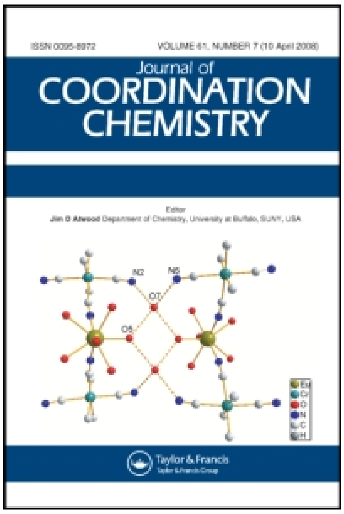

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CYCLIC VOLTAMMETRIC STUDIES OF *TETRAKIS*(ALKYLISOCYANIDE)*BIS*-(TRIALKYLPHOSPHINE)COBALT(III) COMPLEXES

K. R. Barqawi[a][b]; C. A. L. Becker[a]
[a] Department of Chemistry, University of Bahrain, Isa Town, Arabian Gulf, Bahrain [b] Yarmouk University, Jordan

To cite this Article Barqawi, K. R. and Becker, C. A. L.(1996) 'CYCLIC VOLTAMMETRIC STUDIES OF *TETRAKIS*(ALKYLISOCYANIDE)*BIS*-(TRIALKYLPHOSPHINE)COBALT(III) COMPLEXES', Journal of Coordination Chemistry, 38: 3, 237 — 243

To link to this Article: DOI: 10.1080/00958979608022709

URL: http://dx.doi.org/10.1080/00958979608022709

J. Coord. Chem., 1996, Vol 38, pp. 237–243
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands under
license by Gordon and Breach Science Publishers SA
Printed in Malaysia

CYCLIC VOLTAMMETRIC STUDIES OF *TETRAKIS*(ALKYLISOCYANIDE)*BIS*-(TRIALKYLPHOSPHINE)COBALT(III) COMPLEXES

K.R. BARQAWI[†] and C.A.L. BECKER*

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

(Received April 3, 1995; in final form September 15, 1995)

Reduction potentials, E_{red}, and subsequent oxidation potentials, E_{ox}, were measured for *tetrakis*-(alkylisocyanide)*bis*(trialkylphosphine)cobalt(III) complexes, $[Co(CNR)_4(PR_3)_2]X_3$, X = ClO_4, BF_4; CNR = $CNCHMe_2$, CNC_4H_9-*n*, CNC_6H_{11}, $CNCH_2Ph$; PR_3 = $P(C_6H_{13}$-*n*$)_3$, $P(C_4H_9$-*n*$)_3$, $P(C_3H_7$-*n*$)_3$; in CH_3CN *vs* SCE. The major reduction peak, −0.35 to −0.43 V, was assigned, $[Co(CNR)_4(PR_3)_2]^{3+} \xrightarrow{+e^-} [Co(CNR)_4(PR_3)_2]^{2+}$. The unstable six-coordinate Co(II) species are expected to disproportionate, $2\,[Co(CNR)_4(PR_3)_2]^{2+} \rightleftharpoons [Co(CNR)_4(PR_3)_2]^{3+} + [Co(CNR)_3(PR_3)_2]^{+} + CNR$, thereby replenishing the Co(III) species and furnishing the Co(I) species subsequently oxidized in the major oxidation peak, at 0.05 to 0.275 V, $[Co(CNR)_3(PR_3)_2]^{+} \xrightarrow{+e^-} [Co(CNR)_3(PR_3)_2]^{2+}$. In the presence of free RNC both Co(II) species should have limited stability, but on rapid scan (1.0 V/s instead of the usual 0.1 V/s) an oxidative shoulder, about −0.25 V, tentatively assigned as oxidation of $[Co(CNR)_4(PR_3)_2]^{2+}$, and a reductive shoulder, about −0.05 V, tentatively assigned as reduction of $[Co(CNR)_3(PR_3)_2]^{2+}$, were observed in all voltammograms. E_{ox} values, for $[Co(CNR)_3(PR_3)_2]^{+}$, are essentially independent of variation in CNR but increase with decreasing electron-donating ability of the PR_3 ligands. This suggests electron-donation of $P(C_3H_7$-*n*$)_3$ > $P(C_4H_9$-*n*$)_3$ > $P(C_6H_{13}$-*n*$)_3$, dictated by steric effects rather than inductive. E_{red} values, for $[Co(CNR)_4(PR_3)_2]^{3+}$, are roughly independent of variation in both CNR and PR_3, but a weak trend for increasingly negative values as CNR varies from CNC_6H_{11}, $CNCH_2Ph$, $CNCHMe_2$, to CNC_4H_9-*n* seems to be present. E_{ox} values for $[Co(CNCH_2Ph)_3(PR_3)_2]^{+}$ complexes appear abnormally high; this may be attributable to CH_3CN substitution in the $[Co(CNCH_2Ph)_4(PR_3)_2]^{3+}$ complexes.

KEYWORDS: Cyclic voltammetry, alkylisocyanides, cobalt(III) complexes, trialkylphosphines.

INTRODUCTION

White, diamagnetic cobalt(III) complexes of the type *trans*-$[Co(CNR)_4(PR_3)_2]X_3$, with X = ClO_4, BF_4; CNR = $CNCHMe_2$, CNC_6H_{11}, CNC_4H_9-*n*, $CNCH_2Ph$; PR_3 = $P(C_6H_{13}$-*n*$)_3$, $P(C_4H_9$-*n*$)_3$, $P(C_3H_7$-*n*$)_3$; have recently been reported.[1-3] Cyclic voltammetric studies of these compounds should give insight into the possible reduction products, and consequent oxidation products, of these species with highly versatile cobalt oxidation states. It has already been noted[2] that subtle conditions

---

* Author for correspondence.

[†] On leave from Yarmouk University, Jordan.

must govern whether Co(II) disproportionates into Co(III) and Co(I), or the more familiar Co(II) to Co(I) reduction takes place, in the reactions of *pentakis*(alkylisocyanide)cobalt(II) complexes with trialkylphosphine ligands. Oxidation of Co(II), in reactions of *pentakis*(alkylisocyanide)cobalt(II) complexes with triarylarsine and triphenylstibine ligands has also been observed.[4–6] A cyclic voltammetric study of cobalt(I) complexes of the type $[Co(CNR)_3(PR_3)_2]X$, CNR = alkylisocyanide, which may serve as a useful comparison, has recently been completed in this laboratory.[7]

EXPERIMENTAL

Reagents

$[Co(CNR)_4(PR_3)_2]X_3$, X = ClO_4, BF_4; CNR = $CNCHMe_2$, CNC_6H_{11}, CNC_4H_9-*n*, $CNCH_2Ph$; PR_3 = $P(C_6H_{13}\text{-}n)_3$, $P(C_4H_9\text{-}n)_3$, $P(C_3H_7\text{-}n)_3$; were prepared from commercial CNR and PR_3 (Strem Chemicals) as previously reported.[1–3] Solutions (5mM) of the compounds were freshly prepared in chromatographic-grade acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte.

Instrumentation

Voltammograms were recorded using a Metrohm VA Scanner (E612) and a Metrohm Polarecord (E506) with a three electrode compartment cell. The working and auxiliary electrodes were glassy carbon and platinum wire, respectively; the reference electrode employed was a saturated calomel electrode (SCE). The voltammograms were recorded in the potential range −0.7 V to +0.7 V *vs* (SCE) on a JJ Instruments X-Y recorder, using sweep rates of 0.1 V/s and 1.0 V/s. Nitrogen gas was bubbled through each solution for 10 min prior to runs.

RESULTS AND DISCUSSION

Oxidation and reduction potentials observed for the $[Co(CNR)_4(PR_3)_2]X_3$ complexes in CH_3CN are reported in Table 1; a representative cyclic voltammogram is pictured in Figure 1.

Assignment of the Potentials

Cyclic voltammograms, in CH_3CN at 0.1 V/s sweep rate, carried out on these compounds showed two major peaks in the potential range −0.7 V to +0.7 V, one major reduction peak in the range -0.35 V to -0.43 V, and a major oxidation peak in the range +0.05 V to +0.275 V (see Figure 1A). The current for the reduction peak is invariably much larger than the current for the oxidation peak, indicating that the reduction and oxidation peaks most probably correspond to different species. It has also been observed that the oxidation peak appears only after reduction has taken place, so it follows necessarily that the oxidation peak is due to a species formed from the reduction process. The potential range in which the

Table I Oxidation and reduction potentials, in volts *vs* SCE, for the $[Co(CNR)_4(PR_3)_2]X_3$ comlexes in acetonitrile solution.

Compound		$E_{ox}(I \rightarrow II)$	$E_{red}(III \rightarrow II)$
I	$[Co(CNCHMe_2)_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$	0.175V	-0.40V
II	$[Co(CNCHMe_2)_4\{P(C_4H_9\text{-}n)_3\}_2](BF_4)_3$	0.17V	-0.42V
III	$[Co(CNCHMe_2)_4\{P(C_3H_7\text{-}n)_3\}_2](ClO_4)_2$	0.05V	-0.38V
IV	$[Co(CNC_4H_9\text{-}n)_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$	0.19V	-0.43V
V	$[Co(CNC_4H_9\text{-}n)_4\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_3$	0.14V	-0.43V
VI	$[Co(CNC_4H_9\text{-}n)_4\{P(C_3H_7\text{-}n)_3\}_2](ClO_4)_3$	0.09V	-0.43V
VII	$[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$	0.18V	-0.36V
VII	$[Co(CNC_6H_{11})_4\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_3$	0.12V	-0.35V
IX	$[Co(CNC_6H_{11})_4\{P(C_3H_7\text{-}n)_3\}_2](ClO_4)_3$	0.05V	-0.35V
X	$[Co(CNCH_2Ph)_4\{P(C_6H_{13}\text{-}n)_3\}_2](BF_4)_3$	0.275V	-0.38V
XI	$[Co(CNCH_2Ph)_4\{P(C_4H_9\text{-}n)_3\}_2](BF_4)_3$	0.25V	-0.39V
XII	$[Co(CNCH_2Ph)_4\{P(C_3H_7\text{-}n)_3\}_2](BF_4)_3$	0.18V	-0.35V

oxidation peak occurs (0.05 V to 0.275 V) is consistent with values reported for oxidation of the $[Co(CNR)_3(PR_3)_2]X$ complexes.[7] Thus, the major oxidation peak is tentatively assigned to oxidation of five-coordinate Co(I) species (involving particular species that could not be isolated in previous work[6]).

$$[Co(CNR)_3(PR_3)_2]^+ \xrightarrow{-e^-} [Co(CNR)_3(PR_3)_2]^{2+} \qquad (1)$$

With possible exception of the $CNCH_2Ph$ derivatives,[6] the $[Co(CNR)_4(PR_3)_2]X_3$ complexes appear to be indefinitely stable in CH_3CN solution, so the major reduction peak, almost certainly, must be reduction of the $[Co(CNR)_4(PR_3)_2]^{3+}$ species, presumably to a Co(II) species, $[Co(CNR)_4(PR_3)_2]^{2+}$.

$$[Co(CNR)_4(PR_3)_2]^{3+} \xrightarrow{+e^-} [Co(CNR)_4(PR_3)_2]^{2+} \qquad (2)$$

A Co(II) species, such as the postulated *trans*-$[Co(CNR)_4(PR_3)_2]^{2+}$ ion, is not expected to be stable, however, as evidenced by previous disproportionat-syntheses,[1-3] and a disproportionation reaction could be expected to take place.

$$2[Co(CNR)_4(PR_3)_2]^{2+} \rightleftharpoons [Co(CNR)_4(PR_3)_2]^{3+} + [Co(CNR)_3(PR_3)_2]^+ + CNR \qquad (3)$$

This equilibrium, rapidly established and probably lying far to the right-hand side, would provide the $[Co(CNR)_3(PR_3)_2]^+$ observed in the subsequent oxidation step and would also replenish $[Co(CNR)_4(PR_3)_2]^{3+}$. The $[Co(CNR)_3(PR_3)_2]^+$ concentration should be substantially less than the $[Co(CNR)_4(PR_3)_2]^{3+}$ concentration, as indicated by the amount of current.

Under the initial reaction conditions, neither the oxidation of $[Co(CNR)_4(PR_3)_2]^{2+}$ nor the reduction of $[Co(CNR)_3(PR_3)_2]^{2+}$ was observed. This is not particularly surprising, since both species should have very limited stability, especially in the presence of free alkylisocyanide ligand, liberated in reaction [3], which will cause reduction to Co(I).[1,8] $[Co(CNR)_4(PR_3)_2]^{3+}$ and $[Co(CNR)_3(PR_3)_2]^+$ must be stable in the presence of free RNC, as they were initially synthesized in the presence of significant excess of free RNC,[1-3,8] but Co(II) in general tends to be reduced by free RNC. There is, however, some argument for low concentrations of Co(II) complex existing in this solution. The Co(II) complex, $[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$, was isolated as minor product from

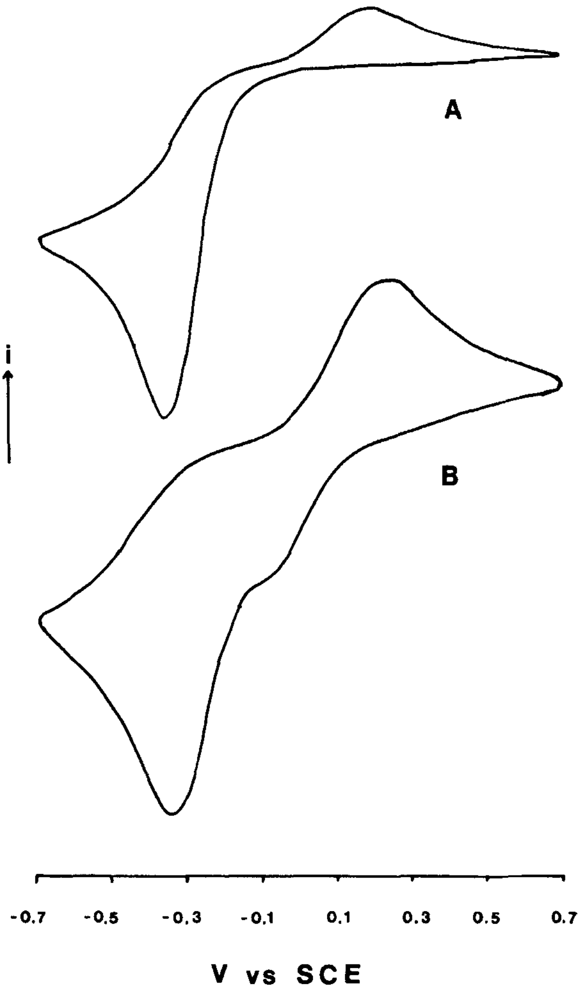

Figure 1 Cyclic voltammograms of $[Co(CNC_6H_{11})_4\{P(C_6H_{13}\text{-}n)_3\}_2](ClO_4)_3$, Compound VII, in CH_3CN containing 0.1 M (TBAH) supporting electrolyte; (A) using 0.1 V/s sweep rate; (B) using 1.0 V/s sweep rate.

reaction of $[Co(CNR)_5](ClO_4)_2$ with PR_3 under reaction conditions least favourable to Co(II) reduction ($[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ was, nevertheless, the major product[9]). This Co(II) complex, believed to be an intermediate in Co(II) reduction/ligand substitution reactions, is stable in solution, including in the presence of free $P(C_6H_4OMe\text{-}p)_3$, but reduces to $[Co(CNCHMe_2)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ in the presence of free $CNCHMe_2$ (5–10 min at room temperature).[9] Low concentrations of $[Co(CNR)_3(PR_3)_2]X_2$ therefore probably exist in the present CH_3CN solutions.

The six-coordinate Co(II) species, $[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_2$, has also been isolated, as minor product, under very specialised reaction conditions.[10,11] Rapid reaction of $[Co(CNC_6H_{11})_5](ClO_4)_2$ in EtOH with PPh_3 produced a minor product of $[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_2$, which precipitated immediately, and a major product of $[Co(CNC_6H_{11})_3(PPh_3)_2]ClO_4$, which remained in solution and required addition of ether for precipitation.[10,11] In rapid recrystallization of the $[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_2$ from CH_2Cl_2/ether only the five-coordinate Co(II) complex, $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$, could be isolated in poor yield.[11] Dissociation of the six-coordinate Co(II) species into a five-coordinate Co(II) species, with liberation of free alkylisocyanide, is probably the first step in the reduction of Co(II).

$$[Co(CNR)_4(PR_3)_2]^{2+} \rightarrow [Co(CNR)_3(PR_3)_2]^{2+} + CNR \qquad (4)$$

Thus, concentrations of $[Co(CNR)_4(PR_3)_2]^{2+}$ even lower than the concentration of $[Co(CNR)_3(PR_3)_2]^{2+}$ could be expected to exist in these present CH_3CN solutions.

By increasing the sweep rate to 1.0 V/s, we were able to observe two additional small peaks, appearing in each voltammogram as shoulders (see Figure 1B). One peak, obtained on sweeping in the cathodic direction, occurs around −0.05 V in all samples, and might be attributed to reduction of small concentrations of $[Co(CNR)_3(PR_3)_2]^{2+}$ to $[Co(CNR)_3(PR_3)_2]^+$.

$$[Co(CNR)_3(PR_3)_2]^{2+} \xrightarrow{+e^-} [Co(CNR)_3(PR_3)_2]^+ \qquad (5)$$

The second, even weaker, peak is obtained on sweeping in the anodic direction and occurs around −0.25 V in all samples. This peak might be attributed to oxidation of very small concentrations of $[Co(CNR)_4(PR_3)_2]^{2+}$ to $[Co(CNR)_4(PR_3)_2]^{3+}$

$$[Co(CNR)_4(PR_3)_2{}^{2+} \xrightarrow{-e^-} [Co(CNR)_4(PR_3)_2]^{3+} \qquad (6)$$

Both the scan rate and relative intensity of these shoulders are significant. Only on rapid scan are the shoulders visible; this indicates a relatively transient species. Both the six-coordinate and five-coordinate Co(II) species should be relatively rapidly decomposed/reduced by free RNC in these solutions. The small time difference between a 0.1 V/s scan and the rapid 1.0 V/s scan could be critical for detection of these short-lived species. Of these two Co(II) species, however, five-coordinate $[Co(CNR)_3(PR_3)_2]^{2+}$ should be the more stable and therefore exist at higher (*albeit* still very low) concentration. The shoulder tentatively assigned to the reduction of this species is more intense (indicating larger current) than the shoulder tentatively assigned to the oxidation of $[Co(CNR)_4(PR_3)_2]^{2+}$. While these tentative assignments of the four observed potentials have certainly not been unambiguously established, they do seem to be compatible with the known chemistry of cobalt complexes with alkylisocyanide and tertiary phosphine ligands.

Trends in the Potentials

Oxidation and reduction of the several cobalt species will depend primarily on the electron density around the cobalt, which in turn is governed by the structure and geometry of the complexes. Values of $E_{ox}(I \rightarrow II)$ (see Table I), assigned to the $[Co(CNR)_3(PR_3)_2]^+ \xrightarrow{-e^-} [Co(CNR)_3(PR_3)_2]^{2+}$ oxidation, are almost independent of variation of the alkylisocyanide ligands involving $CNCHMe_2$, $CNC_4H_9\text{-}n$, and CNC_6H_{11} as long as constant PR_3 is maintained. For $PR_3 = P(C_6H_{13}\text{-}n)_3$, $E_{ox} = 0.175$, 0.18, 0.19 V; with CNR = $CNCHMe_2$ (cpd I), CNC_6H_{11} (VII), $CNC_4H_9\text{-}n$ (IV), respectively. With $P(C_4H_9\text{-}n)_3$ and $CNCHMe_2$, CNC_6H_{11},

CNC_4H_9-*n* (cpd II, VIII, V); E_{ox} = 0.17, 0.12, 0.14 V, respectively (showing slightly more variation); with $P(C_3H_7$-*n*$)_3$ and $CNCHMe_2$, CNC_6H_{11}, CNC_4H_9-*n* (cpd III, IX, VI); E_{ox} = 0.05, 0.05, 0.09V, respectively. This is the same pattern previously reported for $E_{1/2}$ values of the $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes;[7] the oxidation potential is essentially independent of the RNC ligands in these axially-disubstituted trigonal bipryamidal *pentakis*(alkylisocyanide)cobalt(I) complexes.

With variation of PR_3 with respect to fixed CNR ligand, E_{ox} values for $[Co(CNR)_3(PR_3)_2]^+$ show a general trend of decreasing values, $P(C_6H_{13}$-*n*$)_3$ > $P(C_4H_9$-*n*$)_3$ > $P(C_3H_7$-*n*$)_3$, and the difference between complexes with $P(C_3H_7$-*n*$)_3$ and $P(C_4H_9$-*n*$)_3$ is slightly greater than the difference between complexes with $P(C_4H_9$-*n*$)_3$ and $P(C_6H_{13}$-*n*$)_3$ (this parallels observations in the syntheses;[3] in reaction $P(C_4H_9$-*n*$)_3$ is very similar to $P(C_6H_{13}$-*n*$)_3$, but $P(C_3H_7$ *n*$)_3$ reacts somewhat differently). With $CNCHMe_2$, E_{ox} = 0.175, 0.17, 0.05 V; for $P(C_6H_{13}$-*n*$)_3$, $P(C_4H_9$-*n*$)_3$, $P(C_3H_7$-*n*$)_3$, respectively; with CNC_6H_{11}, E_{ox} = 0.18, 0.12, 0.05 V, respectively; with CNC_4H_9-*n*, E_{ox} = 0.19, 0.14, 0.09 V, respectively. Although these three trialkylphosphines should differ very little chemically, E_{ox} for $[Co(CNR)_3(PR_3)_2]^+$ is clearly far more sensitive to the relatively small changes in PR_3 than to the more substantial changes in CNR. This is also the same pattern previously reported for $E_{1/2}$ of $[Co(CNR)_3(PR_3)_2]ClO_4$ complexes;[7] variation of the tertiary phosphine ligand (over a much wider range than in this present work) had a pronounced effect on the $E_{1/2}$ values. As the electron donating ability of the P atom decreased, the oxidation potential of the Co(I) was observed to increase.[7] This trend would imply relative electron donating ability for trialkylphosphine ligands as $P(C_3H_7$-*n*$)_3$ > $P(C_4H_9$-*n*$)_3$ > $P(C_6H_{13}$-*n*$)_3$, which would have to be explained in terms of decreased steric hindrance (in $P(C_3H_7$-*n*$)_3$ over $P(C_6H_{13}$-*n*$)_3$) rather than a pure inductive effect. $P(C_6H_{13}$-*n*$)_3$, having a larger cone angle,[12] would be less effective in σ-donation to Co, than would be $P(C_3H_7$-*n*$)_3$, with a smaller cone angle. $E_{1/2}$ for $[Co(CNCHMe_2)_3\{P(C_6H_{13}$-*n*$)_3\}_2]^+$ is about equal to $E_{1/2}$ for $[Co(CNCHMe_2)_3\{P(C_4H_9$-*n*$)_3\}_2]^+$ (0.08 V *vs* 0.07 V).[7]

The shoulders attributed to reduction of $[Co(CNR)_3(PR_3)_2]^{2+}$ and oxidation of $[Co(CNR)_4(PR_3)_2]^{2+}$, all at approximately −0.05 V and −0.25 V, respectively, are too poorly resolved to merit further interpretation. Suffice to say that the respective reductions and oxidations require relatively low voltages, indicating how easily these reactions take place as would be anticipated from the limited stability of these species.

Values of E_{red} (III→II) (see Table I) have been assigned as reduction of *trans*-$[Co(CNR)_4(PR_3)_2]^{3+}$, previously characterized as having regular tetragonal structure (D_{4h}) in solution.[3] Change in E_{red} value is relatively small for variation of the CNR or the PR_3 ligand. Considering that the experimental error for E_{red} may be as large as ±0.02 V, no trend with variation of PR_3 can be observed. This is really not very surprising, since $P(C_3H_7$-*n*$)_3$, $P(C_4H_9$-*n*$)_3$ and $P(C_6H_{13}$-*n*$)_3$ are very analogous trialkylphosphines. For exchange of CNR with respect to fixed PR_3 in $[Co(CNR)_4(PR_3)_2]^{3+}$, there could be a trend toward increasingly negative E_{red} values as CNR changes from CNC_6H_{11} < $CNCH_2Ph$ < $CNCHMe_2$ < CNC_4H_9-*n*. Since the total change in E_{red}, from least negative $[Co(CNC_6H_{11})_4(PR_3)_2]^{3+}$ to most negative $[Co(CNC_4H_9$-*n*$)_4(PR_3)_2]^{3+}$, is only 0.07 - 0.08 V, this is rather insignificant. Again, however, the reason for this trend may be the same as that for the E_{ox} pattern, steric hindrance of the R groups rather than induction, but now in the CNR ligands rather than the PR_3.

E_{ox} values for complexes involving the $CNCH_2Ph$ ligand (see Table I) appear anomalous in that they are substantially higher (by 0.08–0.13 V) than other values; E_{red} values fall within the range defined by complexes with the other CNR ligands. This anomaly may be traceable to the instability of $[Co(CNCH_2Ph)_4(PR_3)_2]^{3+}$ in CH_3CN solution. In the electronic spectra of $[Co(CNCH_2Ph)_4(PR_3)_2]X_3$ (at $\approx 10^{-5}$ M concentrations) in CH_3CN solution, but not in CH_2Cl_2 and CF_3CH_2OH, the lone intense band at 293.0–297.5 nm ($\varepsilon \approx 30{,}000$) begins to disappear and a new band at 237.5–238.5 nm appear during measurement of the spectrum.[3] It is postulated, but not confirmed, that CH_3CN replaces one or more of the ligands in $[Co(CNCH_2Ph)_4(PR_3)_2]^{3+}$. Thus, E_{red} and E_{ox} may involve species other than $[Co(CNCH_2Ph)_4(PR_3)_2]^{3+}$ and $[Co(CNCH_2Ph)_3(PR_3)_2]^{+}$, respectively, in these particular solutions. Further investigation of the $[Co(CNCH_2Ph)_4(PR_3)_2]X_3$ complexes is clearly required.

Acknowledgements

The authors wish to thank the University Research Council of the University of Bahrain for support of this research.

References

1. C.A.L. Becker, S.A. Al-Qallaf and J.C. Copper, *Inorg. Chim Acta,* **188**, 99 (1991).
2. C.A.L. Becker, M.A.S. Biswas and J.C. Cooper, *Inorg. Chim. Acta,* **188**, 191 (1991).
3. C.A.L. Becker and M.A.S. Biswas, *J. Coord. Chem.*, **29**, 277 (1993).
4. C.A.L. Becker, 204th National Meet. American Chemical Society, Washington, DC, Aug. 1992, Abstr. no. 381 (Inorg. Div.).
5. C.A.L. Becker, *Inorg. Chim. Acta,* **203**, 175 (1993).
6. C.A.L. Becker, *J. Coord. Chem.*, **31**, 337 (1994).
7. C.A.L. Becker and K.R. Barqawi, *J. Coord. Chem.*, **34**, 273 (1995).
8. C.A.L. Becker, A. Anisi, G. Myer and J.D. Wright, *Inorg. Chim. Acta,* **111**, 11 (1986).
9. C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 99 (1992).
10. C.A.L. Becker and O. Al-Jowder, 208th National Meet. American Chemical Society, Washington, DC, Aug. 1994, Abstr. no. 511 (Inorg. Div.).
11. C.A.L. Becker, unpublished results.
12. C.A. Tolman, *Chem. Rev.*, **77**, 313 (1977).