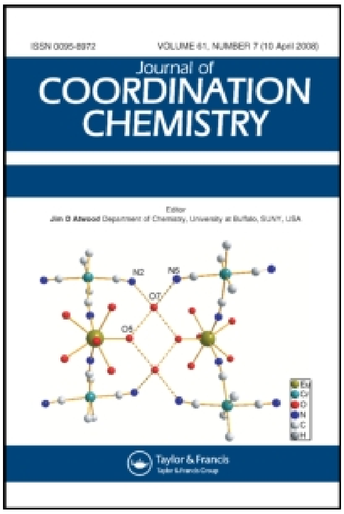

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Clifford A. L. Becker[a]
[a] Department of Chemistry, University of Botswana, Gaborone, Botswana

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Syntheses of *tris*(*t*-butylisocyanide)*bis*(tri-*p*-dimethylaminophenylphosphine)cobalt(I) and cobalt(II) perchlorates: a reversal of the usual stabilities of cobalt oxidation states

CLIFFORD A. L. BECKER*

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

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The complexes $[Co(CNCMe_3)_3\{P(C_6H_4NMe_2\text{-}p)_3\}_2](ClO_4)_2$ and $[Co(CNCMe_3)_3\{P(C_6H_4NMe_2\text{-}p)_3\}_2]ClO_4$ are reported. The Co(II) complex, formed by reaction of excess triarylphosphine with the alkylisocyanide Co(II) complex, is stable and the favoured product. The Co(I) complex, formed by hydrazine reduction of the Co(II) complex, has limited stability in solution, readily oxidizing to the Co(II) species. Upon prolonged irradiation of the Co(II) complex in acetone, $[Co\{OP(C_6H_4NMe_2\text{-}p)_3\}_4](ClO_4)_2$ is produced.

Keywords: *t*-Butylisocyanide; Tri-*p*-dimethylaminophenylphosphine; Cobalt(II); Cobalt(I); Redox reactions

1. Introduction

Reactions of triarylphosphine ligands with Co(II) complexes of alkylisocyanides typically favour reduction/ligand substitution, yielding products of general formula $[Co(CNR)_3(PR'_3)_2]X$, $X = ClO_4$, BF_4 [1–6]. Co(II) complexes have been isolated as minor products under special conditions [7–9], and some Co(I) complexes can be reversibly oxidized to the corresponding Co(II) complexes $[Co(CNR)_3(PR'_3)_2]X_2$ [10, 11], but Co(I) is clearly the favoured product. This trend is particularly well developed for reactions of $[Co(CNCMe_3)_4H_2O](ClO_4)_2$ (**1**) with the complexes $[Co(CNCMe_3)_3(PR'_3)_2]ClO_4$, $R' = C_6H_4CF_3\text{-}p$, $C_6H_4F\text{-}p$, $C_6H_4Cl\text{-}p$, C_6H_5, $C_6H_4Me\text{-}p$, $C_6H_4OMe\text{-}p$ [4–6].

This article reports the reaction of $P(C_6H_4NMe_2\text{-}p)_3$ with **1**, for which the relative stabilities of the Co(I) and Co(II) states are reversed, $[Co(CNR)_3(PR'_3)_2]X_2$ now being the favoured product and $[Co(CNR)_3(PR'_3)_2]X$ being obtained through N_2H_4 reduction; the latter has limited stability in solution. The complex $[Co\{OP(C_6H_4NMe_2\text{-}p)_3\}_4](ClO_4)_2$ [12, 13] is also obtained.

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*Email: beckerca@mopipi.ub.bw

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2. Experimental

Commercially available $CNCMe_3$ (Fluka) and $P(C_6H_4NMe_2\text{-}p)_3$ (Strem) were used without further purification. Complex **1** was synthesized as previously reported [4]. Anhydrous diethylether was filtered through an alumina column before use.

IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer. Solution electronic spectra were recorded on a Shimadzu UV365 spectrophotometer. Molar conductivities were measured on 0.001 M solutions at 25°C using a Crison 525 conductimeter. Magnetic susceptibilities were measured at room temperature using a Johnson Matthey Alfa balance. Effective magnetic moments were calculated assuming Curie Law behaviour using diamagnetic corrections from the literature [7, 14, 15]. An Allen and Co. lamp was used for irradiation at 365 nm. Elemental analyses were performed using a Carlo Erba 1106 instrument.

Cautionary Note: Complexes reported in this article are perchlorate salts. Complex **1** is substantially easier to prepare and store than $[Co(CNCMe_3)_4H_2O](BF_4)_2 \cdot 2.5H_2O$ [4, 16]. Although the complexes show no explosive tendency, all perchlorate salts must be considered as potentially hazardous. Please see comments regarding the use of perchlorate salts [8].

2.1. $[Co(CNCMe_3)_3\{P(C_6H_4NMe_2\text{-}p)_3\}_2](ClO_4)_2$ (2)

Complex **1** (200 mg, 0.329 mmol) was dissolved in CH_3CN (1.5 cm^3), filtered through cotton with a CH_3CN rinse (0.5 cm^3), and chilled in ice. $P(C_6H_4NMe_2\text{-}p)_3$ (383 mg, 0.978 mmol; 3 : 1 P : Co mol ratio), in CH_2Cl_2 (4.5 cm^3), was added dropwise while the reaction mixture was stirred. The colour of the solution changed from dark blue to intense yellow-brown. Diethylether was added dropwise, 8.5 cm^3 for initial precipitation, 18.0 cm^3 in total. The reaction mixture was chilled in ice (30 min), and the yellow-brown product filtered off and washed twice with diethylether. The product (337 mg, 53% yield) was recrystallized from CH_2Cl_2 (5.5 cm^3) and diethylether (7.5 cm^3), producing a yellow-green microcrystalline solid. Yield: 316 mg (50%), m.p. 213–218°C (dec). Anal. Calcd for $C_{63}H_{87}Cl_2CoN_9O_8P_2$ (%): C, 58.65; H, 6.80; N, 9.77. Found: C, 58.44; H, 6.95; N, 9.78. IR (cm^{-1}): $\nu(N{\equiv}C)$ 2193w(sh), ~2179vw(sh), 2170vs (Nujol); 2170vs (CH_2Cl_2); 2172vs (CH_3NO_2); 2171vs (CF_3CH_2OH). Molar conductivity: Λ_M ($ohm^{-1}\,cm^2\,mol^{-1}$) 275 (CH_3CN), 220 (acetone), 140 (CH_3OH), 175 (CH_3NO_2), 51 (CH_2Cl_2). Electronic spectrum: λ_{max} (ε, $M^{-1}\,cm^{-1}$) 905br (320), ~620sh (1,400), 465 (10,000), 385 (9,900), 290 (86,000) nm (CH_2Cl_2); 880br (310), ~620sh (1,400), 454 (9,000), 376 (8,900), 290 (81,000) nm (CH_3CN); ~895br (280), ~620sh (1,200), 459 (9,200), ~383br (9,000), 287 (82,000) nm (CF_3CH_2OH). Magnetic susceptibility: $\chi_g = 1.37 \pm 0.09 \times 10^{-6}$ (cgs), $\mu_{eff} = 2.45 \pm 0.05$ BM.

2.2. $[Co(CNCMe_3)_3\{P(C_6H_4NMe_2\text{-}p)_3\}_2]ClO_4$ (3)

Complex **2** (200 mg, 0.155 mmol) was dissolved in CH_2Cl_2 (2.0 cm^3) and filtered through cotton. $N_2H_4 \cdot H_2O$ (15 microdrops) was added dropwise, and the solution stirred vigorously for 5 min while the dark yellow-brown colour became increasingly red-brown. The reaction mixture was decanted and twice filtered through cotton. Diethylether was added dropwise to the clear, red-orange solution, 2.2 cm^3 for cloudiness, 5.0 cm^3 in total. The reaction mixture was chilled in ice (30 min) and a pale yellow microcrystalline product filtered off and washed twice with diethylether. This product (110 mg, 60% yield) was recrystallized from CH_2Cl_2 (1.5 cm^3) and diethylether (3.0 cm^3). Yield: 75 mg (40%), m.p. 263–270°C (dec). Anal. Calcd for $C_{63}H_{87}ClCoN_9O_4P_2$ (%): C, 63.55; H, 7.36; N, 10.59. Found: C, 63.66; H, 7.37; N, 10.57. IR (cm^{-1}): $\nu(N{\equiv}C)$ ~2090m, 2045vs (br) (Nujol); ~2090m(sh), 2055vs (CH_2Cl_2); ~2080m (br,sh), 2052vs (CH_3NO_2). Molar conductivity: Λ_M (ohm^{-1} cm^2 mol^{-1}) 120 (CH_3CN), 125 (acetone), 71 (CH_3NO_2), 62 (CH_2Cl_2).

2.3. *[Co{OP(C$_6$H$_4$NMe$_2$-p)$_3$}$_4$](ClO$_4$)$_2$ (4)*

Complex **2** (200 mg, 0.155 mmol) was dissolved in acetone (9.5 cm^3), filtered through cotton, and irradiated at 365 nm for 70 h at room temperature. During this exposure in a quartz tube, the opaque yellow-brown solution gradually assumed a less intense, greenish-grey colour. After irradiation, the sample was filtered through cotton, and diethylether was slowly added. After addition of 3.0 cm^3 of diethylether, the sample was again filtered, leaving a clear, blue-green solution. Another 7.0 cm^3 of diethylether was added, and the reaction mixture chilled in ice (1 h). A dark blue, microcystalline solid was filtered from a pale yellow filtrate and washed twice with diethylether. Crude product was recrystallized from CH_2Cl_2 (1.0 cm^3) and diethylether (1.5 cm^3). Yield: 81 mg (55%), m.p. 258–264°C (dec). Anal. Calcd for $C_{96}H_{120}Cl_2CoN_{12}O_{12}P_4 \cdot 0.5CH_2Cl_2$ (%): C, 60.00; H, 6.32; N, 8.71. Found: C, 59.86; H, 6.34; N, 8.67. Molar conductivity: Λ_M (ohm^{-1} cm^2 mol^{-1}) 300 (CH_3CN), 295 (acetone), 180 (CH_3NO_2), 71 (CH_2Cl_2). Electronic spectrum: λ_{max} (ε, M^{-1} cm^{-1}) 638 (440), 608 (385), 587 (360), 562 (280), 553 (265), ~480sh (23), 287 (180,000) nm (CH_2Cl_2); 637 (381), 608 (337), 587 (315), 562 (247), 552 (232), ~480sh (21), 284 (193,000) nm (CH_3CN). Magnetic susceptibility: $\chi_g = 4.79 \pm 0.23 \times 10^{-6}$ (cgs), $\mu_{eff} = 5.0 \pm 0.1$ BM.

3. Results and discussion

3.1. *Syntheses*

The synthesis of **2** uses basically the same procedure for Co(I) complexes with other triarylphosphines. $P(C_6H_4NMe_2\text{-}p)_3$ is less soluble than the other triarylphosphines, requiring greater volumes of CH_2Cl_2, and the colour of the reaction mixture is noticeably more intense. In some attempts, a small crop of **3** was also isolated, but **2** is the major, often only, product. Over prolonged reaction times, complex **4** can be detected. The synthesis of **3** is analogous to hydrazine reduction of other five-coordinate Co(II) complexes [10], except the yield is low, especially in recrystallization. Complex **3** is oxidized to Co(II) in CF_3CH_2OH solution, and has limited stability in CH_3CN and CH_3OH.

The synthesis of complex **4** is similar to that for $[Co(OAsR_3)_4](ClO_4)_2$, R = C_6H_5, $C_6H_4Me\text{-}p$ [17], and $[Co(OPPh_3)_4](ClO_4)_2$ [8], by solution decomposition of $[Co(CNC_6H_{11})_4(AsR_3)_2](ClO_4)_2$ and $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$, respectively. These syntheses are described as photochemically-assisted, not photochemical reactions, since they do take place in the dark, *albeit* more slowly [17]. Complex **4** is best synthesized in acetone, although reaction also takes place in CH_2Cl_2. $[Co(CNC_6H_{11})_3(PPh_3)_2](ClO_4)_2$ readily reacted in CH_2Cl_2 or CH_3NO_2, but in acetone or CH_3CN appeared to decompose to octahedral Co(II) species [8]. $[Co(CNC_6H_{11})_4(AsR_3)_2](ClO_4)_2$ converted to the arsine oxide complex in CH_2Cl_2, CH_3NO_2, CH_3CN, acetone or CF_3CH_2OH [17]. This synthesis, in which a triarylphosphine is oxidized to the phosphine oxide, displacing alkylisocyanide ligands to convert low-spin trigonal bipyramidal Co(II) into a high-spin tetrahedral complex, is quite different to the case of simply reacting Co(II) perchlorate with the triarylphosphine oxide [13].

3.2. *Characterization of the complexes*

The molar conductivities (Λ_M) for complexes **2**, **3**, and **4** are within, or very close to, the ranges expected for 1 : 1 and 2 : 1 electrolytes in CH_3CN, acetone, CH_3OH, and CH_3NO_2 [18], except for **4** in acetone, which is above the expected range (160–200 $ohm^{-1}\,cm^2\,mol^{-1}$). Λ_M values for the $[Co(OAsR_3)_4]X_2$ complexes were also high in acetone [17]. The Λ_M values for **2** especially, and **4**, in CH_2Cl_2 show ion-pairing, customary for Co(II) complexes [19]. Complexes **3** and **4** were unstable in CH_3OH. The effective magnetic moment for complex **2** (2.45 BM) is within the range previously observed for five-coordinate alkylisocyanide–triarylphosphine complexes of Co(II) [10] and within the range normally observed for low-spin Co(II) (1.8–2.7 BM) [14]. The moment for **4** (5.0 BM) is higher than the temperature-varied fit to the Curie–Weiss law (4.76 BM, $\theta = -6$) [12], but clearly indicates a three-electron paramagnetic species. Complex **3** is expected to be diamagnetic.

Solution electronic spectra of complex **2** are analogous to spectra of other $[Co(CNR)_3(PR'_3)_2]X_2$ complexes [10]; a crystal field band around 900 nm and intense charge transfer bands in the UV are observed. For **2** both the CF and most intense CT band are at longer wavelengths. Electronic spectra of **3** are not reported since oxidation to **2** takes place for dilute solution (CH_3CN, CH_2Cl_2 and CF_3CH_2OH). Spectra for complex **4** give a multiplet of bands assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transitions characteristic of tetrahedral Co(II) [20]. The extremely intense band in the UV is undoubtedly an intraligand transition should be divided by four. There is then good agreement between complex **4** and free $OP(C_6H_4NMe_2\text{-}p)_3$ ligand spectra for this band: 287 nm ($\varepsilon = 45{,}000$) (**4**) *versus* 288 (47,000) in CH_2Cl_2, 284 (48,000) (**4**) *versus* 284 (48,000) in CH_3CN.

The $\nu(-N{\equiv}C)$ IR spectra for complexes **2** and **3** are analogous to those of other alkylisocyanide–triarylphosphine complexes of Co(I) and Co(II) [4–6, 10, 11]. Complex **3** would thus be assigned a distorted trigonal bipyramidal solution structure, while **2** would be expected to be regular trigonal bipyramidal. Comparing the major band for $[Co(CNCMe_3)_3(PPh_3)_2]ClO_4$, $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]ClO_4$ and **3**, and for $[Co(CNCMe_3)_3(PPh_3)_2](ClO_4)_2$, $[Co(CNCMe_3)_3\{P(C_6H_4OMe\text{-}p)_3\}_2](ClO_4)_2$ and **2**, one notices that $\nu(-N{\equiv}C)$ values systematically decrease. Slightly larger $\Delta\nu$ values are seen for replacing $P(C_6H_4OMe\text{-}p)_3$ with $P(C_6H_4NMe_2\text{-}p)_3$ than for replacing PPh_3 with $P(C_6H_4OMe\text{-}p)_3$ [11]. This is in accord with the NMe_2 group being a stronger electron-donating substituent than OMe. Herein is also the probable explanation for the increased stability of the Co(II) complex. Through the series

$[Co(CNCMe_3)_3(PR'_3)_2]ClO_4$, $R' = C_6H_4CF_3$-*p*, C_6H_4F-*p*, C_6H_4Cl-*p*, C_6H_5, C_6H_4Me-*p*, C_6H_4OMe-*p*, $C_6H_4NMe_2$-*p*, the triarylphosphine ligand becomes a stronger σ-donator and weaker π^*-acceptor. For $R' = C_6H_4CF_3$-*p*, C_6H_4F-*p*, C_6H_4Cl-*p* only the Co(I) complex is stable [10]. For $R' = C_6H_5$, C_6H_4Me-*p*, C_6H_4OMe-*p* both Co(I) and Co(II) complexes are stable, and for $R' = C_6H_4NMe_2$-*p*, the Co(II) complex is the favoured species with Co(I) having limited stability in solution. This is a significant change in reactivity for a seemingly minor change in the triarylphosphine ligand.

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