Synthesis and characterization of *Tetrakis*(Alkylisocyanide) *Bis*(Triarylphosphine)Cobalt(III) complexes by Labile ligand substitution in intermediate-spin six-coordinate Co(III) complexes

Clifford A. L. Becker[a]; Edward Eddie Mmatli[a]

[a] Department of Chemistry, University of Botswana, Gaborone, Botswana

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND CHARACTERIZATION OF *TETRAKIS*(ALKYLISOCYANIDE) *BIS*(TRIARYLPHOSPHINE)COBALT(III) COMPLEXES BY LABILE LIGAND SUBSTITUTION IN INTERMEDIATE-SPIN SIX-COORDINATE Co(III) COMPLEXES

CLIFFORD A.L. BECKER* and EDWARD EDDIE MMATLI

Department of Chemistry, University of Botswana, P/Bag 0022, Gaborone, Botswana

Three intermediate-spin six-coordinate Co(III) complexes, $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ (**1**), $[Co(CNC_6H_{11})_4(OSbPh_3)_2](ClO_4)_3$ (**2**), and $[Co(CNCH_2Ph)_4(OSbPh_3)_2](BF_4)_3$ (**3**), undergo rapid ligand substitution with selected triarylphosphines at 0°C. Complexes **1**, **2**, and **3** react with $P(C_6H_4OMe\text{-}p)_3$, **1** and **2** react with PPh_3, and **2** reacts with $P(C_6H_4Me\text{-}p)_3$, to produce *trans*-$[Co(CNR)_4(PR'_3)_2]X_3$ complexes in very high yields. Attempted reaction with $P(C_6H_4Cl\text{-}p)_3$ yields a Co(I) complex. The triarylphosphine-alkylisocyanide Co(III) complexes were characterized by magnetic susceptibility, and solution and solid state IR and electronic spectra. The Co(III) complexes are diamagnetic, but exhibit various degrees of reduction in different solvents.

Keywords: Alkylisocyanide; Triarylphosphine; Cobalt(III) complexes; Ligand substitution; Intermediate-spin complexes

INTRODUCTION

The inert nature of diamagnetic six-coordinate cobalt(III) complexes toward ligand substitution is well-known, this sluggish behaviour often restricting synthesis of Co(III) complexes to oxidation of the corresponding Co(II) complex [1]. High-spin (i.e., four unpaired electrons) or intermediate-spin (i.e., two unpaired electrons) six-coordinate Co(III) complexes, however, are not expected to follow this pattern of inert behaviour [2]. Three intermediate-spin Co(III) complexes, *trans*-$[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$ $\{\mu_{\text{eff}} = 3.58\,\text{BM}\}$ (**1**), *trans*-$[Co(CNC_6H_{11})_4(OSbPh_3)_2](ClO_4)_3$ $\{\mu_{\text{eff}} = 3.70\,\text{BM}\}$ (**2**), and *trans*-$[Co(CNCH_2Ph)_4(OSbPh_3)_2](BF_4)_3$ $\{\mu_{\text{eff}} = 3.30\,\text{BM}\}$ (**3**), have

---

*Corresponding author. Fax: +267-355-2482. E-mail: Beckerca@mopipi.ub.bw

been synthesized [3,4] and shown to undergo labile ligand substitution with trialkyl-phosphine ligands ($P(C_3H_7\text{-}n)_3$, $P(C_4H_9\text{-}n)_3$) [5,6]. The less stable species *trans*-[Co(CNCH_2Ph)_4{OAs(C_6H_4Me\text{-}p)_3}_2](ClO_4)_3 has also been prepared and shown to undergo labile ligand substitution, but intermediate-spin could not be confirmed over high-spin [7]. The white, diamagnetic (inert) Co(III) complexes, *trans*-[Co(CNR)_4 (PR'_3)_2]X_3, (PR'_3 = trialkylphosphine), previously synthesized in Co(II) disproportionation reactions [8], were chosen as initial target products because of their stability against reduction in solution. Labile ligand substitution with these intermediate-spin six-coordinate Co(III) complexes, however, should not be restricted to trialkylphosphine ligands.

In this article, ligand substitutions of the three intermediate-spin six-coordinate Co(III) complexes (**1**, **2**, and **3**) were investigated with selected triarylphosphine ligands. The [Co(CNR)_3(PR''_3)_2]X complexes (CNR = CNCMe_3, CNC_6H_{11}, CNCHMe_2, CNCH_2Ph; PR''_3 = P(C_6H_4OMe\text{-}p)_3, P(C_6H_4Me\text{-}p)_3, PPh_3; X = ClO_4, BF_4) are readily oxidized to [Co(CNR)_3(PR''_3)_2]X_2 complexes [9], so these specific triarylphosphine ligands may be able to stabilize Co(III)-alkylisocyanide complexes. Triarylphosphines with electron-withdrawing substituents, e.g., $P(C_6H_4Cl\text{-}p)_3$, $P(C_6H_4F\text{-}p)_3$, $P(C_6H_4CF_3\text{-}p)_3$, however, stabilize Co(I) complexes so strongly that oxidation to Co(II) is not observed [9], and would not be expected to stabilize Co(III) complexes. Alkylisocyanide–triarylphosphine mixed-ligand complexes of cobalt, previously confined primarily to the Co(I) oxidation state [10–16] with limited examples of Co(II) [9,17,18], may now be extended to the Co(III) state by ligand substitution.

EXPERIMENTAL

Reagents

Commercially available CNCH_2Ph (Aldrich) and CNC_6H_{11} (Fluka) were used without redistillation. Complexes **1**, **2**, and **3** were synthesized as previously reported [1,4]. As(C_6H_4Me\text{-}p)_3 was custom-synthesized by Strem Chemicals, Inc. P(C_6H_4OMe\text{-}p)_3, P(C_6H_4Me\text{-}p)_3, and P(C_6H_4Cl\text{-}p)_3 were purchased from Aldrich Chemicals. Anhydrous diethyl ether was filtered through an alumina column immediately before use.

Instrumentation

IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrophotometer. Solution electronic spectra were recorded on a Shimadzu UV-2501PC spectrometer over the range 1100–200 nm. Diffuse reflectance spectra of solid samples were measured using an integrating sphere (model ISR-240A) over the range 800–240 nm. Magnetic suscepti-bilities were measured at room temperature using a Johnson Matthey Alfa magnetic susceptibility balance. Elemental analyses were performed at the microanalytical laboratories of the University of Cape Town (SA) and the University of Durham (UK).

Cautionary Note

Some of the complexes reported in this article are perchlorate salts because Co(II) complexes of CNC_6H_{11} crystallize better with the ClO_4^- anion than with BF_4^-, while

$CNCH_2Ph$ complexes crystallize better as BF_4^- salts. Although these complexes have shown no explosive tendency, all perchlorate salts must be considered as potentially hazardous. Please see comments regarding the use of perchlorate salts [18].

$[Co(CNC_6H_{11})_4(PPh_3)_2](ClO_4)_3$ (4)

Complex **2** (300 mg, 0.196 mmol) was dissolved in CH_2Cl_2 (3.5 cm³), filtered through cotton with CH_2Cl_2 rinse (0.5 cm³), and chilled in ice. PPh_3 (180 mg, 0.686 mmol; 3.5 : 1 P : Co mol ratio) was added in small amounts to the stirred Co(III) solution. The colour of the reaction mixture changed from bright yellow to dark orange during ligand addition. Diethyl ether (5.0 cm³) was added in small aliquots to induce precipitation, and a bright lemon-yellow product was filtered off and washed twice with diethyl ether. Yield: 255 mg (87% for a 1 : 2 CH_2Cl_2 adduct), m.p. 184–188°C (dec). Anal. Calcd. for $C_{64}H_{74}Cl_3CoN_4O_{12}P_2 \cdot 1.2CH_2Cl_2$(%): C, 55.13; H, 5.42; N, 3.94. Found: C, 55.10; H, 5.34; N, 3.88. IR: $\nu(N{\equiv}C)$ 2241 vs, ~2195 vw(sh) cm⁻¹ (Nujol); 2239 vs(br), ~2196 w(sh) (CH_2Cl_2); 2232 vs, 2211 s, 2191 m (CH_3NO_2); 2231 s, 2209 s, 2187 s (CF_3CH_2OH). Electronic spectrum (reflectance): λ_{max} (**A**): ~630 sh (0.13), ~355 br (1.70), ≈315 sh (1.62), ≈245 (1.64) nm; λ_{max} (ε, $M^{-1}cm^{-1}$): 405 (19 000), ≈270 sh (8600), ≈255 sh (13 000) nm (CH_2Cl_2); 410 (9400), ~310 sh (4200), ≈272 sh (7700), ≈265 sh (9700), ≈259 sh (10 000) (CH_3CN); 412 (4300), ~315 sh (5100), ≈286 sh (5800), ≈271 sh (7600), ≈264 sh (8900), ~218 sh (53 000) (CF_3CH_2OH). Magnetic susceptibility: $\chi_g = -286 \pm 38 \times 10^{-9}$ (cgs), $\chi_M = -380 \pm 50 \times 10^{-6}$ (cgs).

Analogous synthesis of $[Co(CNCH_2Ph)_4(PPh_3)_2](BF_4)_3$ (**5**) was performed by reaction of **1** (400 mg, 0.264 mmol) with PPh_3 (242 mg, 0.953 mmol). Yield: 346 mg (94% for a 1 : 1 CH_2Cl_2 adduct), bright lemon-yellow powder; m.p. 136–142°C (dec). Anal. Calcd. for $C_{68}H_{58}B_3CoF_{12}N_4P_2 \cdot 0.15CH_2Cl_2$(%): C, 61.77; H, 4.43; N, 4.23. Found: C, 61.73; H, 4.43; N, 4.26. IR: $\nu(N{\equiv}C)$ 2251 vs, ~2211 w(sh) cm⁻¹ (Nujol); 2091 vs, ≈2142 vw(sh), 2191 w (CH_2Cl_2); 2243 w, 2222 w, 2200 s, 2175 vw, ~2132 w(sh), 2117 s (CH_3NO_2); 2250 vs, 2218 w, 2197 s (CF_3CH_2OH). Electronic spectrum: λ_{max} (**A**): ~620 sh (0.17), ≈430 br, sh (1.44), ~368 br (1.90) nm; λ_{max} (ε, $M^{-1}cm^{-1}$): 411 (18 000), 306 (6700), ~258 sh (16 000), 230 (40 000) nm (CH_2Cl_2); 412 (18 000), ~357 (5800), 291 (4900), 272 (5500), 266 (6500), 260 (6200), ~222 sh (52 000) (CH_3CN); 415 (14 000), ≈330 sh (7000), ≈258 sh (16 000), ≈240 sh (26 000) (CF_3CH_2OH). Magnetic susceptibility: $\chi_g = -165 \pm 15 \times 10^{-9}$ (cgs), $\chi_M = -220 \pm 20 \times 10^{-6}$ (cgs). Attempted synthesis of **5** by reaction of **3** (250 mg, 0.164 mmol) with PPh_3 (150 mg, 0.573 mmol) at 0°C yielded only unreacted **3** (215 mg, 86%).

$[Co(CNCH_2Ph)_4\{P(C_6H_4OMe-p)_3\}_2](BF_4)_3$ (6)

Complex **1** (225 mg, 0.148 mmol) was dissolved in CH_2Cl_2 (6.5 cm³ total), filtered through cotton and chilled in ice. $P(C_6H_4OMe-p)_3$ (183 mg, 0.519 mmol; 3.5 : 1 P : Co mol ratio) was slowly added to the stirred Co(III) solution. The colour of the reaction mixture rapidly changed from bright yellow to dark red-orange during ligand addition. Diethyl ether (15.0 cm³) was added in small aliquots, and a red-orange solid was filtered and washed twice with diethyl ether. Yield: 195.4 mg (84% for a 1 : 1 CH_2Cl_2 adduct), m.p. 183–185°C (dec). Anal. Calcd. for $C_{74}H_{70}B_3CoF_{12}N_4O_6P_2 \cdot 0.15CH_2Cl_2$(%): C, 59.16; H, 4.71; N, 3.72. Found: C, 59.10; H, 4.73; N, 3.76. IR: $\nu(N{\equiv}C)$ 2258 s,

2245 vs, ~2215 vw(sh), ~2208 vw(sh) cm^{-1} (Nujol); ~2245 w, ~2188 w(sh), 2173 w, ~2136 w(sh), 2110 m (CH$_2$Cl$_2$); 2244 s, 2196 w, ~2162 vw, ~2112 vw (CH$_3$NO$_2$); 2242 s, 2214 m, 2193 s (CF$_3$CH$_2$OH). Electronic spectrum: λ_{max} (**A**): ≈500 sh (1.58), ~420 br (1.95), ~375 sh (1.88), ~270 sh (1.67), ~250 (1.77) nm; λ_{max} (ε, M^{-1} cm^{-1}): 476 (30 000), ≈385 sh (9800), 262 (75 000), 248 (74 000) nm (CH$_2$Cl$_2$); 481 (17 000), ≈395 sh (6600), 264 (45 000), 246 (61 000) (CH$_3$CN); 487 (8700), 397 (5800), ≈278 sh (24 000), ≈269 sh (36 000), 245 (76 000) (CF$_3$CH$_2$OH). Magnetic susceptibility: $\chi_g = -140 \pm 20 \times 10^{-9}$ (cgs), $\chi_M = -210 \pm 30 \times 10^{-6}$ (cgs).

Analogous synthesis of **6** was performed by reaction of **3** (215 mg, 0.141 mmol) with P(C$_6$H$_4$OMe-p)$_3$ (174 mg, 0.494 mmol). Yield: 204 mg (92%), m.p. 175–180°C (dec). Anal. Calcd. for C$_{74}$H$_{70}$B$_3$CoF$_{12}$N$_4$O$_6$P$_2$·1.0CH$_2$Cl$_2$(%): C, 57.10; H, 4.60, N, 3.55. Found: C, 56.85; H, 4.45; N, 3.62. Magnetic susceptibility: $\chi_g = -110 \pm 20 \times 10^{-9}$ (cgs), $\chi_M = -165 \pm 30 \times 10^{-6}$ (cgs).

[Co(CNC$_6$H$_{11}$)$_4${P(C$_6$H$_4$OMe-p)$_3$}$_2$](ClO$_4$)$_3$ (7)

Complex **2** (300 mg, 0.196 mmol) was dissolved in CH$_2$Cl$_2$ (5.0 cm^3 total) and chilled in ice. P(C$_6$H$_5$OMe-p)$_3$ (242 mg, 0.687 mmol; 3.5 : 1 P : Co mol ratio) was added to the stirred Co(III) solution. The colour of the reaction mixture changed from bright yellow to dark blood-red during ligand addition. Diethyl ether (15.0 cm^3) was added in small aliquots and a vermilion red powder was immediately filtered and washed thrice with diethyl ether. The crude product (289 mg) was then dissolved in CF$_3$CH$_2$OH (12.0 cm^3 total), precipitated with diethyl ether (22.0 cm^3), immediately filtered and washed thrice with diethyl ether. This sample (255 mg) was recrystallized again from CF$_3$CH$_2$OH (8.0 cm^3) and diethyl ether (13.0 cm^3). Yield: 228 mg (78%), red-orange powder, m.p. 178–186°C (dec). Anal. Calcd. for C$_{70}$H$_{86}$Cl$_3$CoN$_4$O$_{18}$P$_2$(%): C, 56.10; H, 5.78; N, 3.74. Found: C, 55.77; H, 5.72; N, 3.74. IR: ν(N≡C) 2237 vs, ~2198 vw(sh) cm^{-1} (Nujol); 2237 vs, ~2192 vw (CH$_2$Cl$_2$); 2232 vs (CH$_3$NO$_2$); 2232 vs, ~2182 vw(sh) (CF$_3$CH$_2$OH). Electronic spectrum: λ_{max} (**A**): ≈500 sh (1.68), 439 (1.82), ~385 sh (1.76), ≈310 sh (1.61), ~253 (1.70) nm; λ_{max} (ε, M^{-1} cm^{-1}): 470 (12 000), ≈400 sh (5400), 249 (71 000) nm (CH$_2$Cl$_2$); 476 (24 500), ≈398 sh (10 000), ~262 (57 000), 246 (62 000) (CH$_3$CN); 487 (13 500), ~412 sh (6300), ≈270 sh (42 000), 246 (73 000) (CF$_3$CH$_2$OH). Magnetic susceptibility: $\chi_g = 0.39 \pm 0.02 \times 10^{-6}$ (cgs), $\chi_M = 580 \pm 30 \times 10^{-6}$ (cgs).

[Co(CNC$_6$H$_{11}$)$_4${P(C$_6$H$_4$Me-p)$_3$}$_2$](ClO$_4$)$_3$ (8)

Complex **2** (250 mg, 0.163 mmol) was dissolved in CH$_2$Cl$_2$ (3.5 cm^3 total) and chilled in ice. P(C$_6$H$_5$Me-p)$_3$ (174 mg, 0.572 mmol; 3.5 : 1 P : Co mol ratio) was slowly added to the stirred Co(III) solution. The colour of the reaction mixture changed from bright yellow to dark yellow upon ligand addition. Diethyl ether was added in small aliquots. Extensive precipitation occurred after addition of 10.0 cm^3, so the golden-yellow product was immediately filtered off and washed twice with diethyl ether. Yield: 210 mg (87% for a 1 : 1 CH$_2$Cl$_2$-adduct), m.p. 192–200°C (dec). Anal. Calcd. for C$_{70}$H$_{86}$Cl$_3$CoN$_4$O$_{12}$P$_2$·0.8CH$_2$Cl$_2$(%): C, 57.82; H, 6.00; N, 3.81. Found: C, 57.80; H, 5.93; N, 3.76. IR: ν(N≡C) 2245 vs cm^{-1} (Nujol); 2240 vs, ~2190 w (CH$_2$Cl$_2$); 2235 vs, ~2190 w cm^{-1} (CH$_3$NO$_2$); 2235 vs, ~2185 w (CF$_3$CH$_2$OH). Electronic spectrum: λ_{max} (**A**): ~448 sh (1.82), ~388 (2.01), ≈355 sh (1.96), ~261 (1.80) nm;

λ_{max} (ε, M^{-1} cm^{-1}): 423 (3600), $\sim$331 sh (4100), $\sim$270 sh (10 000), 234 (65 000) nm (CH$_2$Cl$_2$); 431 (6600), $\approx$332 (3100), $\approx$267 sh (8700), $\approx$234 sh (43 000), $\approx$224 sh (52 000) (CH$_3$CN); 437 (3900), 333 (3200), $\approx$287 sh (4100), 232 (69 000) (CF$_3$CH$_2$OH). Magnetic susceptibility: $\chi_g = 0.058 \pm 0.03 \times 10^{-6}$ (cgs), $\chi_M = 80 \pm 40 \times 10^{-6}$ (cgs).

RESULTS AND DISCUSSION

Synthesis of the Complexes

Reactions of the three intermediate-spin Co(III) complexes with selected triarylphosphine ligands gave anticipated, and some unanticipated, results. All ligand substitutions that took place were labile. The inert nature of six-coordinate Co(III) complexes toward ligand substitution thus applies to diamagnetic complexes only, and cannot be extended to intermediate-spin complexes. Attempted reaction of P(C$_6$H$_4$Cl-p)$_3$ with **1** yielded unreacted **1** (39%) and modest isolation (29%) of the Co(I) complex, but absence of any Co(II) or Co(III) species. This confirms the initial suggestion that triarylphosphines with electron-withdrawing substituents will not stabilize Co(III) complexes.

Tri-p-methoxyphenylphosphine is the best ligand to produce Co(III) complexes, giving high yields in reactions with **1**, **2**, and **3**, the initial product with **2** being contaminated by [Co(CNC$_6$H$_{11}$)$_3${P(C$_6$H$_4$OMe-p)$_3$}$_2$](ClO$_4$)$_2$ (i.e., IR(Nujol) ν(C$\equiv$N) 2188 br, sh cm^{-1}) [9]. Double recrystallization from CF$_3$CH$_2$OH/diethyl ether, using twice the minimum required volume of CF$_3$CH$_2$OH, provided a pure sample. The initial product was a CF$_3$CH$_2$OH-adduct (i.e., IR(Nujol) ν(O–H) 3445 w cm^{-1}), giving high apparent yield. Adduct formation with CH$_2$Cl$_2$ may also contribute to artificially high yields for the other complexes.

Triphenylphosphine gave high yields of **5** and **4** with **1** and **2**, respectively, but failed to react with **3**. The saturated solution of **3** is more dilute than **1** or **2** (about 0.013, 0.049, and 0.025 M, respectively), but this is not expected to have a drastic effect. In these reactions there appears to be an order of reactivity, **2** > **1** > **3**. Since reaction times must be kept short to minimize decomposition of the starting materials and/or reduction of the Co(III) products, insufficient time may have been available for this reaction to occur.

Tri-p-tolyphosphine appears to be least reactive in promoting ligand substitution. Rapid reactions with **1** and **3** yield only starting material. Products from prolonged reaction with **3** failed to precipitate, but residues from the evaporated solution indicated Co(II) and Co(I) species (i.e., IR (CF$_3$CH$_2$OH} ν(N$\equiv$C) 2195 s, 2089 vs cm^{-1}), but not Co(III). Reaction with **2** required a slightly longer time. Products with shorter reaction times showed a weak IR(Nujol) ν(N$\equiv$C) $\sim$2231–2232 (sh) cm^{-1}, which may be due to unreacted **2**. Triarylphosphine stabilization of the Co(III) complexes is expected to be in the order P(C$_6$H$_4$OMe-p)$_3$ > P(C$_6$H$_4$Me-p)$_3$ > PPh$_3$, so possibly a kinetic, rather than a thermodynamic, effect is observed.

IR Spectra

IR patterns with respect to ν(N$\equiv$C) in Nujol mull for **6**, **5**, and **8** are pictured in Fig. 1. Patterns of one strong band with a lower- or higher-energy shoulder are compatible with tetragonal coordination; i.e., *trans*-[Co(CNR)$_4$(PR$'_3$)$_2$]X$_3$. Rigorous D_{4h} symmetry
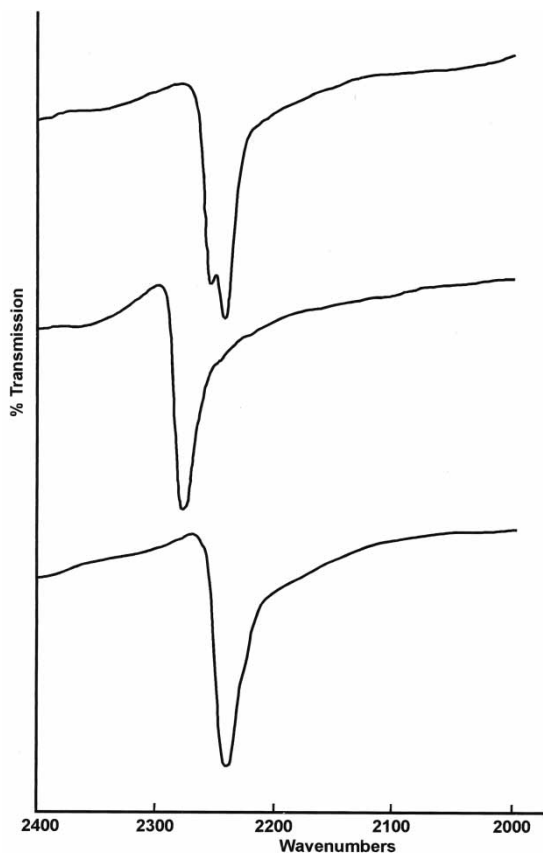
FIGURE 1 The $\nu(N\equiv C)$ IR patterns for $[Co(CNCH_2Ph)_4\{P(C_6H_4OMe\text{-}p)_3\}_2](BF_4)_3$, $[Co(CNCH_2Ph)_4 (PPh_3)_2](BF_4)_3$, and $[Co(CNC_6H_{11})_4\{P(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_3$, top to bottom, respectively, in Nujol mull.

of the $Co(CNR)_4$ moiety requires a single $\nu(N\equiv C)$ band (i.e., E_u), so the weak shoulder suggests slight distortion.

The $\nu(N\equiv C)$ values for complexes with the same CNR ligand lie within a narrow range, often not highly shifted from starting materials. When $OAs(C_6H_4Me\text{-}p)_3$ in **1** is replaced by $P(C_6H_4OMe\text{-}p)_3$, $\Delta\nu(N\equiv C) = -13\,cm^{-1}$; by PPh_3, $-7\,cm^{-1}$; $OSbPh_3$ in **2** replaced by $P(C_6H_4OMe\text{-}p)_3$, $+8\,cm^{-1}$; by PPh_3, $+12\,cm^{-1}$; by $P(C_6H_4Me\text{-}p)_3$, $+16\,cm^{-1}$; $OSbPh_3$ in **3** replaced by $P(C_6H_4OMe\text{-}p)_3$, $+2\,cm^{-1}$. $\Delta\nu(N\equiv C)$ values for **7**, **4**, and **8**, implying $P(C_6H_4OMe\text{-}p)_3 > PPh_3 > P(C_6H_4Me\text{-}p)_3$, correlate the unexpected relative reactivities of these triarylphosphines. The $Co(CNR)_4$ moiety seems to be only slightly affected by significant changes in axial ligands, suggesting, possibly, only weak coordination by the axial ligands.

Solution IR spectra in CH_2Cl_2, CH_3NO_2, and CF_3CH_2OH show various degrees of reduction to Co(II) and/or Co(I) species. Complexes **7** and **8** are essentially stable in all three solvents, **4** in CH_2Cl_2 only. Complex **4** in CH_3NO_2 and CF_3CH_2OH, **6** in all solvents, and **5** in CF_3CH_2OH, exhibit Co(III) and Co(II) species, while **5** in CH_2Cl_2 and CH_3NO_2 appears to be extensively reduced to Co(I). The $CNCH_2Ph$ complexes are less stable in solution than CNC_6H_{11} complexes. Solution $\nu(N\equiv C)$ may be shifted up to $10\,cm^{-1}$ lower than in Nujol.

Magnetic Susceptibilities

The triarylphosphine-substituted Co(III) complexes, unlike their starting materials, are diamagnetic. Measured diamagnetism is less negative than diamagnetic corrections for the composite ions and ligands, however [8,9,19,20]; $\chi_M(4)$, -380×10^{-6} ($vs - 721 \times 10^{-6}$); $\chi_M(5)$, -220×10^{-6} ($vs - 720 \times 10^{-6}$); $\chi_M(6)$, -210 and -165×10^{-6} ($vs - 788 \times 10^{-6}$). Complexes **7** and **8** show apparent paramagnetism, $\chi_M(7)$, $+ 580 \times 10^{-6}$; $\chi_M(8)$, $+ 80 \times 10^{-6}$; but μ_{eff} calculated from these values, 1.77, 1.38 BM, respectively, are unrealistic for intermediate- or high-spin Co(III). Results for **7** are anomalous probably because **7** had to be recrystallized. These complexes are easily recrystallized from CH_2Cl_2/diethyl ether, with no change in IR pattern, but with apparent introduction of slight paramagnetism.

Electronic Spectra

Diffuse reflectance spectra for the triarylphosphine complexes are similar to those for the trialkylphosphine complexes [8,21], with shift to longer wavelengths accounting for the intense lemon-yellow (**4**, **5**), golden-yellow (**8**), red-orange (**6**), and red (**7**) colours observed, while the trialkylphosphine complexes are pure white. For the PPh₃ complexes (**4**, **5**) a weak shoulder ∼620 nm may be a d–d transition; otherwise the spectra consist of charge-transfer bands.

Solution electronic spectra (Fig. 2 shows **7** in CH_3CN) are more complex than spectra for the trialkylphosphine complexes [8,21]. A pattern of one band, ∼490–400 nm, with a shoulder, ∼400–300 nm, and one or more high-energy, intense bands emerges for all
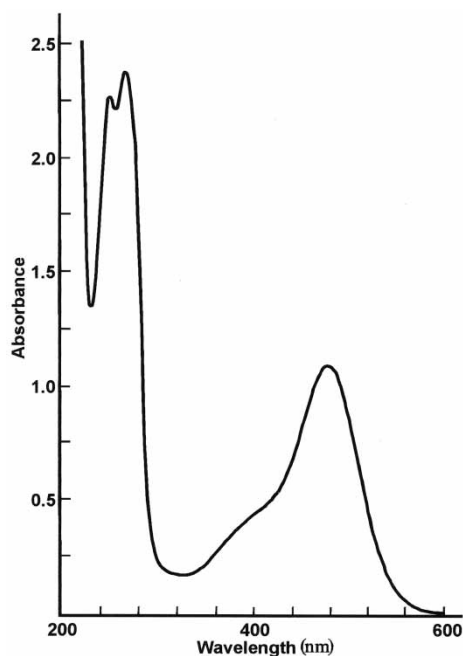

FIGURE 2   The electronic spectrum for $[Co(CNC_6H_{11})_4\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_3$ {4.2×10^{-5} M} in CH_3CN solution.

complexes in all solvents. The first band is dependent on PR_3', $P(C_6H_4OMe\text{-}p)_3 \gg P(C_6H_4Me\text{-}p)_3 > PPh_3$, independent of CNR, but slightly solvent dependent, $CH_2Cl_2 < CH_3CN < CF_3CH_2OH$. From the ε values (which may be low due to partial reduction in solution) all bands must be charge-transfer in nature. Cobalt(I) complexes, formed by reduction in solution, have very intense charge transfer bands that may contribute to the intensity seen in the UV region. If the first band is a ligand $\rightarrow$ metal charge transfer, the triarylphosphine ligands are expected to show increasing electron-donating ability, $PPh_3 < P(C_6H_4Me\text{-}p)_3 < P(C_6H_4OMe\text{-}p)_3$, thereby decreasing the energy of this band.

Acknowledgments

References

[1] N.N. Greenwood and A. Earnshaw, Chemistry of the Elements (Butterworth-Heinemann, Oxford, 1997), 2nd Edn., p. 1123.
[2] G.L. Miessler and D.A. Tarr, Inorganic Chemistry (Prentice-Hall, Upper Saddle River, N.J., 1999), 2nd Edn., pp. 384–393.
[3] C.A.L. Becker, *Inorg. Chim. Acta* **203**, 175 (1993).
[4] C.A.L. Becker, G.S. Sebobi and N.T. Simane, *Inorg. Chim. Acta* **334**, 327 (2002).
[5] C.A.L. Becker and S. Motladiile, *Synth. React. Inorg. Met.-Org. Chem.* **31**, 1545 (2001).
[6] C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.* (in press).
[7] C.A.L. Becker and O.C. Malete, *Synth. React. Inorg. Met.-Org. Chem.* **33**, 1635 (2003).
[8] C.A.L. Becker and M.A.S. Biswas, *J. Coord. Chem.* **29**, 277 (1993).
[9] C.A.L. Becker, *J. Coord. Chem.* **50**, 89 (2000).
[10] R.B. King and M.S. Saran, *Inorg. Chem.* **11**, 2112 (1972).
[11] J.W. Dart, M.K. Lloyd, R. Mason, J.A. McCleverty and J. Williams, *J. Chem. Soc.*, *Dalton Trans.* 1747 (1973).
[12] E. Bordignon, U. Croatto, U. Mazzi and A.A. Orio, *Inorg. Chem.* **13**, 935 (1974).
[13] C.A.L. Becker, A. Anisi, G. Myer and J.D. Wright, *Inorg. Chim. Acta* **111**, 11 (1986).
[14] C.A.L. Becker, S.A. Al-Qallaf and J.C. Cooper, *Inorg. Chim. Acta* **188**, 99 (1991).
[15] I. Beaumont and A.H. Wright, *J. Organomet. Chem.* **425**, C11 (1991).
[16] C.A.L. Becker and K.R. Barqawi, *J. Coord. Chem.* **34**, 273 (1995).
[17] C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.* **22**, 99 (1992).
[18] C.A.L. Becker, *Synth. React. Inorg. Met.-Org. Chem.* **27**, 1527 (1997).
[19] B.N. Figgis and J. Lewis, In: J. Lewis and R.G. Wilkins (Eds.), Modern Coordination Chemistry (Interscience, New York, 1960), Ch. 6.
[20] JM Magnetic Susceptibility Balance Instruction Manual (Johnson Matthey Chemicals, York Way, Royston, Hertfordshire, UK).
[21] C.A.L. Becker, M.A.S. Biswas and J.C. Cooper, *Inorg. Chim. Acta* **188**, 191 (1991).