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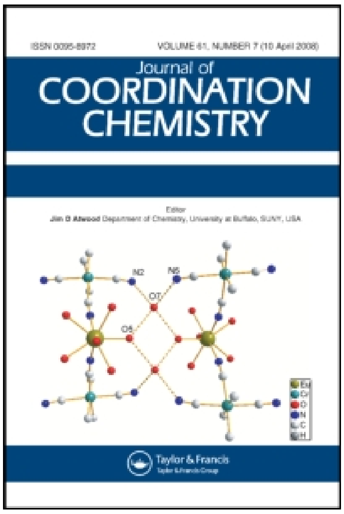

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F. Foster Mbaiwa[a]; C. A. L. Becker[a]
[a] Department of Chemistry, University of Botswana, Gaborone, Botswana

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Chelate complexes from diphosphine substitution in pentakis(arylisocyanide)cobalt(I) complexes

F. FOSTER MBAIWA and C. A. L. BECKER*

Department of Chemistry, University of Botswana,
P/Bag 00704, Gaborone, Botswana

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Four chelate complexes, $[Co(CNC_6H_3iPr_2\text{-}2,6)_3P(C_6H_4Me\text{-}p)_2CH_2CH_2P(C_6H_4Me\text{-}p)_2]BF_4$, $[Co(CNC_6H_3iPr_2\text{-}2,6)_3PPh_2CH{=}CHPPh_2\text{-}cis]BF_4$, $[Co(CNC_6H_3iPr_2\text{-}2,6)_3PPh_2C_6H_4PPh_2\text{-}o]BF_4$, and $[Co(CNC_6H_3iPr_2\text{-}2,6)_3P(C_6H_4CF_3\text{-}p)_2CH_2CH_2P(C_6H_4CF_3\text{-}p)_2]BF_4$, have been synthesized by substitution reactions of $[Co(CNC_6H_3iPr_2\text{-}2,6)_5]BF_4$ at elevated temperatures and/or prolonged reaction times. The complexes have been characterized by IR and electronic spectra, ^{31}P NMR, cyclic voltammetry, and mass spectrometry. Comparisons are made with the pentakis(arylisocyanide)cobalt(I) complexes mono-substituted with diphosphine ligands.

Keywords: Arylisocyanide; Diphosphine; Cobalt(I) complex; ^{31}P-NMR; Cyclic voltammetry

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1. Introduction

An important characteristic of diphosphine ligands is the way in which the spacer backbone can be varied to suit the various bonding modes required. For example, while 1,4-bis(diphenylphosphino)benzene cannot chelate, 1,2-bis(diphenylphosphino)benzene can easily chelate and its mode of chelation can differ from one complex to another. For an initially trigonal bipyramidal complex there are generally three classes of compounds that can be obtained by reacting these with a diphosphine ligand, chelate complexes, mono-coordinate complexes, and bridged complexes. An examination of the literature shows that most diphosphine complexes of trigonal bipyramidal geometry are chelated, assuming, of course, that the diphosphine can assume this mode of coordination. The abundance of such complexes is due to the extra stability arising from the chelate effect. Numerous diphosphines used in the hydroformylation process form chelate complexes of the type $[RhH(CO)_2P\text{-}P]$ [1]. Two diphosphines can replace four ligands forming a complex of the type $[M(P\text{-}P)_2L]^{n+}$, such as $[Co(NO)(P\text{-}P)_2](BF_4)_2$ (P-P = alkyl or phenyl substituted ditertiary phosphine) [2].

Chelated diphosphines can assume three possible modes of coordination, equatorial–equatorial, equatorial–axial, and axial–axial. The equatorial–equatorial and equatorial–axial isomers are usually present in equilibrium in solution, with the relative amounts depending on the steric and electronic nature of the diphosphine [1, 3].

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*Corresponding author. Email: Beckerca@mopipi.ub.bw

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The axial–axial isomer is uncommon, because such a complex requires a very wide bite angle diphosphine. $[RuCl(CO)(dppf)(PPh_3)]BF_4$ (dppf = 1,1′-bis(diphenylphosphino)-ferrocene) exhibits this coordination, although it may be better described as coordinately unsaturated with the sixth site sterically shielded by the ferrocene moiety [4].

Except for complexes with bis(diphenylphospino)methane, few complexes containing monodentate-coordinated diphosphines have been reported and these have not been systematically studied [5]. The complex $[Fe(PMe_2CH_2CH_2PMe_2)_3]$ is approximately trigonal bipyramidal, with one diphosphine coordinated in monodentate fashion in an equatorial position having the second P atom left dangling [6]. Such non-bonded P atoms can often coordinate to a second metal centre, producing a bridged bimetallic complex. In most cases the bridging diphosphine occupies equatorial sites in both metal fragments, as in $[\{Fe(PMe_2CH_2CH_2PMe_2)_2\}_2(\mu\text{-}PMe_2CH_2CH_2PMe_2)]$ [6]. In rare cases the diphosphine P atoms occupy axial positions in both metal centres, but then another small molecule usually spans the metal centres, as in $Rh_2(\mu\text{-}CO)(CO)_4(PEt_2CH_2CH_2PPhCH_2CH_2PEt_2)$ [7].

Diphosphine substitution in pentakis(arylisocyanide)cobalt(I) complexes having sterically hindered organoisocyanide ligands, $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ [8, 9] and $[Co(CNC_6H_3\mathit{i}Pr_2\text{-}2,6)_5]X$, $X = ClO_4$, BF_4 [10], appears to be somewhat exceptional to these trends. Numerous mono-coordinate monometallic and bridged bimetallic complexes of the types $[Co(CNR)_4P\text{-}P]X$ and $[(RNC)_4CoP\text{-}PCo(CNR)_4]X_2$, respectively, were synthesized, but with no observation of chelation taking place even for diphosphines such as $PPh_2CH_2CH_2PPh_2$ and $PPh_2CH_2CH_2CH_2PPh_2$. Attempted reactions of $P(C_6H_4Me\text{-}\mathit{p})_2CH_2CH_2P(C_6H_4Me\text{-}\mathit{p})_2$ and $P(C_6H_4CF_3\text{-}\mathit{p})_2CH_2CH_2P(C_6H_4CF_3\text{-}\mathit{p})_2$ with $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ failed to yield products [8]. The steric bulkiness of these arylisocyanides was credited with effectively blocking possible chelation [10], unlike the less sterically demanding *t*-butylisocyanide ligand in $[Co(CNCMe_3)_5]^+$ which allows multiple chelation by polydentate tertiary phosphines [11]. In this present work possible chelation reactions are re-investigated, using ligands such as $PPh_2C_6H_4PPh_2\text{-}\mathit{o}$ or $PPh_2CH{=}CHPPh_2\text{-}\mathit{cis}$ to encourage chelation and increasing reaction temperatures and/or times.

2. Experimental

2.1. *Reagents*

$PPh_2CH{=}CHPPh_2\text{-}\mathit{cis}$ and $PPh_2C_6H_4PPh_2\text{-}\mathit{o}$ were supplied by Sigma-Aldrich Chemie S.A. and used without further purification, while $P(C_6H_4Me\text{-}\mathit{p})_2CH_2CH_2P(C_6H_4Me\text{-}\mathit{p})_2$ and $P(C_6H_4CF_3\text{-}\mathit{p})_2CH_2CH_2P(C_6H_4CF_3\text{-}\mathit{p})_2$ were supplied by Strem Chemicals, Inc. Tetra-*n*-butylammonium perchlorate (electrochemical grade) was supplied by Fluka. $[Co(CNC_6H_3\mathit{i}Pr_2\text{-}2,6)_5]BF_4$ was synthesized as previously reported [10]. Anhydrous diethylether was filtered through an alumina column immediately before use.

2.2. *Instrumentation*

NMR measurements were performed on a Bruker Avance DPX 300 spectrometer. Chemical shift standards were internal tetramethylsilane for ^1H and external 85%

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H_3PO_4 for ^{31}P; the solvent was $CDCl_3$. Elemental analyses were carried out on a Vario EL CHNOS system. For cyclic voltammetry ~1.0 mM solutions of the compounds were prepared in dichloromethane containing 0.05 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. Cyclic voltammetry measurements were performed using a Metrohm 757 VA Computrace 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 −1.0 to 1.0 V *versus* Ag/AgCl at various scan rates, ranging from 0.05 to 0.25 V s^{-1}. Nitrogen gas was bubbled through each solution for 500 s prior to each run. IR spectra were measured in the 4000–400 cm^{-1} range with a Spectrum 2000 Perkin-Elmer FT-IR spectrophotometer using Nujol mulls and in solutions of spectroscopic grade CH_2Cl_2, CH_3NO_2 and CF_3CH_2OH. Electronic spectra were recorded using a Shimadzu UV-2401 PC spectrophotometer using CH_3CN, CF_3CH_2OH and CH_2Cl_2 as solvents. Mass spectrometry data were obtained using a Finnigan LCQ deca ion trap quadrupole mass spectrometer at atmospheric pressure and a capillary temperature of 300°C. The solvent used was CH_2Cl_2.

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2.3. *[Co(CNC$_6$H$_3$iPr$_2$-2,6)$_3$P(C$_6$H$_4$Me-p)$_2$CH$_2$CH$_2$P(C$_6$H$_4$Me-p)$_2$]BF$_4$ (1)*

To a filtered solution of $P(C_6H_4Me\text{-}p)_2CH_2CH_2P(C_6H_4Me\text{-}p)_2$ (208 mg, 0.46 mmol) in 1,2-dichloroethane (5.0 cm^3) was added solid $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$ (495 mg, 0.46 mmol). The mixture was allowed to react for 12 h at 75°C. During this time the solvent was replenished as necessary to keep the volume at ~5 cm^3. At the end of the reaction time diethylether (10.0 cm^3) was added and the unreacted $P(C_6H_4Me\text{-}p)_2CH_2CH_2P(C_6H_4Me\text{-}p)_2$ that precipitated was filtered off. Further addition of diethylether (20 cm^3) and allowing the solution to stand at room temperature for thirty minutes resulted in the formation of brownish crystals (298 mg). Allowing the filtrate from the above to stand in the refrigerator for one week afforded a second crop (47 mg). Total yield: 65%, m.p. 198–200°C (dec.). Anal. Calcd for $C_{69}H_{83}BCoF_4N_3P_2 \cdot 0.4CH_2Cl_2$ (%): C, 69.69; H, 7.06; N, 3.51. Found: C, 69.64; H, 7.40; N, 3.49.

2.4. *[Co(CNC$_6$H$_3$iPr$_2$-2,6)$_3$PPh$_2$CH=CHPPh$_2$-cis]BF$_4$ (2)*

$PPh_2CH{=}CHPPh_2$-*cis* (182 mg, 0.46 mmol) was dissolved in CH_2Cl_2 (2.0 cm^3) and the solution filtered through cotton to remove any undissolved material. Solid $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$ (500 mg, 0.46 mmol) was then added with continued stirring. The mixture was allowed to react at room temperature for 3 h. At the end of this period diethylether (25 cm^3) was added to precipitate a powder (420 mg). The crude residue was recrystallized from CH_2Cl_2 (2.0 cm^3) and diethylether (15 cm^3). Yield: 238 mg (47%), m.p. 244–246°C (dec.). Anal. Calcd for $C_{65}H_{73}BCoF_4N_3P_2 \cdot 0.5CH_2Cl_2$ (%): C, 68.62; H, 6.51; N, 3.67. Found: C, 68.81; H, 6.97; N, 3.96.

2.5. *[Co(CNC$_6$H$_3$iPr$_2$-2,6)$_3$PPh$_2$C$_6$H$_4$PPh$_2$-o]BF$_4$ (3)*

$PPh_2C_6H_4PPh_2$-*o* (71 mg, 0.16 mmol) was dissolved in CH_2Cl_2 (1.0 cm^3) and filtered through cotton. To the solution was added solid $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$

(172 mg, 0.16 mmol). After about three hours, diethylether (8.0 cm^3) was added and any trace of unreacted ligand removed by filtration. Further addition of diethylether (4.0 cm^3) and cooling in an ice bath for half an hour crystallized out all unreacted $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$. To the filtrate was added 20 cm^3 of diethylether and the solution cooled in an ice bath for 40 min. This afforded brown crystalline $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_3PPh_2C_6H_4PPh_2\text{-}\textit{o}]BF_4$, yield: 39 mg (31%), m.p. 280–282°C (dec.). Anal. Calcd for $C_{69}H_{75}BCoF_4N_3P_2 \cdot CH_2Cl_2$ (%): C, 67.86; H, 6.26; N, 3.39. Found: C, 68.81; H, 6.43; N, 3.26.

2.6. *$[Co(CNC_6H_3iPr_2\text{-}2,6)_3P(C_6H_4CF_3\text{-}p)_2CH_2CH_2P(C_6H_4CF_3\text{-}p)_2]BF_4$ (4)*

To a solution of $P(C_6H_4CF_3\text{-}\textit{p})_2CH_2CH_2P(C_6H_4CF_3\text{-}\textit{p})_2$ (186 mg, 0.28 mmol) dissolved in 1,2-dichloroethane (10.0 cm^3) was added $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$ (300 mg, 0.28 mmol). The mixture was allowed to react at 80°C for 15 h. At the end of the reaction time, the solvent was evaporated off. The solid obtained was dissolved in a minimum of CH_2Cl_2 (2.0 cm^3) and recrystallized by addition of diethylether (5.0 cm^3), chilling in ice for 30 min and filtering out the orange powder. Yield: 121 mg (32%), m.p. 208–210°C (dec.). Anal. Calcd for $C_{69}H_{71}BCoF_{16}N_3P_2 \cdot 0.2CH_2Cl_2$ (%): C, 59.58; H, 5.16; N, 3.01. Found: C, 59.41; H, 5.42; N, 3.06.

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3. Results and discussion

3.1. *Synthesis*

Chelate complexes were obtained when the diphosphine ligands $PPh_2CH{=}CHPPh_2\text{-}\textit{cis}$, $PPh_2C_6H_4PPh_2\text{-}\textit{o}$, $P(C_6H_4Me\text{-}\textit{p})_2CH_2CH_2P(C_6H_4Me\text{-}\textit{p})_2$ and $P(C_6H_4CF_3\text{-}\textit{p})_2CH_2CH_2P(C_6H_4CF_3\text{-}\textit{p})_2$ reacted with $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$, but in all instances the reactions required increased temperatures and/or reaction times as compared to previous diphosphine monosubstitution reactions with $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]X$, $X = ClO_4$, BF_4 [10], and with $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ [8]. Reactions with $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ do not appear viable at elevated temperatures, as attempted reaction even at 30–40°C indicated slight decomposition of this starting material. Reaction of $PPh_2CH_2CH_2PPh_2$ with $[Co(CNC_6H_3\textit{i}Pr_2\text{-}2,6)_5]BF_4$ at room temperature for 45 min indicated, from the ^{31}P NMR, slight amounts of a second product that could have been the chelate complex. This minor product was subsequently lost in recrystallization. Preparation of additional chelate complexes may be possible by allowing prolonged reaction times.

The non-*cis*-enforcing ligands $P(C_6H_4Me\text{-}\textit{p})_2CH_2CH_2P(C_6H_4Me\text{-}\textit{p})_2$ and $P(C_6H_4CF_3\text{-}\textit{p})_2CH_2CH_2P(C_6H_4CF_3\text{-}\textit{p})_2$ could not react at room temperature, but at elevated temperatures the energy barrier to chelation is apparently overcome. The $-CF_3$ substituents in $P(C_6H_4CF_3\text{-}\textit{p})_2CH_2CH_2P(C_6H_4CF_3\text{-}\textit{p})_2$ make the P atoms better π^*-accepting (weaker σ-donating) than in $PPh_2CH_2CH_2PPh_2$, but the –Me substituents in $P(C_6H_4Me\text{-}\textit{p})_2CH_2CH_2P(C_6H_4Me\text{-}\textit{p})_2$ should make these P atoms weaker π^*-accepting, so steric bulkiness, rather than inductive effects, should account for the decreased reactivity of these substituted diphosphines.

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3.2. *Electronic and infrared spectra*

The ν(–N≡C) IR patterns for the four chelate complexes in solid (Nujol) and solution (CH_2Cl_2, CF_3CH_2OH, CH_3NO_2) states are all very similar (table 1). This suggests analogous structures for the complexes and little structural change between solid and solution states. A maximum of three ν(–N≡C) bands is observed, and this would fit every reasonable structure based on idealized geometries; e.g. axial–equatorial substituted trigonal bipyramid: C_s, $2A' + A''$ allowed; equatorial–equatorial substituted trigonal bipyramid: C_{2v}, $2A_1 + B_1$ allowed; basal–basal substituted square pyramid: C_s; apical–basal substituted square pyramid: C_s. Therefore it is not possible to speculate about the structures of these complexes from infrared data alone. Electronic spectra (table 1) show one, two or three charge transfer bands at ~330–340, ~260–265, and ~230–235 nm, depending on the particular complex and solvent. Only intense charge transfer bands would be expected for these complexes.

3.3. *NMR spectroscopy*

^{31}P NMR data for the chelate complexes are shown in table 2. ^1H NMR was used to judge the purity of the compounds synthesized, prior to elemental analysis, by comparing the ratio of aromatic with non-aromatic proton integrals. Adducted CH_2Cl_2 could also be confirmed by ^1H NMR, the CH_2Cl_2 protons appearing at about 5.1 ppm in the proton spectrum. Chemical shift values for the chelates show a completely different pattern from those of the mono-substituted diphosphine complexes [10]. The P atoms in these complexes are generally more deshielded than those of the mono-substituted complexes, evidenced by larger coordination shifts, $\Delta\delta$. Because only singlets are obtained for the chelates, this could imply that they are equatorial–equatorial isomers since only then can the two P atoms become equivalent, if rigid trigonal bipyramidal geometry is assumed. However, with the noted preference for axial substitution in d^8 complexes [12], the structures of the chelate complexes may not be limited to trigonal bipyramidal. It is possible that upon reaction of the ligand with [Co($CNC_6H_3i Pr_2$-2,6)$_5$]X, the axial–equatorial isomer of [Co($CNC_6H_3iPr_2$-2,6)$_3$P-P]X is initially formed followed by pseudo-rotation to give an overall square pyramidal complex in which the two P atoms occupy basal positions (scheme 1). With slight distortion of bond angles there is really little actual difference between these two geometries.

3.4. *Cyclic voltammetry studies*

Cyclic voltammetric data for the chelate complexes are summarized in table 3. The oxidation of Co(I) to Co(II) occurs at E_{ox} values between 0.52 and 0.71 V *versus* Ag/AgCl, substantially lower than values for the mono-substituted mono- and bimetallic complexes (0.73–1.01 V) [10]. Since E_{ox} for [Co($CNC_6H_3iPr_2$-2,6)$_5$]BF_4 is 0.95 V *versus* Ag/AgCl (and only quasi-reversible), the chelate complexes are significantly easier to oxidize to the corresponding Co(II) complexes than is the non-substituted pentakis(arylisocyanide)cobalt(I) complex.

These cycles are reversible, using the non-variance of peak potentials with change in the scan rate as the criterion for reversibility [13–15]. The non-aqueous nature of the

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Table 1. Electronic and infrared data for the chelate compounds.

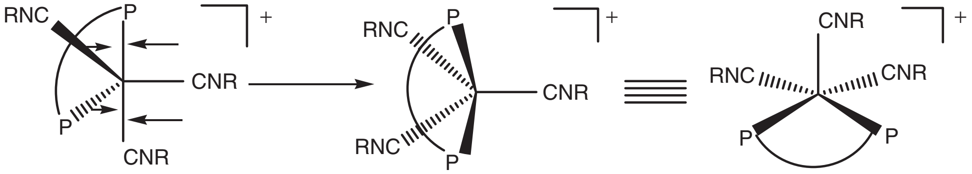
	Electronic spectra, λ_{max} (ε) in nm ($M\,cm^{-1}$)			Infrared spectra[a] ν(–N≡C) in cm^{-1}			
Compound	CH_2Cl_2	CF_3CH_2OH	CH_3CN	Nujol	CH_2Cl_2	CF_3CH_2OH	CH_3NO_2
1	342 (16,200)	339 (17,200)	338 (16,300)	2052 (s)	2058 (br)	2058 (s, br)	2054 (vs)
	261 (45,200)	263 (41,000)		2074 (w)	2079 (sh)	2081 (sh)	2077 (sh)
		231 (65,000)		2122 (m)	2126 (s)	2127 (s)	2125 (s)
2	333 (14,000)	329 (15,300)	331 (15,200)	2077 (vs, br)	2071 (vs)	2072 (vs)	2070 (v)
		261 (42,100)	263 (41,700)	2118 (s)	2087 (w)	2089 (sh)	2087 (sh)
					2132 (s)	2133 (s)	2131 (s)
3	330 (13,800)	330 (13,300)	330 (14,200)	2066 (s)	2068 (vs)	2070 (vs)	2068 (vs)
	265 (40,300)	261 (37,600)	263 (39,100)	2081 (w)	2083 (sh)	2086 (sh)	2083 (sh)
				2125 (m)	2127 (s)	2129 (s)	2127 (s)
4	335 (16,500)	334 (16,800)	340 (18,200)	2074 (s, br)	2072 (s)	2075 (vs)	2072 (vs)
	262 (40,900)	261 (38,700)	267 (39,600)	2092 (w)	2089 (sh)	2095 (sh)	2089 (sh)
			235 (61,700)	2130 (s)	2131 (s)	2133 (m)	2132 (s)

[a] For ν(–N≡C), s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, vs = very strong, br = broad.

Table 2. ^{31}P NMR data for the chelate compounds.

	^{31}P Chemical shift, δ (ppm)		
Compound	Chelate complex	Free ligand	$\Delta\delta^a$
1	80.9	−13.1	94.0
2	89.4	−21.9	111.3
3	77.9	−12.6	90.5
4	83.2	−11.8	95.0

$^a\Delta\delta$ is defined as the difference between the ^{31}P chemical shifts of the free ligand and the metal coordinated phosphorus.



Scheme 1. Pseudo-rotation of equatorial–axial [Co(CNC$_6$H$_3$*i*Pr$_2$-2,6)$_3$P-P]X to give a square pyramidal complex in which the diphosphine P atoms occupy basal sites.

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Table 3. Cyclic voltammetric data for the chelate compounds.^{a}

Compound	E_{ox}	E_{red}	$E_{1/2}$	ΔE
1	0.52	0.38	0.45	0.14
2	0.60	0.45	0.53	0.15
3	0.55	0.43	0.49	0.12
4	0.71	0.48	0.60	0.23

^{a}In *V vs.* Ag/AgCl in CH$_2$Cl$_2$ solution at the scan rate of 0.1 Vs^{-1}.

solvent (CH$_2$Cl$_2$) and the low concentration (0.05 M) of the background electrolyte cause the solutions to have high solution resistance between the working and reference electrodes. This ohmic (iR) drop [14], combined with the higher junction potential created across the ion bridge between the reference electrode and sample solution [16], contribute to the apparent non-conformity of non-aqueous systems to the criterion for reversibility in aqueous systems, $\Delta E < 57$ mV.

Consistent with data from similar compounds [17, 18], the stabilities of the Co(II) species formed in solution seem to depend on the electron donating capacity of the diphosphine ligand. E_{ox} for complex **1** is the lowest while E_{ox} for **4** is the highest, in line with expected behaviour. The electron withdrawing nature of the –CF$_3$ groups in P(C$_6$H$_4$CF$_3$-*p*)$_2$CH$_2$CH$_2$P(C$_6$H$_4$CF$_3$-*p*)$_2$ makes this ligand the strongest π^*-acceptor (weakest σ-donor), best able to stabilize Co(I) and poorest to stabilize Co(II). The electron donating –Me groups in P(C$_6$H$_4$Me-*p*)$_2$CH$_2$CH$_2$P(C$_6$H$_4$Me-*p*)$_2$, however, make this ligand the strongest σ-donor (weakest π^*-acceptor), best able to stabilize Co(II) with more-effective σ-donation. PPh$_2$CH=CHPPh$_2$-*cis* and PPh$_2$C$_6$H$_4$PPh$_2$-*o* are ligands with intermediate σ-donating/π^*-accepting capabilities.

Table 4. Characteristic fragments (*m*/*z* (% relative abundance)) of the chelate complexes.

Fragment	**1**	**2**	**3**	**4**
$[Co(CNR)_3PP]^+$	1074.0 (1.5)	1016.5 (1.4)	1065.9 (1.1)	1290.0 (2.3)
$[Co(CNR)_2PP]^+$	887.0 (12.4)	829.3 (4.0)	879.0 (19.3)	1103.1 (38.4)
$[Co(CNR)PP]^+$	700.0 (65.7)	642.1 (26.1)	692.0 (100)	916.2 (100)
$[CoPP]^+$	513.1 (100)	455.1 (100)	505.1 (24.6)	729.1 (12.1)
$[Co(CNR)_3]^+$		620.1 (28.7)		620.2 (2.1)
$[Co(CNR)_2]^+$		433.2 (83.1)		

3.5. *Mass spectrometry*

All peaks in the mass spectra were identified by the most intense peak in the isotope mass distribution. In all cases, experimental and calculated isotopic mass distributions agreed well. The fragmentation patterns for the complexes are shown in table 4. Fragments are represented in abbreviated form in order to show clearly the patterns of fragmentation. Unlike mass spectra for mono-substituted mono- and bimetallic complexes [10], the molecular ions for these chelate complexes are observed, albeit not as the most abundant peaks. The most abundant peaks are the two-coordinate $[CoPP]^+$ species for compounds **1** and **2**, and the three-coordinate $[Co(CNR)PP]^+$ species for **3** and **4**. This is analogous to data for mono-substituted Co(I) complexes having potentially chelating diphosphines, while the $[Co(CNR)_3]^+$ or $[Co(CNR)_2]^+$ species were the most abundant for complexes having diphosphines that cannot chelate, $PPh_2C{\equiv}CPPh_2$ and $PPh_2CH{=}CHPPh_2$-*trans* [10]. Why the $[Co(CNR)_2]^+$ and $[Co(CNR)_3]^+$ species are so abundant (83.1%, 28.7%, respectively) for compound **2** only is not understood. The $PPh_2CH{=}CHPPh_2$-*cis* ligand (**2**) would be expected to coordinate analogously to $PPh_2C_6H_4PPh_2$-*o* (**3**).

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