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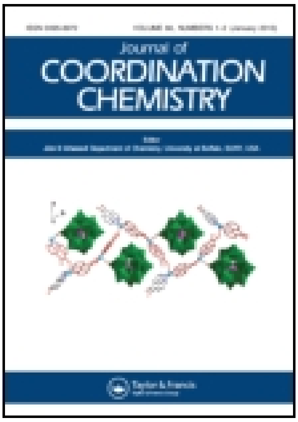

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Dynamics of the reactions of pentakis(t-octylisocyanide)cobalt(II) complex with triarylphosphines

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Dynamics of the reactions of *pentakis*(t-octylisocyanide)cobalt(II) complex with triarylphosphines

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The reactions of freshly prepared solutions of $[Co(CNC_8H_{17}\text{-t})_5](ClO_4)_2$ with three triarylphosphines, PR_3 ($R = Ph$, C_6H_4Me-p, C_6H_4OMe-p), were investigated in dichloromethane under pseudo-first-order conditions and with temperatures maintained at ±0.1 °C. Addition of each of the phosphines to the Co(II) complex solutions results in a shift in the λ_{max} of the electronic spectra accompanied by a change in color of the solution. The shift is attributed to ligand substitution. Analyses of the kinetic data suggest a general rate law given by:

$$\text{Rate} = -\frac{d[Co(CNC_8H_{17}\text{-t})_5]^{2+}}{dt} = ks[\{Co(CNC_8H_{17}\text{-t})_5\}^{2+}] = (k_1 + k_2[PR_3])[\{Co(CNC_8H_{17}\text{-t})_5\}^{2+}].$$

Overall, the reactions of the cobalt(II) complex $[Co(CNC_8H_{17}\text{-t})_5]^{2+}$ with the triarylphosphines are proposed to proceed via substitution/reduction mechanisms with final formation of disubstituted Co(I) complexes. The order of reactivity of the complex with the triarylphosphines was $P(C_6H_4OMe\text{-p})_3 > P(C_6H_4Me\text{-p})_3 > PPh_3$. This order is explained in terms of the electron donating/π-acceptor properties of the phosphines.

Keywords: Pentakis(t-octylisocyanide)cobalt(II) complex; Triarylphosphines; Rate constants; Infrared spectra; Kinetics

1. Introduction

Although isocyanides (C≡N-R) are versatile ligands in organometallic chemistry, their roles and applications in chemical systems have always been overshadowed by those of CO [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 back donation of electrons from the filled dπ orbitals of the metal center to the empty π^* orbitals of the isocyanide. Phosphine ligands exhibit synergic interactions when they bond to metal centers, utilizing 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

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*Corresponding author. Email: oyetunji@mopipi.ub.bw to assess the binding capabilities of phosphorus ligands [3]. The predominant bonding ability of trialkyl phosphines is from their very strong electron donation 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 arylisocyanide ligands have been reported [4–10]. Reactions of cobalt(II)-alkylisocyanide complexes with triarylphosphines have been studied and characterized as ligand substitution/reduction [10] with most reactions giving corresponding di-substituted five-coordinate cobalt(I) complexes as final products.

It has been postulated from earlier studies that free arylisocyanide (CNR) does the reduction from Co(II) to Co(I) and not the phosphine ligands [6, 7]. The six-coordinate $[Co(CNR)_4(PR_3)_2]^{2+}$ is believed to be an intermediate in the reduction/ligand substitution reactions of *pentakis*(organoisocyanide)cobalt(II) complexes with triarylphosphines.

Reactions of cobalt(II) perchlorate hexahydrate with t-octylisocyanide, $CNCMe_2CH_2CMe_3$, in absolute ethanol are said to be different from known reactions of the same cobalt (II) complex with other alkylisocyanides but similar to reactions with arylisocyanide in that the monomeric five-coordinate complex is formed [11] according to equation (1).

$$Co(ClO_4)_2 \cdot 6H_2O(al) + 5CNC_8H_{17}\text{-t}(al) \rightarrow [Co(CNC_8H_{17}\text{-t})_5](ClO_4)_2(s) \quad (1)$$

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 less attention. Such five-coordinate complexes can exhibit different ligand substitution/redox behavior. In this paper, substitution and redox reactions of *pentakis*(t-octyl isocyanide)cobalt(II)perchlorate with triarylphosphines were investigated and kinetic studies on the reactions of this complex were performed to provide insight into their reaction mechanisms.

2. Experimental

2.1. *Chemicals*

Cobalt(II) perchlorate hexahydrate, $Co(ClO_4)_2{\cdot}6H_2O$, 1,1,3,3-tetramethylbutylisocyanide (t-octylisocyanide), CNC_8H_{17}-t, triphenylphosphine, PPh_3, tris(4-methoxyphenyl)phosphine, $P(C_6H_4OMe\text{-p})_3$ and tri(p-tolyl)phosphine, $P(C_6H_4Me\text{-p})_3$ were purchased from Aldrich Chemicals and used without purification. Absolute ethanol was obtained from Rochelle and analar grade dichloromethane was obtained from Saarchem Chemicals. All other reagents used were of analar grade.

2.2. *Instrumentation*

Infrared (IR) spectra were recorded on a Perkin Elmer 2000 FT-IR spectrophotometer from 2300 to 1950 cm^{-1}. Solution electronic spectra were recorded on a Shimadzu UV2501PC Ultraviolet/Visible spectrophotometer equipped with a Peltier TC 240A temperature regulator attachment over the range 1100–190 nm. Dichloromethane was used for background subtraction. Kinetic studies, under pseudo-first-order conditions, were carried out using the Shimadzu UV2501PC spectrophotometer and a Hi Tech Scientific SF-61 DX2 single mixing stopped flow spectrophotometer.

2.3. *Synthesis of pentakis(t-octylisocyanide)cobalt(II) perchlorate, $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$*

$[Co(CNC_8H_{17}\text{-t})_5](ClO_4)_2$ was prepared as reported [11]. The yield was 96%. The purity of the complex was confirmed by infrared spectroscopy and ultraviolet spectrophotometry. The isocyanide stretching frequency values and the electronic spectra peaks for the complex were in excellent agreement with known values [11]. Freshly prepared complex was used for each kinetic study unless otherwise stated.

2.4. *Kinetic studies on the reactions of $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ with triarylphosphines in dichloromethane*

Dichloromethane (CH_2Cl_2) was chosen as the appropriate solvent for the reactions as both the cobalt(II) complex and triarylphosphines (i.e. PPh_3, $P(C_6H_4OMe\text{-p})_3$ and $P(C_6H_4Me\text{-p})_3$) completely dissolve in it. $[Co(CNC_8H_{17}\text{-t})_5]$ $(ClO_4)_2$ was stable in CH_2Cl_2.

For preliminary kinetic runs, stock solutions of $0.134\,mol\,dm^{-3}$ PR_3 and $1.34 \times 10^{-2}\,mol\,dm^{-3}$ Co(II) solutions in dichloromethane were prepared in 5 mL volumetric flasks. Dichloromethane was used for background subtraction. 1.5 mL of each stock solution ($6.67 \times 10^{-2}\,mol\,dm^{-3}$ PR_3 and $6.67 \times 10^{-3}\,mol\,dm^{-3}$ Co(II)) were mixed together in a 3.5 mL cuvette and repeated scans of the mixture were carried out on the UV–visible spectrophotometer over a period of about 3 h for each phosphine. This allowed the choice of fixed wavelengths for detailed kinetic investigations. Similar concentrations of the reactants were used for detailed kinetic studies at fixed wavelengths of 450 nm for PPh_3, 955 nm for $P(C_6H_4Me\text{-p})_3$ and 908 nm for $P(C_6H_4OMe\text{-p})_3$.

At fixed wavelength, the reaction between cobalt(II) complex and PPh_3 showed complex kinetics involving three different stages when monitored over a period of 1½ to 3 h. However, reactions with the other two phosphines showed single exponential decay curves. The first of the three-stage reaction profile for the reaction involving PPh_3 was followed using stopped-flow technique and the pseudo-first-order rate constants were obtained using the upgraded KineTyst™ software on the stopped-flow spectrophotometer computer. These rate constants were obtained at different concentrations of the phosphine and also at different temperatures. Each pseudo-first-order rate constant is an average of rate constants from at least 10 kinetic traces for each set of experimental conditions.

The second-order rate constants (k_2) obtained at different temperatures were subjected to Eyring plots [12] according to equation (2) below:

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(\frac{k}{h}\right) + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT} \tag{2}$$

From such plot, the activation enthalpy ($\Delta H^{\neq}$) and the activation entropy ($\Delta S^{\neq}$) were obtained from the slope and intercept of the plot [13].

For infrared studies, solutions of similar concentrations were used for stopped-flow experiments (for both the phosphines and the cobalt(II) complex), mixed together in the NaCl cell and the infrared spectra recorded at different time intervals on a Perkin Elmer 2000 FT-IR spectrometer. Dichloromethane was used for background subtraction.

3. Results and discussion

3.1. *Reaction of [Co(CNC$_8$H$_{17}$-t)$_5$](ClO$_4$)$_2$ with triphenylphosphine in dichloromethane*

Reactions of cobalt(II) perchlorate hexahydrate with t-octylisocyanide, $CNCMe_2CH_2CMe_3$, in absolute ethanol are dissimilar to reactions with other alkylisocyanides but rather similar to reactions with arylisocyanide in that the monomeric five-coordinate complex is formed [11].

$$\mathrm{Co(ClO_4)_2 \cdot 6H_2O(al) + 5CNC_8H_{17}\text{-}t(al) \rightarrow [Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2}(s) \qquad (3)$$

Electronic absorption peaks of 724 and 486 nm as well as the isocyanide infrared stretching frequencies of 2218 and 2193 cm^{-1} are in agreement with literature values [11]. Stability of $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ in dichloromethane was tested by repeated scans of the ultraviolet/visible (UV/vis) spectrum for 3 h and after 24 h of preparation time. There were practically no changes in λ_{max} and absorbance.

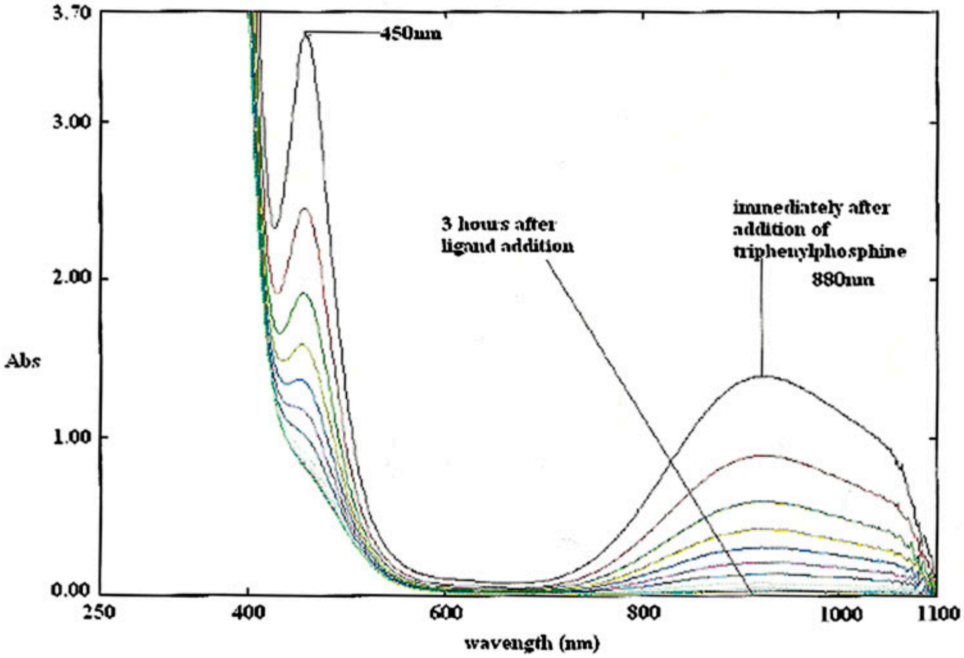

Figure 1. Typical repeated scans of the reaction of $[Co(CNC_8H_{17}\text{-}t)_5]^{2+}$ with PPh_3 in CH_2Cl_2 at 298 K.

When PPh_3 was added to solution of the t-octylisocyanidecobalt(II) complex in CH_2Cl_2, there was an immediate shift in the peaks, one from 724 to 880 nm and another from 486 to 450 nm with attendant decrease in absorbance at both new wavelengths as the reaction progressed. The initial violet/blue color of the Co(II) solution immediately changed to orange on addition of the phosphine; this orange color then changed to clear yellow as the reaction progressed. This shift is attributed to ligand substitution followed by reduction, an observation similar to that reported in earlier studies [14–17]. Figure 1 shows the repeated UV/vis spectra of the reaction mixture taken at intervals of time for 3 h.

Stopped-flow kinetic trace for the fast, substitution process between freshly prepared $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ and PPh_3 showed a perfect fit to a single exponential function (figure 2) showing a first-order dependence on the Co(II) complex.

The observed rate constants, k_s, were found to increase with concentration of PPh_3 (table 1) and plots of observed rate constant, k_s, against concentration of PPh_3 were linear with non-zero intercepts, with a first-order dependence on triphenylphosphine (figure 3). The rate law due to substitution by PPh_3 can thus be written as:

$$\text{Rate} = \frac{-d[\mathrm{Co(CNR)_5}]^{2+}}{dt} = k_s[\{\mathrm{Co(CNR)_5}\}^{2+}] = (k_1 + k_2[\mathrm{PPh_3}])[\{\mathrm{Co(CNC_8H_{17}\text{-}t)_5}\}^{2+}]$$

The second-order rate constants, k_2, were determined from slopes of plots of (k_s) against $[PPh_3]$. An investigation of the reactions at different temperatures showed increased rate constants with increase in temperature. The enthalpy and entropy of activation were then calculated from Eyring plots (table 1 and figure 4).

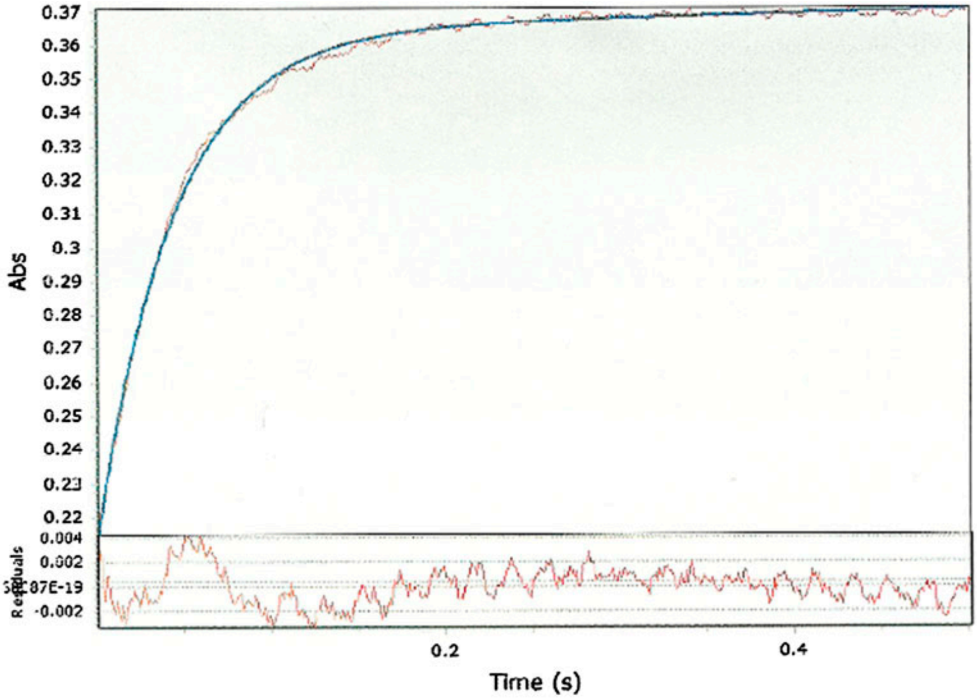

Figure 2. Typical kinetic trace for the reaction between $[Co(CNC_8H_{17}\text{-}t)_5]^{2+}$ and PPh_3 fitted to a single exponential function.

Table 1. Pseudo-first-order rate constants, k_s, for reaction between $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ and PPh_3 in CH_2Cl_2; $[Co(II)] = 1.12 \times 10^{-3}$ M.

	k_s, s^{-1}				
10^2 $[PPh_3]$, M	293 K	298 K	303 K	308 K	313 K
1.12	31.6	33.0	35.7	36.5	42.4
1.78	37.3	37.4	43.1	45.6	51.8
2.23	41.1	43.1	47.3	50.3	57.5
2.67	44.7	48.5	52.2	55.8	64.6
3.12	48.5	52.0	57.3	61.6	69.8
3.57	51.9	54.8	61.9	66.2	75.2
10^{-3} k_2, M^{-1} s^{-1}	0.829 ± 0.007	0.943 ± 0.008	1.06 ± 0.01	1.21 ± 0.01	1.35 ± 0.02
k_1, s^{-1}	22.5 ± 0.2	23.0 ± 0.2	23.8 ± 0.3	24.4 ± 0.4	25.3 ± 0.6

Notes: For the PPh_3 substitution process, $\Delta H^{\neq} = 16.1 \pm 0.3$ kJ mol^{-1}; $\Delta S^{\neq} = -133.9 \pm 0.9$ J mol^{-1} K^{-1}.

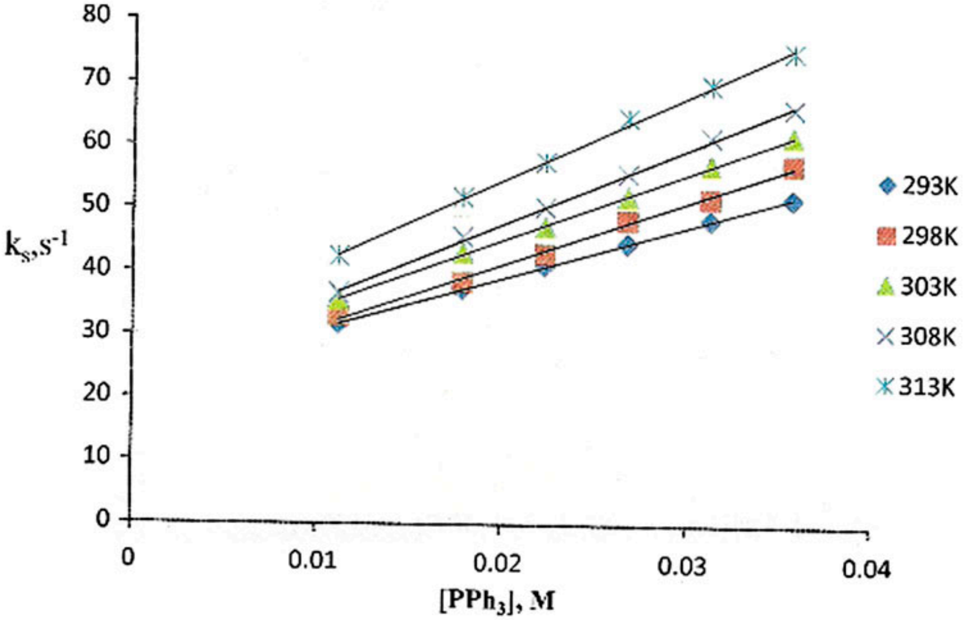

Figure 3. Plots of observed rate constants (k_s) against triphenylphosphine concentration for the reaction between $[Co(CNC_8H_{17}\text{-}t)_5]^{2+}$ and PPh_3; $[Co(II)] = 1.12 \times 10^{-3}$ M.

The rate constant k_1 can be ascribed to the solvent (medium) effect on reaction involving both uni- and bimolecular reaction paths, i.e. a solvent-assisted ligand exchange process. Such effect on kinetic patterns has been described earlier by Tobe and Burgess [18], where plots of k_{obs} against ligand concentration were linear with intercepts.

A suggested process in agreement with the observed kinetic data is one involving substitution of one isocyanide with a phosphine ligand,

$$[Co(CNR)_5]^{2+} + PPh_3 \rightarrow [Co(CNR)_4PPh_3]^{2+} + CNR \qquad (4)$$

A similar mono-substituted complex (though without kinetic data to support it) was suggested earlier as an intermediate in the reaction of $[Co(CNC_6H_{11})_5]^{2+}$ with PPh_3 where the final

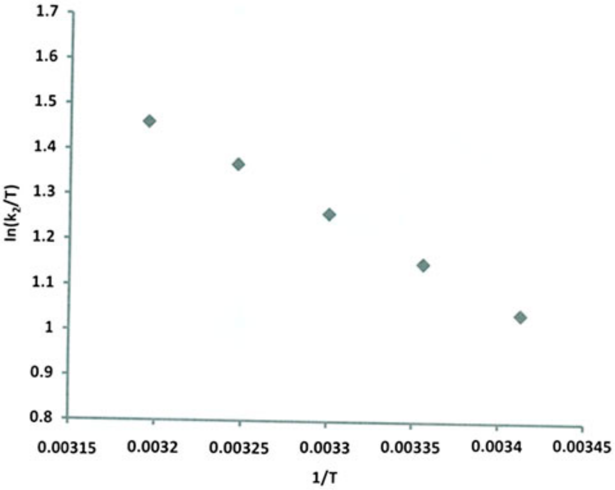

Figure 4. Eyring plot of $\ln(\frac{k_2}{T})$ against $\frac{1}{T}$ for reaction between $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ solution and PPh_3; $[\{Co(CNC_8H_{17}\text{-}t)_5\}^{2+}] = 1.12 \times 10^{-3}$ M.

stable product was also the di-substituted Co(I) analog of the starting complex [19]. The observation of these intercepts could also indicate a small dissociative pathway to the mainly associative substitution process as suggested earlier by Sweigart and others in their work on ligand substitution at five-coordinate centers of some cobalt-dithiolene complexes [20].

The relatively low enthalpy of activation is consistent with fast formation of an activated complex in the substitution process while the negative entropy of activation implies increased orderliness in the transition state, an observation that would support the formation of an associative activated complex which is not a true intermediate. This is similar to a proposition that has been suggested earlier in the reduction/ligand–substitution reactions of some *pentakis*(organoisocyanide)cobalt(II) complexes [10, 19]. An I_a mechanism can be suggested at this stage.

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 scans taken over a period of 3 h 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. Moreover, we have shown similar substitution process with tetrakis-isocyanide complexes [14] while Becker [10] had earlier synthesized related complexes with two coordinated phosphine ligands. This observation is an indication of a slow reaction between $[Co(CNC_8H_{17}\text{-}t)_5]^{2+}$ and PPh_3 probably involving some multistep processes including pre-equilibria. This could explain the observed behavior where attempts to synthesize triarylphosphine-t-octylisocyanide complexes were not successful [11]. The results show that reactions of PPh_3 with solutions of $[Co(CNC_8H_{17}\text{-}t)_5]^{2+}$ proceed via a mechanism which could include the following reaction pathways:

$$2[\mathrm{Co(CNR)_5}]^{2+} + 3\mathrm{PR_3} \leftrightharpoons [\mathrm{Co(CNR)_4(PR_3)}]^{2+} + [\mathrm{Co(CNR)_3(PR_3)_2}]^{2+} + 3\mathrm{CNR} \qquad (5a)$$

$$[\mathrm{Co(CNR)_4(PR_3)}]^{2+} + \mathrm{PR_3} \rightarrow [\mathrm{Co(CNR)_3(PR_3)_2}]^{2+} + \mathrm{CNR} \qquad (5b)$$

$$[\mathrm{Co(CNR)_3(PR_3)_2}]^{2+} + \mathrm{e} \rightarrow [\mathrm{Co(CNR)_3(PR_3)_2}]^{+} \qquad (5c)$$

$$\mathrm{CNR} = \mathrm{CNC_8H_{17}\text{-}t}; \quad \mathrm{PR_3} = \mathrm{PPh_3}$$

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

Separate additions of $\mathrm{P(C_6H_4Me\text{-}p)_3}$ and $\mathrm{P(C_6H_4OMe\text{-}p)_3}$ to solutions of the cobalt(II) complex also showed shifts in absorption peaks to higher wavelengths, from 724 nm to approximately 955 nm for $\mathrm{P(C_6H_4Me\text{-}p)_3}$ and 724–904 nm for $\mathrm{P(C_6H_4OMe\text{-}p)_3}$ with attendant color changes. However, these reactions did not show the complex kinetics exhibited by $\mathrm{PPh_3}$ under similar experimental conditions. Repeated studies show single exponential decays at fixed wavelengths. It was thus suspected that these two phosphines must be reacting at a faster rate than triphenylphosphine. Although these reactions also involve different pre-equilibria and equilibria in addition to the reduction of Co(II) to Co(I), the reactions must be occurring at a relatively fast rate such that the first substitution step became too fast to be observed with our instrumentation and that the single exponential decay observed can be attributed mainly to the reduction of the Co(II) complex to its Co(I) analog.

Figure 5 shows a typical kinetic trace of the reaction between the Co(II) complex and $\mathrm{P(C_6H_4OMe\text{-}p)_3}$. Concentration dependence studies were investigated at 298 K for the two phosphines and the results are shown in table 2. Plots of k_s against

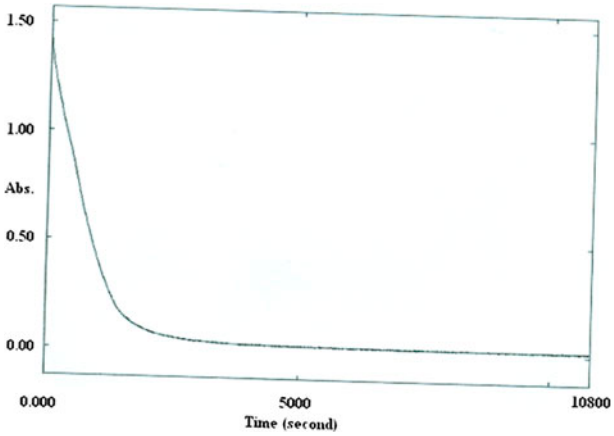

Figure 5. Typical absorbance decay curve for the reaction of $[\mathrm{Co(CNC_8H_{17}\text{-}t)_5}](\mathrm{ClO_4})_2$ with $\mathrm{P(C_6H_4OMe\text{-}p)_3}$ at 904 nm.

Table 2. Pseudo-first-order rate constants, k_s, for reaction between two phosphines ($P(C_6H_4Me\text{-}p)_3$ and $P(C_6H_4OMe\text{-}p)_3$) and $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ in CH_2Cl_2; $[Co(II)] = 1.12 \times 10^{-3}$ M.

	k_s, s^{-1}	
10^2 [PR_3], M	$P(C_6H_4Me\text{-}p)_3$	$P(C_6H_4OMe\text{-}p)_3$
1.12	0.821	0.982
1.78	1.02	1.24
2.23	1.11	1.44
2.67	1.25	1.62
3.12	1.34	1.75
3.57	1.48	1.92
10^2 k_2, M^{-1} s^{-1}	2.63 ± 0.07	3.8 ± 0.1
10^4 k_1, s^{-1}	5.3 ± 0.2	5.6 ± 0.3

concentration of the phosphines were linear for both phosphines with the attendant second-order rate constants showing that $P(C_6H_4OMe\text{-}p)_3$ reduces the cobalt(II) complex faster than $P(C_6H_4Me\text{-}p)_3$ does.

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 the addition of these phosphines. This supports the designation of the single exponential decays mainly to the Co(II) to Co(I) reduction. While traces of the Co(II) starting material were still observed 12 h after reactions with PPh_3 started (as seen in the infrared peaks), these traces were almost completely gone 3 h after the reactions with $P(C_6H_4Me\text{-}p)_3$ started and 45 minutes after the reactions with $P(C_6H_4OMe\text{-}p)_3$ commenced. The suggested reaction pathways are therefore largely based on evidence from the infrared spectra. Among the possible processes that take place in these reactions are:

$$[Co(CNR)_5]^{2+} + 2PR_3 \overset{\text{fast}}{\rightarrow} [Co(CNR)_4(PR_3)_2]^{2+} + CNR \tag{6a}$$

$$[Co(CNR)_5]^{2+} + 2PR_3 \leftrightharpoons [Co(CNR)_3(PR_3)_2]^{2+} + 2CNR \tag{6b}$$

$$2[Co(CNR)_4(PR_3)_2]^{2+} \leftrightharpoons [Co(CNR)_4(PR_3)_2]^{3+} + [Co(CNR)_3(PR_3)_2]^{+} + CNR \tag{6c}$$

$$[Co(CNR)_3(PR_3)_2]^{2+} + e \rightarrow [Co(CNR)_3(PR_3)_2]^{+} \tag{6d}$$

$$CNR = CNC_8H_{17}\text{-t and } PR_3 = P(C_6H_4Me\text{-}p)_3; \quad P(C_6H_4OMe\text{-}p)_3$$

4. Conclusion

The results of this study show that the electron-donating ability of aryl phosphines plays a significant role in the substitution rates of the ligands when reacted with *pentakis* (t-octylisocyanide)cobalt(II) with the order of reactivity being $P(C_6H_4OMe\text{-}p)_3 > P(C_6H_4Me\text{-}p)_3 > PPh_3$. All reactions involve multi-step mechanisms including substitution, ligand rearrangement, and reduction.

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