}$-n)$_3$. The ν(-N≡C) for disubstituted complexes are significantly lower than for analogous monosubstituted complexes, indicating more π*-acceptance and/or less σ-donation by the remaining RNC ligands when the second RNC has been replaced by a P-ligand.

Trialkylphosphines are expected to be weaker π*-acceptors than triarylphosphines, since electron-releasing alkyl groups should increase σ-donating ability of the phosphorus and decrease tendency for π*-acceptance. Strong electron-withdrawing ability of the -CN substituent, however, apparently displaces π*-accepting ability of P(C$_2$H$_4$CN)$_3$ into the range of triarylphosphines, since ν(-N≡C) values imply the following order: RNC ≫ P(OMe)$_3$ >

TABLE II. Dominant ν(-N≡C) and First λ_{max} Values for Selected $[Co(CNR)_3L_2]X$ and $[Co(CNR)_4L]X$.[a]

L\RNC	p-ClC_6H_4NC	C_6H_5NC	o-MeC_6H_4NC	2,6-$Et_2C_6H_3NC$
$P(NEt_2)_3$	2076 M 345	2077 M 329	2074 M 325	2061 M 320
$P(C_6H_{13}$-n$)_3$	2048 D	2045 D 341	2036 D 338	2068 M 324 2035 D 334
$P(C_6H_4OMe$-$p)_3$	2065 D 365	2054[d] D 358	2048 D 354	2074 M 337 2040 D 354
$P(C_2H_4CN)_3$	2090[b] M 335[c] 2068[b] D 339[c]	2068[b] D 333[c]	2064[b] D 322[c]	2082[b] M 324
$P(C_6H_5)_3$	2070 D 360	2069 D 353	2067 D 349	2078 M 335 2045 D 350
$P(C_6H_4Cl$-$p)_3$	2091 M 342 2073 D 351	2070 D 345	2091 M 334 2068 D 341	2082 M 331 2048 D 343
$P(OMe)_3$	2086 D 338	2088 D 331	2084 D 332	
RNC	2114 335	2114 329	2109 327	2106 323

[a] The IR and electronic spectra measured in CH_2Cl_2 unless otherwise noted; upper values, ν(-N≡C) in cm^{-1}; lower values, λ_{max} in mn (mμ); M indicates monosubstituted complex, D indicates disubstituted complex. [b] The ν(-N≡C) measured in CH_3NO_2. [c] The λ_{max} measured in CH_3CN. [d] The complex prepared for this study. *Anal.* Calcd for $[Co(CNC_6H_5)_3\{P(C_6H_4OCH_3)_3\}_2]$-$BF_4\cdot0.96CH_2Cl_2$: C, 61.88; H, 4.78; N, 3.38. Found: C, 61.85; H, 4.97; N, 3.28; m.pt. 248–253 °C (decomp); $\lambda_{max}(\epsilon)$: 354-(29,600), 307(35,300), ~282(sh), ~274(sh), 243(72,100), 228(75,200); -N≡C IR: 2058s(br), ~1995w(sh) (CH_2Cl_2); 2052s(br), ~2005w(sh) (nujol).

$P(C_6H_4Cl$-$p)_3 > P(C_6H_5)_3 \gtrsim P(C_2H_4CN)_3 > P(C_6H_4$-$OMe$-$p)_3 > P(C_6H_{13}$-n$)_3 > P(NEt_2)_3$ (Table II). Increase in ν(-N≡C) reflects increase in π^*-acceptance and/or decrease in σ-donation by the P-ligands, so behavior for $P(C_2H_4CN)_3$ may be reflecting significantly decreased σ-donating ability.

Electronic Spectra

Electronic spectra of the new complexes are tabulated in Table I and representative examples pictured in Fig. 3. Band maxima (λ_{max}) and molar extinction coefficients (ϵ) are reported without Gaussian resolution. Spectra were recorded in CH_2Cl_2, except for $P(C_2H_4CN)_3$ complexes where solubility necessitated CH_3CN. The pattern of three intense absorption bands in the UV region previously observed for unsubstituted, monosubstituted, and disubstituted pentakis(arylisocyanide)cobalt(I) complexes [1, 6, 8, 10, 46] is retained with additional shoulders in CH_2Cl_2, but spectra in CH_3CN (where shorter wavelength is possible) show at least one additional high-energy band. Comparison of ϵ values (Table I) with those for analogous triarylphosphine complexes [6, 8] shows the decreased intensity expected whenever ligands with aliphatic nature are substituted for analogous aromatic ligands. The ϵ values are still high enough for interpretation as metal-to-ligand charge-transfer bands [1, 5, 6], rather than as one crystal field band and the rest charge-transfer bands [47, 10].

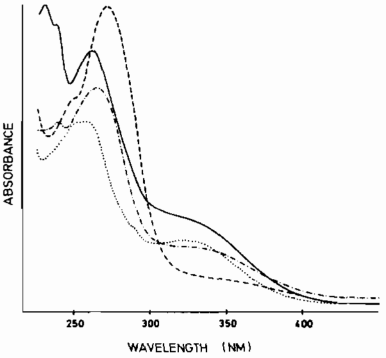

Fig. 3. Solution electronic spectra (CH_2Cl_2, 25 °C) for selected arylisocyanidetrialkylphosphine cobalt(I) complexes (~1.5 × 10^{-5} M); $[Co(CNC_6H_3Et_2$-2,6$)_4P(NEt_2)_3]ClO_4$ (——); $[Co(CNC_6H_3Et_2$-2,6$)_4P(C_6H_{13}$-n$)_3]ClO_4$ (– · –); $[Co(CNC_6H_3Et_2$-2,6$)_3\{P(C_6H_{13}$-n$)_3\}_2]ClO_4$ (- - -); and $[Co(CNC_6H_3Et_2$-2,6$)_4P(C_2H_4CN)_3]ClO_4$ (· · ·).

Three one-electron, symmetry-allowed transitions from the highest-energy filled metal orbital into π^* group-ligand orbitals based on equatorial RNC are possible if D_{3h} symmetry is assumed for $[Co(CNR)_3L_2]^+$ in solution [1]:

$$
\begin{aligned}
&{}^{1}A'_{1}[(e''\{d_{\pi}\})^{4}(e'\{d_{\pi,\sigma}\})^{4}] \longrightarrow \\
&\qquad {}^{1}E'[(e'')^{4}(e')^{3}(E'\{eq,\pi^{*}\})^{1}] \\
&\qquad + {}^{1}E'[(e'')^{4}(e')^{3}(A'_{2}\{eq,\pi^{*}\})^{1}] \\
&\qquad + {}^{2}A''_{2}[(e'')^{4}(e')^{3}(E''\{eq,\pi^{*}\})^{1}]
\end{aligned}
$$

If a C_{2v} solution-structure is assumed, as evidenced by IR/Raman spectra, five one-electron, symmetry-allowed $d_{\pi} \rightarrow \pi^{*}(eq)$ charge-transfer bands are allowed:

$$
\begin{aligned}
&{}^{1}A_{1}[b_{1}\{d_{\pi}\}^{2}b_{2}\{d_{\pi}\}^{2}a_{1}\{d_{\pi,\sigma}\}^{2}a_{2}\{d_{\pi,\sigma}\}^{2}] \longrightarrow \\
&\qquad {}^{1}A_{1}[(b_{1})^{2}(b_{2})^{2}(a_{1})^{2}(a_{2})^{1}(A_{2}\{eq,\pi^{*}\})^{1}] \\
&\qquad + 2\,{}^{1}B_{1}[(b_{1})^{2}(b_{2})^{2}(a_{1})^{2}(a_{2})^{1}(B_{2}\{eq,\pi^{*}\})^{1}] \\
&\qquad + 2\,{}^{1}B_{2}[(b_{1})^{2}(b_{2})^{2}(a_{1})^{2}(a_{2})^{1}(B_{1}\{eq,\pi^{*}\})^{1}]
\end{aligned}
$$

Mixing of axial ligand (PR_3) character into $\pi^{*}(eq)$ is symmetry-possible in both $D_{3h}(E' + E'')$ and C_{2v}-$(A_1 + A_2 + B_1 + B_2)$, so even if the charge-transfer bands are of primarily RNC character, the ϵ values can still reflect aliphatic *vs.* aromatic nature in the axial ligands. For C_{3v} $[Co(CNR)_4L]^+$ solution-structure all four one-electron $d_{\pi} \rightarrow \pi^{*}(eq)$ transitions are symmetry allowed:

$$
\begin{aligned}
&{}^{1}A_{1}[(e\{d_{\pi}\})^{4}(e\{d_{\pi,\sigma}\})^{4}] \longrightarrow \\
&\qquad {}^{1}E[(e)^{4}(e)^{3}(A_{2}\{eq,\pi^{*}\})^{1}] \\
&\qquad + {}^{1}E[(e)^{4}(e)^{3}(A_{1}\{eq,\pi^{*}\})^{1}] \\
&\qquad + 2\,{}^{1}A_{1},{}^{1}E[(e)^{4}(e)^{3}(E\{eq,\pi^{*}\})^{1}]
\end{aligned}
$$

and with C_s solution-structure six one-electron transitions are symmetry-allowed:

$$
\begin{aligned}
&{}^{1}A'[(a''\{d_{\pi}\})^{2}(a''\{d_{\pi}\})^{2}(a'\{d_{\pi,\sigma}\})^{2}(a'\{d_{\pi,\sigma}\})^{2}] \longrightarrow \\
&\qquad 3\,{}^{1}A'[(a'')^{2}(a'')^{2}(a')^{2}(a')^{1}(A'\{eq,\pi^{*}\})^{1}] \\
&\qquad + 3\,{}^{1}A''[(a'')^{2}(a'')^{2}(a')^{2}(a')^{1}(A''\{eq,\pi^{*}\})^{1}]
\end{aligned}
$$

so the number of electronic bands observed for mono- and disubstituted complexes could all be $d_{\pi} \rightarrow \pi^{*}(eq)$ charge-transfer transitions.

Accepting the first electronic transition as $d_{\pi} \rightarrow \pi^{*}(eq)$, electronic data are in accord with π^{*}-accepting ability: $P(C_2H_4CN)_3 > P(C_6H_{13}\text{-}n)_3 > P(NEt_2)_3$. Weaker π^{*}-accepting ligands substituted for one or two RNC force the remaining RNC to become stronger π^{*}-accepting, thereby lowering the energy (increasing λ_{max}) for $d_{\pi} \rightarrow \pi^{*}(eq)$ transitions. The $P(NEt_2)_3$ is difficult to assess because of monosubstitution, and λ_{max} may reflect a long Co–P bond. Extending this reasoning to other P-ligands (Table II) results in unexpected ordering of $d_{\pi} \rightarrow \pi^{*}$ accepting ability: $RNC > P(OMe)_3 > P(C_2H_4CN)_3 > P(C_6H_{13}\text{-}n)_3 > P(NEt_2)_3 > P(C_6H_4Cl\text{-}p)_3 > P(C_6H_5)_3 > P(C_6H_4OMe\text{-}p)_3$. Electronic data may be valid indication of relative π^{*}-accepting ability within a given ligand type, but perhaps cannot be extended over the range of different ligand types.

Pattern of Trialkylphosphine Substitution Reactions

Substitution pattern in the trialkylphosphine reactions may be relatable to π^{*}-accepting/σ-donating ability of the P-ligands. In Co(I) reactions, presence of $CNC_6H_3Et_2$-2,6 or $P(NEt_2)_3$ dictates monosubstitution, which is probably due to steric hindrance rather than electron-inductive effects. For the remaining phosphine ligands (trialkyl- and triaryl-), substitution pattern parallels apparent π^{*}-accepting ability. The strongest π^{*}-acceptor, $P(C_6H_4Cl\text{-}p)_3$, tends to monosubstitute [7, 8]; $P(C_2H_4CN)_3$, being a slightly weaker π^{*}-acceptor, shows mono- and disubstitution, with preference for disubstitution. Approximately-equal and weaker π^{*}-accepting ligands $P(C_6H_5)_3$, $P(C_6H_4OMe\text{-}p)_3$, and $P(C_6H_{13}\text{-}n)_3$; tend to disubstitute with all arylisocyanides except the sterically-hindered $CNC_6H_3Et_2$-2,6. The weakest π^{*}-accepting ligand, $P(NEt_2)_3$, would be expected to disubstitute on the basis of inductive effects, were it not so severely sterically hindered.

The Co(II) direct reduction/substitution reactions further specify preference for mono- and disubstitution in cases for which Co(I) reactions monosubstituted. (For reactions disubstituting with Co(I) there is no need to perform the Co(II) reaction.) That monosubstituted products were obtained with $P(NEt_2)_3$ reacted with $[Co(CNR)_5](ClO_4)_2$, R = C_6H_5, C_6H_4Me-*o*; further underscores the strong preference for monosubstitution by this sterically-hindered ligand. The apparently less severe steric-hindrance of $CNC_6H_3Et_2$-2,6 is effectively overridden in Co(II) reactions with all phosphines except $P(C_2H_4CN)_3$ (and $P(NEt_2)_3$, which was not attempted). This result could suggest that $P(C_2H_4CN)_3$ has π^{*}-accepting ability comparable to that of $P(C_6H_4Cl\text{-}p)_3$. Similarity of these two phosphines is further emphasized in that $P(C_2H_4CN)_3$ gave a mixture of mono- and disubstituted products with $[Co(CNC_6H_4Cl\text{-}p)_5]BF_4$, while $P(C_6H_4Cl\text{-}p)_3$ gave a mixture when reacted with $Co(BF_4)_2 \cdot 6H_2O$ and CNC_6H_4Cl-*p* [8]. Tendency for monosubstitution with $P(C_2H_4CN)_3$ may be more dependent on decreased ability for σ-donation than on enhanced π^{*}-accepting ability. Substitution reactions are kinetically, not thermodynamically, controlled, and decreased σ-donating ability may limit the effective reactivity of both $P(C_2H_4CN)_3$ and $P(C_6H_4Cl\text{-}p)_3$.

Acknowledgements

The authors wish to thank the American University of Beirut and Washburn University of Topeka for grants supporting this research.

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