

Cyclic voltammetric studies of tris(alkylisocyanide)-bis(triarylphosphine)cobalt(II) and tris-(alkylisocyanide)bis(triarylphosphine)cobalt(I) complexes exhibiting synthetic interconvertibility

Jamil Ahmad, Florence Bothata-Nareetsile, and Clifford A.L. Becker

Abstract: Nine pairs of corresponding $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$, $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ complexes — where $\text{X} = \text{ClO}_4$, BF_4 ; $\text{CNR} = \text{CNCMe}_3$, CNCHMe_2 , $\text{CNC}_6\text{H}_{11}$, CNCH_2Ph ; $\text{PR}'_3 = \text{PPh}_3$, $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$, $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ — have been studied using cyclic voltammetry in CH_3CN solutions. All cycles are reversible, and $E_{1/2}$ for the Co(I) complexes, initially oxidized, are within experimental error identical to $E_{1/2}$ values for the corresponding Co(II) complexes, initially reduced. $E_{1/2}$ values are strongly dependent on the triarylphosphine ligand, decreasing in the order $\text{PPh}_3 > > \text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3 > \text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$, and weakly dependent on the alkylisocyanide ligand, decreasing in the order $\text{CNCH}_2\text{Ph} > \text{CNCMe}_3 > \text{CNC}_6\text{H}_{11} \geq \text{CNCHMe}_2$. Solution $\nu(\text{N}=\text{C})$ IR patterns reveal that the $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ complexes do not have regular trigonal bipyramidal coordination, their structure being determined by the particular CNR ligand, while the $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ complexes, specifically in $\text{CF}_3\text{CH}_2\text{OH}$, appear to have regular trigonal bipyramidal coordination.

Key words: cyclic voltammetry, cobalt(I) complexes, cobalt(II) complexes, alkylisocyanide ligands, triarylphosphine ligands.

Résumé : Utilisant la voltamétrie cyclique on a étudié neuf paires de complexes de $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$, et de $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ dans lesquels $\text{X} = \text{ClO}_4$, BF_4 ; $\text{CNR} = \text{CNCMe}_3$, CNCHMe_2 , $\text{CNC}_6\text{H}_{11}$, CNCH_2Ph ; $\text{PR}'_3 = \text{PPh}_3$, $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$, $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$. Tous les cycles sont réversibles et les valeurs de $E_{1/2}$ pour les complexes de Co^{I} , préalablement oxydés sont, à l'intérieur des erreurs expérimentales, identiques aux valeurs de $E_{1/2}$ des complexes correspondants de Co^{II} préalablement réduits. Les valeurs de $E_{1/2}$ dépendent fortement du ligand triarylphosphine et décroissent dans l'ordre : $\text{PPh}_3 > > \text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3 > \text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$; ces valeurs également dépendent faiblement du ligand alkylisocyanure et décroissent dans l'ordre : $\text{CNCH}_2\text{Ph} > \text{CNCMe}_3 > \text{CNC}_6\text{H}_{11} \geq \text{CNCHMe}_2$. L'allure des spectres IR $\nu(\text{N}=\text{C})$ révèle que les complexes $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ n'ont pas une coordination bipyramidale trigonale régulière, la structure étant déterminée par le ligand particulier CNR, tandis que les complexes $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ spécifiquement dans le $\text{CF}_3\text{CH}_2\text{OH}$ semblent avoir une coordination bipyramidale trigonale régulière.

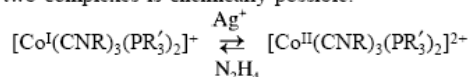
Mots clés : voltamétrie cyclique, complexes de cobalt (I), complexes de cobalt (II), ligands alkylisocyanures, ligands triarylphosphines.

[Traduit par la Rédaction]

Introduction

Reactions of triarylphosphines with cobalt(II)-alkylisocyanide complexes have been characterized by reduction – ligand-substitution, producing disubstituted Co(I) complexes, $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ ($\text{X} = \text{ClO}_4$, BF_4) in good yields (1–5). Cyclic voltammograms of some tris(alkylisocyanide)bis-(triarylphosphine)cobalt(I) complexes showed quasi-reversible behavior for oxidative cycles (5), suggesting the existence of stable $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]^{2+}$ species, however, and a number

of tris(alkylisocyanide)bis(triarylphosphine)cobalt(II) complexes have since been synthesized (6). The pairs of corresponding Co(I) and Co(II) complexes, $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ and $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$, having the same alkylisocyanide (CNR) and triarylphosphine (PR'_3) ligands show what may be termed “regular behavior” in that mutual interconversion of the two complexes is chemically possible:



This is opposed to “irregular behavior” for cases where only the Co(I) or only the Co(II) complex has been synthesized and where it has not been possible to isolate the corresponding Co(II) or Co(I) complex, respectively. Co(I) complexes showing clearly irreversible cyclic voltammograms, for example, cannot be oxidized to the corresponding Co(II) complexes with AgClO_4 or AgBF_4 (6).

In this paper, corresponding pairs of Co(I) and Co(II) complexes are investigated using cyclic voltammetry; cycles

Received 20 November 2002. Published on the NRC Research Press Web site at <http://canjchem.nrc.ca> on 12 August 2003.

J. Ahmad, F. Bothata-Nareetsile, and C.A.L. Becker.¹
Department of Chemistry, University of Botswana,
P/Bag 0022, Gaborone, Botswana.

¹Corresponding author (e-mail: Beckerca@mopipi.ub.bw).

for the Co(I) complexes were initially scanned oxidatively, and cycles for the Co(II) complexes were initially scanned reductively. If results of these two scans are equivalent, within experimental error, this should confirm that the Co(II) species observed in the voltammograms of the Co(I) species are indeed the recently synthesized $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ complexes. Since there are a limited number of known series of transition metal complexes, differing only in the oxidation state of the metal, this should be a worthwhile study.

Results

The equilibrium cyclic voltammetric data for the $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$, $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ corresponding pairs of complexes are summarized in Table 1. The equilibrium scans are quite similar in shape to the respective first scans and have quite close E values. A characteristic set of cyclic voltammograms for $[\text{Co}^{\text{I}}(\text{CNC}_6\text{H}_{11})_3(\text{PPh}_3)_2]\text{ClO}_4$ at various scan rates is pictured in Fig. 1. The dependence of the peak currents from these voltammograms on the scan rate is shown in Fig. 2. This dependence was used as a diagnostic tool to decide if the electrochemical processes were reversible. The $\nu(\text{N}\equiv\text{C})$ IR values for the five-coordinate Co(I) and Co(II) complexes in $\text{CF}_3\text{CH}_2\text{OH}$, CH_3NO_2 , and CH_2Cl_2 are tabulated in Table 2, and the four distinct patterns for the $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ complexes are pictured in Fig. 3.

Interpretation of the voltammograms

The plots of the peak current vs. the square root of the scan rate are linear for all of the complexes (see Fig. 2 for compound (9)). The peak potentials also do not change significantly with the scan rate. According to these criteria, the electrode processes are reversible (7–9). This system has a high solution resistance between the working and the reference electrode because of the non-aqueous nature of the solvent and the low concentration (0.05 M) of the background electrolyte, which is necessitated by its low solubility in CH_3CN . The measured potential is increased by an amount equal to this ohmic (iR) drop. The net result is an increase in the peak separation between the anodic and cathodic peak potential values (8). This “ohmic distortion” contributes to the apparent nonconformity of the system to a third criterion of reversibility, namely the requirement that the peak separation be around 57 mV.

Another source of this discrepancy for high ΔE values is the junction potential created across the ion bridge between the reference electrode and the sample solution. This is caused by the difference in the diffusion coefficients of the cations and the anions of the supporting electrolyte (10). Measurements made on ferrocene–ferrocenium, which is a known reversible couple, under conditions identical to those reported herein gave a peak separation of 110 mV at a 0.1 V s^{-1} scan rate, thereby confirming that the observed peak separation is inherent in the experimental conditions and not characteristic of the redox couple.

Interpretation of the $E_{1/2}$ values

Experimental error of $\pm 10 \text{ mV}$ in measurement of the $E_{1/2}$ values was estimated by repetitive scans of the same samples. Within this margin of error, the $E_{1/2}$ values measured

for the Co(I) complexes, initially oxidized, and the $E_{1/2}$ values measured for the Co(II) complexes, initially reduced, are essentially identical (see Table 1). This experimental fact, observed for nine pairs of corresponding Co(I), Co(II) complexes, would seem to confirm that the recently synthesized $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ complexes are indeed the same Co(II) species observed in cyclic voltammetric oxidation of the previously known $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ complexes.

Alternately, these Co(II) complexes are reduced by cyclic voltammetry to the same Co(I) complexes that are obtained by chemical reduction with hydrazine or that served as starting materials for synthesis of the Co(II) complexes. Generation of the same chemical species electrolytically and by N_2H_4 reduction – Ag^+ oxidation is thus confirmed.

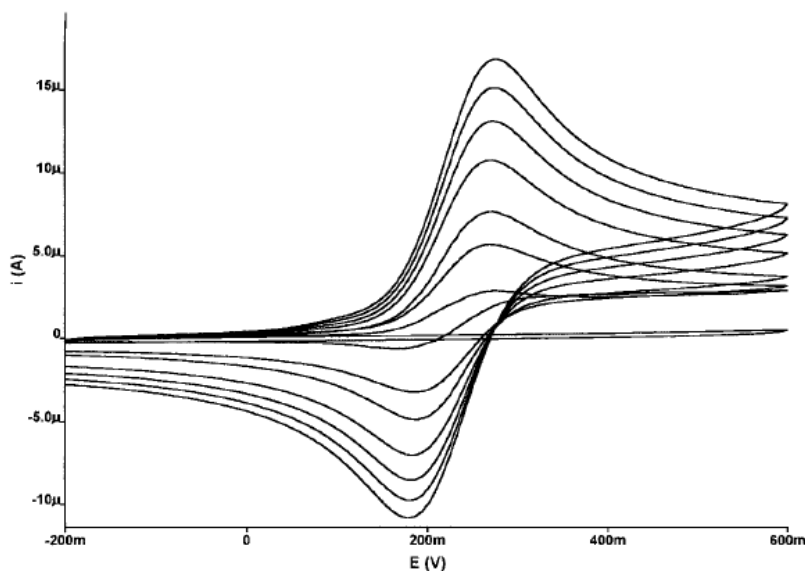
The $E_{1/2}$ dependence on variation of the PR'_3 ligand with respect to constant CNR ligands for both Co(I) and Co(II) complexes is very pronounced, with the definite trend in decreasing $E_{1/2}$ values, $\text{PPh}_3 >> \text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3 > \text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$. This is expected since *para*-substituents with increasing electron-donating ability should make the phosphines both stronger σ -donating and less π^* -accepting, favoring stabilization of Co(II) over Co(I). This trend also correlates with the ease or difficulty of synthesizing the Co(II) complexes as opposed to isolating only Co(I). Decreasing Co(II) and (or) increasing Co(I) stability for the species $[\text{Co}(\text{CNR})_3(\text{PR}'_3)_2]^m$ has been observed to be favored by $\text{P}(\text{C}_6\text{H}_4\text{NMe}_2-p)_3 > \text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3 > \text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3 > \text{PPh}_3 > \text{P}(\text{C}_6\text{H}_4\text{F-}p)_3 \approx \text{P}(\text{C}_6\text{H}_4\text{Cl-}p)_3 > \text{P}(\text{C}_6\text{H}_4\text{CF}_3-p)_3$ (6, 11), this trend running to both extremes. $[\text{Co}^{\text{I}}(\text{CNCMe}_3)_3\{\text{P}(\text{C}_6\text{H}_4\text{NMe}_2-p)_3\}_2]\text{ClO}_4$, prepared by N_2H_4 reduction in CH_2Cl_2 of the initially isolated $[\text{Co}^{\text{II}}(\text{CNCMe}_3)_3\{\text{P}(\text{C}_6\text{H}_4\text{NMe}_2-p)_3\}_2](\text{ClO}_4)_2$, for example, spontaneously oxidizes back to the Co(II) complex in $\text{CF}_3\text{CH}_2\text{OH}$ solution (11), while $[\text{Co}^{\text{I}}(\text{CNCMe}_3)_3(\text{PR}'_3)_2]\text{ClO}_4$ complexes with $\text{PR}'_3 = \text{P}(\text{C}_6\text{H}_4\text{F-}p)_3$, $\text{P}(\text{C}_6\text{H}_4\text{Cl-}p)_3$, and $\text{P}(\text{C}_6\text{H}_4\text{CF}_3-p)_3$ are not oxidized by AgClO_4 (6). These latter Co(I) complexes show irreversible voltammograms under oxidation (5). No substantial difference in ease of synthesis for $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PPh}_3)_2]\text{X}_2$ vs. $[\text{Co}^{\text{II}}(\text{CNR})_3\{\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3\}_2]\text{X}_2$ complexes sufficient to justify these $E_{1/2}$ values has been observed, but the Hammett σ constants do indicate a much larger difference between reactivity involving a $-\text{C}_6\text{H}_5$ group and the $-\text{C}_6\text{H}_4\text{Me-}p$ group than between $-\text{C}_6\text{H}_4\text{Me-}p$ and $-\text{C}_6\text{H}_4\text{OMe-}p$ groups (12), so this may be reflected in the $E_{1/2}$ values.

The $E_{1/2}$ dependence on variation of the CNR ligand with respect to constant PR'_3 ligands is relatively small but seems to follow the trend in decreasing $E_{1/2}$ values, $\text{CNCH}_2\text{Ph} > \text{CNCMe}_3 > \text{CNC}_6\text{H}_{11} > \text{CNCHMe}_2$. This trend parallels the decreasing ability of the alkylisocyanide substituent to stabilize a δ^+ charge on the C atom adjacent to the isocyanide functional group. Analogous variation of $E_{1/2}$ values with alkylisocyanide ligands was reported by Dart et al. (2) for $[\text{Co}(\text{CNR})_3(\text{PPh}_3)_2]\text{PF}_6$ complexes (measured in CH_2Cl_2 solution), with $E_{1/2}$ values decreasing in the order $\text{R} = t\text{-Bu}$ (0.29 V) $> i\text{-Pr}$ (0.20 V) $> \text{Me}$ (0.12 V). $E_{1/2}$ values reported for $[\text{M}(\text{CO})_4\text{L}_2]$ complexes (where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{CNCHMe}_2, \text{CNCMe}_3$), however, show very little difference (13). Previous work from this laboratory (5) indicated a narrow range of $E_{1/2}$ values for variation in CNR ligands (i.e., $0.20\text{--}0.25 \text{ V}$), but the trend of $\text{CNCMe}_3 > \text{CNCHMe}_2$ values was detected. For $[\text{PtL}_2(\text{CNR})\text{Me}]^+$ ($\text{L} = \text{PMePh}_2, \text{PMe}_2\text{Ph}$)

Table 1. Cyclic voltammetric results for corresponding pairs of tris(alkylisocyanide)bis(triarylphosphine)cobalt(I) and tris(alkylisocyanide)bis(triarylphosphine)cobalt(II) complexes in acetonitrile solution at 0.1 V s⁻¹ scan rate.

Compound	$E_{\text{oxidation}}$ (mV vs. Ag–AgCl)	$E_{\text{reduction}}$ (mV)	$E_{1/2}$	ΔE
1 [Co ^I (CNCHMe ₂) ₃ {P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂]ClO ₄	155	70	113	85
2 [Co ^{II} (CNCHMe ₂) ₃ {P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂](ClO ₄) ₂	163	96	130	67
3 [Co ^I (CNC ₆ H ₁₁) ₃ {P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂]ClO ₄	179	116	148	63
4 [Co ^{II} (CNC ₆ H ₁₁) ₃ {P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂](ClO ₄) ₂	179	109	144	70
5 [Co ^I (CNCMe ₃) ₃ {P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂]ClO ₄	193	126	160	67
6 [Co ^{II} (CNCMe ₃) ₃ {P(C ₆ H ₄ OMe- <i>p</i>) ₃ } ₂](ClO ₄) ₂	207	137	172	70
7 [Co ^I (CNCHMe ₂) ₃ (PPh ₃) ₂]ClO ₄	246	183	215	63
8 [Co ^{II} (CNCHMe ₂) ₃ (PPh ₃) ₂](ClO ₄) ₂	253	175	214	78
9 [Co ^I (CNC ₆ H ₁₁) ₃ (PPh ₃) ₂]ClO ₄	267	190	229	77
10 [Co ^{II} (CNC ₆ H ₁₁) ₃ (PPh ₃) ₂](ClO ₄) ₂	270	193	232	77
11 [Co ^I (CNCMe ₃) ₃ (PPh ₃) ₂]ClO ₄	295	218	257	77
12 [Co ^{II} (CNCMe ₃) ₃ (PPh ₃) ₂](ClO ₄) ₂	284	200	242	84
13 [Co ^I (CNCH ₂ Ph) ₃ (PPh ₃) ₂]BF ₄	298	235	267	63
14 [Co ^{II} (CNCH ₂ Ph) ₃ (PPh ₃) ₂](BF ₄) ₂	312	231	272	81
15 [Co ^I (CNCHMe ₂) ₃ {P(C ₆ H ₄ Me- <i>p</i>) ₃ } ₂]ClO ₄	204	105	155	99
16 [Co ^{II} (CNCHMe ₂) ₃ {P(C ₆ H ₄ Me- <i>p</i>) ₃ } ₂](ClO ₄) ₂	207	109	158	98
17 [Co ^I (CNC ₆ H ₁₁) ₃ {P(C ₆ H ₄ Me- <i>p</i>) ₃ } ₂]ClO ₄	225	112	169	113
18 [Co ^{II} (CNC ₆ H ₁₁) ₃ {P(C ₆ H ₄ Me- <i>p</i>) ₃ } ₂](ClO ₄) ₂	227	133	180	94

Fig. 1. Cyclic voltammograms of [Co^I(CNC₆H₁₁)₃(PPh₃)₂]ClO₄, cpd 9 (1 mM in CH₃CN), with 0.05 M tetrabutylammonium hexafluorophosphate background electrolyte. The flat (innermost) trace is for the background electrolyte only, at a scan rate of 0.1 V s⁻¹. The other curves are, in order, for scan rates of 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 V s⁻¹.

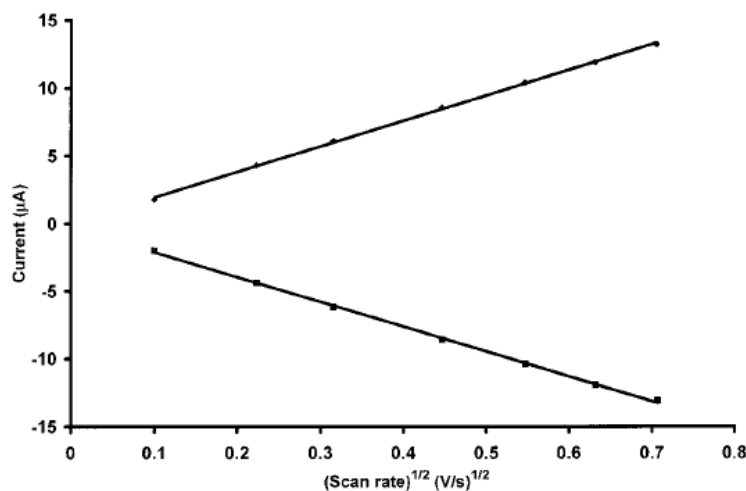


it is suggested that the σ -donor strength of CNR is essentially independent of the inductive properties of R, making variation in $E_{1/2}$ dependent only on the relatively slight differences in π^* -accepting ability of the CNR (14).

Strong $E_{1/2}$ dependence on the triarylphosphine ligands, with relatively little sensitivity to the alkylisocyanide ligands, has been attributed to effective σ -donation from the

phosphines in axial positions and ineffective σ -donation by the alkylisocyanides in equatorial positions of trigonal bipyramidal coordination in the Co(I) complexes (5). For diamagnetic d^8 Co(I) complexes in trigonal bipyramidal coordination, the electronic configuration of $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{x^2-y^2})^2$ should hinder σ -donation from the equatorial ligands (i.e., the alkylisocyanides) while allowing effective σ -donation

Fig. 2. Plots of anodic and cathodic currents vs. square root of scan rate for cpd 9 (i.e., $[\text{Co}^{\text{I}}(\text{CNC}_6\text{H}_{11})_3(\text{PPh}_3)_2]\text{ClO}_4$) from the voltammograms in Fig. 1.



from the axial ligands (i.e., the triarylphosphines) by electron donation into the empty $3d_{2z^2-x^2-y^2}$ orbital on the Co(I) (5). Possibly spectral data can provide insight into this question.

Interpretation of solution $\nu(\text{N}\equiv\text{C})$ IR patterns

In previous cyclic voltammetric studies of five-coordinate Co(I) complexes, when quasi-reversible behavior was assigned on the basis of ΔE values exceeding 57 mV, two alternate explanations were offered for quasi-reversibility. One explanation was that Co(I) in a regular trigonal bipyramidal (TBP) coordination is oxidized to Co(II) in a regular TBP structure that rapidly undergoes chemical change to a square pyramidal (SP) solution structure of C_{2v} symmetry (15). The other explanation was that Co(I) in a distorted TBP coordination is oxidized to Co(II) in a regular TBP structure (5). The $\nu(\text{N}\equiv\text{C})$ IR patterns in the solid state (i.e., Nujol mull) are significantly different for the Co(I) (3–5) and Co(II) (6, 16) complexes, but solution structures are more relevant in this study. Solution structures for $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]^+$ species in general have been considered only approximately TBP, the strongest evidence for deviation from rigorous (D_{3h}) TBP coordination coming from combined IR and Raman data for the arylisocyanide complexes (17). Spectral data for the Co(I) complexes in this paper were measured over a period of years on different spectrophotometers, so solution IR measurements have now been repeated on superior instrumentation under identical conditions. These data, in Table 2, reveal trends in the $\nu(\text{N}\equiv\text{C})$ IR patterns hitherto unrecognized.

The shape of the $\nu(\text{N}\equiv\text{C})$ IR patterns for these $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ complexes in solution is unique for each alkylisocyanide, but independent of the particular triarylphosphine and solvent used. Figure 3 illustrates these four distinct patterns, corresponding to Co(I) complexes with the $\text{CNC}_6\text{H}_{11}$, CNCH_2Ph , CNCHMe_2 , and CNCMe_3 ligands, respectively (top to bottom). The patterns for CNCMe_3 (seen for cpd 5, 11) and CNCHMe_2 (cpd 1, 7, 15) are clearly in-

compatible with D_{3h} symmetry (one, E' , allowed band), and even $\text{CNC}_6\text{H}_{11}$ (cpd 3, 9, 17) suggests some distortion in the solution state. Only CNCH_2Ph (represented by one complex, 13) could be assigned D_{3h} symmetry and only if the weak, albeit persistent, higher energy shoulder is ignored. Solution structures of the $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ complexes cannot be assumed to be regular TBP.

The shapes of the $\nu(\text{N}\equiv\text{C})$ IR patterns for the $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ complexes in solution are distinctly different from those for the Co(I) complexes and seem to vary mostly depending on solvent. In $\text{CF}_3\text{CH}_2\text{OH}$ almost all spectra exhibit a lone strong band, expected for D_{3h} (regular) TBP structure (see Table 2). Cpds 12 and 14 in $\text{CF}_3\text{CH}_2\text{OH}$ and many Co(II) complexes in CH_2Cl_2 and especially in CH_3NO_2 , however, exhibit additional shoulders and (or) weak bands in the energy region appropriate for Co(II). These additional bands are normally accompanied by weak to medium bands attributed to the corresponding $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ complex (produced by reduction in solution), except for cpd 14 where reduction is extensive. These data could indicate that a non-TBP structure for Co(II) is more prone to reduction than TBP coordination. These data also suggest that the $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}_2$ complexes in $\text{CF}_3\text{CH}_2\text{OH}$ at least tend to be TBP.

Now that the Co(I)–Co(II) couples have been recognized as being reversible, a difference in the solution coordination structures for the two oxidation states is interesting. This would imply that identical coordination structures for oxidized and reduced species is not a requirement for reversibility.

Experimental

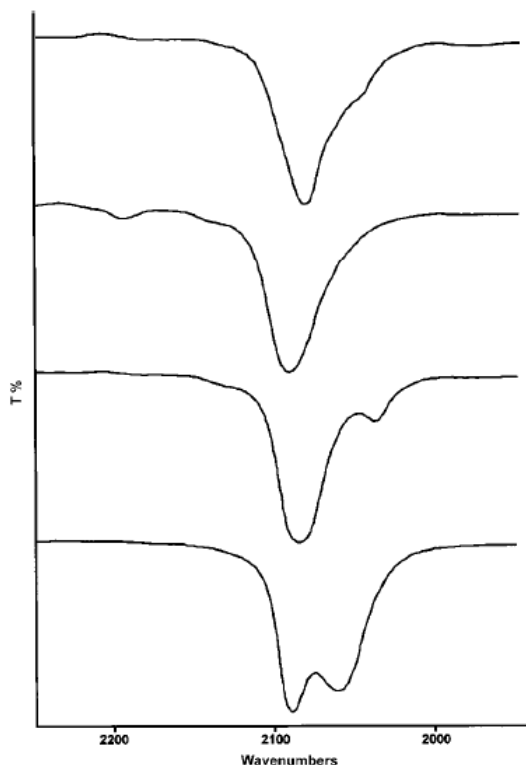
Commercially available alkylisocyanides — i.e., CNCMe_3 , CNCHMe_2 , $\text{CNC}_6\text{H}_{11}$, and CNCH_2Ph (Fluka, Strem, Fluka, and Aldrich Chemicals, respectively) — were used without redistillation. Commercially available triarylphosphines —

Table 2. Solution $\nu(\text{N}=\text{C})$ IR patterns for the $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}$ and $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}_2$ complexes.

Compound ^a	$\nu(\text{N}=\text{C})$ IR pattern ^b		
	$\text{CF}_3\text{CH}_2\text{OH}$	CH_3NO_2	CH_2Cl_2
1	~2132 w(sh) 2085 vs 2039 m	~2131 w(sh) 2082 vs 2038 m	~2130 w(sh) 2079 vs 2036 m
2	2186 vs	~2211 vw(sh) 2189 vs ~2086 m ^c ~2035 vw ^c	2189 vs
3	2083 vs ~2050 w(sh)	2081 vs ~2047 w(sh)	2079 vs ~2048 w(sh)
4	2183 vs	2186 vs ~2081 m ^c	2186 vs ~2153 vw(sh) ~2079 vw ^c
5	2091 s 2062 s	2089 s 2061 s	2088 s 2059 s
6	2175 vs	~2202 vw(sh) 2177 vs ~2144 vw(sh) ~2090m ^c ~2060m ^c	~2201 vw(sh) 2177 vs ~2144 vw(sh)
7	~2132 w(sh) 2091 vs 2038 m	~2135 w(sh) 2090 vs 2037 m	~2133 w(sh) 2088 vs 2036 m
8	2189 vs	~2212 vw(sh) 2193 vs 2091 m ^c 2037 vw ^c	~2214 vw(sh) 2194 vs 2157 w 2088 m ^c ~2034 vw ^c
9	2087 vs ~2049 w(sh)	2086 vs ~2048 w(sh)	2085 vs ~2046 w(sh)
10	2187 vs	2190 vs 2086 s ^c	2192 vs ~2155 vw(sh) ~2085 w ^c
11	2093 vs 2066 s	2092 vs 2064 s	2090 vs 2063 s
12	~2200 w(sh) 2179 vs	2204 m 2181 vs 2092 m ^c ~2064 m ^c	2204 w 2182 vs 2149 m 2091 m ^c ~2060 w ^c
13	~2142 w(sh) 2092 vs	~2142 w(sh) 2093 vs	~2140 w(sh) 2090 vs
14	~2220 vw(sh) 2197 vs 2094 m ^c	2196 m ~2144 w(sh) 2095 vs	2192 w ~2142 w(sh) 2091 vs
15	2188 m ^d ~2134 w(sh) 2087 vs 2039 m	2134 w(sh) 2085 vs 2037 m	~2132 w(sh) 2082 vs 2037 m
16	2188 vs	~2213 w(sh) 2191 vs ~2088 m ^c ~2035 vw ^c	~2214 vw(sh) 2191 vs 2155 w 2082 w ^c
17	2083 vs ~2050 w(sh)	2083 vs ~2048 w(sh)	2081 vs ~2047 w(sh)

Table 2 (concluded).

Compound ^a	$\nu(\text{N}=\text{C})$ IR pattern ^b		
	$\text{CF}_3\text{CH}_2\text{OH}$	CH_3NO_2	CH_2Cl_2
18	2185 vs	~2210 w(sh) 2188 vs 2083 m ^c	2189 vs 2080 vw ^c

^aComplexes listed in the same order as in Table 1.^bThe $\nu(\text{N}=\text{C})$ in cm^{-1} ; w = weak, m = medium, s = strong, v = very, sh = shoulder.^cBands due to the corresponding $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}$ complex formed in solution.^dBands due to the corresponding $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}_2$ complex formed in solution.**Fig. 3.** The $\nu(\text{N}=\text{C})$ IR patterns for $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}$ complexes. Top to bottom: $[\text{Co}(\text{CNC}_6\text{H}_{11})_3\{\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3\}_2]\text{ClO}_4$, $[\text{Co}(\text{CNCH}_2\text{Ph})_3(\text{PPh}_3)_2]\text{BF}_4$, $[\text{Co}(\text{CNCHMe}_2)_3\{\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3\}_2]\text{ClO}_4$, and $[\text{Co}(\text{CNCMe}_3)_3\{\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3\}_2]\text{ClO}_4$ all in $\text{CF}_3\text{CH}_2\text{OH}$ solution.

i.e., PPh_3 , $\text{P}(\text{C}_6\text{H}_4\text{Me-}p)_3$, and $\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3$ (Aldrich Chemicals) — were used without recrystallization. Anhydrous AgClO_4 and AgBF_4 were supplied by Strem Chemicals, Inc. 2,2,2-Trifluoroethanol (puriss grade) from Fluka was used for IR spectra. Anhydrous diethyl ether was filtered through an alumina column immediately before use. The $[\text{Co}^{\text{I}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}$ and $[\text{Co}^{\text{II}}(\text{CNR})_3(\text{PR}'_2)_2]\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) complexes were synthesized as previously re-

ported (3–6). Ferrocene, which was used to test the experimental setup, was prepared by standard procedure (18).

For cyclic voltammetry, 1 mM solutions of the compounds were freshly prepared in chromatographic-grade acetonitrile containing 0.05 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Cyclic voltammetry measurements were performed using a Metrohm 757 VA Computerace system with a three-electrode compartment cell. The working and auxiliary electrodes were both made of glassy carbon. The reference electrode was a double junction Ag–AgCl system. The voltammograms were recorded in the potential range, -0.2 to $+0.6$ V vs. Ag–AgCl, at various scan rates ranging from 0.01 V s^{-1} to 0.5 V s^{-1} . Nitrogen gas was bubbled through each solution for 500 s prior to the run. IR spectra were recorded on a PerkinElmer 2000 FT-IR spectrophotometer in spectro-grade CH_2Cl_2 , CH_3NO_2 , and CF_3CH_2OH .

Acknowledgements

The authors wish to thank the Faculty of Science Research and Publications Committee of the University of Botswana for a grant supporting this research.

References

1. R.B. King and M.S. Saran. *Inorg. Chem.* **11**, 2112 (1972).
2. J.W. Dart, M.K. Lloyd, R. Mason, J.A. McCleverty, and J. Williams. *J. Chem. Soc. Dalton Trans.* 1747 (1973).
3. C.A.L. Becker, A. Anisi, G. Myer, and J.D. Wright. *Inorg. Chim. Acta*, **111**, 11 (1986).
4. C.A.L. Becker, S.A. Al-Qallaf, and J.C. Cooper. *Inorg. Chim. Acta*, **188**, 99 (1991).
5. C.A.L. Becker and K.R. Barqawi. *J. Coord. Chem.* **34**, 273 (1995).
6. C.A.L. Becker. *J. Coord. Chem.* **50**, 89 (2000).
7. R. Nicholson and I. Shain. *Anal. Chem.* **36**, 706 (1964).
8. W.E. Geiger. *Laboratory techniques in electrochemistry*. Edited by P.T. Kissinger and W.R. Heineman. Marcel Dekker, New York, 1996. pp. 683–717.
9. J.J. Van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston, and P.T. Kissinger. *J. Chem. Educ.* **60**, 773 (1983).
10. G.A. Mabbott. *J. Chem. Educ.* **60**, 699 (1983).
11. C.A.L. Becker and O. Al-Jowder. 208th National Meeting of the American Chemical Society, Washington, DC, August 1994. Abstract No. 511 (Inorg. Div.).
12. N.S. Issacs. *Physical organic chemistry*. Longman Scientific & Technical, New York, 1987. Chap 4.
13. M.K. Lloyd, J.A. McCleverty, D.G. Orchard, J.A. Connor, M.B. Hall, I.H. Hillier, E.M. Jones, and G.K. McEwen. *J. Chem. Soc. Dalton Trans.* 1743 (1973).
14. H.C. Clark, W.J. Cherwinski, and L.E. Manzer. *Inorg. Chem.* **11**, 1511 (1972).
15. J. Hanzlik, G. Albertin, E. Bordignon, and A.A. Orio. *Inorg. Chem.* **38**, 207 (1980).
16. C.A.L. Becker. *Synth. React. Inorg. Met.-Org. Chem.* **22**, 99 (1992).
17. C.A.L. Becker and G.C. Papavassiliou. 180th National Meeting of the American Chemical Society, August 1980, Abstract No. 295 (Inorg. Div.).
18. W.L. Jolly. *Inorg. Synth.* **11**, 120 (1968).