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Preparation of Tetrakis(t-butylisocyanide)aquacobalt(II) Perchlorate and Reaction with Tertiary Phosphine Ligands*

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Abstract

Reaction of t-butylisocyanide with $Co(ClO_4)_2\cdot 6H_2O$ in 4:1 molar ratio in EtOH at 0 °C produces $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ in near quantitative yields. Ligand substitution/reduction reactions of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ (in CH_3CN) with triarylphosphines (in CH_2Cl_2) at 25 °C are rapid and in good yield; $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$, $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$, and $[Co(CNCMe_3)_3\{P(C_6H_5)_3\}_2]ClO_4$ were prepared. Analogous reaction with $As(C_6H_5)_3$ caused intense color change, but only unsubstituted $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was recovered. Reaction of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ with trialkylphosphines produced $[Co(CNCMe_3)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$, $[Co(CNCMe_3)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$, and $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$, but anticipated monosubstituted product with $P(NEt_2)_3$ was not recovered. Infrared, ^1H NMR and electronic spectra give some indication of coordination structure.

Introduction

Pentakis(methylisocyanide)cobalt(II) perchlorate, $[Co(CNMe)_5](ClO_4)_2$, as red (diamagnetic) and blue (paramagnetic) crystals, was initially reported [1–3] for reaction of $Co(ClO_4)_2\cdot 6H_2O$ with excess CNMe in ethanol. The red compound was later established as a metal–metal bonded dimer, $[(MeNC)_5Co{-}Co(CNMe)_5](ClO_4)_4$, by X-ray crystallography [4], and the blue compound could not be reproduced, speculation being that $[Co(CNMe)_6](ClO_4)_2$ or $[Co(CNMe)_5H_2O](ClO_4)_2$ was prepared [5]. Analogous $[(EtNC)_5Co{-}Co(CNEt)_5](ClO_4)_4$ has also been reported [6]. Monomeric pentacoordinate Co(II) complexes with arylisocyanides have been prepared in anhydrous and/or hydrated forms: $[Co(CNR)_5](ClO_4)_2\cdot xH_2O$, $R = C_6H_5$, $C_6H_4Me\text{-}o$, $C_6H_4Me\text{-}p$, $C_6H_4F\text{-}p$, $C_6H_4Et\text{-}o$, $C_6H_3Me_2\text{-}2,6$, $C_6H_3Et_2\text{-}2,6$, $C_6H_2Me_3\text{-}2,4,6$ [1, 3, 5, 7–9]. Significantly no less than five RNC ligands coordinated per Co(II) has been reported for complexes with the non-coordinating perchlorate anion, although numerous complexes with four or two RNC ligands have been prepared with coordinating anions, X = Cl, Br, I, SCN [3, 8].

The $[Co(CNBu\text{-}t)_5]PF_6$ was prepared by reduction of the Co(II) complex without attempted isolation [10], and substituted Co(I) complexes, $[Co(CNBu\text{-}t)_3(PPh_3)_2]PF_6$, $[Co(CNBu\text{-}t)_4AsPh_3]PF_6$, $[Co(CNBu\text{-}t)_3(PMePh_2)_2]PF_6$, $[Co(CNBu\text{-}t)_3Ph_2PCH_2CH_2PPh_2]PF_6$, $[Co(CNBu\text{-}t)_3(cis\text{-}Ph_2PCH{=}CHPPh_2)]PF_6$, $[Co(CNBu\text{-}t)_2PhP(CH_2CH_2PPh_2)_2]PF_6$, $[Co(CNBu\text{-}t)_2PhP(CH_2CH_2AsPh_2)_2]PF_6$, and $[Co(CNBu\text{-}t)P(CH_2CH_2PPh_2)_3]PF_6$; have been prepared in ligand-substitution reaction [10] or reaction of CNBu-t with CoL_2Cl_2 [11]. Direct ligand substitution/reduction reactions of triarylphosphine, triarylphosphite, trialkylphosphine, trialkylphosphite, and triphenylarsine ligands on $[Co(CNR)_5](ClO_4)_2\cdot xH_2O$ and $[Co(CNR)_5](BF_4)_2\cdot xH_2O$ have been investigated for arylisocyanide complexes, and shown to favor disubstitution almost exclusively [12–16]. This present work investigates the Co(II) complex formed in reaction of $Co(ClO_4)_2\cdot 6H_2O$ with $CNCMe_3$, and reactions of this tetrakis(t-butylisocyanide)aquacobalt(II) complex, $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, with triarylphosphine and trialkylphosphine ligands.

Experimental

Commercial $CNCMe_3$ (Strem), $Co(ClO_4)_2\cdot 6H_2O$ (Alfa), $P(C_6H_5)_3$, $P(C_6H_4OMe\text{-}p)_3$ (Strem), $P(C_6H_4Cl\text{-}p)_3$ (Strem), $As(C_6H_5)_3$, $P(NMe_2)_3$ (Fluka), $P(NEt_2)_3$ (Fluka), $P(C_2H_4CN)_3$ (Strem), and $P(C_6H_{13}\text{-}n)_3$ (Alfa) were used without further purification. Anhydrous diethyl ether was filtered through an alumina column immediately before use; spectro-

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grade CH_2Cl_2, CH_3CN, and CH_3NO_2 were used without further purification. Infrared spectra were recorded on a Perkin-Elmer 398 spectrophotometer in Nujol mull and CH_2Cl_2, CH_3NO_2, or CH_3CN solution (~1%) using 0.106 mm pathlength matched NaCl cells. Electronic spectra were measured in CH_2Cl_2 or CH_3CN (~5×10^{-3}–5×10^{-5} M) using a Perkin-Elmer 552 UV/VIS spectrophotometer. Proton-NMR spectra were recorded on a Varian EM 390 spectrometer in 99.6% dichloromethane-d_2 (Aldrich) with added TMS as primary internal reference. Elemental analyses were performed commercially.

Preparation of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$

A solution of 3.95 g $CNCMe_3$ in 4.0 ml EtOH was added dropwise to a filtered, stirred solution of 4.83 g $Co(ClO_4)_2 \cdot 6H_2O$ (*i.e.*, 4:1 molar ratio) in 71 ml EtOH at 0 °C. Initial drops gave blue color, the pink solution rapidly becoming blue-purple with precipitation of blue-grey solid during ligand addition. Upon atmospheric filtration, the iron-grey solid rapidly became pale beige or flesh-color. Yield: 7.01 g (97%); m.p. 110–112 °C (dec). The IR: ν(O–H), 3511, 3498 cm^{-1}; ν(N≡C), ~2238 unresolv(sh), 2230s(br), ~2190, 2196vw(sh), 2042w cm^{-1} [nujol]; ν(N≡C), ~2278 (CH_3CN interference), 2237s, ~2212w(sh), 2030w cm^{-1} [CH_3CN]; ν(N≡C), 2240s cm^{-1} [CH_3NO_2]; $CNCMe_3$ [neat] ν(N≡C), 2147s, 2112vw(sh), 2079w cm^{-1}. Electronic spectra: 738 (ϵ = 150), ~520sh (100), 440sh (120), ~315sh (525), ~270sh (2400), 256 (5100), 230 nm (4900) [CH_2Cl_2]; 740 (ϵ = 110), ~468 (30), ~357sh (3300), 280 (17,700), 240 (19,800), 216 nm (23,.900) [CH_3CN]. Sample treated with 10% molar excess of acetone dimethyl acetal ($CH_3C(OCH_3)_2CH_3$) in CH_3NO_2 similar to spectra in CH_3NO_2. *Anal.* Calcd for $CoC_{20}H_{38}Cl_2N_4O_9$: C, 39.48; H, 6.30; N, 9.21; Cl, 11.65. Found: C, 39.21; H, 6.30; N, 9.18; Cl, 11.94%.

The $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is very slightly soluble/effectively insoluble (≲2 mg ml^{-1}) in $CHCl_3$, CH_2Cl_2, CH_2ClCH_2Cl, C_4H_8O (THF), C_2H_5OH, and $CH_3COC_2H_5$; slightly soluble in H_2O (~4 mg ml^{-1}) and CH_3COCH_3 (~6 mg ml^{-1}); moderately soluble in CH_3OH (~14 mg ml^{-1}); soluble in C_9H_7N, quinoline (~30 mg ml^{-1}, partial decomposition), CH_3NO_2 (~34 mg ml^{-1}), and C_5H_5N (~38 mg ml^{-1}); and very soluble in CH_3CN (~110 mg ml^{-1}), $(CH_3)_2SO$ (~150 mg ml^{-1}, partial decomposition), and $(CH_3)_2NCHO$ (~165 mg ml^{-1}, partial decomposition). Re-crystallization is possible from CH_3CN/ether. A 1.00 g sample was dissolved in 7.5 ml CH_3CN, filtered through cotton (0.5 ml CH_3CN rinse), and precipitated by dropwise addition of 10.0 ml ether. After cooling in ice and filtration under suction/air, a second crop was recovered by adding 10.0 ml ether to the filtrate. Total yield: 839 mg (84%).

Preparation of $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$

A 500 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 4.0 ml CH_3CN and filtered through cotton. Then 1.45 g $P(C_6H_4OMe\text{-}p)_3$ (5:1 mole ratio) in 4.0 ml CH_2Cl_2 was added dropwise with swirling at 25 °C. The dark blue solution turned intense, opaque red-brown, then became clear red-orange during ligand addition. Odor of RNC was noted. The solution was allowed to stand 10 min at 25 °C. Addition of 28.0 ml ether produced cloudiness, which was removed by filtration through cotton. Fine yellow crystals formed after addition of 37.0 ml ether. Total volume of 40.0 ml ether was added, the solution was cooled in ice (1 hr), and the resulting orange crystals were filtered and dried under suction/air. Addition of 5.0 ml ether to the filtrate and overnight refrigeration produced a second crop. Crude product (605 mg, 66%) was re-crystallized from 2.5 ml CH_2Cl_2 and 7.2 ml ether. Yield: 560 mg (61%). *Anal.* Calcd for $CoC_{57}H_{69}ClN_3O_{10}P_2$: C, 61.53; H, 6.25; N, 3.78; Cl, 3.19. Found: C, 61.63; H, 6.40; N, 3.77; Cl, 3.46%.

Analogous preparation of $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4 \cdot 1.6CH_2Cl_2$. Yield: 53%. *Anal.* Calcd for $CoC_{52.6}H_{54.2}Cl_{10.2}N_3O_4P_2$: C, 49.55; H, 4.29; N, 3.30, Cl, 28.36. Found: C, 49.88; H, 4.40; N, 3.27; Cl, 28.66%.

Analogous preparation of $[Co(CNCMe_3)_3\{P(C_6H_5)_3\}_2]ClO_4 \cdot 0.40CH_2Cl_2$. Yield: 78%. *Anal.* Calcd for $CoC_{51.4}H_{57.8}Cl_{1.8}N_3O_4P_2$: C, 63.89; H, 6.03; N, 4.35; Cl, 6.60. Found: C, 63.90; H, 6.38; N, 4.36; Cl, 6.61%.

Preparation of $[Co(CNCMe_3)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$

A 500 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 4.0 ml CH_3CN, filtered through cotton, and chilled in ice. Then 1.18 g $P(C_6H_{13}\text{-}n)_3$ (5:1 mole ratio) diluted with 1.0 ml CH_2Cl_2 was added dropwise with swirling at 0 °C. The dark blue solution changed through green to yellow with precipitation of pale yellow crystals during ligand addition. The first crop was filtered after 20 min cooling in ice, and addition of 25.0 ml ether to the filtrate with refrigeration (overnight) produced a second crop of pale yellow needle crystals. Crude product (370 mg total, 52%) was re-crystallized from 1.5 ml CH_2Cl_2 and 4.0 ml ether; yield: 325 mg (46%). *Anal.* Calcd for $CoC_{51}H_{105}ClN_3O_4P_2$: C, 62.46; H, 10.79; N, 4.28, Cl, 3.61. Found: C, 62.73; H, 10.75; N, 4.25, Cl, 3.62%.

Preparation of $[Co(CNCMe_3)_3\{P(C_2H_4CN)_3\}_2]ClO_4$

A 500 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 4.0 ml CH_3CN and filtered through cotton. A solution of 0.698 g $P(CH_2CH_2CN)_3$ (5:1 mole ratio) in 8.0 ml CH_3CN was filtered through cotton and added dropwise at 25 °C. The dark blue

Co(II) solution changed to a bright, clear yellow and odor of RNC was evident. Addition of 10.0 ml ether dropwise and scratching the walls of the flask produced a white solid (excess $P(C_2H_4CN)_3$) which was filtered out after brief cooling (10 min). Addition of 7.0 ml ether dropwise to the filtrate produced light yellow crystals. After cooling in ice (25 min) the crystalline product was collected in a sintered glass frit, and another 3.0 ml ether was carefully added to the filtrate to effect precipitation of a third crop. After cooling in ice (45 min) and filtration, another 2.0 ml ether was added to the filtrate and it was refrigerated overnight. This fourth crop was a mixture of white ($P(C_2H_4CN)_3$) and yellow crystals, which were crudely separated by hand. Combined second, third, and fourth crops (308, 202, 44 mg, respectively) were dissolved in 3.5 ml CH_3CN, filtered through cotton, and precipitated by dropwise addition of 7.0 ml ether. Yield: 510 mg (89%) of bright yellow needle crystals.

Anal. Calcd for $CoC_{33}H_{51}ClN_9O_4P_2$: C, 49.91; H, 6.47; N, 15.87; Cl, 4.46. Found: C, 49.84; H, 6.52; N, 16.06; Cl, 4.25%.

This complex decomposes slowly upon storage. After two weeks the compound had changed to a light brown color; dissolving in CH_3CN produced a bright yellow filtrate from which $[Co(CNCMe_3)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ was recovered by dropwise addition of ether, and a purple residue insoluble in CH_3CN.

Preparation of $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$

A 500 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 4.0 ml CH_3CN, filtered through cotton, and chilled in ice. Then 671 mg $P(NMe_2)_3$ (5:1 mole ratio) was added dropwise with swirling at 0 °C. The dark blue solution turned green with slight precipitation during ligand addition, but became golden yellow with extensive precipitation of pale yellow hexagonal platelet crystals after prolonged (3.0 h) standing at 25 °C. Then 15.0 ml ether was carefully added dropwise, and the solution thoroughly cooled in ice (1 h). After filtration, another 6.0 ml ether added to the filtrate produced a second crop. Crude product (540 mg total, 89%) was recrystallized from 2.0 ml CH_2Cl_2 and 3.0 ml ether; yield: 453 mg (75%). *Anal.* Calcd for $CoC_{27}H_{63}ClN_9O_4P_2$: C, 44.17; H, 8.65; N, 17.17; Cl, 4.83. Found: C, 44.02; H, 8.62; N, 17.26; Cl, 5.01%.

Results and Discussion

Novelty of the $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ Complex

In view of previous results with both alkylisocyanides [1–3, 5, 6] and arylisocyanides [1, 3, 5, 7–9], preparation of the tetrakis(t-butylisocyanide) complex was unexpected. Stoichiometric ratio of 4:1 t-BuNC to Co(II) maximizes yield but does not effectively determine product composition. Just as $[Co(CNPh)_5](ClO_4)_2\cdot H_2O$ is prepared with an excess or deficiency of PhNC [17], the $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ appears to be the major, possibly only, product in reactions with 5:1 mole ratios as well. In reaction under approximately anhydrous conditions (*i.e.*, $[Co(H_2O)_6](ClO_4)_2$ in EtOH under $N_2(g)$ de-hydrated with 10% molar excess acetone dimethyl acetal, $CH_3C(OCH_3)_2CH_3$), multiple fractions with different $\nu(N{\equiv}C)$ were obtained. The $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is recovered, however, upon re-crystallization from CH_3CN/ether. This work does not imply that $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is necessarily the only product obtained by reaction of t-BuNC with $Co(ClO_4)_2$ under all conditions, but is prepared in near-quantitative yield under the specific conditions reported. Why four, rather than five, t-butylisocyanide ligands coordinate is not evident.

Solubility of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is significantly different from that of the arylisocyanide complexes, specifically that in chlorohydrocarbons. The $[Co(CNPh)_5](ClO_4)_2\cdot 1.0H_2O$, for example is soluble to the extent of ~33 mg ml^{-1} in $CHCl_3$, CH_2Cl_2, CH_2ClCH_2Cl, $CHCl_2CH_3$; and ~27 mg ml^{-1} in $CHCl_2CH_2Cl$ [17]. That $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is moderately to highly soluble in polar solvents such as CH_3OH, CH_3NO_2, C_5H_5N, CH_3CN, $(CH_3)_2SO$, and $(CH_3)_2NCHO$; and only sparingly soluble in semi-polar solvents such as $CHCl_3$, CH_2Cl_2, and THF; is reasonable, therefore expected, behavior. The high solubility of $[Co(CNPh)_5](ClO_4)_2\cdot H_2O$, and other arylisocyanide complexes, in chlorohydrocarbons is actually the abnormal or unexpected behavior.

Reduction/Ligand-substitution Reactions

Reaction of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ in 1:5 mole ratio with $P(C_6H_5)_3$, $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4OMe\text{-}p)_3$, $P(C_6H_{13}\text{-}n)_3$, and $P(C_2H_4CN)_3$ is analogous to the reduction/ligand-substitution reactions of the pentakis(arylisocyanide)cobalt(II) complexes [12–16]. Reaction is effectively immediate, exothermic in various degrees, and produces disubstituted product in good yield. Acetonitrile must be substituted for dichloromethane as solvent for $[Co(CNCMe_3)_4H_2O](ClO_4)_2$, but CH_2Cl_2 is a better solvent for recrystallization of the products, due to greater ease of precipitation, and is therefore also used when a second solvent is needed in reaction. The $P(C_2H_4CN)_3$ produces disubstitution, in analogy with reactions of less sterically hindered arylisocyanides, C_6H_5NC, *o*-MeC_6H_4NC, and *p*-ClC_6H_4NC (mono- and disubstituted); rather than monosubstitution, as observed with the sterically-hindered arylisocyanide,

TABLE I. Physical Properties of t-Butylisocyanide-Tertiary Phosphine Complexes of Cobalt(I)

Compound[a]	Color	M.P.[b] (°C)	Isocyanide IR[c]		Electronic spectra[d]	^{1}H NMR spectra[e]	
			CH_2Cl_2	Nujol		$CNCMe_3$	PR_3
$[Co(CNR)_3L_2{}^a]ClO_4$	red-orange	195–200	~2074m(sh) 2104s ~2156vw(sh)	2068m 2100s 2147w	~460 (175) ~340 (5500) ~281sh (44000) 276 (47000) ~270sh (45000) 244 (85000) ~226sh (65000)	δ0.77s	δ7.55m^{h}
$[Co(CNR)_3L_2{}^b]ClO_4$	orange	200–205	2076m 2104s	2062s 2100m 2134vw(sh)	~340sh (4100) ~292sh (30000) ~282sh (39000) 275 (40000) 249 (75000) 227sh (54000)	δ0.75s	δ3.85s δ6.99d(*J*, ~8Hz) δ7.42m
$[Co(CNR)_3L_2{}^c]ClO_4$	orange	214–215	2075m 2104s	2070s 2100s ~2145w(sh)	~465 (150) ≈330br (8800) ~275sh (43000) 270 (45000) ~265sh (42000) 231 (59000)	δ0.68s	δ7.55d(*J*, ~4Hz)
$[Co(CNR)_3L_2{}^d]ClO_4$	pale yellow	160–166	2054s 2090m(sh) ~2130vw(sh)	2049s(br) ~2088m(sh) ~2162vw(sh)	~410sh (200) 278(15000) 237 (41000)	δ0.97s(br)	δ1.50s(br) δ1.68s(br)
$[Co(CNR)_3L_2{}^e]ClO_4$	pale yellow	120–125	2048m^{f} 2085s ~2133w(sh) 2257m^{g}	2040m 2078s ~2128w(sh) 2236m^{g} 2246m^{g}	~642sh (14) 625 (15) ~563sh (8.5) ~395br,sh (200) ~382br,sh (220) 273 (12000) 230 (27000)	Not Sufficiently Soluble in CD_2Cl_2	
$[Co(CNR)_3L_2{}^f]ClO_4$	pale yellow	164–170	2057s 2093m(sh)	2055s 2098m(sh) ~2154vw(sh)	~532sh (10) ~485sh (370) ~465 (490) ~425 (690) ~395 (1100) ~375sh (1300) 279 (31000) 228 (23000)	~δ1.43s(br)	~δ2.73s(br)

[a] R = $-C(CH_3)_3$, $L^a = P(C_6H_4Cl\text{-}p)_3$, $L^b = P(C_6H_4OMe\text{-}p)_3$, $L^c = P(C_6H_5)_3$, $L^d = P(C_6H_{13}\text{-n})_3$, $L^e = P(CH_2CH_2CN)_3$, $L^f = P(NMe_2)_3$. [b] Melting (decomposition) range, uncorrected. [c] The ν(N≡C) in cm^{-1}; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [d] The λ_{max} (ϵ) in mμ (nm), ϵ without Gaussian resolution. [e] Symbols: s = singlet, d = doublet, m = partially-resolved, high-order multiplet, br = broad band. [f] Spectrum in CH_3NO_2. [g] The ν(N≡C) from $P(C_2H_4CN)_3$. [h] Asymmetric AB pattern.

$2,6\text{-}Et_2C_6H_3NC$ [16]. Solubility of $[Co(CNCMe_3)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ is limited, as with previous complexes [16]. Reaction with $P(NMe_2)_3$ is analogous to other P-ligands except that longer reaction time is required; solubility of $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$ is unexpectedly limited.

Reaction with $P(NEt_2)_3$, a ligand observed to monosubstitute in arylisocyanide reactions of $[Co(CNR)_5](ClO_4)_2\cdot xH_2O$ as well as $[Co(CNR)_5]ClO_4$ [16], did not yield a crystalline product. This problem of inability to isolate the product was observed in most reduction/ligand-substitution reactions expected to yield monosubstituted derivatives [12]. Several reaction conditions were attempted. The $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ in minimum volume CH_3CN was reacted with 1:5 mole ratio

$P(NEt_2)_3$, neat and in CH_2Cl_2, at 0, 15 and 25 °C; and in the presence of 1:1 mole ratio $CNCMe_3$. In all reactions, solution color rapidly changed from dark blue, through red purple/maroon, to yellow-brown, becoming golden yellow after the first filtration. Addition of even excessive volumes of ether, multiple filtrations through cotton to remove cloudiness, and prolonged refrigeration, however, produced only initial trace amounts of flocculant, pale yellow solid, and eventual separation of dark green-grey, intractable tar and darkened color of the filtrate. With sufficient patience, a monosubstituted product could possibly have been isolated.

Reaction of $As(C_6H_5)_3$ in 5:1 mole ratio with $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ produced vivid color changes, but only unsubstituted starting material was recovered. Reacting $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ in CH_3CN with 1:5 mole ratio $As(C_6H_5)_3$ in CH_2Cl_2 at 25 °C, and 2:10:1 mole ratio $As(C_6H_5)_3$ and hydrazine in CH_2Cl_2 at 0 °C; caused a color change to opaque yellow–brown during ligand addition, but only $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was recovered (67%, 84%, respectively) upon addition of ether. The filtrate underwent multiple color changes. The $As(C_6H_5)_3$ is less reactive than $P(C_6H_5)_3$, causing disubstitution with $[Co(CNC_6H_5)_5](ClO_4)_2 \cdot H_2O$ [13], but only monosubstitution with $[Co(CNCMe_3)_5]PF_6$ in refluxing ethanol [10] and no substitution with $[Co(CNR)_5]X$, R = aryl; X = ClO_4, BF_4; under various reaction conditions [18, 13]; so failure to substantially react with $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is not unexpected.

Characterization of the Disubstituted Complexes

Physical properties of color, melting point (decomposition range), $\nu(N\equiv C)$ infrared, electronic spectrum, ^1H NMR for the disubstituted complexes are listed in Table I. Colors of these crystalline complexes are typical of previous results with arylisocyanides: orange to red–orange for triarylphosphine disubstituted complexes [14, 15] and pale yellow for trialkylphosphine disubstituted complexes [16]. This trend is in accord with increased π-interaction from aromatic ligands over aliphatic. Decomposition temperature ranges are also analogous to those observed with arylisocyanide complexes, both in absolute values and that temperatures for triarylphosphine derivatives are significantly higher than for trialkylphosphine complexes [14, 16]. These values reflect reasonably high thermal stability, especially for the triarylphosphine complexes; but notably lower for the $P(C_2H_4CN)_3$ complex, the one compound unstable in the solid state.

The $[Co(CNCMe_3)_3\{P(C_6H_5)_3\}_2]ClO_4$ changes color from red–orange to dark blue when slowly heated at 190 °C (decomposition, 214–215 °C), and $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ changes to dark green–blue at its decomposition temperature (198 °C). From $\nu(N\equiv C)$ for the first crude product (*i.e.*, ~2185 cm^{-1} [nujol]), this reaction could be air oxidation of the Co(I) complexes at elevated temperature; further investigation is necessary. The $[Co(CNCMe_3)_3L_2]ClO_4$, L = $P(C_6H_4OMe\text{-}p)_3$, $P(C_6H_{13}\text{-}n)_3$, $P(C_2H_4CN)_3$, and $P(NMe_2)_3$; simply show discoloration/decomposition at their melting points.

The ^1H NMR data are quite routine. Signals for PR_3 show partial resolution of the high multiplicities that are possible: splitting from ^{31}P (I = ½) is evident for $P(C_6H_5)_3$, while $P(C_6H_4Cl\text{-}p)_3$ shows resolution (albeit asymmetric) into a (pseudo) AB pattern, and $P(C_6H_4OMe\text{-}p)_3$ exhibits a doublet for its *ortho*-protons (probably ^{31}P splitting) and a higher-order multiplet (five resolved bands) for its *meta*-protons. The $P(CH_2CH_2CH_2CH_2CH_2CH_3)_3$ protons are resolved only into two broad (asymmetrical) peaks, and the $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$ spectrum shows two very broad peaks, broadening probably due to both the electric quadrupole moment of ^{14}N (I = 1) and slight decomposition in solution.

The chemical shift (δ) for $CNC(CH_3)_3$ shows progressive displacement to lower field (increased deshielding) with the ligands $P(C_6H_5)_3 < P(C_6H_4OMe\text{-}p)_3 \lesssim P(C_6H_4Cl\text{-}p)_3 \ll P(C_6H_{13}\text{-}n)_3 \ll P(NMe_2)_3$. This behavior can be explained in the following manner. Increased σ-donation/decreased π^*-acceptance from the P-ligands causes increasing electron density at the $C\equiv N-$, since there is decreased σ-donation/increased π^*-acceptance from RNC in this series. However, increased electron density increases, not decreases, electronic shielding at this site through local diamagnetic effects. Paramagnetic electronic circulation about the $C\equiv N-$ would also increase shielding (decrease δ) in the adjacent $-C(CH_3)_3$, but these protons could be effectively deshielded (increased δ) through a diamagnetic anisotropic effect from the $C\equiv N-$ [19]. More detailed NMR spectra are necessary to confirm this interpretation. Exception to the orderly progression of P-ligands is the apparent displacement of $P(C_6H_4Cl\text{-}p)_3$ relative to $P(C_6H_5)_3$ and $P(C_6H_4OMe\text{-}p)_3$.

Infrared Spectra

The $\nu(N\equiv C)$ values in CH_2Cl_2 solution and nujol mull for the new complexes are listed in Table I, and representative spectra pictured in Fig. 1. This $N\equiv C$ IR pattern, previously observed with arylisocyanide complexes [10–16, 20–26], clearly identifies disubstitution. Solution and mull spectra are very similar in pattern (although mull spectra tend to be more broad), suggesting similar structure in solution and solid state. The disubstituted pattern for $\nu(N\equiv C)$ is a strong, broad band with higher and

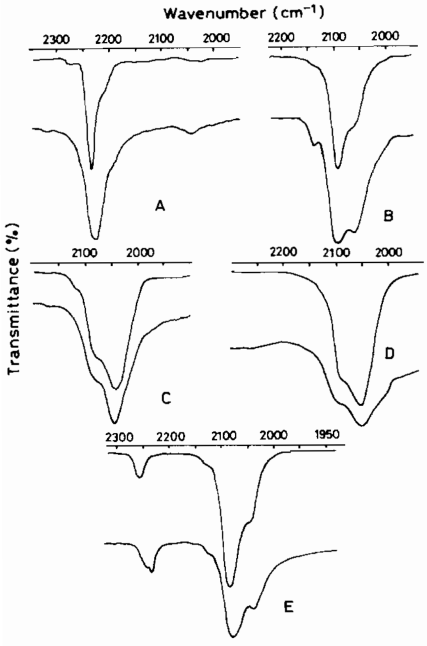

Fig. 1. Selected IR spectra for t-butylisocyanide complexes. A. $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ (top, CH_3CN; bottom, nujol); B. $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ (top, CH_2Cl_2; bottom, nujol); C. $[Co(CNCMe_3)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ (top, CH_2Cl_2; bottom, nujol); D. $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$ (top, CH_2Cl_2; bottom, nujol); E. $[Co(CNCMe_3)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ (top, CH_3NO_2; bottom, nujol).

lower energy shoulders, the shoulders showing varying degrees of resolution and intensity. Initially the solution-structure for disubstituted pentakis(organoisocyanide)cobalt(I) complexes was assumed to be regular axially-disubstituted trigonal bipyramidal (D_{3h}; one allowed ν(N≡C)) [10–12, 14, 20, 22, 24, 25], the IR shoulders being treated as nonfundamental absorptions [27]. Distortion from regular (*i.e.*, D_{3h}) trigonal bipyramidal structure was suggested for the crystalline state, however [12, 14, 20–22, 24]; especially after crystallographic C_{2v} site-symmetry was observed in $[Co(CNC_6H_4F\text{-}p)_3\{P(OMe)_3\}_2]BF_4$ [28]. Raman spectra in CH_2Cl_2 solution, coupled with IR investigation, suggests C_{2v} symmetry for triarylphosphine and trialkylphosphite disubstituted complexes of pentakis(arylisocyanide)cobalt(I) [29]. Similarity between the N≡C IR patterns for t-butylisocyanide-cobalt(I) complexes and those for arylisocyanide complexes suggests analogous structure. A C_{2v} structure would have three allowed ν(N≡C): $2A_1 + B_2$, as is experimentally observed.

Changes in ν(N≡C) assess the relative π^*-accepting ability of the substituting P-ligands. The ν(N≡C) increases for σ-donation to Co(I) and decreases for π^*-acceptance ($d_\pi \rightarrow \pi^*$ backbonding) from Co(I). With two P-ligands and three $CNCMe_3$ bonded to Co(I), the $CNCMe_3$ exhibit more or less π^*-acceptance as the P-ligands are weaker or stronger π^*-acceptors, respectively. Increased or decreased π^*-acceptance by $CNCMe_3$ is reflected by decreased or increased ν(N≡C), respectively, relative to the value for $[Co(CNCMe_3)_5]X$. In accord with recognized [30] decreasing $d_\pi \rightarrow \pi^*$ electron-accepting ability: $RNC > PR_3$; the ν(N≡C) for these tertiary phosphine disubstituted complexes are lower than ν(N≡C) for $[Co(CNMe_3)_5]PF_6$ (*i.e.*, 2120vs, 2152s) [10].

Using the strongest IR band in solution spectra as the most accurate values, ν(N≡C) shows the trend: $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_5)_3$, $P(C_6H_4OMe\text{-}p)_3 > P(C_2H_4CN)_3 > P(NMe_2)_3 \gtrsim P(C_6H_{13}\text{-}n)_3$ (*i.e.*, 2104, 2104, 2104, 2085, 2057, 2054 cm^{-1}, respectively). Within experimental error, the triarylphosphine complexes are not distinguished; expected behavior would be: $P(C_6H_4Cl\text{-}p)_3 > P(C_6H_5)_3 > P(C_6H_4OMe\text{-}p)_3$. This trend has been observed in arylisocyanide complexes [15]. The trend, $P(C_2H_4CN)_3 > P(NMe_2)_3 \gtrsim P(C_6H_{13}\text{-}n)_3$, is unexpected, since on inductive effects the behavior $P(C_2H_4CN)_3 > P(C_6H_{13}\text{-}n)_3 > P(NMe_2)_3$ is expected, as was observed in arylisocyanide complexes [16]. Steric hindrance of $P(NMe_2)_3$ could be involved. Trialkylphosphines are expected to be weaker π^*-acceptors than triarylphosphines, because of electron-releasing ability of alkyl groups, so PR_3 (R = aryl) $> P(C_2H_4CN)_3$ is expected behavior, despite the strong electron-withdrawing ability of the CN substituent. In arylisocyanide complexes [16], however, ν(N≡C) for $[Co(CNR)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ is displaced into the range for triarylphosphines: $P(C_6H_4Cl\text{-}p)_3 > P(C_6H_5)_3 \gtrsim P(C_2H_4CN)_3 > P(C_6H_4OMe\text{-}p)_3$.

Electronic Spectra

Electronic spectra of the disubstituted complexes are tabulated in Table I, and representative examples pictured in Fig. 2. Band maxima (λ_{max}) and molar extinction coefficients (ϵ) are reported without Gaussian resolution. Three intense absorption bands only were observed for pentakis(arylisocyanide)cobalt(I) complexes [5, 24] and for arylisocyanide complexes mono- and disubstituted with trialkylphosphite [24], triarylphosphite [26], and triarylphosphine [11, 13, 15, 26] ligands. Arylisocyanide complexes mono- and disubstituted with trialkylphosphines, however, show additional shoulders and/or major bands, which are interpreted to support deviation from idealized symmetry [16] (*i.e.*, C_{3v} and D_{3h}, respectively, lowered to C_s and C_{2v}). Electronic spectra observed for disubstituted complexes of t-butylisocyanide are more complex. Molar extinction values occur in four ranges: $\epsilon \lesssim 15$, $150 \lesssim \epsilon \lesssim 700$, $1000 \lesssim \epsilon \lesssim 9000$, and $12\,000 \lesssim \epsilon \lesssim 85\,000$.

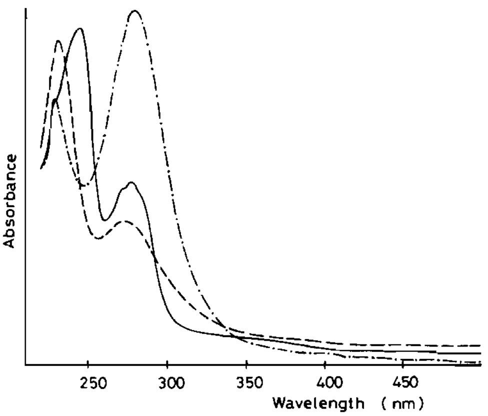

Fig. 2. Solution electronic spectra (CH_2Cl_2, 25 °C, ~1.5 × 10^{-5} M) for selected disubstituted t-butylisocyanide cobalt-(I) complexes; $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ (——), $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$ (–·–), $[Co(CNCMe_3)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ (– – –).

Very weak ($\epsilon \lesssim 15$) absorption bands below 500 nm are observed for $[Co(CNCMe_3)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ and $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$. Since these two complexes show limited stability, very weak bands are probably due to slight decomposition in solution. Intermediate-intensity ($150 \lesssim \epsilon \lesssim 9000$) bands below 330 nm are all probably crystal field transitions. The weak ($\epsilon \approx 200$) bands at 460–465 nm in $P(C_6H_4Cl\text{-}p)_3$ and $P(C_6H_5)_3$ complexes, and 380–410 nm in $P(C_6H_{13}\text{-}n)_3$ and $P(C_2H_4CN)_3$ complexes, are undoubtedly crystal field in nature. Transition metal complexes with unsaturated/aromatic ligands sometimes have very intense crystal field bands, as well as very intense charge transfer bands, so the relatively-intense bands ($4000 \lesssim \epsilon \lesssim 9000$) at 330–340 nm in the triarylphosphine complexes are probably also crystal field transitions. These bands are still significantly less intense than the charge transfer bands above 300 nm ($30\,000 \lesssim \epsilon \lesssim 85\,000$). With trialkylphosphine ligands, the charge transfer bands are less intense ($12\,000 \lesssim \epsilon \lesssim 40\,000$), as expected, but still commence above 280 nm. The five bands for $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$ between 485–375 nm ($370 < \epsilon < 1300$) are interpreted as crystal field transitions.

Appearance of crystal field bands is unlike previous spectra for arylisocyanidecobalt(I) complexes [5, 11, 13, 15, 16, 24, 26], and further supports assigning the first band in $[Co(CNR)_5]X$ ($\bar{\epsilon} \simeq 7000$, $R = CH_3$; $\epsilon \simeq 26\,000$, $R = C_6H_4Cl\text{-}p$) and in $[Co(CNR)_3\{P(C_6H_5)_3\}_2]X$ ($\epsilon \simeq 30\,000$–$35\,000$) as charge transfer [24] rather than crystal field [31, 11]. Unfortunately the crystal field spectra are not sufficiently resolved under these conditions to allow meaningful assignments.

As previously discussed [24, 16], only three one-electron, symmetry-allowed transitions from the highest-energy filled metal orbital into π^* group-ligand orbitals based on equatorial $CNCMe_3$ are possible if rigorous D_{3h} solution-symmetry is assumed for $[Co(CNCMe_3)_3L_2]^+$. Five such metal-to-ligand charge transfer bands are allowed under the C_{2v} distorted trigonal bipyramidal symmetry evidenced by IR/Raman studies with arylisocyanide complexes [29]. Coupled with the IR data, these electronic spectra containing numerous charge transfer bands for triarylphosphine complexes further support a distorted (C_{2v}), rather than regular (D_{3h}), axially-disubstituted trigonal bipyramidal solution structure.

If the charge transfer bands can be interpreted [24, 16] as $d_\pi \rightarrow \pi^*(eq)$ transitions, the λ_{max} suggest π^*-accepting ability: $P(C_6H_5)_3 > P(C_6H_4OMe\text{-}p)_3 \gtrsim P(C_6H_4Cl\text{-}p)_3$ (comparing the first major bands, not shoulders: 270, 275, 276nm); $P(C_2H_4CN)_3 > P(C_6H_{13}\text{-}n)_3 \gtrsim P(NMe_2)_3$ (273, 278, 279 nm); and $P(C_6H_5)_3 > P(C_2H_4CN)_3 > P(C_6H_4OMe\text{-}p)_3 \gtrsim P(C_6H_4Cl\text{-}p)_3 > P(C_6H_{13}\text{-}n)_3 \gtrsim P(NMe_2)_3$. The interpretation of λ_{max} is that ligands which are weaker π^*-accepting than $CNCMe_3$ force the three (equatorial) $CNCMe_3$ to become progressively stronger π^*-accepting, thereby lowering the energy (increasing λ_{max}) for the $d_\pi \rightarrow \pi^*(eq)$ transitions. Result for the trialkylphosphines is expected from inductive effects; an electron-withdrawing substituent (e.g., CN) decreases σ-donation, increases π^*-acceptance of the phosphine. For the triarylphosphines, λ_{max} of the $P(C_6H_4Cl\text{-}p)_3$ complex is displaced to lower energy relative to the $P(C_6H_5)_3$ and $P(C_6H_4OMe\text{-}p)_3$ complexes. By inductive effects, $P(C_6H_4Cl\text{-}p)_3$ should be the strongest, not weakest, π^*-accepting triarylphosphine. The $P(C_6H_4Cl\text{-}p)_3$ ligand was similarly displaced in ^1H NMR data. Except for $P(C_6H_4Cl\text{-}p)_3$ displacement, this ordering of tertiary-phosphine π^*-accepting ability is the same as observed with arylisocyanide-cobalt(I) complexes according to $\nu(N{\equiv}C)$ IR data [16]. Trialkylphosphines are expected to be weaker π^*-acceptors than triarylphosphines, but the strong electron-withdrawing ability of the CN substituent has apparently displaced π^*-accepting ability of $P(C_2H_4CN)_3$ into the range of triarylphosphines, on the basis of the electronic data.

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