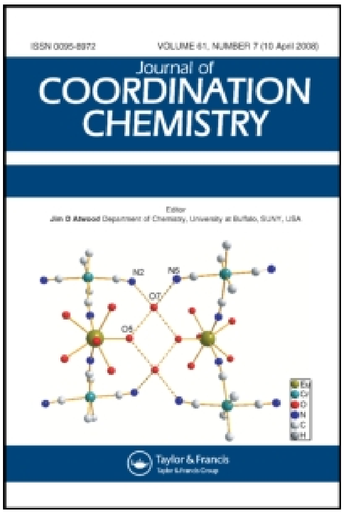

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SYNTHESIS AND LIGAND SUBSTITUTION OF *TETRAKIS*(ALKYLISOCYANIDE) *BIS*(TRI-2-FURYLPHOSPHINE)-COBALT(III) COMPLEXES

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The complexes $[Co(CNC_6H_{11})_4\{P(C_4H_3O)_3\}_2](ClO_4)_3$ and $[Co(CNCH_2Ph)_4\{P(C_4H_3O)_3\}_2](BF_4)_3$ have been synthesized by ligand substitution of tri-2-furylphosphine in the intermediate-spin complexes $[Co(CNC_6H_{11})_4(OSbPh_3)_2](ClO_4)_3$ and $[Co(CNCH_2Ph)_3(OSbPh_3)_2](BF_4)_3$, respectively. Physical properties are reported. These diamagnetic complexes undergo labile ligand-substitution reactions with trialkylphosphines [$P(C_3H_7\text{-}n)_3$, $P(C_4H_9\text{-}n)_3$], producing the complexes $[Co(CNR)_4(PR'_3)_2]X_3$ in good yields at room temperature, This behaviour is in apparent contradiction to the inert nature expected for diamagnetic, six-coordinate Co(III) complexes.

Keywords: Tri-2-furylphosphine; Alkylisocyanide; Cobalt(III) complexes; Ligand substitution; Labile reactions

INTRODUCTION

While almost all known six-coordinate Co(III) complexes are diamagnetic, three alkylisocyanide complexes have been identified as intermediate-spin (*i.e.*, two electron paramagnetic), $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](BF_4)_3$(**1**), $\mu_{eff} = 3.58$ BM [1], $[Co(CNC_6H_{11})_4(OSbPh_3)_2](ClO_4)_3$ (**2**), $\mu_{eff} = 3.70$ BM [2], and $[Co(CNCH_2Ph)_4(OSbPh_3)_2](BF_4)_3$ (**3**), $\mu_{eff} = 3.30$ BM [2], with a fourth complex, $[Co(CNCH_2Ph)_4\{OAs(C_6H_4Me\text{-}p)_3\}_2](ClO_4)_3$ (**4**), appearing to be high-spin [3]. The inert nature of diamagnetic six-coordinate cobalt(III) complexes toward ligand substitution is well established, but intermediate-spin complexes are not expected to share this rule of inert behaviour [4–7] and have been shown to undergo labile ligand substitution.

Complex **1** was initially observed to rapidly substitute trialkylphosphines (*i.e.*, $P(C_3H_7\text{-}n)_3$ and $(P(C_4H_9\text{-}n)_3)$ at room temperature [8], leading to the previously known, stable Co(III) complexes $[Co(CNCH_2Ph)_4(PR'_3)_2](BF_4)_3$ [9], but yields were significantly increased when reactions were repeated at low temperatures [10]. Complexes **2**, **3** and **4** were also shown to rapidly substitute the trialkylphosphines

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at 0°C [3,10]. Complexes **1**, **2** and **3** are observed to react rapidly with $(P(C_6H_4OMe\text{-}p)_3$, **1** and **2** with PPh_3, and **2** with $(P(C_6H_4Me\text{-}p)_3$, at 0°C, to produce $[Co(CNR)_4(PR''_3)_2]X_3$ complexes in high yields [11]. Reactions that failed to substitute rapidly yielded unreacted starting material, or, upon prolonged reaction, a Co(I) or Co(II) complex [11].

Tri-2-furylphosphine, $P(C_4H_3O)_3$, is not a trialkylphosphine or a triarylphosphine, but is intermediate to these two classes of tertiary phosphines, and may also ligand substitute in these intermediate-spin six-coordinate Co(III) complexes. This paper reports ligand substitutions and some apparently labile ligand substitutions of the products obtained.

EXPERIMENTAL

Reagents

Commercially available $CNCH_2Ph$ (Aldrich) and CNC_6H_{11} (Fluka) were used without redistillation. Complexes **2** and **3** were synthesized as previously reported [2]. $P(C_3H_7\text{-}n)_3$ (Aldrich) and $P(C_4H_9\text{-}n)_3$ (Fluka) were used without redistillation. $P(C_4H_3O)_3$ was 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 FTIR spectrophotometer. Solution electronic spectra were recorded on a Shimadzu UV-2501PC spectrophotometer 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 susceptibilities 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).

Cautionary Note

Some of the complexes reported in this paper are perchlorate salts because Co(II) complexes of CNC_6H_{11} crystallize better with the ClO_4^- anion than 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 the comments regarding the use of perchlorate salts [12].

$[Co(CNC_6H_{11})_4\{P(C_4H_3O)_3\}_2](ClO_4)_3$ (5)

Complex **2** (400 mg, 0.261 mmol) was dissolved in CH_2Cl_2 (6.5 cm^3) and filtered through cotton with CH_2Cl_2 (1.0 cm^3 rinse). $P(C_4H_3O)_3$ (212 mg, 0.913 mmol; *i.e.*, 3.5:1 P:Co mol ratio) was slowly added to the stirred Co(III) solution at room temperature. The colour of the reaction mixture rapidly changed from bright yellow to intense orange. Diethyl ether (4.0 cm^3) was added in small aliquots to induce precipitation, and the reaction mixture was chilled in ice (20 min) before a bright-orange powder was filtered from a golden-yellow filtrate and washed twice with diethyl ether. Yield: 310 mg (94%), m.p. 138–142°C (dec). Anal. Calcd. for $C_{52}H_{62}Cl_3CoN_4O_{18}P_2$(%): C, 49.64; H, 4.97; N, 4.45. Found: C, 49.26; H, 4.83; N, 4.43.

IR (cm^{-1}): ν(N≡C) 2252 vs (Nujol); 2253 vs (CH_2Cl_2); 2250 w(sh), 2226 vs, ≈2206 w(sh), 2155 w, 2109 w (CH_3NO_2); 2250 vs, 2223 w, 2205 m (CF_3CH_2OH). Electronic spectrum (reflectance): λ_{max} (A): 495 (1.64), ~391 (1.84), ≈343 sh (1.78) nm; λ_{max}(ε, $M^{-1}cm^{-1}$): 437 (23 000), ≈370 sh (8300), 243 (42 000) nm (CH_2Cl_2); 438 (25 000), ≈372 sh (9000), 244 (41 000) nm (CH_3CN); 438 (18 000), ≈370 sh (7700), 240 (41 000) nm (CF_3CH_2OH). Magnetic susceptibility: $\chi_g = -195 \pm 15 \times 10^{-9}$ (cgs), $\chi_m = -250 \pm 20 \times 10^{-6}$ (cgs).

$[Co(CNCH_2Ph)_4\{P(C_4H_3O)_3\}_2](BF_4)_3$ (6)

Complex **3** (400 mg, 0.262 mmol) was dissolved in CH_2Cl_2 (26 cm^3) and filtered through cotton with CH_2Cl_2 (0.5 cm^3 rinse). $P(C_4H_3O)_3$ (213 mg, 0.917 mmol; *i.e.*, 3.5:1 P:Co mol ratio) was slowly added to the stirred Co(III) solution at room temperature. The colour of the reaction mixture rapidly changed from light yellow to dark orange during the ligand addition. Diethyl ether (25 cm^3) was added in small aliquots, and the reaction mixture was chilled in ice (20 min) before a bright-orange, flocculent solid was filtered from a light-yellow filtrate and washed twice with diethyl ether. Yield: 306 mg (93%), m.p. 124–130°C (dec). Anal. Calcd. for $C_{56}H_{46}B_3CoF_{12}N_4O_6P_2$(%): C, 53.71; H, 3.70; N, 4.47. Found: C, 53.68; H, 3.68; N, 4.35.

IR (cm^{-1}): ν(N≡C) 2263 vs (Nujol); 2231 m, 2200 w, 2165 s, 2130 s (CH_2Cl_2); 2237 m, 2166 s, 2131 s (CH_3NO_2); ≈2252 vw(sh), 2232 vs, 2215 s (CF_3CH_2OH). Electronic spectrum (reflectance): λ_{max} (A): ≈472 sh (1.64), ~392 (1.90), ≈355 sh (1.87) nm; λ_{max} (ε, $M^{-1}cm^{-1}$): 442 (17 000), ~374 sh (6900), 243 (37 000) nm (CH_2Cl_2); 446 (18 000), ~378 sh (8000), 243 (39 000) nm (CH_3CN); 448 (5900), ~334 sh (6100), 283 (16 000), 238 (48 000) nm (CF_3CH_2OH). Magnetic susceptibility: $\chi_g = -180 \pm 30 \times 10^{-9}$ (cgs), $\chi_m = -230 \pm 40 \times 10^{-6}$ (cgs).

$[Co(CNC_6H_{11})_4\{P(C_3H_7\text{-}n)_3\}_2](ClO_4)_3$

Complex **5** (290 mg, 0.230 mmol) was dissolved in CF_3CH_2OH (4.5 cm^3) and filtered through cotton with CF_3CH_2OH (0.5 cm^3 rinse). $P(C_3H_7\text{-}n)_3$ (277 mg, 1.73 mmol; *i.e.*, 7.5:1 P:Co mol ratio), diluted with CF_3CH_2OH (0.5 cm^3), was added dropwise to the stirred Co(III) solution at room temperature. The dark-orange colour of the reaction mixture faded to pale greenish-yellow in about 90 s, but a 5-min reaction period was allowed. Diethyl ether (8.0 cm^3) was then added in small aliquots, and the reaction mixture was chilled in ice (20 min). A pure-white, finely divided powder was filtered from a clear, light-yellow filtrate, and washed twice with diethyl ether. The crude product (167 mg) was recrystallized from CH_3CN (5.0 cm^3) and diethyl ether (12.0 cm^3). Yield: 153 mg (60%), m.p. 196–202°C (dec). Anal. Calcd. for $C_{46}H_{86}Cl_3CoN_4O_{12}P_2$(%): C, 49.58; H, 7.78; N, 5.03. Found: C, 49.89; H, 7.68; N, 5.02.

Analogous synthesis of $[Co(CNC_6H_{11})_4\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_3$ was performed by reaction of **5** with $P(C_4H_9\text{-}n)_3$ in 7.5:1 P:Co mol ratio; yield: 60% (crude), 54% (recryst.), m.p. 210–212°C (dec). Anal. Calcd. for $C_{52}H_{98}Cl_3CoN_4O_{12}P_2$(%): C, 52.10; H, 8.24; N, 4.60. Found: C, 51.85; H, 8.21; N, 4.65.

[Co(CNCH$_2$Ph)$_4${P(C$_4$H$_9$-*n*)$_3$}$_2$](BF$_4$)$_3$

Complex **6** (300 mg, 0.240 mmol) was dissolved in CF$_3$CH$_2$OH (4.0 cm^3) and filtered through cotton with CF$_3$CH$_2$OH (0.5 cm^3 rinse). P(C$_4$H$_9$-*n*)$_3$ (170 mg, 0.840 mmol; *i.e*., 3.5:1 P:Co mol ratio), diluted with CF$_3$CH$_2$OH (0.5 cm^3), was added dropwise to the stirred Co(III) solution at room temperature. The dark-orange colour of the reaction mixture immediately faded to pale greenish-yellow during ligand addition. Diethyl ether (12.0 cm^3) was then added in small aliquots and the reaction mixture was chilled in ice (20 min). An off-white, flocculent solid was filtered from a clear, light-yellow filtrate, and washed twice with diethyl ether. The crude product (135 mg) was recrystallized from CH$_3$CN (10.5 cm^3) and diethyl ether (15.0 cm^3). Yield: 115 mg (41%), m.p. 203–205°C (dec). Anal. Calcd. for C$_{56}$H$_{82}$B$_3$CoF$_{12}$N$_4$P$_2$(%): C, 56.40; H, 6.93; N, 4.70. Found: C, 56.46: H, 6.78; N, 4.68.

Analogous synthesis of [Co(CNCH$_2$Ph)$_4${P(C$_3$H$_7$-*n*)$_3$}$_2$](BF$_4$)$_3$ was performed by reaction of **6** with (P(C$_3$H$_7$-*n*)$_3$ in 3.5:1 P:Co mol ratio; yield: 50% (crude), 44% (recryst.), m.p. 218–220°C (dec). Anal. Calcd. for C$_{50}$H$_{70}$B$_3$CoF$_{12}$N$_4$P$_2$(%): C, 54.18; H, 6.37; N, 5.05. Found: C, 54.07; H, 6.25; N, 5.08.

RESULTS AND DISCUSSION

Synthesis of the Complexes

Tri-2-furylphosphine substitutes in complexes **2** and **3** to produce [Co(CNR)$_4$ {P(C$_4$H$_3$O)$_3$}$_2$X$_3$ complexes in a labile manner; reactions are effectively immediate at room temperature and yields are high. The reactions with P(C$_4$H$_3$O)$_3$ are similar to those reported for triarylphosphines [11], although the products are more stable in solution.

Reactions of the two diamagnetic [Co(CNR)$_4${P(C$_4$H$_3$O)$_3$}$_2$]X$_3$ complexes with trialkylphosphines [P(C$_3$H$_7$-*n*)$_3$, P(C$_4$H$_9$-*n*)$_3$] are also labile, and this is unexpected behaviour as it appears to contradict the rule of inert ligand substitution in diamagnetic six-coordinate Co(III) complexes. 2,2,2-Trifluoroethanol was used as solvent because **6** has limited solubility in dichloromethane. Complex **6** is substantially more reactive than **5**; **6** reacted immediately at room temperature with 3.5:1 mol ratio of trialkylphosphine, while **5** required more than one minute reaction time with 7.5:1 trialkylphosphine mol ratio. Reaction of **6** with 5.0:1 mol ratio of trialkylphosphine resulted in a lower yield (19%), suggesting possible loss of product in excess trialkylphosphine. Complex **5** did not appear to react with P(C$_4$H$_9$-*n*)$_3$ in a 5.0:1 mol ratio at 0°C. Ligand substitutions in the [Co(CNR)$_4${P(C$_4$H$_3$O)$_3$}$_2$]X$_3$ complexes are being further investigated.

Characterization of the Complexes

Physical properties of the complexes are included with their synthesis. [Co(CNR)$_4${P(C$_4$H$_3$O)$_3$}$_2$]X$_3$ complexes are unambiguously established as diamagnetic, as expected for six-coordinate Co(III) complexes. Measured molar susceptibilities (χ_M) are less negative than diamagnetic measurements for the separate ligands and ions [9,13], **5**, -250×10^{-6} *vs*. -627×10^{-6}; **6**, -230×10^{-6} *vs*. -626×10^{-6} (cgs). The values $\chi_g = -0.518 \pm 0.009 \times 10^{-6}$ and $\chi_M = -120 \pm 2 \times 10^{-6}$ (cgs) are measured for P(C$_4$H$_3$O)$_3$.

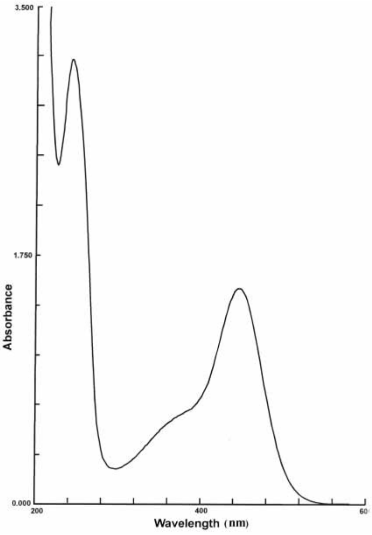

FIGURE 1 Electronic spectrum for $[Co(CNCH_2Ph)_4\{P(C_4H_3O)_3\}_2](BF_4)_3$ $\{7.1 \times 10^{-5}\,M\}$ in CH_3CN.

Solution electronic spectra for **5** and **6** are very similar to the complex spectra seen for triarylphosphine-Co(III) complexes [11] and dissimilar to the single-band spectra for triarylphosphine-Co(III) complexes [9,10]. A typical solution spectrum is pictured in Fig. 1. Molar extinction coefficients (ε), which are probably somewhat diminished due to slight reduction in solution, indicate that all bands must be considered charge transfer in nature. $P(C_4H_3O)_3$ complexes appear to be more stable in solution than triarylphosphine complexes [11].

The $\nu(N{\equiv}C)$ IR patterns for **5** and **6** are quite informative. One intense band in the solid state (Nujol mull) for both complexes is compatible with regular tetragonal (D_{4h}) coordination, *i.e.*, *trans*-$[Co(CNR)_4\{P(C_4H_3O)_3\}_2]X_3$, as expected. Following the solution IR patterns, a regular tetragonal structure appears to be maintained for **5** in CH_2Cl_2, while **6** undergoes apparent reduction to Co(I) in CH_2Cl_2 and CH_3NO_2. The behaviour of **6** in CF_3CH_2OH, and **5** in CF_3CH_2OH and CH_3NO_2, is more complex. There appear to be two bands attributable to Co(III) species and one to Co(II). The highest frequency band approximates values seen in Nujol, but a second band ($\sim 2225\,cm^{-1}$ for **5**, $\sim 2235\,cm^{-1}$ for **6**) should also be attributed to Co(III). The band $\sim 2205\,cm^{-1}$ for **5**, $\sim 2215\,cm^{-1}$ for **6**, is probably due to Co(II). Presence of a second Co(III) species in solution could resolve the dilemma of labile behaviour for supposedly inert diamagnetic six-coordinate Co(III) complexes. In CF_3CH_2OH and CH_3NO_2 solutions there could be a dissociation equilibrium of six-coordinate Co(III) into five or four-coordinate Co(III), which would be expected to be labile to ligand substitution. This possibility is being investigated.

Significance of the Results

Tri-2-furylphosphine reacts with intermediate spin Co(III) complexes as expected. Being intermediate to trialkylphosphines and triarylphosphines, $P(C_4H_3O)_3$ is expected to substitute in these Co(III) complexes to yield diamagnetic Co(III) complexes. The fact that these complexes are highly coloured, show a tendency towards reduction in

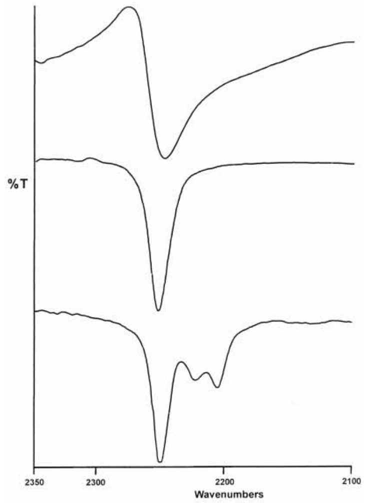

FIGURE 2 ν(N≡C) IR patterns for $[Co(CNC_6H_{11})_4\{P(C_4H_3O)_3\}_2](ClO_4)_3$ in Nujol, CH_2Cl_2, and CF_3CH_2OH, top to bottom, respectively.

solution (*albeit* less so than the triarylphosphine complexes), and have electronic spectra similar to the triarylphosphine complexes [11] suggest that tri-2-furylphosphine behaves more like a triarylphosphine than a trialkylphosphine in these complexes. That the diamagnetic $[Co(CNR)_4\{P(C_4H_3O)_3\}_2]X_3$ complexes undergo labile ligand substitution with trialkylphosphines is curious but not altogether novel, since diamagnetic Co(III) in vitamin B_{12} is also known to exibit labile behaviour [14].

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