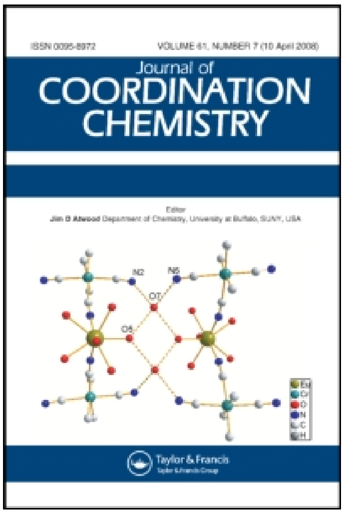

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Synthesis and selected reactions of <i>pentakis</i>(<i>t</i>-octylisocyanide)cobalt(II) complexes

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Synthesis and selected reactions of *pentakis*(*t*-octylisocyanide)cobalt(II) complexes

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The ligand 1,1,3,3-tetramethylbutylisocyanide, $CNCMe_2CH_2CMe_3$, i.e. *t*-octylisocyanide, with $Co(ClO_4)_2 \cdot 6H_2O$ or $Co(BF_4)_2 \cdot 6H_2O$ in ethanol, produces *pentakis*(alkylisocyanide)cobalt(II) complexes, $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ (**1**) and $[Co(CNC_8H_{17}\text{-}t)_5](BF_4)_2 \cdot 2.0H_2O$ (**2**). These Co(II) complexes undergo reduction/substitution upon reaction with trialkylphosphine ligands to produce $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$ (**3**), $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$ (**4**), and $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$ (**5**). Complex **3** is oxidized with $AgClO_4$ to produce $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ (**6**). Complex **1** yields $[Co(CNC_8H_{17}\text{-}t)_4py_2](ClO_4)_2$ (**7**) upon dissolving in pyridine. Reactions with triarylphosphine and triphenylarsine ligands were unsatisfactory. The chemistry of **1** and **2** is therefore more similar to that of Co(II) complexes with $CNCMe_3$ than with $CNCHMe_2$, other alkylisocyanides, or arylisocyanides, but shows some behavior dissimilar to any known Co(II) complexes of alkylisocyanides or arylisocyanides. Infrared and electronic spectra, magnetic susceptibility, molar conductivities, and cyclic voltammetry are reported and compared with known complexes. ^1H, ^{13}C, and ^{31}P NMR data were also measured for the diamagnetic complexes **3**, **4**, and **5**.

Keywords: *t*-Octylisocyanide; Cobalt(II) complexes; Cobalt(I) complexes; Trialkylphosphine; Alkylisocyanide; Cyclic voltammetry

1. Introduction

Reactions of alkylisocyanide ligands with cobalt(II) perchlorate or tetrafluoroborate occur in two different patterns. A dimeric, six-coordinate, diamagnetic complex in the solid state, dissociating into a monomeric, one-electron paramagnetic species in solution, has been observed with most alkylisocyanides studied. *Pentakis*(methylisocyanide)cobalt(II) perchlorate, $[Co(CNMe)_5](ClO_4)_2$, as red (diamagnetic) and blue (paramagnetic) crystals, was initially reported for reaction of $Co(ClO_4)_2 \cdot 6H_2O$ with excess CNMe in ethanol [1–4]. The red complex was later established as a metal-metal bonded dimer, $[(MeNC)_5Co–Co(CNMe)_5](ClO_4)_4$ [5], but the blue complex could not be reproduced, speculation being that possibly $[Co(CNMe)_6](ClO_4)_2$ or $[Co(CNMe)_5H_2O](ClO_4)_2$ had been observed [6]. Analogous $[Co_2(CNEt)_{10}](ClO_4)_4$ was subsequently reported [7]. Other diamagnetic

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alkylisocyanide-Co(II) complexes, as hydrates, containing CNR:Co mole ratio of 5 : 1 have been synthesized, $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ [8], $[Co_2(CNCHMe_2)_{10}](BF_4)_4 \cdot 5H_2O$ [8], $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ [9], and $[Co_2(CNCH_2Ph)_{10}](ClO_4)_4 \cdot 5H_2O$ [10]. These complexes presumably contain Co–Co bonds in the solid state. A maroon-red, very hygroscopic, complex assumed to be $[Co_2(CNC_4H_9\text{-}n)_{10}](ClO_4)_4 \cdot xH_2O$, has been noted [8].

The *t*-butylisocyanide ligand, however, has been unique in forming low-spin *tetrakis*(alkylisocyanide)aquacobalt(II) complexes, $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ [11] and $[Co(CNCMe_3)_4H_2O](BF_4)_2 \cdot 2.5H_2O$ [8], upon initial reaction with Co(II) in ethanol. Monomeric, low-spin pentacoordinate Co(II) complexes in anhydrous or hydrated forms are reported with arylisocyanide ligands, $[Co(CNR)_5]X_2 \cdot xH_2O$, $X = ClO_4$, BF_4; R = Ph, C_6H_4Me-*o*, C_6H_4Me-*p*, C_6H_4F-*p*, C_6H_4Et-*o*, $C_6H_3Me_2$-2,6, $C_6H_2Me_3$-2,4,6 [1, 3, 4, 6, 12, 13]. Sterically-hindered arylisocyanides also form *tetrakis*(arylisocyanide)*bis*(perchlorato)cobalt(II) complexes, $[Co(CNR)_4(ClO_4)_2]$, while retaining the *pentakis*(arylisocyanide)cobalt(II) structure as the BF_4^- salt, R = $C_6H_3Me_2$-2,6 [14], $C_6H_3Et_2$-2,6 [15], $C_6H_3\{CHMe_2\}_2$-2,6 [16], C_6H_4Me-*o* [17].

In this article a new alkylisocyanide ligand, 1,1,3,3-tetramethylbutylisocyanide, i.e. *t*-octylisocyanide, is investigated in reactions with $Co(ClO_4)_2 \cdot 6H_2O$ and $Co(BF_4)_2 \cdot 6H_2O$ in ethanol. The Co(II) compounds thus prepared are then studied in reactions with trialkylphosphines, $P(C_4H_9\text{-}n)_3$ and $P(C_3H_7\text{-}n)_3$, and with pyridine and 4-picoline to yield products analogous to known alkylisocyanide-tertiary phosphine Co(I) complexes [11, 18–26] and organoisocyanide-pyridine complexes of Co(II) [27–29]. Unsuccessful reactions with triarylphosphines and triphenylarsine are also discussed, since organoisocyanide-cobalt complexes are also well known with these ligands [11, 16–22, 26, 30–39].

2. Experimental

2.1. *Reagents*

1,1,3,3-tetramethylbutylisocyanide (*t*-octylisocyanide), CNC_8H_{17}-*t*, was purchased from Merck and Aldrich, and used as supplied. Commercial $P(C_3H_7\text{-}n)_3$ (Aldrich) and $P(C_4H_9\text{-}n)_3$ (Fluka) were used without redistillation. $Co(ClO_4)_2 \cdot 6H_2O$, $Co(BF_4)_2 \cdot 6H_2O$, $P(C_6H_4OMe\text{-}p)_3$, and $AgClO_4$ were purchased from Aldrich Chemicals. Anhydrous diethyl ether was filtered through an alumina column immediately before use. For cyclic voltammetry, 1 mM solutions of the compounds were freshly prepared in chromatographic-grade acetonitrile containing 0.05 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte.

2.2. *Instrumentation*

IR spectra were recorded on a Perkin–Elmer 2000 FT-IR. Solution electronic spectra were recorded on a Shimadzu UV-2501 PC spectrometer over the range 1100–200 nm. Diffuse reflectance electronic spectra were measured with an integrating sphere on a Shimadzu UV-2401PC spectrometer over the range 800–240 nm. Magnetic susceptibility was measured at room temperature using a Johnson Matthey Alfa magnetic susceptibility balance. Molar conductivities were measured on ~0.001 M solutions at 25°C using a Crison Basic 30 conductimeter and calculated as $\Lambda_M = 1000 (L_{solution} - L_{solvent})/C_M$ in $\Omega^{-1}\,cm^2\,mol^{-1}$. NMR measurements were performed on a Bruker Avance DPX 300 spectrometer. Chemical shift standards were internal tetramethylsilane for ^1H and ^{13}C, and external 85% H_3PO_4 for ^{31}P. The ^{13}C and ^{31}P spectra were routinely proton decoupled. The C, H, and N elemental analyses were performed using a Vario EL CHNOS elemental analyzer. 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. Voltammograms were recorded in the potential range −1.2 to +1.2 V *versus* Ag–AgCl, at a 0.1 Vs^{-1} scan rate. Nitrogen was bubbled through each solution for 500 s before the run.

2.3. *Cautionary note*

Some complexes reported in this article are perchlorate salts. None of these complexes show explosive tendency, but all perchlorate salts should be considered as potentially hazardous. Please see comments regarding the use of perchlorate salts [39].

2.4. *$[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ (1)*

A solution of $CNCMe_2CH_2CMe_3$ (1.011 g, 7.26 mmol) in ethanol (1.0 mL) was added dropwise to a filtered, well-stirred solution of $Co(ClO_4)_2 \cdot 6H_2O$ (540 mg, 1.48 mmol; i.e. 5 : 1 CNR : Co mol ratio) in ethanol (7.5 mL) at 0°C. During ligand addition, the pink solution rapidly turned dark blue-purple with precipitation of a blue-purple solid. The reaction mixture was filtered, and the solid was washed with cold ethanol and dried under suction/air, producing a pale blue-purple powder. Yield: 1.349 g (97%), m.p. 66–70°C (dec). Anal. Calcd for $C_{45}H_{85}Cl_2CoO_8N_5$ (%): C, 56.65; H, 8.98; N, 7.34. Found: C, 57.07; H, 9.12; N, 7.46.

IR (cm^{-1}): $\nu(N{\equiv}C)$ 2211 vs, 2180 s (Nujol); 2247 w, 2220 vs, ~2198 w(sh) (CF_3CH_2OH); 2245 w, 2219 vs, 2191 m (CH_2Cl_2); 2246 w, 2220 vs, ~2180 w(sh) (CH_3NO_2). Electronic spectra: λ_{max} (ε, $M^{-1}\,cm^{-1}$): 837 (270), 463 (40), 316 sh (480), 265 (3200), 224 (7600) nm (CF_3CH_2OH); 722 (200), ~487 sh (20), ≈335 sh (440), 268 (3500), 231 (7000) nm (CH_2Cl_2); 697 (150), ≈340 sh (260), 267 (2000), 241 (5400), 228 (5100) nm (CH_3CN). Diffuse reflectance electronic spectrum: λ_{max} (A): 528 br (0.408), 310 (1.282) nm. Molar conductivities: Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 250 ($CH_3CN$), 150 ($CH_3NO_2$), 140 (acetone), 45 ($CH_2Cl_2$). Cyclic voltammogram: $E_{ox} = 148$ mV, $E_{red} = 65.3$ mV, $E_{1/2} = 107$ mV *versus* Ag–AgCl, $\Delta E = 83$ mV. Magnetic susceptibility: $\chi_g = 2.34 \pm 0.09 \times 10^{-6}$ cgs, $\mu_{eff} = 2.60 \pm 0.04$ BM.

Analogous synthesis of $[Co(CNC_8H_{17}\text{-}t)_5](BF_4)_2 \cdot 2H_2O$ (**2**), as a pale red-purple powder. Yield: 90%, m.p. 82–84°C (dec). Anal. Calcd for $C_{45}H_{85}B_2CoF_8N_5 \cdot 2H_2O$ (%): C, 56.02; H, 9.30; N, 7.26. Found: C, 56.34; H, 9.59; N, 7.34. IR (cm^{-1}): $\nu(N{\equiv}C)$ ~2252 m(br), 2212 vs, 2181 m; ν(O–H) ~3484 w(br) (Nujol); 2213 vs, 2180 m(br) (CF_3CH_2OH); 2219 w(sh), 2205 vs, 2174 m, 2135 w, 2116 w (CH_2Cl_2); 2219 vs, 2177 m, 2136 w (CH_3NO_2). Electronic spectra: λ_{max} (ε, $M^{-1}\,cm^{-1}$): 861 (305), 458 (20), 316 sh (490), 265 (3100), ~219 sh (8900) nm (CF_3CH_2OH); 762 (250), 482 (21), 317 sh (550), 267 (2300), 230 (6400) nm (CH_2Cl_2); 698 (180), ≈330 sh (350), 272 (2200), 265 (5000), ~238 sh (12,000), 228 (13,000), 204 (22,000) nm (CH_3CN). Diffuse reflectance electronic spectrum: λ_{max} (A): 531 br (0.450), 307 (1.430) nm. Molar conductivities: Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 270 ($CH_3CN$), 165 ($CH_3NO_2$), 185 (acetone), 50 ($CH_2Cl_2$). Cyclic voltammogram: $E_{ox} = 184$ mV, $E_{red} = 77.2$ mV, $E_{1/2} = 131$ mV *versus* Ag–AgCl, $\Delta E = 107$ mV. Magnetic susceptibility: $\chi_g = 1.26 \pm 0.03 \times 10^{-6}$ cgs, $\mu_{eff} = 2.11 \pm 0.01$ BM.

2.5. *[Co(CNC$_8$H$_{17}$-t)$_3${P(C$_4$H$_9$-n)$_3$}$_2$]ClO$_4$ (3)*

Complex **1** (700 mg, 0.734 mmol) was dissolved in CH_2Cl_2 (3.5 mL), filtered through cotton with a CH_2Cl_2 (0.5 mL) rinse, and chilled in ice (10 min). Then $P(C_4H_9\text{-}n)_3$ (665 mg, 3.29 mmol; 1 : 4.5 Co : P mol ratio) dissolved in CH_2Cl_2 (1.5 mL) was added rapidly dropwise while the chilled Co(II) solution was stirred. The dark blue solution changed through brown and green to light yellow during ligand addition, but no precipitate was observed. Four micro drops (~110 mg, 2.2 mmol) of $N_2H_4 \cdot H_2O$ were added, and the heterogeneous mixture was agitated vigorously for 3 min before decanting and filtration through cotton to afford a clear, bright yellow solution. Diethyl ether (5.0 mL) was added, and this solution was then concentrated to ~2 mL by evaporation under a brisk flow of air. After filtration through cotton, diethyl ether was added in small aliquots, 2.5 mL for initial precipitation, 4.5 mL total. The reaction mixture was chilled in ice (25 min), then filtered and washed with diethyl ether. The crude product (425 mg, 59% yield) was recrystallized from CH_2Cl_2 (1.0 mL) and diethyl ether (8.0 mL), producing 365 mg (51% overall yield) of lemon yellow microcrystals, m.p. 122–124°C (dec). Anal. Calcd for $C_{51}H_{105}ClCoN_3O_4P_2$ (%): C, 62.46; H, 10.79; N, 4.28. Found: C, 62.13; H, 10.85; N, 4.22.

IR (cm^{-1}): $\nu(N{\equiv}C)$ 2034 vs (br), ~1996 w(sh) (Nujol); 2164 w, ~2109 vw(sh), 2041 vs (br) (CF_3CH_2OH); ~2107 vw(sh), 2038 vs (br) (CH_2Cl_2); ~2108 vw(sh), 2040 vs (br) (CH_3NO_2). Electronic spectra: λ_{max} (ε, $M^{-1}\,cm^{-1}$): ~410 sh (173), ≈330 sh, ≈278 sh, 240 (12,700) nm (CF_3CH_2OH); ~420 sh (69), 282 (14,900), 238 (39,800) nm (CH_2Cl_2); 281 (13,800), 238 (35,600) nm (CH_3CN). Molar conductivities: Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 130 ($CH_3CN$), 80 ($CH_3NO_2$), 140 (acetone), 65 ($CH_2Cl_2$). Cyclic voltammogram: $E_{ox} = 53.4$ mV, $E_{red} = -29.9$ mV, $E_{1/2} = 11.8$ mV *versus* Ag–AgCl, $\Delta E = 83.3$ mV. NMR: see tables 1, 3, and 5 for ^1H, ^{13}C, and ^{31}P NMR data, respectively.

Analogous synthesis of $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$ (**4**). Yield: 76% (crude), 49% (recryst), m.p. 118-120°C (dec). Anal. Calcd for $C_{51}H_{105}BCoF_4N_3P_2$ (%): C, 63.27; H, 10.93; N, 4.34. Found: C, 63.75; H, 10.89; N, 4.35. IR (cm^{-1}): $\nu(N{\equiv}C)$ 2035 vs (br), ~1973 w(sh) (Nujol); ~2110 vw(sh), 2041 vs (br) (CF_3CH_2OH); ~2109 vw(sh), 2039 vs (br) (CH_2Cl_2); ~2110 vw(sh), 2040 vs (br) (CH_3NO_2). Electronic spectra: λ_{max} (ε, $M^{-1}\,cm^{-1}$): ~413 sh (290), ≈305 sh, ≈275 sh, 241 (12,700) nm (CF_3CH_2OH); 281 (13,300), 242 (28,500) nm (CH_2Cl_2); 281 (13,900), 238 (41,400) nm (CH_3CN). Molar conductivities: Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 135 ($CH_3CN$), 85 ($CH_3NO_2$), 150 (acetone), 70 ($CH_2Cl_2$). Cyclic voltammogram: $E_{ox} = 17.7$ mV, $E_{red} = -59.7$ mV, $E_{1/2} = -21.0$ mV *versus* Ag–AgCl, $\Delta E = 77.4$ mV. NMR: see tables 1, 3, and 5 for ^1H, ^{13}C, and ^{31}P NMR data, respectively.

Analogous synthesis of $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$ (**5**). Yield: 67% (crude), 55% (recryst), m.p. 95–98°C (dec). Anal. Calcd for $C_{45}H_{93}ClCoN_3O_4P_2 \cdot 0.5\ CH_2Cl_2$ (%): C, 58.20; H, 10.09; N, 4.47. Found: C, 58.17; H, 10.10; N, 4.45. IR (cm^{-1}): $\nu(N{\equiv}C)$ ~2106 vw(sh), ~2065 vw(sh), 2034 vs (br) (Nujol); 2164 w, ~2109 vw(sh), 2040 vs (br) (CF_3CH_2OH); ~2108 vw(sh), 2039 vs (br) (CH_2Cl_2); 2039 vs (br) (CH_3NO_2). Electronic spectra: λ_{max} (ε, $M^{-1}\,cm^{-1}$): ~413 sh (194), ~329 sh (35), ≈273 sh, 240 (13,200) nm (CF_3CH_2OH); 282 (13,600), 239 (33,500) nm (CH_2Cl_2); 280 (12,700), 238 (32,400) nm (CH_3CN). Molar conductivities: Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 135 ($CH_3CN$), 85 ($CH_3NO_2$), 145 (acetone), 65 ($CH_2Cl_2$). Cyclic voltammogram: $E_{ox} = 77.2$ mV, $E_{red} = -71.6$ mV, $E_{1/2} = 2.8$ mV *versus* Ag–AgCl, $\Delta E = 148.8$ mV. NMR: see tables 2, 4, and 5 for ^{1}H, ^{13}C, and ^{31}P NMR data, respectively.

2.6. *$[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ (6)*

Complex **3** (200 mg, 0.204 mmol) was dissolved in CH_2Cl_2 (1.0 mL total) and filtered through cotton. $AgClO_4$(s) (46.5 mg, 0.22 mmol; 1 : 1.1 Co : Ag mol ratio) was added at room temperature and continuously triturated with a glass stirring rod for 3 min.

Table 1. ^{1}H NMR data, δ_H ($CDCl_3$, 300 MHz), for $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$ and $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$.

H atom	Free ligand	Complex **1**[a]	Complex **2**[b]
$P(CH^1_2CH^2_2CH^3_2CH^4_3)_3$			
H^1, H^2, H^3	1.19–1.32 envelope	1.69–1.81 envelope	1.65–1.80 envelope
H^4	0.78 t, $J = 6.9$ Hz	0.98 t, $J = 6.6$ Hz	0.98 s
$CNC(CH^5_3)_2CH^6_2C(CH^7_3)_3$			
H^5	1.46 t, $^3J_{H–N} = 2.0$ Hz	1.50 s	1.50 s
H^6	1.58 t, $^3J_{H–N} = 2.2$ Hz	1.62 s	1.61 s
H^7	1.06 s	1.04 s	1.04 s

[a]Complex **1** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$.
[b]Complex **2** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$.

Table 2. ^{13}C NMR data, δ_C ($CDCl_3$, 75.5 MHz), for $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$ and $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$.

C atom	Free ligand	Complex **1**[a]	Complex **2**[b]
$P(C^1H_2C^2H_2C^3H_2C^4H_3)_3$			
$–C^1–$	26.9 d, $^1J_{C–P} = 12.3$ Hz	28.2 t, $^1J_{C–P} = 13.4$ Hz	28.2 t, $^1J_{C–P} = 13.4$ Hz
$–C^2–$	24.4 d, $^2J_{C–P} = 10.9$ Hz	24.7 t, $^2J_{C–P} = 6.6$ Hz	24.7 t, $^2J_{C–P} = 6.6$ Hz
$–C^3–$	28.0 d, $^3J_{C–P} = 7.6$ Hz	26.5 s	26.5 s
$–C^4$	13.6 s	14.1 s	14.1 s
$C^5NC^6(C^7H_3)_2C^8H_2C^9(C^{10}H_3)_3$			
$C^5–$	155.1 t, $^1J_{C–N} = 4.5$ Hz		156.9 t, $^1xJ_{C–N} = 31.7$ Hz
$–C^6–$	56.7 t, $^1J_{C–N} = 4.8$ Hz	54.7 s	54.7 s
$–C^7–$	31.6 s	31.3 s	31.2 s
$–C^8–$	57.0 s	60.2 s	60.2 s
$–C^9–$	31.7 s	31.6 s	31.5 s
$–C^{10}$	30.9 s	31.1 s	31.1 s

[a]Complex **1** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$.
[b]Complex **2** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$.

Table 3. ^{1}H NMR data, δ_H ($CDCl_3$, 300 MHz), for $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$.

H atom	Free ligand	Complex **3**[a]
$P(CH^1_2CH^2_2CH^3_2)_3$		
H^1	1.095–1.165 m	1.67–1.79 envelope
H^2	1.185–1.300 m	1.67–1.79 envelope
H^3	0.78 t, $J = 7.2$ Hz	1.05 m
$CNC(CH^4_3)_2CH^5_2C(CH^6_3)_3$		
H^4	1.46 t, $^3J_{H-N} = 2.0$ Hz	1.50 m
H^5	1.58 t, $^3J_{H-N} = 2.2$ Hz	1.61 m
H^6	1.06 s	1.05 m

[a]Complex **3** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$.

Table 4. ^{13}C NMR data, δ_C ($CDCl_3$, 75.5 MHz), for $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$.

C atom	Free ligand	Complex **3**[a]
$P(C^1H_2C^2H_2C^3H_3)_3$		
$-C^1-$	19.2 d, $^1J_{C-P} = 13.7$ Hz	17.9 t, $^1J_{C-P} = 14.3$ Hz
$-C^2-$	29.8 d, $^2J_{C-P} = 12.5$ Hz	30.8 t, $^2J_{C-P} = 13.4$ Hz
$-C^3$	15.8 d, $^3J_{C-P} = 11.4$ Hz	16.0 t, $^3J_{C-P} = 6.9$ Hz
$C^4NC^5(C^6H_3)_2C^7H_2C^8(C^9H_3)_3$		
C^4-	155.1 t, $^1J_{C-N} = 4.5$ Hz	157.0 s
$-C^5-$	56.7 t, $^1J_{C-N} = 4.8$ Hz	54.5 s
$-C^6-$	31.6 s	31.5 s
$-C^7-$	57.0 s	60.1 s
$-C^8-$	31.7 s	31.6 s
$-C^9$	30.9 s	31.1 s

[a]Complex **3** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_3H_7\text{-}n)_3\}_2]ClO_4$.

Table 5. ^{31}P NMR data, δ_P ($CDCl_3$, 121.46 MHz), for **1**, **2**, and **3**.

Free ligand	Complex **1**[a]	Complex **2**[b]	$\Delta\delta$[c]
$P(CH_2CH_2CH_2CH_3)_3$			
−31.1	50.3	50.3	81.4
	Complex **3**[d]	$\Delta\delta$[c]	
$P(CH_2CH_2CH_3)_3$			
−33.2	49.7	82.9	

[a]Complex **1** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]ClO_4$.
[b]Complex **2** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$.
[d]Complex **3** = $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_7\text{-}n)_3\}_2]ClO_4$.
$\Delta\delta$[c] is the difference between the ^{31}P chemical shift of the free ligand and the metal coordinated P atom.

The $AgClO_4$ rapidly darkened and a silver mirror deposited on the bottom of the flask. The heterogeneous reaction mixture was decanted and filtered twice through cotton with a CH_2Cl_2 (1.0 mL) rinse each time. Diethyl ether was added in small aliquots to the clear, dark yellow solution; 2.0 mL for initial precipitation, 4.0 mL total. The reaction mixture was chilled in ice (30 min) and the greenish-yellow microcrystalline product was filtered and washed with diethyl ether. Crude product (135 mg) was recrystallized from CH_2Cl_2 (1.5 mL) and diethyl ether (4.0 mL). Yield: 121 mg (55%), m.p. 106–109°C (dec). Anal. Calcd for $C_{51}H_{105}Cl_2CoN_3O_8P_2$ (%): C, 56.71; H, 9.80; N, 3.89. Found: C, 56.42; H, 9.65; N, 3.89.

IR (cm^{-1}): $\nu(N\equiv C)$ ~2179 vw(sh), 2155 vs (br), ~2120 vw(sh) (Nujol); 2163 vs, ~2130 w(sh) (CF_3CH_2OH); ~2190 vw(sh), 2162 vs, ~2128 w (CH_2Cl_2); ~2190 vw(sh), 2163 vs, ~2130 w (CH_3NO_2). Electronic spectra: λ_{max} (ε, $M^{-1}\,cm^{-1}$): 962 (303), 626 (14), 415 (339), ~319 sh (3900), 278 (13,100), 241 (16,100) nm (CF_3CH_2OH); 938 (317), 413 (378), ~329 sh (1700), 276 (12,700), 242 (18,100) nm (CH_2Cl_2); 951 (284), ~628 (5), 416 (323), ~334 sh (1900), 278 (12,800), 243 (15,000), 212 (12,500) nm (CH_3CN). Molar conductivities: Λ_M ($\Omega^{-1}\,cm^2\,mol^{-1}$): 275 ($CH_3CN$), 180 ($CH_3NO_2$), 230 (acetone), 45 ($CH_2Cl_2$). Cyclic voltammogram: $E_{red} = -41.5$ mV, $E_{ox} = 41.8$ mV, $E_{1/2} = 0.15$ mV *versus* Ag–AgCl, $\Delta E = 83.3$ mV. Magnetic susceptibility: $\chi_g = 1.07 \pm 0.03 \times 10^{-6}$ cgs, $\mu_{eff} = 2.08 \pm 0.02$ BM.

2.7. *[Co(CNC$_8$H$_{17}$-t)$_4$(C$_5$H$_5$N)$_2$](ClO$_4$)$_2$ (7)*

Complex **1** (300 mg, 0.314 mmol) was dissolved in pyridine (4.0 mL), filtered through cotton with a C_5H_5N (0.5 mL) rinse, and allowed to stand at room temperature for 15 min. Diethyl ether was then added in small aliquots to the dark blue solution; 1.0 mL for initial precipitation, 3.0 mL total. The reaction mixture was chilled in ice (15 min) and the pale sky blue powder was filtered from a light yellow filtrate, washed with diethyl ether, and dried under suction/air. Yield: 224 mg (73%), m.p. 145–150°C (dec). Anal. Calcd for $C_{46}H_{78}Cl_2CoN_6O_8$ (%): C, 56.78; H, 8.08; N, 8.64. Found: C, 56.96; H, 8.24; N, 8.74. IR (cm^{-1}): $\nu(N\equiv C)$ 2207 vs, ~2180 vw(sh) (Nujol); 2220 vs, ~2196 vw(sh) (CF_3CH_2OH); 2218 vs, 2191 w (CH_2Cl_2); 2207 vs (CH_3NO_2). Diffuse reflectance electronic spectrum: λ_{max} (A): 639 br (0.680), ~400, 326 (1.687), 257 (1.736) nm. Magnetic susceptibility: $\chi_g = 2.83 \pm 0.04 \times 10^{-6}$ cgs, $\mu_{eff} = 2.82 \pm 0.02$ BM.

3. Results and discussion

3.1. *Synthesis of the complexes*

Reactions of 1,1,3,3-tetramethylbutylisocyanide, $CNCMe_2CH_2CMe_3$, with $Co(ClO_4)_2 \cdot 6H_2O$ or $Co(BF_4)_2 \cdot 6H_2O$ in ethanol solution, i.e.

$$\begin{gathered} CoX_2(al) + 5CNC_8H_{17}\text{-}t(al) \rightarrow [Co(CNC_8H_{17}\text{-}t)5]X_2(s) \\ X = ClO_4, BF_4 \end{gathered} \tag{1}$$

are dissimilar to known reactions with other alkylisocyanides [1–10], but are analogous to reactions with the arylisocyanides not promoting reduction to Co(I) [1, 3, 4, 6, 12, 13]. Dimerization through a Co–Co bond is therefore lacking in the solid state, and *pentakis*-coordination is retained in these monomeric complexes. The $\nu(N\equiv C)$ IR pattern, but not frequencies of course, for **1** (see figure 1a), is essentially identical to that reported for $[Co(CNPh)_5](ClO_4)_2 \cdot 1.5H_2O$ [6], while the pattern for **2** (figure 1b) is similar to those for a number of other hydrated arylisocyanide–Co(II) complexes [13]. Extent of hydration appears to influence the $\nu(N\equiv C)$ pattern, since as **1** ages, slowly hydrating as evidenced from the IR $\nu(O–H)$ region, the $\nu(N\equiv C)$ pattern begins to approximate that for **2**. Complex **2** is sometimes obtained anhydrous, however, and then its $\nu(N\equiv C)$ pattern is essentially identical to that for **1**. That the BF_4^- salt is more

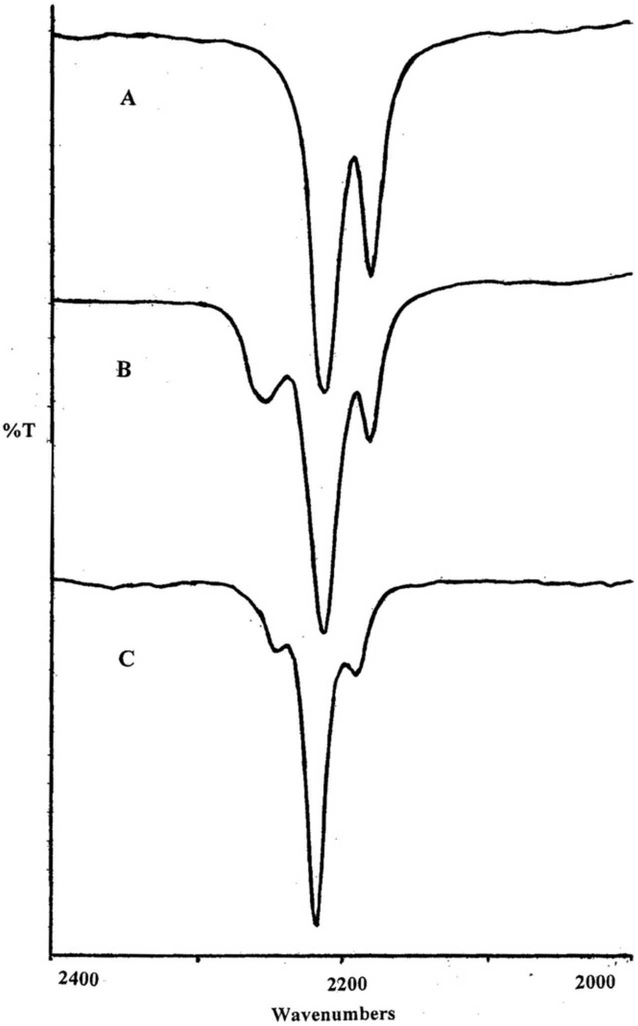

Figure 1. The $\nu(N{\equiv}C)$ IR patterns for *t*-octylisocyanide-Co(II) complexes: (a) $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ (Nujol), (b) $[Co(CNC_8H_{17}\text{-}t)_5](BF_4)_2 \cdot 2.0H_2O$ (Nujol), (c) $[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2$ (CH_2Cl_2 solution).

prone to being hydrated, or more extensively hydrated, than the ClO_4^- salt is typical for the arylisocyanide–Co(II) complexes [13].

Reactions of **1** and **2** with excess trialkylphosphine ligands, i.e.

$$[Co(CNC_8H_{17}\text{-}t)_5]X_2(CH_2Cl_2) + PR_3(\text{excess}) \rightarrow [Co(CNC_8H_{17}\text{-}t)_3\{PR_3)_2\}_2]X$$
$$X = ClO_4, \quad BF_4; \quad PR_3 = P(C_4H_9\text{-}n)_3, \quad P(C_3H_7\text{-}n)_3 \qquad (2)$$

closely parallel reactions of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ [11]. Reduction/substitution reactions produce disubstituted five-coordinate Co(I) complexes, $[Co(CNR)_3(PR'_3)_2]X$, rather than disproportionation/substitution reactions producing Co(I) and Co(III) complexes, $[Co(CNR)_3(PR'_3)_2]X$ and $[Co(CNR)_4(PR'_3)_2]X_3$, respectively, as with Co(II) complexes of $CNCHMe_2$, CNC_6H_{11}, $CNC_4H_9\text{-}n$, and $CNCH_2Ph$ [22–24].

In the absence of added hydrazine the reduction to Co(I) tends to be incomplete, however, and in one instance pure $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ was obtained. Reactions with $P(C_3H_7\text{-}n)_3$ reduce more readily, but N_2H_4 was used in all reported reactions.

The five-coordinate Co(I) complexes are oxidizable to the corresponding five-coordinate Co(II) complexes with Ag^+, i.e.

$$[Co(CNC_8H_{17}\text{-}t)_3\{PR_3)_2\}_2]ClO_4 + 1.1AgClO_4(s) \rightarrow [Co(CNC_8H_{17}\text{-}t)_3\{PR_3)_2\}_2](ClO_4)_2$$
$$PR_3 = P(C_4H_9\text{-}n)_3 \quad (3)$$

This reaction is analogous to the synthesis of $[Co(CNCMe_3)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ [25].

Synthesis of *tetrakis*(*t*-octylisocyanide)*bis*(pyridine)cobalt(II) perchlorate by reaction of **1** with pyridine, i.e.

$$[Co(CNC_8H_{17}\text{-}t)_5](ClO_4)_2 \xrightarrow[2.\ Et_2O]{1.\ C_5H_5N(l)} [Co(CNC_8H_{17}\text{-}t)_4(py)_2](ClO_4)_2(s) \quad (4)$$

is analogous to reactions of Co(II) complexes of $CNCMe_3$, $CNCHMe_2$, and $CNC_6H_3i Pr_2$-2,6 with pyridine [27–29], except that this reaction is more sluggish. The reduction of **1** in pyridine is also apparently much more sluggish. When **1** was left in C_5H_5N solution for only a few minutes before precipitation with diethyl ether, the product obtained was primarily unreacted starting material and the filtrate was very pale yellow indicating only slight reduction to Co(I). With the other Co(II)-alkylisocyanide complexes, either the solution in pyridine had to be precipitated immediately ($CNCMe_3$ [27]) or the starting material was treated as a slurry, not actually dissolved, in C_5H_5N ($CNCHMe_2$ [28], $CNC_6H_3i Pr_2$-2,6 [29]). Extensive reduction to Co(I) was also clearly evident for the other alkylisocyanide-Co(II) complexes [29]. In an attempted, presumably analogous, reaction with 4-picoline, in which **1** was allowed to remain dissolved for 20 min before addition of diethyl ether, only unreacted **1** was recovered, in 62% yield. This behavior is somewhat unexpected, since 4-picoline should behave as a better ligand than pyridine in this particular reaction, and complexes of $4\text{-}MeC_5H_4N$ have been obtained in reactions with Co(II) complexes of $CNCMe_3$ [27], $CNCHMe_2$ [28], and $CNC_6H_3i Pr_2$-2,6 [29].

Attempts to synthesize triarylphosphine-*t*-octylisocyanide complexes with **1** and **2** were unsuccessful. Alkyl- and arylisocyanide-Co(II) complexes are well known to yield disubstituted Co(I) products in reactions with triarylphosphine ligands, i.e. $[Co(CNR)_3(PR'_3)_2]X$, $X = ClO_4$, BF_4 [11, 18, 19, 22, 30–35, 38]; in order to present a more complete survey of the reaction chemistry for **1** and **2**, data for these failed reactions are included. Reactions of **2** in CH_2Cl_2 solution, for example, with either $P(C_6H_4OMe\text{-}p)_3$ or PPh_3 in CH_2Cl_2 or reacted as solids, in several different P : Co mole ratios, all effected rapid solution color change from dark blue to red orange, but the anticipated Co(I) products could not be purified from unreacted (excess) triarylphosphine despite multiple recrystallizations. The $\nu(N{\equiv}C)$ IR patterns for these samples suggest Co(I) complexes of 3 : 2 RNC : PR'_3 composition were indeed obtained: e.g. for the presumed $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]BF_4$ complex, 2059 vs (br) cm^{-1} (Nujol), 2066 vs (br) (CH_2Cl_2), 2068 vs (br) (CH_3NO_2), 2068 vs (br) (CF_3CH_2OH); $[Co(CNC_8H_{17}\text{-}t)_3(PPh_3)_2]BF_4$: 2065 s, 2045 s cm^{-1} (Nujol), 2069 vs (br) (CH_2Cl_2), 2071 vs (br) (CH_3NO_2), 2071 vs (br) (CF_3CH_2OH). Reason for difficulty in isolating pure products is presumably the high solubility of these Co(I) complexes. A 4 : 1 RNC : PR'_3 composition of the Co(I) complexes would be expected to be more soluble [30, 34], but this composition is not substantiated by the $\nu(N{\equiv}C)$ pattern.

Attempted synthesis of a *t*-octylisocyanide-triphenylarsine complex was also unsuccessful. Cobalt(II) complexes with $CNCHMe_2$, CNC_6H_{11}, CNC_4H_9-*n*, and $CNCH_2Ph$ yield green paramagnetic Co(II) complexes of general formula $[Co(CNR)_4(AsPh_3)_2]X_2$, $X = ClO_4$, BF_4, in rapid reactions at room temperature [37]. Reactions of triphenylarsine with *pentakis*(arylisocyanide)cobalt(II) complexes produce several different products. Reaction with $[Co(CNPh)_5](ClO_4)_2 \cdot H_2O$ yielded $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ [33], in a reduction/substitution reaction analogous to that for PPh_3 [32], while reactions with $[Co(CNC_6H_3Me_2\text{-}2,6)_5](ClO_4)_2 \cdot 0.5H_2O$ and $[Co(CNC_6H_4Me\text{-}o)_5](ClO_4)_2$ produced the $[Co(CNR)_4(ClO_4)_2]$ complexes [14, 17]. Reactions with the tetrafluoroborate salts of Co(II)-arylisocyanide complexes, however, effected only modest yields of the $[Co(CNR)_5]BF_4$ [14]. Even reaction of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ with $AsPh_3$ showed an immediate, vivid color change, although only starting material could be recovered [11]. Reaction of **1** with $AsPh_3$, 5 : 1 As : Co mole ratio in CH_2Cl_2, however, only showed a subtle color change of the solution from blue to blue-green in 5 min at room temperature, and **1** was recovered in 75% yield upon addition of diethyl ether. This reaction behavior is thus unlike that observed for any other Co(II) complexes of alkylisocyanides or arylisocyanides.

3.2. *Physical properties of the complexes*

The $\nu(N{\equiv}C)$ IR patterns for **1** and **2** are so analogous to those for five-coordinate arylisocyanide-Co(II) complexes [6, 13] that similar coordination structures are suggested. $[Co(CNPh)_5](ClO_4)_2 \cdot 1.5H_2O$, formulated as $[Co(CNPh)_5H_2O](ClO_4)_2 \cdot 0.5H_2O$, is postulated to contain a six-coordinate cation with five CNPh ligands in square pyramidal coordination and a water occupying the sixth, pseudo-octahedral site [6]. This blue complex is easily reversibly dehydrated to yellow $[Co(CNPh)_5](ClO_4)_2$, which is believed to be square pyramidal [6]. Re-crystallization leads to $[Co(CNPh)_5](ClO_4)_2 \cdot 0.5CH_2ClCH_2Cl$ [40], for which square pyramidal coordination has been confirmed by X-ray crystallography [41]. Square pyramidal coordination of the five CNC_8H_{17}-*t* ligands in **1** and **2** is therefore highly probable, even though this has not been confirmed by X-ray crystallography. The $\nu(N{\equiv}C)$ IR patterns for **3**, **4**, and **5** in solid and solution are basically a single strong band, which is compatible with D_{3h} axially-disubstituted trigonal bipyramidal coordination. This is dissimilar to IR spectra for other *tris*(alkylisocynaide)*bis*(trialkylphosphine)cobalt(I) complexes [11, 22], where lower symmetry (i.e. C_{2v}) was postulated. The $\nu(N{\equiv}C)$ IR patterns for **6** are essentially one strong band, compatible with D_{3h} symmetry. These patterns are not analogous to data seen for $[Co(CNCMe_3)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ [25], but are similar to spectra for *tris*(alkylisocyanide)*bis*(triarylphosphine)cobalt(II) complexes in solution which were postulated to be regular trigonal bipyramids [38]. The $\nu(N{\equiv}C)$ IR pattern for **7** in Nujol is similar to data reported for the other $[Co(CNR)_4py_2](ClO_4)_2$ complexes [27–29], so analogous tetragonal coordination is assumed. Unlike the other pyridine complexes, however, **7** retains its chemical integrity and apparent coordination structure in solution. The other complexes were rapidly reduced to Co(I).

Solution electronic spectra for **1** show solvent dependence for the first (broad) crystal field band, ranging from 840 ($\varepsilon = 270$), 720 (200), 700 (150) nm in CF_3CH_2OH, CH_2Cl_2, CH_3CN, respectively. Decreasing λ and ε values with increasing coordinating ability of the solvent may indicate progressive change from $[Co(CNR)_5]^{2+}$ species to $[Co(CNR)_5solvent]^{2+}$. The UV regions of the spectra, probably charge transfer in nature, show less solvent dependency. Spectra for **1** and **2** show larger differences for the crystal field band in CF_3CH_2OH and CH_2Cl_2 than would be expected if the only difference were non-coordinating ClO_4^- or BF_4^- anions, respectively, but are similar in CH_3CN. This could be due to presence or absence of H_2O molecules in the coordination sphere. Spectra for **1** and **2** are analogous to $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ in CF_3CH_2OH and CH_2Cl_2 but not in CH_3CN [8], for $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ in CF_3CH_2OH but not in CH_3CN [8], and for $[Co_2(CNCH_2Ph)_{10}](BF_4)_4 \cdot H_2O$ in CH_2Cl_2 and CH_3CN [9]. Clearly there is solvent interaction in the spectra of these complexes. Electronic spectra for **3**, **4**, and **5** are primarily charge transfer in nature, very similar to each other despite change in anion or phosphine, showing two bands in CH_2Cl_2 and CH_3CN solution but only one band in CF_3CH_2OH. These spectra are similar to analogous $CNCMe_3$ complexes [11,22]. Electronic spectra for **6** exhibit crystal field and charge transfer bands as expected for a trigonal bipyramidal Co(II) complex, and spectra in all three solvents are very similar. These spectra are analogous to those for $[Co(CNCMe_3)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ [25].

The diffuse reflectance electronic spectrum for **7** shows one well-resolved crystal field band and two apparent charge transfer bands. The pattern and wavelengths are very similar to Co(II)-pyridine complexes with $CNCHMe_2$ and $CNCMe_3$ [27, 28]. The diffuse reflectance spectrum for **1** consists of one crystal field band and one probable charge transfer band, dissimilar to data reported for $[Co_2(CNCHMe_2)_{10}](ClO_4)_4 \cdot 5H_2O$ and $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ [8], as would be expected, but quite similar to data for $[Co(CNPh)_5](ClO_4)_2 \cdot 1.5H_2O$ [6], with maxima shifted to shorter wavelengths. Similarities between complexes of this alkylisocyanide ligand and complexes with arylisocyanides is again very apparent.

Effective magnetic moments for the Co(II) complexes were calculated assuming Curie law behavior. Diamagnetic corrections for the ligands and ions were taken from the literature [8, 15, 16, 42]; magnetic susceptibility for $CNC_8H_{17}\text{-}t$ was measured as $\chi_g = -787 \pm 3 \times 10^{-9}$, $\chi_M = -109.5 \pm 0.5 \times 10^{-6}$ cgs. The Co(II) complexes are within the general range 1.8–2.7 BM [42] for low-spin, one-electron paramagnetism as expected for strong field ligands. The effective moment for **1** (2.60 BM) is higher than **2** (2.11 BM), perhaps reflecting the presence of H_2O in **2**, approximating octahedral coordination with expected range 1.7–2.0 BM [43], while **1** is square pyramidal. The moment for **7** (2.82 BM) is higher than μ_{eff} reported for other Co(II) alkylisocyanide-pyridine complexes (1.90, 2.24 BM) [27, 28], but not unreasonable for one-electron paramagnetism of Co(II) [43].

The cyclic voltammograms for **1**–**6** are all reversible, as judged by the criteria of non-variance of $E_{1/2}$ with a change in scan rate [44–46]. The non-aqueous nature of the solvent and the consequent relatively low concentration of the background electrolyte cause the solutions to have high solution resistance between the working and reference electrodes. This Ohmic (iR) drop [45], combined with the higher junction potential created across the ion bridge between the reference electrode and sample solution [47, 48], contribute to the apparent non-conformity of non-aqueous systems to the criterion for reversibility in aqueous systems of $\Delta E < 57$ mV. Solubility of these complexes restricts choice of solvent to CH_3CN or CH_2Cl_2, so these problems are unavoidable. Within experimental error, estimated at ±10 mV, the $E_{1/2}$ value measured for **3**, initially oxidized, and the $E_{1/2}$ value for **6**, initially reduced, are equal, indicating that the species observed in the voltammograms are the two complexes isolated. This is the same behavior previously observed for pairs of alkylisocyanide-Co(I), Co(II) complexes with triarylphosphine ligands, $[Co^{I}(CNR)_3(PR'_3)_2]X$, $[Co^{II}(CNR)_3(PR'_3)_2]X_2$, $X = ClO_4$, BF_4 [48]. That the voltammograms for **1** and **2** exhibit reversible behavior is somewhat unexpected, however, as $[Co(CNR)_5]ClO_4$, $R = C_6H_3Et_2$-2,6, $C_6H_3i Pr_2$-2,6, showed poor quasi-reversibility in CH_2Cl_2 [49].

Molar conductivity values (Λ_M) confirm the assumption that **1**–**6** are monomeric and ionic in solution; **7** decomposes in solution state. The Λ_M values for **1**, **2**, and **6** are within the known range of 2 : 1 electrolytes in CH_3CN and CH_3NO_2 solution, and values for **3**, **4**, and **5** are within range of 1 : 1 electrolytes [50]. The Λ_M value for **1** in acetone is slightly low, the value for **2** is normal, and the value for **6** is slightly high for expected 2 : 1 behavior. The Λ_M values in acetone for **3**, **4**, and **5** are at the upper range for expected 1 : 1 behavior, a trend previously observed with Co(I)-alkylisocyanide complexes [22, 23]. The Λ_M values in CH_2Cl_2 for **3**, **4**, and **5** are within the range observed for Co(I)-alkylisocyanide complexes, i.e. 50–70 $\Omega^{-1}\,cm^2\,mol^{-1}$ [22, 23], but values for **1**, **2**, and **6** indicate extensive ion-pairing, which is expected for this solvent of relatively low dielectric constant [8, 9, 37].

^1H, ^{13}C, and ^{31}P NMR chemical shifts for **3**, **4**, and **5**, together with the $CNC(Me)_2CH_2C(Me)_3$, $P(CH_2CH_2CH_2CH_3)_3$, and $P(CH_2CH_2CH_3)_3$ free ligands, are summarized in tables 1–5, and the ^{13}C-NMR spectrum for $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3]BF_4$ is shown in figure 2. The ^1H spectra are poorly resolved and therefore of little interest. For $CNC(Me)_2CH_2C(Me)_3$, the two equivalent CH_3 and the CH_2 sets of protons are nicely split into triplets by coupling with N, however, but the $CH_2CH_2CH_2$ protons in $P(C_4H_9\text{-}n)_3$ are unresolved while the CH_2CH_2 protons in $P(C_3H_7\text{-}n)_3$ are high-order multiplets that are not clearly assigned. In **3** and **4** the equivalent sets of protons can be identified, but in **5** proton signals from the isocyanide and phosphine ligands are scrambled. The ^{13}C spectra are more informative. The CN signal from $CNC_8H_{17}\text{-}t$ is split by N but little affected by Co in multiplicity or frequency, and is very weak, so it is undetected in **3**. N-coupling to the two equivalent CH_3 groups in $CNC_8H_{17}\text{-}t$ is well-resolved in the free ligand but undetected in the complexes. Assignments for C^2 and C^3 in $P(C_4H_9\text{-}n)_3$ and C^1 and C^2 in $P(C_3H_7\text{-}n)_3$ would appear interchanged as judged by their frequencies, but values of C–P coupling constants and relative intensities dictate the assignments given. For the Co(I) complexes, signals for C^1 and C^2 in $P(C_4H_9\text{-}n)_3$ from **3** and **4**, and C^1, C^2, and C^3 in $P(C_3H_7\text{-}n)_3$ from **5**, are all split into symmetrical triplets with progressively decreasing coupling constants (see tables 2 and 4). These patterns are best explained in terms of virtual coupling with both P atoms [51]. To confirm that the signals observed are indeed triplets, not fortuitous overlap of doublets of doublets, ^{13}C NMR spectra for **3** were scanned in methanol-d_4 and acetone-d_6, in addition to chloroform-d_1. Results in these three deuterated solvents, $DCCl_3$, CD_3OD, and $CD_3C(O)CD_3$, respectively, for C^1 and C^2 (see table 2 for notation) were, C^1: 28.2 t, $^1J_{C\text{–}P} = 13.4$ Hz; 28.0 t, $^1J_{C\text{–}P} = 13.5$ Hz; 29.0 t, $^1J_{C\text{–}P} = 13.7$ Hz; and C^2: 24.7 t, $^2J_{C\text{–}P} = 6.6$ Hz; 24.4 t, $^2J_{C\text{–}P} = 6.8$ Hz; 25.4 t, $^2J_{C\text{–}P} = 6.7$ Hz. Chemical shifts and coupling constants are slightly changed, as expected, but the triplet patterns for the two different C atoms were retained, thereby supporting this argument. Virtual coupling confirms *trans*-coordination for the

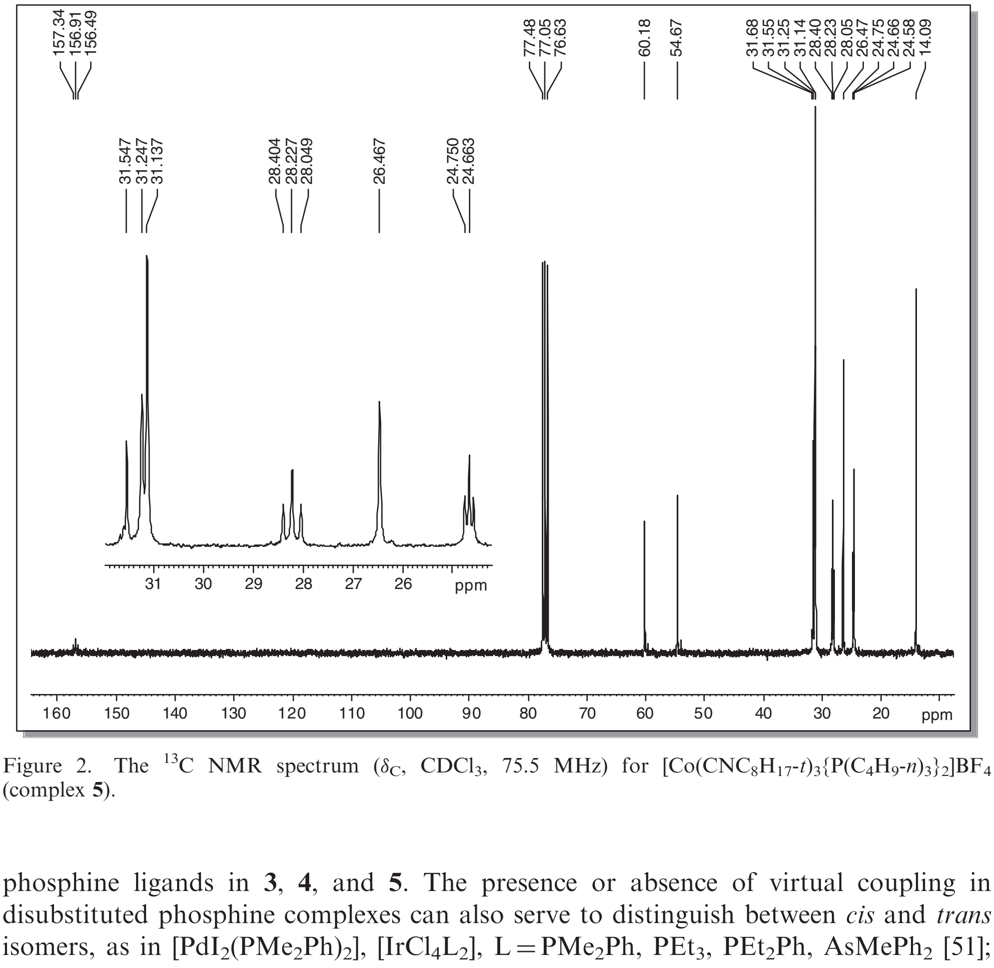

Figure 2. The ^{13}C NMR spectrum (δ_C, $CDCl_3$, 75.5 MHz) for $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2]BF_4$ (complex **5**).

phosphine ligands in **3**, **4**, and **5**. The presence or absence of virtual coupling in disubstituted phosphine complexes can also serve to distinguish between *cis* and *trans* isomers, as in $[PdI_2(PMe_2Ph)_2]$, $[IrCl_4L_2]$, L = PMe_2Ph, PEt_3, PEt_2Ph, $AsMePh_2$ [51]; $[Rh(CNR)_3(PPh_3)_2][PF_6]$, R = Me, Et, C_6H_{11} [52]; $[NiCl_2(HL)_2]$, $[PdCl_2(HL)_2]$, HL = Ph_2PCH_2COMe [53]; $[PtBr_2\{PPh_2(CF{=}CF_2)\}_2]$, $[PtBr_2\{PPh_2(CCl{=}CF_2)\}_2]$, $[PtI_2\{PPh_2(CX{=}CF_2)\}_2]$ [54]; $[PdCl_2(PPh_2CH_2\text{-}2,4,6\text{-}C_6H_2Me_3)_2]$ [55], to list a few examples. The ^{31}P spectra are routine: one signal shifted significantly down-field relative to the free ligand ($\Delta\delta = 81$–83 ppm). These data also support the assumed solution structures of axially-disubstituted trigonal bipyramidal coordination for **3**, **4**, and **5**.

4. Conclusions

Cobalt-organoisocyanide chemistry has been extended to include 1,1,3,3-tetramethylbutylisocyanide, $CNC(Me)_2CH_2C(Me)_3$, i.e. *t*-octylisocyanide. Surprisingly the Co(II) reaction products are not analogous to the complexes with $CNCMe_3$ or with $CNCHMe_2$, but are similar to complexes of non-sterically hindered arylisocyanides, i.e. $[Co(CNR)_5]X_2 \cdot xH_2O$, X = ClO_4, BF_4, in both composition and ν(N≡C) IR patterns. Monomeric and ionic nature of these Co(II) complexes (i.e. **1** and **2**) are confirmed by one-electron paramagnetism in solid state and conductivity measurements (Λ_M) in solution. Cyclic voltammetry measurements (in acetonitrile) are unexpectedly reversible.

The Co(II)-*t*-octylisocyanide complexes undergo reduction/substitution reactions upon treatment with excess trialkylphosphine ligands, yielding $[Co(CNR)_3(PR'_3)_2]X$, $R' = C_4H_9$-*n*, C_3H_7-*n* (**3**, **4**, and **5**), similar to complexes with $CNCMe_3$ but dissimilar to Co(II) complexes of $CNCHMe_2$, CNC_6H_{11}, $CNCH_2Ph$, and CNC_4H_9-*n*, which undergo disproportionation/substitution reactions. These five-coordinate complexes, $[Co(CNC_8H_{17}\text{-}t)_3(PR_3)_2]X$, $X = ClO_4$, BF_4, are essentially identical under exchange of phosphine ligand or anion. Diamagnetism in solution is affirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectra, and virtual coupling of the two P nuclei confirms linearity of the P–Co–P bond in the axially disubstituted trigonal bipyramidal coordination. The Co(I) complex is oxidized to the five-coordinate Co(II) complex, $[Co(CNC_8H_{17}\text{-}t)_3\{P(C_4H_9\text{-}n)_3\}_2](ClO_4)_2$ (**6**), with Ag^+. Upon treatment of **1** with pyridine, a six-coordinate Co(II) complex, *trans*-$[Co(CNC_8H_{17}\text{-}t)_4py_2](ClO_4)_2$ (**7**), is isolated and is surprisingly stable to reduction in solution. Anticipated reduction/substitution reactions of **1** and **2** with triarylphosphine ligands were unsatisfactory, as the disubstituted Co(I) complexes, evidenced by definitive $\nu(N{\equiv}C)$ IR patterns, are too soluble to be purified by conventional methods. Complex **2** is surprisingly inert to reaction with $AsPh_3$. Thus a wealth of new chemistry has been discovered in cobalt complexes of *t*-octylisocyanide.

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References

[1] A. Sacco. *Gazz. Chim. Ital.*, **84**, 370 (1954).
[2] A. Sacco, M. Freni. *Gazz. Chim. Ital.*, **89**, 1800 (1959).
[3] L. Malatesta. *Prog. Inorg. Chem.*, **1**, 283 (1959).
[4] L. Malatesta, F. Bonati. *Isocyanide Complexes of Metals*, Ch. 7, John Wiley, New York (1969).
[5] F.A. Cotton, T.G. Dunne, J.S. Wood. *Inorg. Chem.*, **3**, 1495 (1964).
[6] J.M. Pratt, P.R. Silverman. *Chem. Commun.*, 117 (1967); *J. Chem. Soc. A*, 1286 (1967).
[7] P.M. Boorman, P.J. Craig, T.W. Swaddle. *Can. J. Chem.*, **48**, 838 (1970).
[8] C.A.L. Becker. *J. Coord. Chem.*, **28**, 147 (1993).
[9] C.A.L. Becker. *Inorg. Chim. Acta*, **203**, 175 (1993).
[10] C.A.L. Becker, O.C. Malete. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 1635 (2003).
[11] C.A.L. Becker, A. Anisi, G. Myer, J.D. Wright. *Inorg. Chim. Acta*, **111**, 11 (1986).
[12] L. Malatesta, A. Sacco. *Z. Anorg. Allg. Chem.*, **273**, 247 (1953).
[13] C.A.L. Becker. *Inorg. Chim. Acta*, **27**, L105 (1978).
[14] C.A.L. Becker, J.C. Cooper. *Inorg. Chim. Acta*, **158**, 141 (1989).
[15] C.A.L. Becker, J.C. Cooper. *Inorg. Chim. Acta*, **182**, 25 (1991).
[16] C.A.L. Becker. *Synth. React. Inorg. Met.-Org. Chem.*, **22**, 437 (1992).
[17] C.A.L. Becker. *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 1455 (1995).

[18] R.B. King, M.S. Saran. *Inorg. Chem.*, **11**, 2112 (1972).

[19] J.W. Dart, M.K. Lloyd, R. Mason, J.A. McCleverty, J. Williams. *J. Chem. Soc., Dalton Trans.*, 1747 (1973).

[20] G. Albertin, E. Bordignon, U. Croatto, A.A. Orio. *Gazz. Chim. Ital.*, **104**, 1041 (1974).

[21] E. Bordignon, U. Croatto, U. Mazzi, A.A. Orio. *Inorg. Chem.*, **13**, 935 (1974).

[22] C.A.L. Becker, S.A. Al-Qallaf, J.C. Cooper. *Inorg. Chim. Acta*, **188**, 99 (1991).

[23] C.A.L. Becker, M.A.S. Biswas, J.C. Cooper. *Inorg. Chim. Acta*, **188**, 191 (1991).

[24] C.A.L. Becker, M.A.S. Biswas. *J. Coord. Chem.*, **29**, 277 (1993).

[25] C.A.L. Becker, N. Samarakkody. *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 1111 (1999).

[26] C.A.L. Becker. *J. Coord. Chem.*, **59**, 1407 (2006).

[27] C.A.L. Becker. *J. Coord. Chem.*, **26**, 231 (1992).

[28] C.A.L. Becker, S. Odisitse. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 1547 (2000).

[29] C.A.L. Becker. *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 269 (1995).

[30] S. Otsuka, M. Rossi. *Bull. Chem. Soc. Japan*, **46**, 3411 (1973).

[31] R. Graziani, G. Albertin, E. Forsellini, A.A. Orio. *Inorg. Chem.*, **15**, 2422 (1976).

[32] C.A.L. Becker. *Synth. React. Inorg. Met.-Org. Chem.*, **9**, 445 (1979).

[33] C.A.L. Becker. *Inorg. Chim. Acta*, **36**, L441 (1979).

[34] C.A.L. Becker. *J. Inorg. Nucl. Chem.*, **42**, 27 (1980).

[35] C.A.L. Becker. *Inorg. Chim. Acta*, **77**, L223 (1983).

[36] C.A.L. Becker, N.K. Homsy. *Inorg. Chim. Acta*, **89**, 93 (1984).

[37] C.A.L. Becker. *J. Coord. Chem.*, **31**, 337 (1994).

[38] C.A.L. Becker. *J. Coord. Chem.*, **50**, 89 (2000).

[39] C.A.L. Becker. *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 1527 (1997).

[40] C.A.L. Becker. *Abstracts, 161st National Meeting of the American Chemical Society*, Los Angeles, Calif., No. INORG 85 (April 1971).

[41] F.A. Jurnak, D.R. Greig, K.N. Raymond. *Inorg. Chem.*, **14**, 2585 (1975).

[42] B.N. Figgis, J. Lewis. In: *Modern Coordination Chemistry*, J. Lewis, R.G. Wilkins (Eds), Ch. 6, pp. 403–408, Interscience, New York (1960).

[43] B.N. Figgis, R.S. Nyholm. *J. Chem. Soc.*, 12 (1954).

[44] R. Nicholson, I. Shain. *Anal. Chem.*, **36**, 706 (1964).

[45] W.E. Geiger. In: *Laboratory Procedures in Electrochemistry*, P.T. Kissinger, W.R. Heineman (Eds), pp. 683–717, Marcel Dekker, New York (1996).

[46] J.J. Van Benschoten, J.Y. Lewis, W.R. Heineman, D.A. Roston, P.T. Kissinger. *J. Chem. Educ.*, **60**, 772 (1983).

[47] J. Ahmad, F. Bothata-Nareetsile, C.A.L. Becker. *Can. J. Chem.*, **81**, 982 (2003).

[48] G.A. Mabbot. *J. Chem. Educ.*, **60**, 697 (1983).

[49] F.F. Mbaiwa, C.A.L. Becker. *Inorg. Chim. Acta*, **359**, 1041 (2006).

[50] R.J. Angelici. *Synthesis and Technique in Inorganic Chemistry*, 2nd Edn, Appendix 2 Saunders, Philadelphia (1960).

[51] J.M. Jenkins, B.L. Shaw. *Proc. Chem. Soc London*, 279 (1963).

[52] J.A. McCleverty, J. Williams. *Transition Met. Chem.*, **3**, 205 (1978).

[53] E.M. Georgiev, H.T. Kieck, G. Fendesak, G. Hahn, G. Petrov, M. Kirilov. *J. Chem. Soc., Dalton Trans.*, 1331 (1992).

[54] N.A. Barnes, A.K. Brisdon, J.G. Fay, R.G. Pritchard, J.E. Warren. *Inorg. Chim. Acta*, **358**, 2543 (2005).

[55] L. Chahen, B. Therrien, G. Suss-Fink. *J. Organomet. Chem.*, **691**, 4257 (2006).