

Substitution and Redox Properties of Some Organoisocyanide Cobalt(II) Complexes

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<http://dx.doi.org/10.5772/intechopen.71448>

Abstract

The reactions of four *tetrakis*(arylisocyanide)cobalt(II) complexes, $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ $\{\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**A**), $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (**B**), $2,6\text{-Et}_2\text{C}_6\text{H}_3$ (**C**), and $2,6\text{-iPr}_2\text{C}_6\text{H}_3$ (**D**)\}, with two pyridines, 4-CNpy and 4-Mepy, have been kinetically studied in trifluoroethanol medium. Each of the reactions, which was monitored over a temperature range of 293 to 318 K, exhibited two distinct processes proposed to be an initial fast substitution process followed by a slow reduction process. For each pyridine, steric hindrance was observed to play a significant role in the rates of the reactions, which decrease with increasing size of the aryloisocyanide ligand in the order $k(\text{A}) > k(\text{B}) > k(\text{C}) > k(\text{D})$. Addition of each of three triarylphosphines, PR_3 ($\text{R} = \text{Ph}$, $\text{C}_6\text{H}_4\text{Me-p}$, $\text{C}_6\text{H}_4\text{OMe-p}$), to solutions of *pentakis*(*t*-octylisocyanide)cobalt(II), $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{-t})_5](\text{ClO}_4)_2$, resulted in a shift in the λ_{max} of the electronic spectrum accompanied by a change in color of the solutions. The shift is attributed to ligand substitution. The reactions of the cobalt(II) complex $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{-t})_5]^{2+}$ with the triarylphosphines are proposed to proceed via a combination of substitution, reduction, and disproportionation mechanisms with final formation of disubstituted Co (I) complexes. The order of reactivity of the complex with the triarylphosphines was found to be $\text{P}(\text{C}_6\text{H}_4\text{OMe-p})_3 > \text{P}(\text{C}_6\text{H}_4\text{Me-p})_3 > \text{PPh}_3$. This order is explained in terms of the electron donating/ π -acceptor properties of the phosphines.

Keywords: substitution, redox, organoisocyanide, cobalt(II), kinetics, mechanisms

1. Introduction

Although isocyanides ($\text{C}\equiv\text{N-R}$) are versatile ligands in organometallic chemistry, their roles and applications in chemical systems have always been overshadowed by those of the CO

ligand [1, 2]. Isocyanides show stronger σ -donor and weaker π -acceptor character which can be tuned by the substituent R and the complex fragment to which they are coordinated. The metal fragment has a substantial influence on the reactivity and stability of coordinated isocyanide ligands. Isocyanides form metal-ligand π -bonds by the back donation of electrons from the filled $d\pi$ orbitals of the metal center to the empty π^* orbitals of the isocyanide ligand. Phosphine ligands on their part are phosphorus based, and they exhibit synergic interactions when they bond to metal centers. Phosphines (PR_3) utilize the d -orbitals to accept π -electron density. A number of techniques including infrared, ^{13}C and ^{31}P NMR, molecular mechanics, and reaction chemistry have been used to assess the binding capabilities of phosphorus ligands [3]. The predominant bonding ability of trialkyl phosphines is certainly from their very strong electron donating property, while π^* -acceptance appears to be more significant for triaryl phosphines such as PPh_3 . The synthesis and characterization of many cobalt (I), (II), and (III) complexes containing alkyl-, phenyl-, or aryl-isocyanide ligands have been reported [4–10].

Early studies on alkylisocyanide and arylisocyanide cobalt(II) complexes dating back to the sixties showed that while some of these complexes were reported as cobalt(II) dimers, a number of monomeric pentacoordinate cobalt(II) complexes were also reported [6, 11]. Reactions of cobalt(II)alkylisocyanide complexes with triarylphosphines have been studied and characterized as ligand substitution/reduction [10] with most reactions giving corresponding disubstituted five coordinate cobalt(I) complexes as final products, while the reactions of the cobalt(II) complexes with triarylsines resulted in initial substitution, which at least in one case was accompanied by oxidation of the ligand to triarylsine oxide and that of the cobalt (II) to cobalt(III) [12]. Spectra studies on these complexes suggested that some of them produce tetragonal structures in the solid state, while solution decomposition leads to tetrahedral geometry.

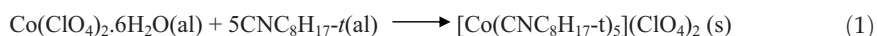
The five-coordinate alkylisocyanide complexes were known to generally react with tertiary phosphines to produce reduction/ligand substitution products of the type $[Co(CNR)_3(PR'_3)_2]X$, $X = ClO_4$ or BF_4 [13–15], exceptions being reactions with tri-*n*-alkylphosphines, which led to disproportionation/ligand substitution products of the types $[Co(CNR)_3(PR'_3)_2]X$ and $[Co(CNR)_3(PR'_3)_2]X_3$, $X = ClO_4$, BF_4 [13–15]. On the other hand, the five-coordinate arylisocyanide cobalt(II) complexes can react with tertiary phosphines to give monosubstituted cobalt(I) products of the type $[Co(CNR)_4(PR'_3)]X$ or di-substituted cobalt(I) products of the type $[Co(CNR)_3(PR'_3)_2]X$ depending principally on the level of steric hindrance in the arylisocyanide ligand [7, 16–20].

Conversely, triarylsine ligands react with five-coordinate alkylisocyanide cobalt(II) complexes to produce primarily ligand-substituted six-coordinate Co(II) complexes of the type $trans-[Co(CNR)_4(AsR'_3)_2]X_2$, $X = ClO_4$, BF_4 ; $PR'_3 = AsPh_3$, $As(C_6H_4Me-p)_3$ [21]; although the Co(III) complex, $[Co(CNCH_2Ph)_4\{OAs(C_4H_4Me-P)_3\}_2](BF_4)_3$, has also been observed [12].

Apart from the many pentakis(arylisocyanide)cobalt(II) complexes that have been prepared, the synthesis and characterization of a number of tetrakis(arylisocyanide)bis(perchlorato) cobalt(II) complexes have also been reported [4, 22–24]. Earlier studies showed that these pentakis and tetrakis cobalt(II) complexes react with amines to undergo reduction to their

corresponding cobalt(I) complexes of the general formula $[\text{Co}(\text{CNR})_5]\text{X}$. In some cases, when R was sufficiently bulky, e.g. $\text{R} = \text{CHMe}_2$, CMe_3 and $\text{C}_6\text{H}_3\text{iPr}_2$, six-coordinate disubstituted intermediates like $[\text{Co}(\text{CNR})_4(\text{py})_2](\text{ClO}_4)_2$ were isolated [25–27]. It has also been observed that arylisocyanide cobalt(II) complexes are reduced in the presence of free arylisocyanide ligands or coordinating anions [6].

Reactions of cobalt(II) perchlorate hexahydrate with *t*-octylisocyanide, $\text{CNCMe}_2\text{CH}_2\text{CMe}_3$, in absolute ethanol are said to be different from known reactions of the same cobalt(II) salt with other alkylisocyanides but rather similar to reactions with arylisocyanide in which the monomeric five-coordinate complex is formed [28] according to the equation



Unlike octahedral transition metal complexes, the formation, stability, and mechanistic behavior of five-coordinate square pyramidal or trigonal bipyramidal first row transition metal complexes have received significantly less attention. Such five-coordinate complexes can exhibit substantially different ligand substitution/redox behavior.

Some isocyno analogues of $[\text{Co}(\text{CO})_4]$ in the -1 , 0 , and $+1$ oxidation states were synthesized a few years back [29] using *m*-terphenyl isocyanide as the stabilizing ligand. The same ligand was later employed in the synthesis of the isocyno counterpart of $\text{HCo}(\text{CO})_4$ followed by a study of its decomposition and catalytic hydrogenation [30]. Figueroa and co-workers [31] most recently synthesized some isocyanide palladium(0) complexes as catalysts for the Suzuki-Miyaura cross-coupling of aryl bromides and arylboronic acids.

Despite the extensive information on the synthesis and characterization of these organo-isocyanide cobalt(II) complexes, little is known about kinetic studies on their substitution/reduction reactions. This chapter reports the kinetic studies on the substitution and redox reactions of two pyridines with some six-coordinate *tetrakis*(arylisocyanide)cobalt(II) complexes as well as those of five-coordinate *pentakis*(*t*-octylisocyanide)cobalt(II) complex with three triarylphosphines.

2. Experimental

2.1. Materials and syntheses of complexes

RNCHO , $\text{R} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$, $2,6\text{-iPr}_2\text{C}_6\text{H}_3$ and $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, were prepared from commercial RNH_2 (Aldrich) and formic acid as described by McKusick and Webster [32]. These formamides were then used in the syntheses of the organo-isocyanides. $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was obtained commercially from Strem Chemicals. Anhydrous diethyl ether was filtered through an alumina column before use and the *tetrakis*(arylisocyanide)cobalt(II) complexes, $[\text{Co}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_4(\text{ClO}_4)_2]$ (**A**), $[\text{Co}(\text{CNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_4(\text{ClO}_4)_2]$ (**B**), $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2\text{-}2,6)_4(\text{ClO}_4)_2]$ (**C**), and $[\text{Co}(\text{CNC}_6\text{H}_3\text{iPr}_2\text{-}2,6)_4(\text{ClO}_4)_2]$ (**D**) were prepared as reported in literature [4, 22, 24, 33]. Analar grade pyridines (Rochelle Chemicals) and trifluoroethanol (Fluka Chemicals) were used without further purification. *Pentakis*(*t*-octylisocyanide)cobalt(II)

perchlorate, $[\text{Co}(\text{CNC}_8\text{H}_{17-t})_5](\text{ClO}_4)_2$, was prepared as reported in the literature [28]. The yield was 96%. Characterization of the complexes was carried out using infrared and electronic spectra as well as elemental analyses. The results are in close agreement with those of earlier workers [4, 22, 24, 28, 33]. The ligands 1,1,3,3-tetramethylbutylisocyanide (*t*-octylisocyanide), $\text{CNC}_8\text{H}_{17-t}$, triphenylphosphine, PPh_3 , tris(4-methoxyphenyl)phosphine, $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$, tri(*p*-tolyl)phosphine, and $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$ were purchased from Aldrich Chemicals and used without further purification. Absolute ethanol was obtained from Rochelle, and Analar grade dichloromethane was obtained from Saar Chem Chemicals. All other reagents used were of Analar grade.

2.2. Instrumentation

IR spectra were recorded on a Perkin Elmer 2000 FTIR spectrophotometer over the range 4000 to 400 cm^{-1} . Samples of the tetrakis(arylisocyanide)cobalt(II) complexes were prepared and run as Nujol mulls on NaCl plates or solution spectra over the range 3000 to 1000 cm^{-1} . The solutions from the reactions of Pyridine with the complexes in $\text{CF}_3\text{CH}_2\text{OH}$ were used in their original state after the reaction was complete. Pyridine- $\text{CF}_3\text{CH}_2\text{OH}$ mixture was used for background subtraction. Solution electronic spectra were recorded on a Shimadzu UV-2501PC spectrophotometer equipped with a Peltier TC 240A temperature regulator attachment over the range 1100–200 nm. Carbon, Hydrogen, and Nitrogen elemental analyses were performed on a Vario EL CHNOS Elemental Analyzer. Kinetic measurements were obtained from the Shimadzu spectrophotometer for the relatively slow reactions and a Hi-tech scientific SF-61 DX2 single mixing stopped-flow spectrophotometer for the fast reactions.

2.3. Kinetics

Kinetic measurements were taken on the Shimadzu UV-Vis spectrophotometer mentioned earlier for the slow reactions as well as on the stopped-flow spectrophotometer for the fast reactions. The cell compartments for both instruments were well thermostatted for constant temperature measurements between the temperatures of 293 and 318 K. This was done using the TC-240A temperature controller with the UV-Vis spectrophotometer, while water was circulated from a Neslab RTE 7 thermocirculator to the cell compartment of the stopped-flow equipment. Prior to kinetic measurements, the stabilities of the *tetrakis* cobalt(II) complexes were investigated in various solvents and were all found to be most stable in trifluoroethanol ($\text{CF}_3\text{CH}_2\text{OH}$). Absorbance changes monitored at the electronic absorption peak of the cobalt (II) complexes were found to remain practically unchanged in trifluoroethanol. Variation in the concentration of the trifluoroethanol did not affect the absorption spectra and the kinetics. For the reactions involving the *pentakis*(*t*-octylisocyanide) cobalt(II) complex, dichloromethane (CH_2Cl_2) was chosen as the appropriate solvent for the reactions as both the cobalt(II) complex and the triarylphosphines used (i.e., PPh_3 , $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$, and $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$) completely dissolve in it. $[\text{Co}(\text{CNC}_8\text{H}_{17-t})_5](\text{ClO}_4)_2$ was also found to be stable in CH_2Cl_2 .

The kinetics were followed under pseudo-first-order conditions with the pyridines in concentrations which were 10 times or more greater than those of the *tetrakis* Co(II) complexes, and the triarylphosphines also had concentrations which were similarly 10 times or more greater

than that of the *pentakis* cobalt(II) complex. All kinetic studies were followed to more than 90% completion. The reactions of the *tetrakis* complexes with the pyridines show an initial fast increase in absorbance followed by a slow gradual absorbance decrease. Conversely, the reaction between the *pentakis t-octyl* complex showed complex kinetics, while those of the same *pentakis* complex with the other two phosphines showed single exponential decay curves. For the slow processes, the pseudo first-order rate constants (k_s) were obtained from linear regression plots of $\ln(A_t - A_\infty)$ against time, t ; where A_t and A_∞ are the absorbances at time t and $t = \infty$, respectively. Similar k_s values for the fast processes were obtained from the stopped-flow instrument kinetic software (KinetAsyst™ 3) by fitting the decay curves to single exponential analysis. These k_s values for the fast processes are averages of four to five runs for each pyridine concentration.

3. Conclusion

3.1. Kinetic studies

3.1.1. Reactions of the four *tetrakis*(arylisocyanide)cobalt(II) complexes **A**, **B**, **C**, and **D** with pyridines

All absorbance decay curves obtained while monitoring the reactions between the pyridines and the *tetrakis* cobalt(II) complexes show an initial fast increase in absorbance attributed to the substitution process, followed by a slow absorbance decrease representing the reduction process. **Figure 1** shows a typical decay curve for the reaction between $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2-2,6)_4(\text{ClO}_4)_2]$ and 4-cyanopyridine (4-CNpy).

It was also noticed that on addition of each pyridine, an immediate change from green to a nearly colorless solution (substitution) followed by slow development of a deep yellow solution (reduction), which persisted at the end of the reactions was observed. Repeated scans of the visible spectra on addition of each pyridine also showed a bathochromic shift of d-d

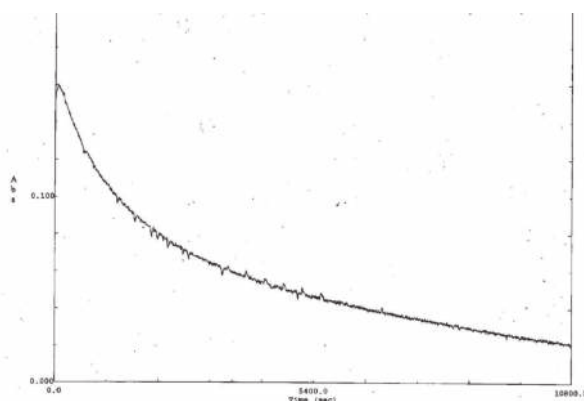


Figure 1. Typical absorbance decay curve for the reduction of $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2)_4(\text{ClO}_4)_2]$ complex by 4-CNpy at 298 K.

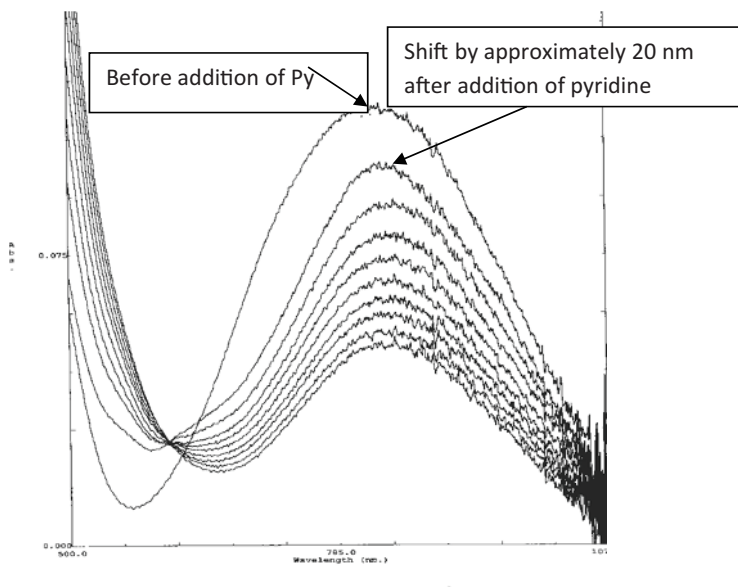


Figure 2. Spectral changes of a $[\text{Co}(\text{CNC}_6\text{H}_4\text{Et}_2\text{-}2,6)_4(\text{ClO}_4)_2]$ solution in trifluoroethanol on addition of pyridine at 298 K.

transition by about 20 to 35 nm (**Figure 2**). This shift can be attributed to the substitution of the solvent molecules from the Co(II) inner shell by the incoming pyridine ligand (Eq. 2).



Similar observations have been reported by Becker [8, 21] in his work on the synthesis of some organoisonocyanide cobalt(II) complexes as well as by other authors [34–37] in their investigations on reactions of cobalt(II) protoporphyrin complexes with amine ligands. The reduction of the *tetrakis*(arylisocyanide)cobalt(II) complexes by the pyridines was found to produce *pentakis*(arylisocyanide)cobalt(I) perchlorate salts as the final products. The isolation and characterization of some of these cobalt(I) complexes have been reported in earlier studies [38–40].

As explained earlier, the fast process was followed using stopped-flow techniques, while the slow process was followed using the conventional ultraviolet-visible spectrophotometry. Linear regression plots were used for the determination of the pseudo first-order rate constants. For convenience, we use k_{1s} for the fast substitution reactions and k_{2s} for the slow reduction processes. The reactions were monitored at different concentrations of the pyridines. For all the reactions, k_{1s} and k_{2s} increased with increasing concentration of pyridine. Plots of k_{1s} versus concentrations of pyridine were linear with intercepts. Using the data in **Tables 1–4**, such plots for the reactions of the four cobalt(II) complexes with 4-CNpy are shown in **Figure 3**.

For pyridine, the corresponding k_1 and k_2 values for the substitution process have been reported earlier [24] and are shown in **Table 4**:

$10^3[4\text{-CNpy}], \text{M}$	$k_{1sr} \text{ s}^{-1}$			
	A	B	C	D
3.30	21.9	18.9	16.4	12.2
4.63	23.8	21.0	18.2	12.9
6.61	27.1	23.2	19.7	15.7
7.60	28.7	24.6	21.3	16.3
9.25	30.9	27.0	23.1	17.6
12.14	38.6	32.9	27.5	20.4
15.18	40.2	34.3	29.8	24.5
19.80	48.1	40.7	35.1	28.1
k_1, s^{-1}	16.6	14.8	12.7	8.7
$k_2, \text{M}^{-1} \text{ s}^{-1}$	1610	1331	1143	992

Table 1. Pseudo-first-order rate constants, k_{1sr} , for the substitution reactions between the four $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes and 4-CNpy in $\text{CF}_3\text{CH}_2\text{OH}$ at 298 K.

$10^4[4\text{-Mepy}], \text{M}$	$k_{1sr} \text{ s}^{-1}$			
	A	B	C	D
3.30	29.9	27.3	23.6	20.8
4.63	34.2	30.8	26.5	23.3
6.61	39.1	34.2	29.5	26.0
7.60	43.1	36.1	31.6	27.9
9.25	47.6	39.8	34.2	30.1
12.14	55.1	45.0	39.3	34.2
15.18	66.0	52.6	43.6	37.5
19.80	78.9	61.5	52.0	44.9
19.80	2.59	1.33	0.35	0.162
k_1, s^{-1}	19.2	17.1	15.1	8.3
$k_2, \text{M}^{-1} \text{ s}^{-1}$	1720	1550	1430	1030
k_1, s^{-1}	21.0	20.6	18.4	16.6
$k_2, \text{M}^{-1} \text{ s}^{-1}$	29,751	20,652	16,909	14,213

Table 2. Pseudo-first-order rate constants, k_{1sr} , for the substitution reactions between the four $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes and 4-Mepy in $\text{CF}_3\text{CH}_2\text{OH}$ at 298 K.

$10^3[4\text{-CNpy}], \text{M}$	$10^5 k'_s, \text{s}^{-1}$			
	A	B	C	D
3.30	1.23	0.67	0.24	0.079
4.63	1.44	0.85	0.27	0.094
6.61	1.90	0.94	0.30	0.106
7.60	1.98	1.08	0.31	0.112
9.25	2.20	1.13	0.33	0.131
12.14	2.27	1.24	0.34	0.138
15.18	2.43	1.29	0.35	0.150
K, M^{-1}	164.2	195.3	260.9	209.2
k_3, s^{-1}	3.49	1.74	0.398	0.198

Table 3. Pseudo-first-order rate constants, k'_s , for the reduction of $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes by 4-CNpy in $\text{CF}_3\text{CH}_2\text{OH}$ at 318 K.

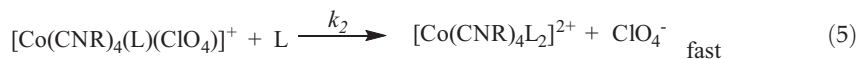
	A	B	C	D
k_1, s^{-1}	19.2	17.1	15.1	8.3
$k_2, \text{M}^{-1} \text{s}^{-1}$	1720	1550	1430	1030

Table 4. k_1 and k_2 values for the substitution reaction between pyridine and the four cobalt(II) complexes at 298 K.

The data fit well to the rate law described by the following equation:

$$\text{Rate} = \frac{-d[\text{Co}(\text{CNR})_4^{2+}]}{dt} = k_{1s}[\text{Co}(\text{CNR})_4^{2+}] \quad (3)$$

This is consistent with octahedral substitution involving a two-step ligand-ligand replacement, according to the following mechanism:



where k_{1s} in Eq. 3 above is given by.

$$k_{1s} = k_1 + k_2[\text{L}].$$

From plots of k_{1s} vs. $[\text{L}]$, values of k_1 and k_2 were obtained from the intercepts and slopes, respectively, and are listed in **Table 1** and **2**. The fact that k_2 is much greater than k_1 indicates attack by the solvent is a much slower process than attack by the nucleophile.

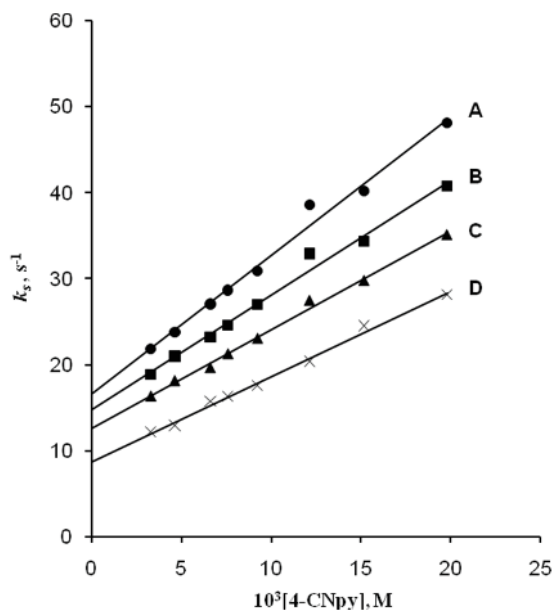
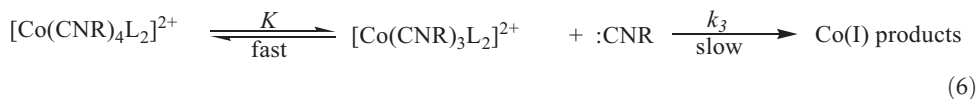


Figure 3. Plots of observed rate constants (k_s) versus 4-CNpy concentration for the reaction between $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes and 4-CNpy at 298 K.

In contrast, the slow reduction processes exhibited different kinetic behavior as compared to the substitution process. Plots of k_s' versus $[L]$ gave curves typical of saturation kinetics (**Figure 4**). Similar observations have been reported in our earlier studies [24] as well as in both the aminolysis of sulfamate esters in chloroform [41] and in the reactions of Co(II) protoporphyrins IX dimethyl ester with pyridine and related compounds [34, 37]. Such saturation kinetics is also typical of the formation of a precursor complex prior to electron transfer as observed in the electron transfer reactions of halopentacyanocobaltate(III) complexes [42]. The above observation fits well with the following mechanism:



giving the rate law:

$$\text{Rate} = k_s' [\text{Co}(\text{CNR})_4\text{L}_2]^{2+} \quad \text{where } k_s' = \frac{k_3 K [L]}{1 + K [L]} \quad (7)$$

Rearrangement of Eq. 5 gives

$$\frac{1}{k_s'} = \frac{1}{k_3 K [L]} + \frac{1}{k_3} \quad (8)$$

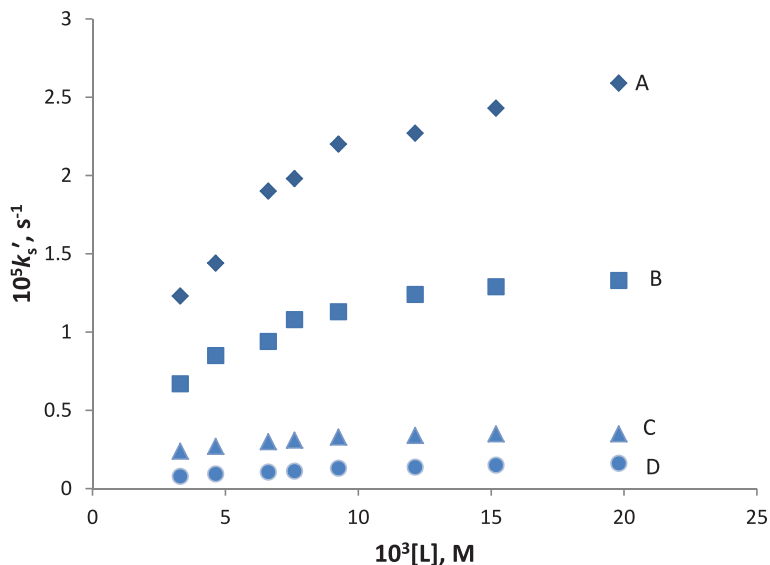


Figure 4. Plots of k_s' against concentration of 4-CNpy for the reduction of the four cobalt(II) complexes at 298 K.

Values of k_3 and K are reported in **Table 3**. It is observed from **Tables 1** and **3** that the rate constants k_2 and k_3 associated with the substitution by the amine ligand and the reduction of Co(II) to Co(I), respectively, decrease with increasing size of the arylisocyanide ligand, a clear evidence of steric hindrance.

For the reactions of the three pyridines under similar conditions, our results show that while 4-CNpy reacted at a slower rate than pyridine, 4-Mepy reacted at a faster rate. This observation can be explained in terms of the basicity of the amines. The CN group is an electron withdrawing substituent and therefore reduces the electron density of the pyridine ring, making 4-CNpy a weaker electron donor and hence less basic than pyridine. On the other hand, the methyl substituent on pyridine increases the electron density of the ring such that 4-Mepy is a better electron donor and a more basic amine than pyridine. Since ligands usually coordinate to metal centers by acting as Lewis bases donating lone pairs of electrons to the empty metal d-orbitals, more basic amines will be better coordinating ligands and will form more stable complexes as compared to less basic amines. This can be used to explain the higher reactivity of 4-Mepy and lower reactivity of 4-CNpy when they are compared to pyridine.

3.1.2. Reaction of $[Co(CNC_8H_{17-t})_5](ClO_4)_2$ complex with triphenylphosphine in dichloromethane

Addition of PPh_3 to solutions of the *pentakis* cobalt(II) complex in CH_2Cl_2 resulted in an immediate shift in the peaks, one from 724 nm to approximately 880 nm and another from 486 nm to approximately 450 nm with attendant decrease in absorbance at both new wavelengths as the reaction progressed. It should be noted that the solutions of the *pentakis* complex

employed in this study are those that have been standing for about 24 hours. The shift in peak on addition of PPh₃ with the attendant decrease in absorbance is attributed to ligand substitution followed by reduction, an observation similar to that reported in earlier studies [24, 43–45]. **Figure 5** shows the repeated UV/Vis spectra of the reaction mixture taken at intervals of time for 3 hours.

When the reaction of [Co(CNC₈H₁₇-t)₅]²⁺ with PPh₃ was monitored at a fixed wavelength on the UV-VIS spectrophotometer over a period of 1 to 3 hours, some complex kinetics were observed as shown in **Figure 6**. Different attempts made to analyze the data did not yield any meaningful result. Repeated infrared scans were then employed to probe further insight into the mechanism of the reactions.

Stopped-flow kinetic trace for the substitution process between [Co(CNC₈H₁₇-t)₅](ClO₄)₂ and PPh₃ showed a perfect fit to a single exponential function (**Figure 7**), showing a first order dependence on the Co(II) complex.

The observed rate constants, *k_s*, were found to increase with concentration of PPh₃ and plots of *k_s* against [PPh₃] were linear with nonzero intercepts, with a first-order dependence on triphenylphosphine. This result is consistent with the following rate law:

$$\text{Rate} = -\frac{d[\text{Co}(\text{CNC}_8\text{H}_{17}-t)_5]^{2+}}{dt} = k_s[\text{Co}(\text{CNC}_8\text{H}_{17}-t)_5]^{2+} = (k_1 + k_2[\text{PR}_3])[\text{Co}(\text{CNC}_8\text{H}_{17}-t)_5]^{2+} \quad (9)$$

where $k_s = k_1 + k_2[\text{PR}_3]$

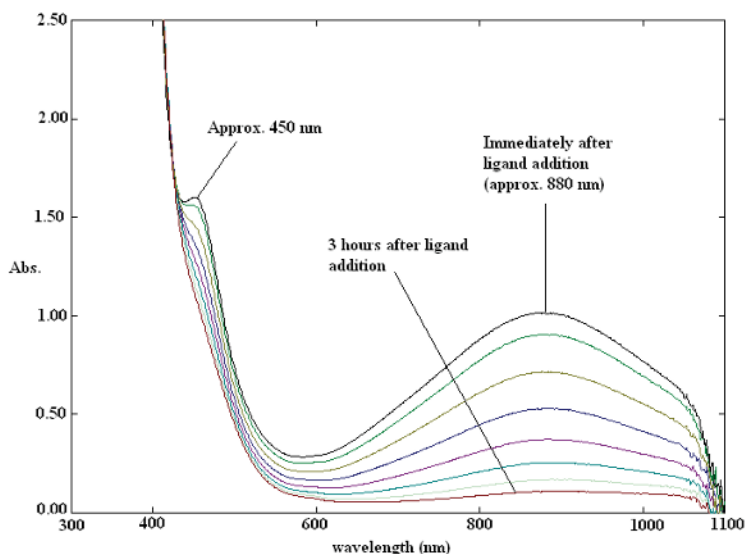


Figure 5. Typical repeated scans of the reaction of [Co(CNC₈H₁₇-t)₅]²⁺ with PPh₃ in CH₂Cl₂ at 298 K.

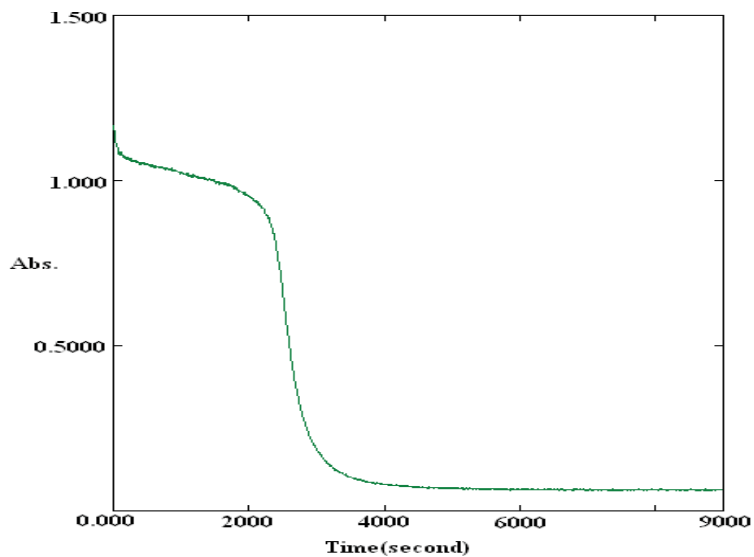


Figure 6. Typical absorbance decay curve for the reaction of $[\text{Co}(\text{CNCHMe}_2)_5]^{2+}$ with PPh_3 at 880 nm.

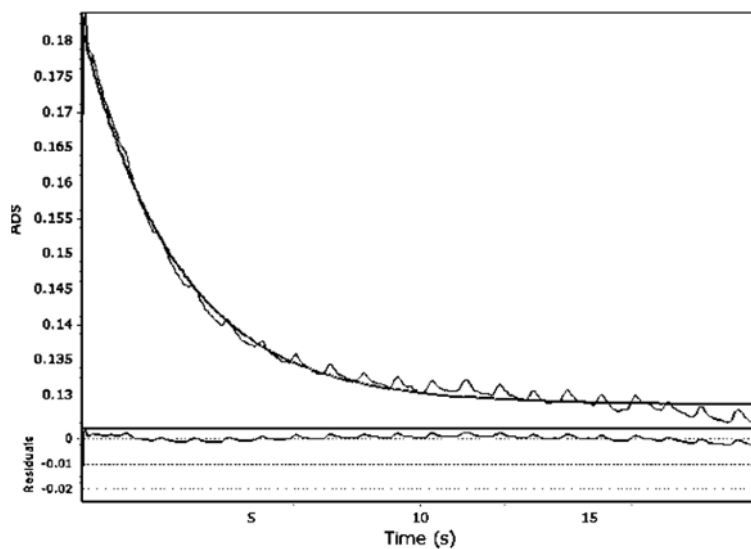
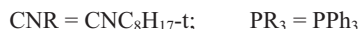


Figure 7. Typical kinetic trace for the reaction between $[\text{Co}(\text{CNC}_8\text{H}_{17-t})_5]^{2+}$ and PPh_3 fitted to a single exponential function.

This is similar to the rate law reported for the substitution reaction between freshly prepared solution of $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{t})_5]^{2+}$ and PPh_3 where it was suggested that the substitution process involved a solvent-assisted replacement of one isocyanide ligand with PPh_3 [46]. However, the stale solutions in this study substitutes at slower rates. For example, while the second order rate constant for the substitution of the isocyanide ligand by PPh_3 in the freshly prepared solution at 298 K was $943 \text{ M}^{-1} \text{ s}^{-1}$, the rate constant for the stale solution was $782 \text{ M}^{-1} \text{ s}^{-1}$. It is suggested that the stale solutions contain solvent molecules in their coordination shells as a cobalt(II) intermediate before undergoing substitution of one isocyanide ligand by PPh_3 .

Attempts to analyze the complex kinetic traces did not yield meaningful results, and therefore, infrared studies were employed in an effort to probe further insight into the mechanism of the reactions. The repeated infrared scan taken over a period of 3 hours for reactions of solutions of the Co(II) complex with PPh_3 show gradual disappearance of the Co(II) peak just as the Co(I) peak became more intense. Twelve hours after the reaction between the *t*-octyl Co(II) complex and PPh_3 started, the infrared spectra of the reaction mixture showed the isocyanide stretching frequencies largely associated with pentakis Co(I) isocyanide complexes as well as some peaks characteristic of mono- and di-substituted Co(II) and the starting Co(II) complex. This observation is an indication of a slow reaction between $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{t})_5]^{2+}$ and PPh_3 probably involving some multistep processes including pre-equilibria. This is similar to what was obtained with freshly prepared solutions of $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{t})_5]^{2+}$ and an indication of similar reaction mechanisms, which could include the following reaction pathways:



3.1.3. Reaction of $[\text{Co}(\text{CNC}_8\text{H}_{17}\text{t})_5]^{2+}$ complex with tri(*p*-tolyl)phosphine and tris(4-methoxyphenyl) phosphine

When $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$ and $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ were separately added to stale solutions of the cobalt(II) complex, shifts in absorption peaks to higher wavelengths from 724 nm to approximately 955 nm for $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$ and 724 nm to 904 nm for $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ were observed with attendant color changes. However, these reactions did not show complex kinetics exhibited by PPh_3 but show single experimental decays under similar experimental conditions. Although these reactions also involve different pre-equilibria and equilibria processes in addition to the reduction of Co(II) to Co(I), the substitution reactions must be occurring at a relatively fast process (too fast to be measured by the available instrumentation) that the single exponential decay observed can be attributed mainly to the reduction of the Co(II) complex to its Co(I) analog. As attempts to analyze the kinetic traces did not give reproducible results, the discussion of the reactions is mainly based on infrared studies.

Infrared spectra taken at different time intervals show that there was fast reduction of the Co(II) complex to Co(I) as strong peaks of the Co(I) complexes appear immediately after addition of these phosphines. Furthermore, the reactions of the two phosphines with stale solutions of the Co(II) complex also resulted in disproportionation reactions. This is evidenced by the observed infrared peaks due to the Co(III) and Co(I) analogues of the Co(II) complex with the di-substituted Co(III) complex, showing its characteristic isocyanide stretching frequency at 2234 cm^{-1} and its Co(I) analogue at 2063 cm^{-1} (**Figure 8**). Earlier studies had recorded similar observation in the reactions of some alkylisocyanide cobalt(II) complexes with tri-(p-tolyl)phosphine and 2-furylphosphine [47, 48].

Among the possible processes that take place in these reactions are:

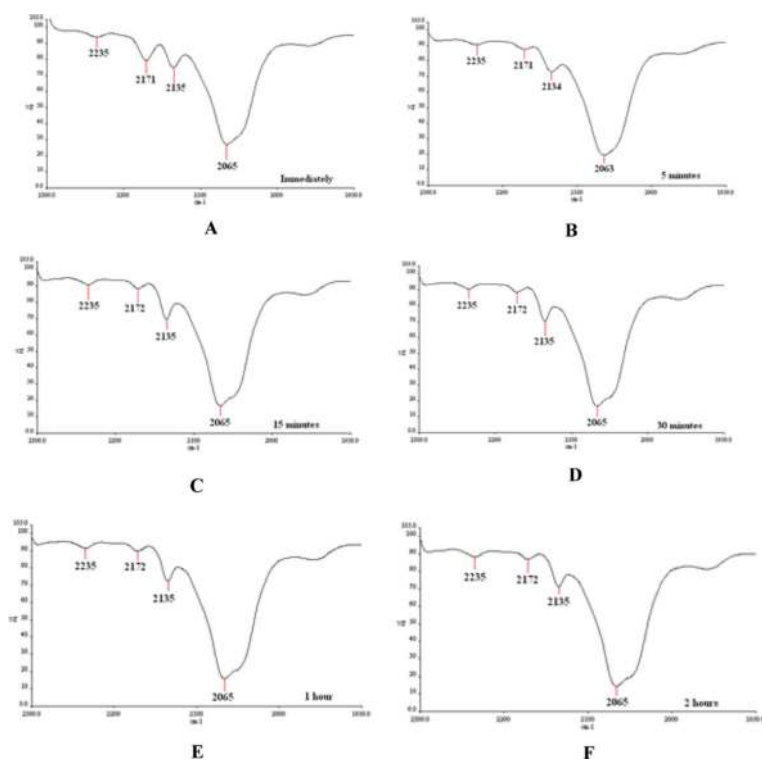
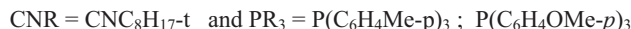
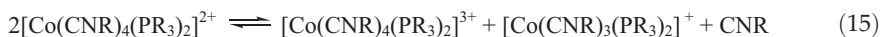


Figure 8. Isocyanide stretching frequencies for the reaction between stale $[\text{Co}(\text{CNC}_6\text{H}_{17-t})_5]$ and tris(4-methoxyphenyl) phosphine at different time intervals (A–F).



Acknowledgements

The authors are grateful to University of Botswana Research Committee for funding.

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