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# Reactions of decakis(isopropylisocyanide)dicobalt(II) complexes with tertiary phosphine ligands

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## Abstract

Reaction of $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ ($X=ClO_4$, $BF_4$) with triarylphosphines and substituted trialkylphosphines produces disubstituted Co(I) complexes, $[Co(CNCHMe_2)_3(PR_3)_2]X$; $R=C_6H_5$, $C_6H_4Cl$-*p*, $C_6H_4OMe$-*p*, $CH_2C_6H_5$, $NMe_2$, $CH_2CH_2CN$. These reduction/ligand-substitution reactions are analogous to those of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$. Reaction with unsubstituted trialkylphosphines produces Co(III) complexes, $[Co(CNCHMe_2)_4(PR_3)_2]X_3$, $R=C_4H_9$-n, $C_6H_{13}$-n; in disproportionation reaction from which the Co(I) complex is not recovered: $[Co_2(CNCHMe_2)_{10}]X_4+4PR_3 \rightarrow [Co(CNR)_4(PR_3)_2]X_3+[Co(CNR)_3(PR_3)_2]X+3CNR$. Solution properties ($\nu(-N\equiv C)$, electronic spectra, $\Lambda_M$) are compared for $CNCHMe_2$ and $CNCMe_3$ complexes. The Co(I) complexes are 1:1 electrolytes in $CH_3CN$, $CH_3NO_2$, $CH_3C(O)CH_3$ and $CH_2Cl_2$; the Co(III) complexes are 3:1 electrolytes in $CH_3CN$ and $CH_3NO_2$, but exhibit increasing ion-pairing in acetone and $CH_2Cl_2$. The $\nu(-N\equiv C)$ suggest decreasing $\pi^*$-acceptance in the order: $CNCHMe_2 \gg P(C_6H_4Cl\text{-}p)_3 > P(C_6H_5)_3 \geqslant P(CH_2CH_2CN)_3 > P(C_6H_4OMe\text{-}p)_3 > P(CH_2Ph)_3 > P(NMe_2)_3$. Solution structure for $[Co(CNCHMe_2)_3(PR_3)_2]X$ is believed to be distorted trigonal bipyramidal, but rigorous $D_{4h}$ for $[Co(CNCHMe_2)_4(PR_3)_2]X_3$.

## Introduction

Direct reduction/ligand-substitution reactions, in which a Co(II)–organoisocyanide complex undergoes both reduction to Co(I) and incomplete substitution of ligands, have been investigated for different arylisocyanide and alkylisocyanide Co(II) perchlorate and tetrafluoroborate salts with various tertiary phosphorus ligands [1–5]. Reactions with tertiary phosphines tend to yield disubstituted Co(I) complexes, $[Co(CNR)_3(PR_3)_2]X$, $X=ClO_4$, $BF_4$; $PR_3=P(C_6H_5)_3$, $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4OMe\text{-}p)_3$, $P(C_6H_{13}\text{-n})_3$, $P(NMe_2)_3$, $P(CH_2CH_2CN)_3$ [1–5]. Exceptional behavior is observed with the sterically-hindered $P(NEt_2)_3$, which yields the monosubstituted complex, $[Co(CNR)_4P(NEt_2)_3]ClO_4$ [4]; and the unique instance of $[Co(CNC_6H_3Et_2\text{-}2,6)_4P(C_2H_4CN)_3]ClO_4$ [4].

This present work extends direct reduction/ligand-substitution reactions to the dimeric complexes $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ ($X=ClO_4$, $BF_4$) reacted with tertiary phosphine ligands. Products are compared with analogous complexes of $CNCMe_3$. While reactions with triarylphosphines may be deemed routine, reactions with trialkylphosphines produce unexpected and highly interesting complexes.

## Experimental

$[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ and $[Co(CNCMe_3)_4H_2O]X_2 \cdot nH_2O$ ($X=ClO_4$, $BF_4$) were prepared from commercial $CNCHMe_2$ (Strem) and $CNCMe_3$ (Fluka) as previously reported [5, 6]. Commercial $PPh_3$, $P(C_6H_4Cl\text{-}p)_3$ (Strem), $P(C_6H_4OMe\text{-}p)_3$ (Strem), $P(CH_2Ph)_3$ (Strem), $P(C_4H_9\text{-n})_3$ (Fluka), $P(C_6H_{13}\text{-n})_3$ (Strem), $P(NMe_2)_3$ (Fluka), $P(NEt_2)_3$ (Fluka) and $P(CH_2CH_2CN)_3$ (Strem) were used without further purification. Anhydrous diethyl ether was filtered through an alumina column immediately before use. IR spectra were recorded on a Perkin-Elmer 1710 FT-IR or a Mattson Polaris FT-IR instrument in nujol mull or $CH_2Cl_2$ and $CH_3NO_2$ solution using a single NaCl cell. Solution electronic spectra in

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$CH_2Cl_2$ and $CH_3CN$ were recorded on a Shimadzu UV-365 in matched silica cells. Melting (decomposition) ranges were measured in capillaries using an Electrothermal melting point apparatus. Molar conductivities were measured on ~0.001 M solutions at 25.0 °C using a Crison model 525 conductimeter with an Ingold flow-through cell. The C, H and N elemental analyses were performed using a Carlo Erba CHN-O/S elemental analyzer, model 1106. Microsamples were weighed on a Sartorius Ultramicro electrobalance. Co was analyzed by atomic emission using a Perkin-Elmer P-II ICP-AES; samples were dissolved in concentrated nitric acid, then diluted 2:5 with millipore water. Standards were also prepared in 40% nitric acid and measured before and after each sample. Several samples precipitated upon dilution and were not analyzed.

### *Synthesis of* $[Co(CNCHMe_2)_3(PPh_3)_2]ClO_4$

A 500 mg sample of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ was dissolved in 1.5 ml $CH_2Cl_2$ and filtered through cotton. This solution was maintained at 0 °C in an ice bath while 1.01 g $PPh_3$ (1:5 Co:P mol ratio) dissolved in 1.0 ml $CH_2Cl_2$ was added dropwise. The dark green solution changed to yellow–brown, then to red–brown, after about half the $PPh_3$ had been added, and an odor of liberated $CNCHMe_2$ was evident. The clear solution was allowed to warm to room temperature (5 min), then diethyl ether was added dropwise. Initial precipitation commenced after addition of 4.5 ml ether and scratching the walls of the flask. A total volume of 5.5 ml ether was added and the solution chilled for 25 min. Bright orange crystals (1.00 g) were filtered from the pale orange filtrate; addition of 1.0 ml ether and further refrigeration produced a second crop (100 mg). The crude product was recrystallized from 1.5 ml $CH_2Cl_2$ and 2.0 ml ether. Yield: 630 mg (82%). The sample was recrystallized from $CH_2Cl_2$/ether a second time. Melting range: 189–197 °C (dec.); $\nu(-N{\equiv}C)$: ~2140vw(sh), ~2091br(sh), 2077vs(br), 2034w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{48}H_{51}ClN_3O_4P_2 \cdot 1.2CH_2Cl_2$: C, 59.56; H, 5.42; N, 4.24; Co, 5.94. Found: C, 59.38; H, 5.40; N, 4.23; Co, 5.92%.

Analogous syntheses produced the following complexes.

$[Co(CNCHMe_2)_3(PPh_3)_2]BF_4 \cdot nCH_2Cl_2$. Melting range: 138–147 °C (dec.); $\nu(-N{\equiv}C)$: ~2140vw(sh), ~2091br(sh), 2077vs(br), 2034w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{48}H_{51}BF_4N_3P_2 \cdot 1.5CH_2Cl_2$: C, 59.16; H, 5.42; N, 4.18. Found: C, 59.02; H, 5.41; N, 4.22%.

$[Co(CNCHMe_2)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$. Melting range: 184–188 °C (dec.); $\nu(-N{\equiv}C)$: ~2135vw(sh), 2081vs, 2036w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{48}H_{45}Cl_7N_3O_4P_2$: C, 52.56; H, 4.13; N, 3.83; Co, 5.37. Found: C, 52.29; H, 4.12; N, 3.51; Co, 5.33%.

$[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$. Melting range: 189–205 °C (dec.); $\nu(-N{\equiv}C)$: ~2135w(sh), 2075vs(br), 2038m $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{54}H_{63}ClN_3O_{10}P_2$: C, 60.58; H, 5.93; N, 3.92; Co, 5.50. Found: C, 59.93; H, 5.90; N, 3.86; Co, 5.48%.

$[Co(CNCMe_3)_3(PPh_3)_2]BF_4 \cdot nCH_2Cl_2$. Melting range: 185–207 °C (dec.); $\nu(-N{\equiv}C)$: ~2136vw(sh), 2092vs, 2057vs(br) $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{51}H_{57}BF_4N_3P_2 \cdot 0.4CH_2Cl_2$: C, 64.74; H, 6.11; N, 4.41; Co, 6.18. Found: C, 64.70; H, 6.28; N, 4.75; Co, 5.80%.

### *Synthesis of* $[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]ClO_4$

A 500 mg sample of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ was dissolved in 1.5 ml $CH_2Cl_2$, filtered through cotton with additional 0.5 ml $CH_2Cl_2$ rinse, and chilled in ice. A solution of 1.17 g $P(CH_2Ph)_3$ (1:5 Co:P mole ratio) in 2.0 ml $CH_2Cl_2$ was added dropwise with stirring. The green reaction mixture turned yellow–brown with precipitation of light yellow solid during ligand addition. The mixture was allowed to warm to room temperature (10 min), then 7.5 ml ether was added dropwise and the mixture chilled 30 min. Bright yellow microcrystalline powder was filtered from the amber filtrate. No second crop was obtained. The crude product (1.215 g) was dissolved in 75 ml $CH_3NO_2$, filtered through cotton twice, and precipitated by addition of 145 ml ether. Yield: 640 mg (85%). The product was recrystallized a second time from $CH_3NO_2$/ether. Yield: 410 mg (64% recovery; 55% overall yield). Melting range: 197–205 °C (dec.); $\nu(-N{\equiv}C)$: 2124w, 2068vs(br), 2035w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{54}H_{63}ClN_3O_4P_2$: C, 66.56; H, 6.52; N, 4.31; Co, 6.05. Found: C, 66.24; H, 6.52; N, 4.05; Co, 6.01%.

$[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]BF_4$. Melting range: 200–212 °C (dec.); $\nu(-N{\equiv}C)$: ~2123w, 2069vs(br), 2035w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{54}H_{63}BF_4N_3P_2$: C, 67.43; H, 6.60; N, 4.37; Co, 6.13. Found: C, 67.10; H, 6.69; N, 4.66; Co, 6.05%.

$[Co(CNCMe_3)_3\{P(CH_2Ph)_3\}_2]ClO_4$. Melting range: 190–196 °C (dec.); $\nu(-N{\equiv}C)$: 2070 m, 2041s $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{57}H_{69}ClN_3O_4P_2$: C, 67.35; H, 6.84; N, 4.13. Found: C, 67.22; H, 7.03; N, 3.79%.

### *Synthesis of* $[Co(CNCHMe_2)_4\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_3$

A 750 mg sample of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ was dissolved in 2.0 ml $CH_2Cl_2$, filtered through cotton, washed with 0.5 ml $CH_2Cl_2$, and chilled in ice. Then 1.17 g $P(C_4H_9\text{-}n)_3$ (neat, 1:5 Co:P mole ratio) was added dropwise while the solution was stirred and maintained at 0 °C. The dark green solution changed to bright red–orange during ligand addition, and flocculent solid precipitated. The mixture was allowed to stand 10 min at room temperature, then 12.0 ml ether was added dropwise, and the pale yellow solid filtered at room temperature. The product was washed twice with 2.0 ml portions of ether and dried under suction/air (500 mg). Addition of more ether failed to yield the crystalline product. The crude product was recrystallized from 6.0 ml $CH_3CN$ and 5.0 ml ether; the mixture was chilled 1 h before the flocculent white product was filtered from the golden yellow solution and dried under suction/air. Yield: 410 mg (34%). This sample was recrystallized from $CH_3CN$/ether a second time (85% recovery). Melting range: 190–195 °C (dec.); $\nu(-N{\equiv}C)$: 2241vs, ~2204vw(sh), 2016w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{40}H_{82}Cl_3N_4O_{12}P_2$: C, 46.27; H, 7.96; N, 5.40; Co, 5.68. Found: C, 46.50; H, 8.01; N, 5.67; Co, 5.61%.

$[Co(CNCHMe_2)_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$. Melting range: 142–147 °C (dec.); $\nu(-N{\equiv}C)$: 2236vs, ~2200vw(sh), 2017w $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{52}H_{106}Cl_3N_4O_{12}P_2$: C, 51.76; H, 8.85; N, 4.64; Co, 4.88. Found: C, 51.97; H, 9.07; N, 4.77; Co, 4.85%.

$[Co(CNCHMe_2)_4\{P(C_4H_9\text{-}n)_3\}_2](BF_4)_3$. Melting range: 178–182 °C (dec.); $\nu(-N{\equiv}C)$: 2244vs, ~2205w(sh), 2016vw $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{40}H_{82}B_3F_{12}N_4P_2$: C, 48.02; H, 8.26; N, 5.60; Co, 5.89. Found: C, 47.81; H, 8.47; N, 5.44; Co, 5.98%.

### *Synthesis of $[Co(CNCMe_3)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$*

A 500 mg sample of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ was dissolved in 3.5 ml $CH_3CN$, filtered through cotton, rinsed with 0.5 ml $CH_3CN$, and chilled in ice. Then 850 mg $P(C_4H_9\text{-}n)_3$ (neat, 1:5 mole ratio) was added dropwise. The dark blue solution changed to clear bright yellow when about half the ligand had been added. After the solution was warmed to room temperature, 18.0 ml ether was added dropwise, and the mixture was chilled 30 min. Pale yellow crystals (390 mg) were filtered, and addition of 5.0 ml ether afforded a second crop (100 mg). The crude product was recrystallized from 2.0 ml $CH_2Cl_2$ and 6.0 ml ether. Yield: 420 mg (62%). Melting range: 140–146 °C (dec.); $\nu(-N{\equiv}C)$: ~2151vw(sh), ≈2080m(sh), 2042vs, ~1945vw(sh) $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{39}H_{81}ClN_3O_4P_2$: C, 57.66; H, 10.05; N, 5.17; Co, 7.25. Found: C, 57.16; H, 10.14; N, 5.00; Co, 7.11%.

### *Synthesis of $[Co(CNCHMe_2)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$*

A 500 mg sample of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ was dissolved in 2.5 ml $CH_3CN$ and filtered through cotton. A solution of 745 mg $P(C_2H_4CN)_3$ in 6.0 ml $CH_3CN$ was added dropwise at room temperature. The green color of the reaction mixture turned to clear red–brown. The solution was allowed to stand for 10 min at room temperature and was then filtered through cotton. The addition of 10.0 ml ether and immediate filtration produced an off-white solid (140 mg). Successive additions of small volumes of ether followed by refrigeration produced three crops of mixed white and yellow crystals and a final crop of white crystals. The second, third and fourth crops were combined (430 mg) and recrystallized from 2.0 ml $CH_3CN$ and 3.0 ml ether. Yield: 230 mg (40%). This sample was recrystallized again from $CH_3CN$/ether. Melting range: 115–135 °C (dec.); $\nu(-N{\equiv}C)$: 2082s, 2044m $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{30}H_{45}ClN_9O_4P_2$: C, 47.91; H, 6.03; N, 16.76. Found: C, 48.27; H, 6.10; N, 16.63%.

### *Synthesis of $[Co(CNCHMe_2)_3\{P(NMe_2)_3\}_2]ClO_4$*

A 750 mg sample of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ was dissolved in 2.5 ml $CH_2Cl_2$, filtered through cotton using additional 0.5 ml $CH_2Cl_2$, and chilled in ice, before 950 mg $P(NMe_2)_3$ (neat, 1:5 Co:P mole ratio) was added dropwise. The yellow–green reaction mixture, allowed to stand at room temperature for 60 min, changed to a clear, yellow–brown color. Careful addition of 7.5 ml ether and refrigeration for several days produced the crystalline product. The pale yellow crystals (245 mg) were rapidly filtered from the cold solution, washed twice with 2.0 ml portions of ether, and immediately recrystallized from 1.5 ml $CH_2Cl_2$ and 8.0 ml ether. Addition of 4.0 ml ether to the original filtrate and extensive refrigeration afforded a second crop (420 mg), which was immediately recrystallized. Total yield: 375 mg (56% recovery; 47% overall yield). This compound was characterized as soon as possible, since it rapidly discolors and eventually decomposes. Melting range: 128–137 °C (dec.); $\nu(-N{\equiv}C)$: ≈2133vw(sh), 2066s, 2035m $cm^{-1}$ (nujol). *Anal.* Calc. for $CoC_{24}H_{57}ClN_9O_4P_2$: C, 41.65; H, 8.30; N, 18.21; Co, 8.51. Found: C, 40.97; H, 8.36; N, 18.16; Co, 8.18%.

Attempts to synthesize the analogous $P(NEt_2)_3$ complex were unsuccessful. Reaction mixtures became yellow–brown during ligand addition, but careful addition of ether, repeated filtrations through cotton, and extensive refrigeration produced only yellow oils on several attempts.

## Results and discussion

### *Syntheses of the complexes*

Reactions of $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ ($X = ClO_4$, $BF_4$) with the triarylphosphines $P(C_6H_5)_3$,

$P(C_6H_4Cl\text{-}p)_3$ and $P(C_6H_4OMe\text{-}p)_3$ are analogous to those of $[Co(CNMe_3)_4H_2O](ClO_4)_2$ [5]. Disubstituted Co(I) complexes with a tendency to adduct $CH_2Cl_2$, $[Co(CNCHMe_2)_3(PR_3)_2]X \cdot nCH_2Cl_2$, are produced in good yields. No significant difference is observed between $ClO_4^-$ and $BF_4^-$ salts.

Reactions with tribenzylphosphine differ only in substantially decreased solubility of the complexes and initial co-precipitation of the side-product, probably $(PhCH_2)_3PO$. Nitromethane gives better solubility than $CH_2Cl_2$ or $CH_3CN$, but still is needed in far greater volumes than solvent used for other Co(I) complexes. Comparison of nujol IR spectra for the crude product with purified $[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]ClO_4$ reveals the additional, medium-intensity band at $\sim 1185\ cm^{-1}$, which is likely to be $\nu(P{=}O)$ [7] from a phosphine oxide impurity. The reaction of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ is similar, including the limited solubility of the product.

Reactions of $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ and $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ with $P(C_4H_9\text{-}n)_3$ and $P(C_6H_{13}\text{-}n)_3$ show significant differences. $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ undergoes typical reduction/ligand substitution with $P(C_6H_{13}\text{-}n)_3$ (46% yield [5]) and $P(C_4H_9\text{-}n)_3$ (62%), but $[Co_2(CNCHMe_2)_{10}]X_4 \cdot nH_2O$ behaves differently: a Co(III) product is obtained. Disproportionation of Co(II) is the probable reaction: $[Co_2(CNCHMe_2)_{10}]X_4 + 4PR_3 \rightarrow [Co(CNCHMe_2)_4(PR_3)_2]X_3 + [Co(CNCHMe_2)_3(PR_3)_2]X + 3CNCHMe_2$, with only the Co(III) complex isolated. Simple oxidation is not suggested. Support for this conclusion is found in the % yield values. High stability and low solubility of the Co(III) complexes should insure high recovery, yet less than half the cobalt is recovered. This suggests a second product. Cobalt(I) complexes of $CNCHMe_2$ tend to be less stable than analogous $CNCMe_3$ complexes, and the $[Co(CNCMe_3)_3(PR_3)_2]ClO_4$ complexes ($R = C_4H_9\text{-}n$, $C_6H_{13}\text{-}n$) already have limited stability, being synthesized in lower than normal yields and decomposing under storage. Cobalt(I) complexes of $CNCHMe_2$ with $P(C_4H_9\text{-}n)_3$ and $P(C_6H_{13}\text{-}n)_3$ could thus be expected to be highly soluble and prone to decomposition. In subsequent work [8], both $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$ and $[Co(CNC_6H_{11})_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ have been isolated in an analogous reaction using $CNC_6H_{11}$. These reactions are analogous to $Co(ClO_4)_2 \cdot 6H_2O$ disproportionation by trialkylphosphites [9–11]: $2Co(ClO_4)_2 \cdot 6H_2O + 11P(OR)_3 \rightarrow [Co\{P(OR)_3\}_6](ClO_4)_3 + [Co\{P(OR)_3\}_5]ClO_4 + 6H_2O$.

Reactions of $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ with $P(C_2H_4CN)_3$ and $P(NMe_2)_3$ are analogous to reactions of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$. Final yields are low due to the limited stability of $[Co(CNCHMe_2)_3\{P(NMe_2)_3\}_2]ClO_4$ (47%) and the fractional recrystallization of $[Co(CNCHMe_2)_3\{P(C_2H_4CN)_3\}_2]ClO_4$ (40%). There is no evidence of Co(III). Trialkylphosphines with electron donating or withdrawing substituents therefore effect reduction/substitution in the $CNCHMe_2$ as well as $CNCMe_3$ complexes of Co(II), while the unsubstituted $P(C_4H_9\text{-}n)_3$ and $P(C_6H_{13}\text{-}n)_3$ selectively disproportionate/substitute $[Co(CNCHMe_2)_5]^{2+}$. What may be required for this disproportionation is a subtle balance of effects, rather than one electronic or steric aspect. Analogous systems are under current investigation.

*Characterization of the complexes*

Solution properties ($\nu(-N{\equiv}C)$, electronic spectra and $\Lambda_M$) for the $CNCHMe_2$ and the corresponding $CNCMe_3$ complexes are reported in Table 1. Typical $\nu(-N{\equiv}C)$ patterns and electronic spectra for the new Co(I) complexes are shown in Figs. 1 and 2, respectively. Melting (decomposition) ranges and mull $\nu(-N{\equiv}C)$ are reported within the 'Experimental'. The nujol $\nu(-N{\equiv}C)$ are similar to solution data, although sometimes exhibiting additional shoulders, possibly indicating lower symmetry in the solid state. Melting ranges are comparable to, or lower than, values for analogous $CNCMe_3$ complexes [5]. Decomposition temperatures for these complexes show a parallel trend with compound stability. Triarylphosphine derivatives appear to be indefinitely stable, but the $P(C_2H_4CN)_3$ and $P(NMe_2)_3$ complexes slowly decompose under desiccation.

Molar conductivities ($\Lambda_M^{25}$) for the Co(I) complexes in $CH_3CN$, $CH_3NO_2$ and $CH_3C(O)CH_3$ are appropriate for fully dissociated 1:1 electrolytes [12], so values in $CH_2Cl_2$ (i.e. 50–70) probably reflect 1:1 electrolyte behavior. Values in acetone are slightly higher than expected. Conductivity values for the Co(III) complexes in $CH_3CN$ and $CH_3NO_2$ indicate 3:1 electrolyte behavior, but values in acetone and $CH_2Cl_2$ (for which solubility is limited) suggest extensive ion-pairing. This behavior parallels the solvent dielectric constant. High $\epsilon$ for $CH_3CN$ (36.2 [12]) and $CH_3NO_2$ (35.9 [12]) allow total dissociation, but moderate $\epsilon$ for acetone (20.7 [12, 13]) supports only partial dissociation and low $\epsilon$ for $CH_2Cl_2$ (9.1 [13]) allows little dissociation of free ions. This is reasonable behavior for highly charged ions in organic solvents.

The $\nu(-N{\equiv}C)$ pattern for $CNCHMe_2$–Co(I) complexes (see Fig. 1) is diagnostic for disubstitution, and well characterized in both alkylisocyanide [5, 14–17] and arylisocyanide [1–4, 15–20] complexes. Resolution of the side band supports deviation from strict trigonal bipyramidal structure in solution and solid state [21]. These spectra suggest the three

TABLE 1. Solution properties of Co(I) and Co(III) complexes with isopropylisocyanide or t-butylisocyanide and tertiary phosphine ligands

| Compound | $\nu(-N\equiv C)$ infrared[a] | | Electronic spectra[b] | | $\Lambda_M^{25\ °C}$ |
|---|---|---|---|---|---|
| | $CH_2Cl_2$ | $CH_3NO_2$ | $CH_2Cl_2$ | $CH_3CN$ | |
| $[Co(CNCHMe_2)_3(PPh_3)_2]ClO_4$ | $\sim$2133vw(sh) | $\sim$2137vw(sh) | $\approx$340sh (4400) | $\approx$340sh (3500) | 135 |
| | 2089vs | 2090vs | $\sim$275sh | $\sim$276sh | 87 |
| | 2037w | 2038w | 271 (45, 200) | 271 (39, 300) | 151 |
| | | | $\sim$266sh | $\sim$266sh | 63 |
| | | | 230 (59, 200) | 229sh (53, 500) | |
| $[Co(CNCHMe_2)_3(PPh_3)_2]BF_4$ | $\sim$2132vw(sh) | $\sim$2134vw(sh) | $\approx$340sh (4500) | $\approx$340sh (3600) | 140 |
| | 2089vs | 2091vs | $\sim$276sh | $\sim$276sh | 86 |
| | 2037w | 2039w | 272 (36, 300) | 271 (39, 200) | 150 |
| | | | $\sim$266sh | $\sim$266sh | 55 |
| | | | 228 (59, 000) | 228sh (53, 600) | |
| $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$ | 2090vs | 2092vs | $\approx$340sh (3600) | $\approx$340sh (3300) | 135 |
| | 2064m(sh) | 2066m(sh) | $\sim$275sh | $\sim$275sh | 77 |
| | | | 270 (43, 000) | 269 (41, 100) | 134 |
| | | | $\sim$265sh | $\sim$265sh | 66 |
| $\{Co(CNCMe_3)_3(PPh_3)_2\}BF_4$ | $\sim$2150vw | 2092vs | $\approx$340sh (3500) | $\approx$335sh (3300) | 136 |
| | 2090vs | 2065m(sh) | $\sim$275sh | $\sim$274sh | 85 |
| | 2064m(sh) | | 270 (42, 000) | 269 (39, 200) | 151 |
| | | | $\sim$265sh | $\sim$264sh | 66 |
| | | | 232 (54, 400) | 230 (50, 000) | |
| $[Co(CNCHMe_2)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ | $\sim$2145vw(sh) | $\sim$2146vw(sh) | $\approx$340sh (3900) | $\approx$340sh (3500) | 131 |
| | $\sim$2133vw(sh) | 2095vs | $\sim$283sh | $\sim$281sh | 77 |
| | 2091vs | 2034w | 277 (42, 800) | 275 (41, 000) | 134 |
| | 2032w | | $\sim$271sh | $\sim$271sh | 51 |
| | | | 243 (75, 100) | 240 (73, 300) | |
| $[Co(CNCMe_3)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$ | $\sim$2133vw(sh) | $\sim$2126vw(sh) | $\approx$345sh (3900) | $\sim$340sh (3800) | 136 |
| | 2089vs | 2092vs | $\sim$283sh | $\approx$282sh | 80 |
| | $\sim$2058m(sh) | $\sim$2059m(sh) | 277 (51, 400) | 275 (50, 400) | 140 |
| | | | $\sim$271sh | $\sim$271sh (49, 800) | 68 |
| | | | 244 (91, 700) | 242 (90, 200) | |
| $[Co(CNCHMe_2)_4\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ | $\sim$2129vw(sh) | $\sim$2129vw(sh) | $\approx$340sh (5000) | $\approx$340sh (4700) | 141 |
| | 2080vs(br) | 2084vs(br) | $\sim$293sh (32, 800) | $\sim$292sh (31, 100) | 96 |
| | 2037w(br) | $\sim$2039w(br) | 282 (39, 600) | 281 (38, 200) | 154 |
| | | | 275 (40, 800) | 274 (39, 200) | 60 |
| | | | 249 (68, 800) | 247 (67, 700) | |
| $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ | 2088vs | $\approx$2127vw(sh) | $\approx$340sh (4700) | $\approx$335sh (4700) | 129 |
| | 2059vs(br) | 2089vs | $\sim$292sh (33, 300) | $\sim$292sh (30, 400) | 73 |
| | | 2060vs(br) | 281 (42, 000) | 281 (39, 200) | 130 |
| | | | 275 (43, 300) | 275 (40, 500) | 61 |
| | | | 249 (73, 100) | 248 (71, 000) | |
| $[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]ClO_4$ | $\sim$2127vw(sh) | $\sim$2128vw(sh) | 287 (12, 100) | $\sim$286 (11, 100) | 134 |
| | 2078vs | 2078vs | 250 (34, 700) | 250 (32, 100) | 82 |
| | 2033w | $\sim$2033vw(sh) | | | 140 |
| | | | | | 56 |
| $[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]BF_4$ | $\sim$2125vw(sh) | $\sim$2127vw(sh) | 288 (11, 400) | $\sim$288 (10, 700) | 133 |
| | 2078vs | 2078vs | 250 (33, 800) | 250 (30, 900) | 83 |
| | $\sim$2033w | $\sim$2033vw(sh) | | | 145 |
| | | | | | 60 |
| $[Co(CNCMe_3)_3\{P(CH_2Ph)_3\}_2]ClO_4$ | 2076vs | 2076vs | $\sim$286 (12, 400) | $\sim$287 (10, 400) | 124 |
| | 2047w | 2048w | 252 (39, 500) | 250 (32, 600) | 76 |
| | | | | | 132 |
| | | | | | 57 |
| $[Co(CNCHMe_2)_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$ | 2240vs | 2237vs | 296.5 (31, 900) | 297.0 (28, 400) | 340 |
| | | | | | 205 |
| | | | | | 130 |
| | | | | | 3.75 |

*(continued)*

TABLE 1. (*continued*)

| Compound | $\nu(-N{\equiv}C)$ infrared[a] | | Electronic spectra[b] | | $\Lambda_M^{25\,°C}$ |
|---|---|---|---|---|---|
| | $CH_2Cl_2$ | $CH_3NO_2$ | $CH_2Cl_2$ | $CH_3CN$ | |
| $[Co(CNCMe_3)_3\{P(C_6H_{13}\text{-}n)_3\}_2]ClO_4$ | ~2118vw(sh)<br>~2075m(sh)<br>2040vs | ~2120w(sh)<br>~2077w(sh)<br>2042vs | 277 (15, 900)<br>236 (42, 400) | 276 (14, 300)<br>236 (35, 100) | 130<br>74<br>143<br>65 |
| $[Co(CNCHMe_2)_4\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_3$ | 2240vs | 2237vs | 295.5 (25, 200) | 295.5 (32, 300) | 350<br>200<br>134<br>d |
| $[Co(CNCHMe_2)_3\{P(C_4H_9\text{-}n)_3\}_2](BF_4)_3$ | 2241vs | 2237vs | 294.0 (28, 600) | 296.0 (27, 500) | 395<br>220<br>141<br>d |
| $[Co(CNCMe_3)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$ | ~2116vw(sh)<br>≈2075m(sh)<br>2042vs<br>~1948vw(sh) | ~2117vw(sh)<br>≈2075m(sh)<br>2043vs<br>~1943vw(sh) | 277 (15, 100)<br>236 (39, 700) | 276 (11, 300)<br>236 (29, 100) | 126<br>83<br>144<br>62 |
| $[Co(CNCHMe_2)_3\{P(NMe_2)_3\}_2]ClO_4$ | ~2131vw(sh)<br>2070vs<br>2037m | ~2133vw(sh)<br>2072vs<br>2039m | 280 (26, 600) | 279 (24, 400) | 147<br>91<br>151<br>62 |
| $[Co(CNCMe_3)_3\{P(NMe_2)_3\}_2]ClO_4$ | ~2145vw(sh)<br>≈2080m(sh)<br>2047vs<br>~1945vw(sh) | ≈2081m(sh)<br>2049vs<br>~1944vw(sh) | 278 (29, 900) | 277 (28, 200) | 144<br>89<br>154<br>63 |
| $[Co(CNCHMe_2)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$ | d | ≈2139vw(sh)<br>2089vs(br)<br>2027w | d | 274 (13, 300)<br>234 (31, 200) | 124<br>77<br>121<br>d |
| $[Co(CNCMe_3)_3\{P(CH_2CH_2CN)_3\}_2]ClO_4$ | 2080vs<br>2044m(sh) | 2081vs(br)<br>~2044w(sh) | d | 274 (13, 700)<br>232 (34, 100) | 110<br>68<br>115<br>d |

[a] The $\nu(-N{\equiv}C)$ in $cm^{-1}$; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [b] The $\lambda_{max}(\epsilon)$ in nm, without Gaussian resolution. [c] Molar conductivity, $\Lambda_M = 1000\ L_{correct}\ C_M^{-1}$ in $ohm^{-1}\ cm^2\ mol^{-1}$, $L_{correct} = L_{solution} - L_{solvent}$, measured at 25.0 °C and $C_M \cong 1.0 \times 10^{-3}$ M; first value in $CH_3CN$, second value in $CH_3NO_2$, third value in $CH_3C(O)CH_3$, fourth value in $CH_2Cl_2$. [d] Insufficient solubility for accurate measurement.

bands ($2A_1 + B_2$) required by the $C_{2v}$ equatorially-distorted, axially-disubstituted trigonal bipyramidal structure suggested for disubstituted pentakis(arylisocyanide)cobalt(I) complexes [21]. This is the solid-state structure for $[Co(CNC_6H_4F\text{-}p)_3\{P(OMe)_3\}_2]BF_4$ [22]. The $\nu(-N{\equiv}C)$ values also assess relative σ-donating/π*-accepting abilities in the phosphorus ligands [4, 5]. Decreasing π*-acceptance is assigned: $CNCHMe_2 \gg P(C_6H_4Cl\text{-}p)_3 > P(C_6H_5)_3 \geqslant P(CH_2CH_2CN)_3 > P(C_6H_4OMe\text{-}p)_3 > P(CH_2Ph)_3 > P(NMe_2)_3$. This agrees with previous observations [3–5].

The $\nu(-N{\equiv}C)$ for the Co(III) complexes suggests tetragonally-distorted octahedral geometry, *trans*-$[Co(CNCHMe_2)_4(PR_3)_2]X_3$. The shoulder in mull spectra suggests solid-state distortion of the $CoC_4$ plane, such as the 'puckering' seen in *trans*-$[Co(CNC_6H_4Me\text{-}p)_4I_2]$ [23]. The single, strong band in solution is compatible with rigorous $D_{4h}$ symmetry.

Electronic spectra for $CNCHMe_2$–Co(I) complexes (Table 1 and Fig. 2) show considerable variation but remain similar to analogous $CNCMe_3$ complexes. With trialkylphosphines only one or two of the expected three [3–5, 15, 19] charge-transfer bands are observed. With triarylphosphines more charge transfer bands are observed, and additionally there is a longer-wavelength ($\lambda > 300$ nm), lower-intensity ($\epsilon \cong 3300$–$5000$) crystal field region. Appearance of this region supports assignment of the first band in $[Co(CNC_6H_4Cl\text{-}p)_3(PPh_3)_2]X$ ($\epsilon \cong 30\,000$–$35\,000$) as charge transfer [19] rather than crystal field [15, 24]. Shoulders in the UV region are difficult to interpret.

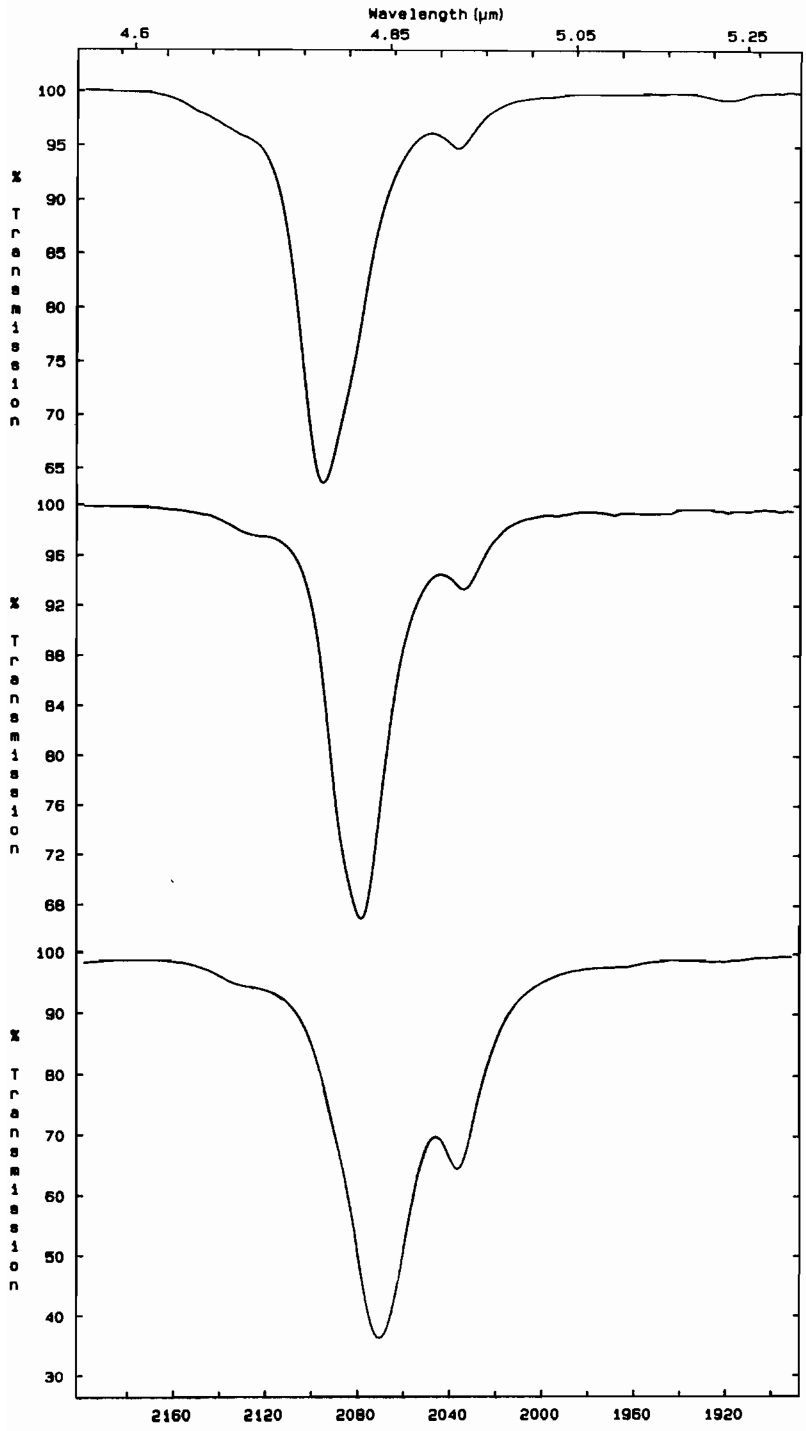

Fig. 1. The $\nu(-N{\equiv}C)$ IR pattern (2200–1900 cm$^{-1}$) for selected Co(I) complexes in $CH_2Cl_2$; top to bottom: $[Co(CNCHMe_2)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$, $[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]ClO_4$, $[Co(CNCHMe_2)_3\{P(NMe_2)_3\}_2]ClO_4$.

These may be extra bands for reduced symmetry: three $d_\pi \rightarrow \pi^*$ (equatorial) charge-transfer bands are expected under $D_{3h}$ symmetry [19], but five one-electron, symmetry-allowed bands become possible under $C_{2v}$ [4].

The single, intense UV band seen for each Co(III) complex is solvent dependent, extremely symmetrical, and probably charge transfer in nature. The pure white solids give colorless solutions with no visible or near IR absorption.

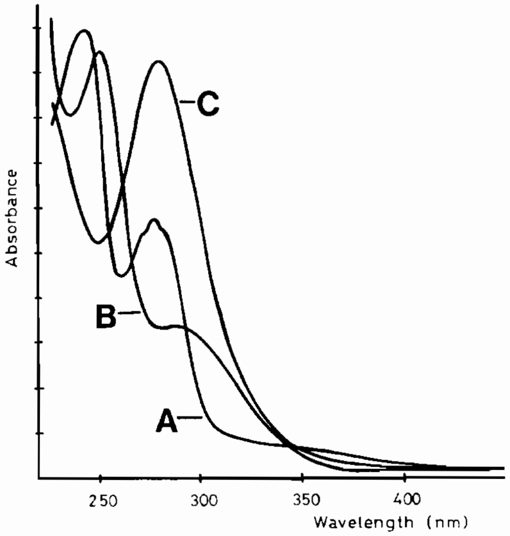

Fig. 2. Electronic spectra (450–225 nm) for selected Co(I) complexes in $CH_2Cl_2$: A, $[Co(CNCHMe_2)_3\{P(C_6H_4Cl\text{-}p)_3\}_2]ClO_4$; B, $[Co(CNCHMe_2)_3\{P(CH_2Ph)_3\}_2]ClO_4$; C, $[Co(CNCHMe_2)_3\{P(NMe_2)_3\}_2]ClO_4$.

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