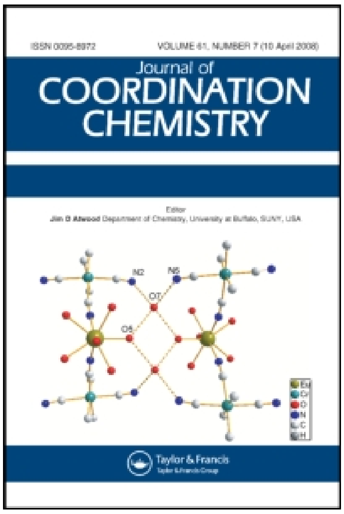

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Clifford A. L. Becker[a]
[a] Department of Chemistry, University of Bahrain, Bahrain, Arabian Gulf

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# SYNTHESIS OF MONOSUBSTITUTED *PENTAKIS*(2,6-DIETHYLPHENYLISOCYANIDE)COBALT(I) COMPLEXES WITH BIDENTATE TERTIARY PHOSPHINE LIGANDS. II. BIMETALLIC COMPLEXES

CLIFFORD A.L. BECKER

*Department of Chemistry, University of Bahrain, P.O. Box 32038, Isa Town, Bahrain — Arabian Gulf*

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Reaction of bidentate tertiary phosphines with excess $[Co(CNR)_5]BF_4$, or reaction of $[Co(CNR)_4L\text{-}L]BF_4$ with excess $[Co(CNR)_5]BF_4$, leads to bimetallic complexes of the form, $[(RNC)_4CoL\text{-}LCo(CNR)_4](BF_4)_2$, R = 2,6-$Et_2C_6H_3$, L-L = *p*-$Ph_2PC_6H_4PPh_2$, $Ph_2PC{\equiv}CPPh_2$, $Me_2PCH_2CH_2PMe_2$, $Ph_2PCH_2CH_2PPh_2$, $Ph_2PCH_2CH_2CH_2PPh_2$. Comparison of the $\nu(-N{\equiv}C)$ IR patterns, electronic spectra, and molar conductivity values of these bimetallic complexes with data for other Co(I)-organoisocyanide complexes indicates that the two -$Co(CNR)_4$ moieties are almost totally independent of each other. Recorded $\lambda_{max}$ values are the same as for the $[Co(CNR)_4L\text{-}L]BF_4$ complexes, but the $\varepsilon$ values, although very large, are less than double. $\Lambda_M$ values in acetone, and probably also in $CH_2Cl_2$, are better interpreted as twice the normal conductivity for 1:1 electrolytes than conductivity for 2:1 electrolytes.

KEYWORDS: 2,6-diethylphenylisocyanide, arylisocyanide, tertiary phosphine, cobalt(I), bidentate ligands

## INTRODUCTION

Syntheses of monosubstituted Co(I) complexes with bidentate tertiary phosphine ligands, $[Co(CNC_6H_3Et_2\text{-}2,6)_4L\text{-}L]BF_4$, have recently been reported.[1] These syntheses raise the question as to whether it is the $[Co(CNR)_5]BF_4$ complexes, or the bidentate phosphines, that are unable to disubstitute. This work investigates the bimetallic complexes, $[(RNC)_4CoL\text{-}LCo(CNR)_4](BF_4)_2$, whose syntheses firmly establish that the bidentate phosphines can indeed bond through both P sites to $Co(CNR)_4$ moieties, but that the $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ complex does not disubstitute under these reaction conditions.

## EXPERIMENTAL

### *Reagents*

Commercial bidentate phosphines (Strem Chemicals) were used without further purification. $[Co(CNR)_5]BF_4$ and $[Co(CNR)_4L\text{-}L]BF_4$, R = 2,6-$Et_2C_6H_3$, L-L = bidentate phosphine, were prepared as previously reported.[1] Anhydrous diethyl ether was filtered through an alumina column immediately before use.

### *Instrumentation*

IR spectra were recorded on a Perkin Elmer 1710 FT-IR instrument. Solution electronic spectra were recorded on a Shimadzu UV-365 spectrophotometer. Molar conductivities were measured on ~0.001 M samples at 25°C using a Crison 525 conductimeter. C, H, N and P analyses were performed commercially.

### *$[(RNC)_4Co(p\text{-}Ph_2PC_6H_4PPh_2)Co(CNR)_4](BF_4)_2$*

A 700 mg sample of $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ was dissolved in 1.0 $cm^3$ of $CH_2Cl_2$, filtered through cotton, and added dropwise with stirring to a filtered solution of 112 mg of *p*-$Ph_2PC_6H_4PPh_2$ (*i.e.*, 3:1 Co:L-L mole ratio) dissolved in 1.7 $cm^3$ of $CH_2Cl_2$. After the addition was complete, the reaction mixture was allowed to remain at room temperature for 30 min. An odour of free RNC was evident. Ether was then added dropwise. Precipitation of fine, gold-coloured crystals commenced after 10.0 $cm^3$ of ether had been added. A total volume of 13.0 $cm^3$ of ether was added, and the solution chilled in ice for 30 min. before filtration. Addition of 5.0 $cm^3$ of ether to the filtrate and 1 h chilling in ice afforded a second crop of golden yellow microcrystals. Refrigeration of this filtrate afforded a third crop, and addition of excess ether and prolonged refrigeration produced a fourth crop. The first three crops (300 mg) were combined and recrystallized from 2.0 $cm^3$ of $CH_2Cl_2$ and 5.5 $cm^3$ of ether. Yield: 265 mg (52%) of orange microcystals. The fourth crop (195 mg) was separately recrystallized from 1.0 $cm^3$ of $CH_2Cl_2$ and 16.0 $cm^3$ of ether. Yield: 145 mg of $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ (identified by its characteristic $\nu(-N{\equiv}C)$ IR).

### *$[(RNC)_4CoPh_2PCH_2CH_2PPh_2Co(CNR)_4](BF_4)_2$*

A 400 mg sample of $[Co(CNC_6H_3Et_2\text{-}2,6)_4Ph_2PCH_2CH_2PPh_2]BF_4$ was dissolved in 1.0 $cm^3$ of $CH_2Cl_2$, filtered through cotton, and added dropwise to a filtered solution of 480 mg of $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ (1:1.5 mole ratio, respectively) dissolved in 1.0 $cm^3$ of $CH_2Cl_2$. The reaction mixture was allowed to remain at room temperature for 60 min. Ether was then added dropwise. Extensive precipitation of a flocculent, bright yellow, microcrystalline product (215 mg) occured after addition of 10.0 $cm^3$ of ether. The product was filtered and washed twice with 1.5 $cm^3$ portions of ether. Addition of small volumes of ether to the filtrates and chilling in ice afforded three more crops (157 mg) of product; a fifth crop (154 mg) was contaminated with unreacted $[Co(CNR)_5]BF_4$ (identified by $\nu(-N{\equiv}C)$ IR) and hence discarded. Combined crude product (372 mg) was dissolved in 1.5 $cm^3$ of $CH_2Cl_2$, filtered through cotton, and precipitated by dropwise addition of 7.5 $cm^3$ of ether. Yield: 315 mg (85% recovery; 47% overall yield).

## RESULTS AND DISCUSSION

The monosubstituted, bimetallic Co(I) complexes formed in reactions between $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ and selected bidentate phosphine ligands are summarized in Table 1 with major physical properties.

### *Synthesis of the complexes*

Bimetallic complexes, in which the bidentate phosphine ligand bridges two $Co(CNR)_4^+$ moieties, can be synthesized by reaction of the bidentate phosphine with excess $[Co(CNR)_5]BF_4$ (Method A; synthesis of $[(RNC)_4Co(p\text{-}Ph_2PC_6H_4PPh_2)Co(CNR)_4](BF_4)_2$), or by reaction of the appropriate $[Co(CNR)_4L\text{-}L]BF_4$ complex with excess $[Co(CNR)_5]BF_4$ (Method B; synthesis of $[(RNC)_4CoPh_2PCH_2CH_2PPh_2Co(CNR)_4](BF_4)_2$). Method A appears to be preferable and was used for most of the complexes. The atmosphere-sensitive $Me_2PCH_2CH_2PMe_2$ ligand was handled by vacuum line, but the $[(RNC)_4CoMe_2PCH_2CH_2PMe_2Co(CNR)_4](BF_4)_2$ complex is stable to the atmosphere. The bimetallic complex with $Ph_2PC{\equiv}CPPh_2$ was synthesized using a procedure usually producing monometallic complexes; a monometallic complex with $Ph_2PC{\equiv}CPPh_2$ could not be obtained.[1] Attempted reaction of $Ph_2PPPh_2$, $(n\text{-}C_4H_9)_2PCH_2CH_2P(C_4H_9\text{-}n)_2$, $(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2$, and $(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2$ (Method A) showed no substitution; only unreacted $[Co(CNR)_5]BF_4$ was recovered. Reaction with $Ph_2PCH_2PPh_2$ (Method A) was very incomplete; only $[Co(CNR)_5]BF_4$ was recovered in the first crop, but some product, probably the monometallic complex, was observed with $[Co(CNR)_5]BF_4$ in the second crop.

Failure of $(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(C_6H_4CF_3\text{-}p)_2$ to react is probably due to the electron-withdrawing effect of the $\text{-}CF_3$ substituent. $P(C_6H_4Cl\text{-}p)_3$ is noticeably less reactive than $PPh_3$ in $[Co(CNR)_5]X$ substitution reactions, forming monosubstituted complexes with all arylisocyanides investigated;[2,3] $P(C_6H_4CF_3\text{-}p)_3$ fails to substitute in $[Co(CNC_6H_3Et_2\text{-}2,6)_5]ClO_4$ at all.[4] Since $P(C_4H_9\text{-}n)_3$ and $P(C_6H_4Me\text{-}p)_3$ both monosubstitute in $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$,[4] failure of $(n\text{-}C_4H_9)_2PCH_2CH_2P(C_4H_9\text{-}n)_2$ and $(p\text{-}MeC_6H_4)_2PCH_2CH_2P(C_6H_4Me\text{-}p)_2$ to react should not be due to electronic effects, but may be due to increased steric hindrance relative to $Ph_2PCH_2CH_2PPh_2$. Retarded reaction of $Ph_2PCH_2PPh_2$ is interesting. Since $[Co(CNR)_4Ph_2PCH_2PPh_2]BF_4$ was prepared in a standard procedure,[1] there should be no difficulty for $Ph_2PCH_2PPh_2$ to substitute in one $[Co(CNR)_5]BF_4$. Possibly the $\text{-}CH_2\text{-}$ linkage between phosphine sites is too short to allow bimetallic complexes. An $(RNC)_4CoPh_2PCH_2\text{-}$ group on the second P should cause considerable steric hindrance.

Syntheses of these bimetallic complexes clearly reaffirm the irresistible tendency of $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ to only monosubstitute.[1] The ability of the L-L ligands to function as bidentates has also been re-established, *albeit* as bridging rather than chelating ligands with the $\text{-}Co(CNC_6H_3Et_2\text{-}2,6)_4$ moiety.

### *Characterization of the complexes*

The $\nu(-N{\equiv}C)$ IR patterns for these five bimetallic complexes show variation ranging from the familiar "fingerprint" pattern for monosubstituted-$[Co(CNR)_5]^+$

**Table 1** Physical properties of the $[(2,6\text{-}Et_2C_6H_3NC)_4CoL\text{-}LCo(CNC_6H_3Et_2\text{-}2,6)_4](BF_4)_2$ complexes

| L-L/M. pt. | $\nu(-N{\equiv}C)$ Infrared[a] | | Electronic spectra[b] | | Molar | Elemental analysis (%) Found/calcd. | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Nujol | $CH_2Cl_2$ | $CH_2Cl_2$ | $CH_3CN$ | conductivity[c] | C | H | N | P |
| $Ph_2PC_6H_4PPh_2$-*p* | 1995 w | ~1996 vw(sh) | 323 (35,600) | 324 (33,400) | 278 | 70.48 | 6.53 | 5.56 | 3.24 |
| 234–238°C (dec) | 2080 vs | 2077 vs | 260 (90,900) | 256 (89,400) | 268 | (70.45) | (6.41) | (5.57) | (3.08) |
| | 2110 w | ~2114 vw(sh) | | ~239sh (88,800) | 181 | | | | |
| | ~2125 vw(sh) | 2162 m | | | 183 | | | | |
| | 2160 m | | | | 81 | | | | |
| $Ph_2PC{\equiv}CPPh_2$ | 1997 vw | ~1996 vw(sh) | 326 (36,500) | 327 (32,100) | 270 | 70.33 | 6.41 | 5.36 | 3.06 |
| 145–153°C (dec) | 2094 vs | ~2068 vw(sh) | 257 (105,000) | 255 (93,100) | 263 | (69.87) | (6.38) | (5.72) | (3.16) |
| | ~2111 vw(sh) | 2087 vs | | ~239sh (92,300) | 184 | | | | |
| | 2131 w | ~2112 vw(sh) | | | 168 | | | | |
| | 2162 w | 2157 m | | | 88 | | | | |
| $Me_2PCH_2CH_2PMe_2$ | 1996 w | ~1995 w(sh) | 320 (32,200) | 323 (28,800) | 300 | 65.79 | 7.04 | 6.33 | 3.48 |
| 147–155°c (dec) | 2072 vs | 2054 vs(br) | 264 (102,000) | 263 (102,000) | 278 | (65.82) | (7.05) | (6.53) | (3.61) |
| | 2105 w | 2102 w | | ~242sh (83,600) | 189 | | | | |
| | 2159 m | 2151 m | | | 185 | | | | |
| | | | | | 75 | | | | |
| $Ph_2PCH_2CH_2PPh_2$ | 1995 w | ~1994 vw(sh) | 326 (29,700) | 327 (27,200) | 282 | 69.62 | 6.63 | 5.78 | 3.35 |
| 153–162°C (dec) | 2081 vs | 2059 vs | 263 (94,300) | 263 (94,400) | 275 | (69.73) | (6.57) | (5.71) | (3.15) |
| | 2110 w | 2076 w | | ~240sh (79,500) | 195 | | | | |
| | ~2122 vw(sh) | 2105 w | | | 190 | | | | |
| | 2160 m | 2158 m | | | 79 | | | | |
| $Ph_2PCH_2CH_2CH_2PPh_2$ | 1997 w | ~1996 vw(sh) | 327 (31,100) | 325 (28,500) | 281 | 70.15 | 6.84 | 5.81 | 3.10 |
| 141–151°C (dec) | 2078 vs | 2067 vs | 262 (93,500) | 261 (89,600) | 276 | (69.84) | (6.63) | (5.67) | (3.13) |
| | 2106 w | 2104 w | | ~240sh (78,900) | 183 | | | | |
| | 2143 w | 2147 m | | | 175 | | | | |
| | 2159 w | 2155 m | | | 91 | | | | |

[a] The $\nu(-N{\equiv}C)$ in $cm^{-1}$; s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad. [b] The $\lambda_{max}(\varepsilon)$ in nm ($Mcm^{-1}$) without Gaussian resolution. [c] Molar conductivity; first value in $CH_3CN$, second value in acetone, third value in $CH_3OH$, fourth value in $CH_3NO_2$, fifth value in $CH_2Cl_2$; $\Omega^{-1}cm^2mol^{-1}$.

complexes[1,2,5-7] to several modifications showing an apparent doubling of at least one of the bands (see Figure 1). Spectra in Nujol and $CH_2Cl_2$ are approximately the same. Two totally isolated but equivalent -$Co(CNR)_4$ moieties could be expected to behave independently of each other, and thus give rise to a single $\nu(-N \equiv C)$ pattern similar to that for $[Co(CNR)_4PR_3]^+$. Only the completely saturated L–L ligand, $Me_2PCH_2CH_2PMe_2$, has a bimetallic complex showing the simple $\nu(-N \equiv C)$ pattern; all other complexes show some degree of "doubling" in the $\nu(-N \equiv C)$ pattern. Complexes with ligands that could be the most conjugated, $Ph_2PC \equiv CPPh_2$ and $Ph_2C_6H_4PPh_2$-*p*, however, show less deviation from the simple $\nu(-N \equiv C)$ pattern, especially for spectra in Nujol mull, than complexes

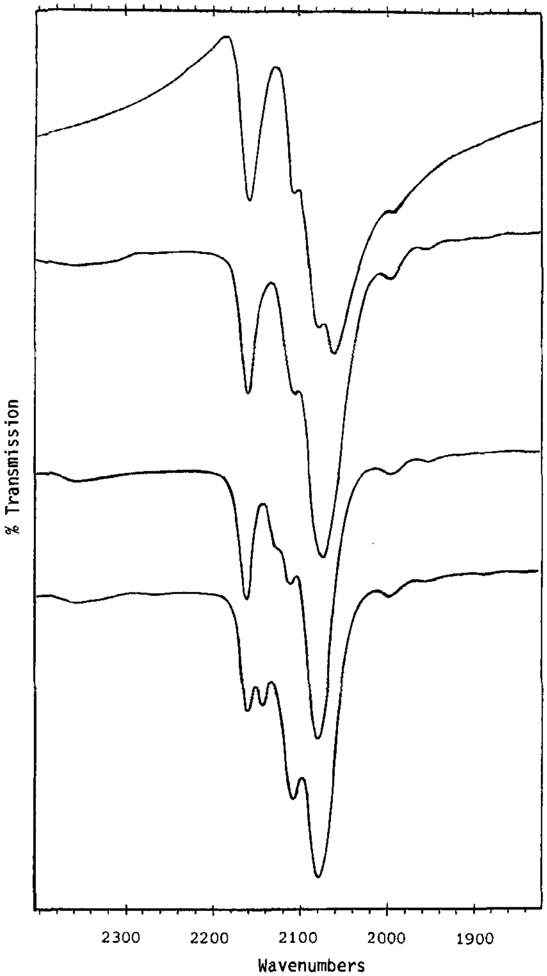

**Figure 1** Representative $\nu(-N{\equiv}C)$ IR patterns for the $[(RNC)_4CoL\text{-}LCo(CNR)_4](BF_4)_2$ complexes, R = 2,6-$Et_2C_6H_3$; in the order top to bottom: L-L = $Ph_2PCH_2CH_2PPh_2$ (in Nujol), L-L = $Me_2PCH_2CH_2PMe_2$ (in $CH_2Cl_2$), L-L = $Ph_2PC_6H_4PPh_2$-*p* (in $CH_2Cl_2$), L-L = $Ph_2PCH_2CH_2CH_2PPh_2$ (in $CH_2Cl_2$).

with $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2CH_2CH_2PPh_2$. In solution, $[(RNC)_4CoPh_2PCH_2CH_2CH_2PPh_2Co(CNR_4)](BF_4)_2$ shows the most pronounced deviation, with doubling of the highest energy band (see Figure 1). Further investigation is necessary to fully interpret these $\nu(-N{\equiv}C)$ IR patterns.

Solution electronic spectra for the $[(RNC)_4CoL\text{-}LCo(CNR)_4](BF_4)_2$ complexes (see Table 1) show an interesting relationship with spectra for $[Co(CNR)_4L\text{-}L]BF_4$ complexes.[1] Where comparison is possible, $\lambda_{max}$ values are approximately the same for corresponding monometallic and bimetallic complexes, but the $\varepsilon$ values for the bimetallic complexes, although very large in some instances, are in general less than double the $\varepsilon$ values for the corresponding monometallic complexes. If there were no interaction of any kind between the two $\text{-}Co(CNR)_4$ moieties, the $\varepsilon$ values for the bimetallic complexes should be expected to be double the $\varepsilon$ values for the corresponding monometallic complexes.

Molar conductivity values ($\Lambda_M$) for the bimetallic complexes (see Table 1) allow an interesting interpretation. The $\Lambda_M$ values in $CH_3CN$ (270–300 $\Omega^{-1}cm^2mol^{-1}$) and $CH_3OH$ (180–195) are within the upper range expected for 2:1 electrolytes, and values in $CH_3NO_2$ (170–190) are borderline high.[8] The $\Lambda_M$ values in acetone (265–280 $\Omega^{-1}cm^2mol^{-1}$) and $CH_2Cl_2$ (75–90), however, are unreasonably high for 2:1 electrolytes.[8] Other $\Lambda_M$ values for Co(II)-organoisocyanide complexes previously measured in acetone are reasonable for 2:1 electrolytes (160–200 $\Omega^{-1}cm^2mol^{-1}$);[8] *e.g.*, $[Co(CNCHMe_2)_5](ClO_4)_2$ (180),[9] $[Co(CNCHMe_2)_5](BF_4)_2$ (165),[9] $[Co(CNCH_2Ph)_5](BF_4)_2$ (170),[10] $[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO)_4)_2$ (180),[11] $[Co(CNR)_4(AsR_3)_2]X_2$, $X = ClO_4$, $BF_4$; $AsR_3 = AsPh_3$, $As(C_6H_4Me\text{-}p)_3$ (180–220);[12] values reported in this paper are thus exceptional. The $\Lambda_M$ values for 1:1 Co(I)-organoisocyanide complexes in $CH_2Cl_2$ have been observed in the range 45–70 $\Omega^{-1}cm^2mol^{-1}$,[1,4,13] but $\Lambda_M$ values for Co(II)-organoisocyanide complexes that are expected to be 2:1 electrolytes have always shown significant ion-pairing; *e.g.*, 17–34 $\Omega^{-1}cm^2mol^{-1}$, for $[Co(CNR)_4(AsR_3)_2]X_2$;[12] 14, for $[Co(CNCH_2Ph)_5](BF_4)_2$;[10] 12, for $[Co(CNCHMe_2)_5](ClO_4)_2$;[4] 32, for $[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$.[11] The $\Lambda_M$ values in $CH_2Cl_2$ for these bimetallic complexes, 75–90 $\Omega^{-1}cm^2mol^{-1}$, clearly indicate a different behaviour in solution.

Molar conductivity values for the $[(RNC)_4CoL\text{-}LCo(CNR)_4](BF_4)_2$ complexes appear to be better interpreted as twice the normal conductivity for 1:1 electrolytes, than conductivity for 2:1 electrolytes. Doubling the expected ranges of $\Lambda_M$ for 1:1 electrolytes in $CH_3CN$, $CH_3NO_2$, and $CH_3OH$ gives approximately the expected ranges for 2:1 electrolytes, so no difference in $\Lambda_M$ values can be observed if these cations were behaving as single dipositive ions or as two monopositive ions. For acetone, however, the doubled 1:1 electrolyte range (200–280 $\Omega^{-1}cm^2mol^{-1}$)[8] is significantly higher than the expected 2:1 range (160–200)[8] and reflects the values observed for these bimetallic complexes (265–280). Thus it appears that these complexes behave more like two 1:1 electrolytes than a single 2:1 electrolyte. Since recognized $\Lambda_M$ ranges are not well-established for $CH_2Cl_2$, a similar conclusion cannot be reached for conductivity behaviour in $CH_2Cl_2$, although $\Lambda_M$ values certainly appear much higher than would be expected for normal 2:1 electrolyte behaviour. With the $\nu(-N{\equiv}C)$ IR patterns and $\varepsilon$ values, the $\Lambda_M$ values for these bimetallic complexes suggest that the two $-Co(CNR)_4$ moieties are almost totally independent of each other.

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