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# Structural variation in cobalt halide complexes supported by *m*-terphenyl isocyanides

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Dedicated to Professor Arnold L. Rheingold, a tremendous mentor and great friend, on the occasion of his 70th birthday.

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#### ABSTRACT

Detailed herein are synthetic, spectroscopic and structural studies on trisisocyanide cobalt halide complexes featuring the encumbering *m*-terphenyl isocyanide  $CNAr^{Mes2}$  (Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub>). Addition of  $CNAr^{Mes2}$  to  $Col_2$  in a 3:1 molar ratio provides the mononuclear complex,  $Col_2(CNAr^{Mes2})_3$ , which can be oxidized to six-coordinate  $Col_3(CNAr^{Mes2})_3$  upon treatment with 0.5 equivalents of  $l_2$ . Contrastingly, addition of  $CNAr^{Mes2}$  to  $CoBr_2$  provided the dinuclear complex  $Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$  irrespective of the molar ratios employed. FTIR analysis on these Co(II) and Co(III) complexes is used to assess the relative  $\pi$ -basicities of the cobalt centers toward the  $CNAr^{Mes2}$  ligands. Treatment of  $CoX_2$  (X = Cl, Br and I) with three  $CNAr^{Mes2}$  ligands followed by the addition of granulated Zn provides the pseudo-tetrahedral complexes  $XCo(CNAr^{Mes2})_3$ . FTIR, magnetic and X-ray crystallographic studies are used to determine both the ground state electronic structure and relative  $\pi$ -basicities of these complexes.

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## 1. Introduction

Longstanding interest in isocyanide complexes of cobalt has arisen because of their isolobal relationship to the classic binary carbonyl  $Co_2(CO)_8$  [1–7]. More specifically, the root of this interest stems from attempts to model the mononuclear intermediates proposed in industrial hydroformylation (oxo catalysis) initiated by  $Co_2(CO)_8$  [8–10]. For example, it has been established that the combination of Co<sub>2</sub>(CO)<sub>8</sub> and H<sub>2</sub> generates two equivalents of monohydride complex  $HCo(CO)_4$  [10]. Interestingly, there is still debate whether  $H_2$  reacts directly with  $Co_2(CO)_8$ , or if the latter undergoes homolytic cleavage to two Co(CO)<sub>4</sub> molecules prior to the H<sub>2</sub> activation step [10,11]. Once formed however, carbon monoxide dissociation from HCo(CO)<sub>4</sub> is proposed to form four-coordinate  $HCo(CO)_3$ , which serves as the catalysis entry point [10]. Despite these proposals, definitive evidence for the presence of either Co(CO)<sub>4</sub> or HCo(CO)<sub>3</sub> during hydroformylation catalysis has remained elusive [12-15].

Accordingly, isocyanides (CNR), which allow for steric and electronic tunability [16], have been employed to model both the structural and electronic aspects of such highly reactive cobalt carbonyls [1–7]. However, one common drawback to the implementation of isocyanides in this context has been their limited success for the simultaneous stabilization of coordinative and electronic unsaturation in mononuclear cobalt centers. In this regard, encum-

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bering isocyanides including CN-*t*-Bu and CNXyl (Xyl = 2,6- $Me_2C_6H_3$ ) mirror the reactivity of CO, rather than diverging from it [17]. Furthermore, these isocyanides have been shown to stabilize higher coordinate cobalt complexes than are typically available with carbonyl ligands. This latter fact is demonstrated by the many examples of penta-coordinate [Co(CNR)<sub>5</sub>]<sup>+</sup> cations [16,18–20], whereas the analogous pentacarbonyl cobalt cation, [Co(CO)<sub>5</sub>]<sup>+</sup> has only recently been isolated in crystalline form [21].

In an effort to stabilize low-coordinate metal isocyanide complexes in general, we have introduced the encumbering *m*-terphenyl isocyanide ligand,  $CNAr^{Mes2}$  [22–24]. As part of our studies, we recently reported a series of homoleptic cobalt tetraisocyanide complexes of the formulation  $[Co(CNAr^{Mes2})_4]^n$  in the +1, 0 and -1 charge states [25]. The neutral species  $Co(CNAr^{Mes2})_4$  is particularly noteworthy as it represents a formal mimic of the reactive unsaturated carbonyl  $Co(CO)_4$ .

In order to gain synthetic entry to this tetraisocyanide system, we found that the salt Na[Co(CNAr<sup>Mes2</sup>)<sub>4</sub>] is accessible from Na/ Hg reduction of CoCl<sub>2</sub> in the presence of CNAr<sup>Mes2</sup>. Interestingly, optimization of the reaction conditions predicated that only three equivalents of CNAr<sup>Mes2</sup> were necessary to achieve both reasonable yields (ca. 60%) of Na[Co(CNAr<sup>Mes2</sup>)<sub>4</sub>] and full consumption of the isocyanide. Indeed, when greater than three equivalents of CNAr<sup>Mes2</sup> are employed, no increase in the yield of Na[Co(C-NAr<sup>Mes2</sup>)<sub>4</sub>] was achieved. Furthermore, significant quantities of free CNAr<sup>Mes2</sup> remained. Thus, this protocol seemingly does not yield low-valent trisisocyanide complexes which may serve as precursors to species such as  $HCo(CNAr^{Mes2})_3$  or  $[Co(CNAr^{Mes2})_3]^n$ 



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(n = +1, 0 and -1). Accordingly, herein we present synthetic details for tris-CNAr<sup>Mes2</sup> cobalt halide complexes which may serve this purpose. Most importantly, the complexes reported here exhibit spectroscopic and structural features which provide insight into  $\pi$ -basicity properties of cobalt halide fragments toward isocyanide ligands.

## 2. Experimental

All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures. Unless otherwise stated, reagent grade starting materials were purchased from commercial sources and used as received. Benzene-d<sub>6</sub> (Cambridge Isotope Laboratories) was degassed and stored over 4 Å molecular sieves for 2 d prior to use. THF-d<sub>8</sub> (Cambridge Isotope Laboratories) was vacuum distilled from Na metal and stored over 4 Å molecular sieves for 1 d prior to use. The isocyanide ligand CNAr<sup>Mes2</sup>,  $[Co(CNAr^{Mes2})_4]BAr_4^F$  and  $NaBAr_4^F$  (Ar<sup>F</sup> = 3,5- $(CF_3)_2C_6H_3$ ) were prepared as previously described [22,25,26]. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use. Nuiol was dried with sodium metal and stored in the glovebox prior to use. Granulated zinc metal was activated with a 2 M hydrochloric acid solution, subsequently washed with dry THF in three cycles and dried under vacuum prior to use.

Solution <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers and a Varian VNMRS 500 spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm relative to SiMe<sub>4</sub> (<sup>1</sup>H and <sup>13</sup>C  $\delta$  = 0.0 ppm) with reference to the residual proton resonances of 7.16 ppm (<sup>1</sup>H) and 128.06 ppm (<sup>13</sup>C) for benzene-*d*<sub>6</sub> and 1.73 ppm (<sup>1</sup>H) and 25.3 ppm (<sup>13</sup>C) for THF-*d*<sub>8</sub>, respectively [27]. <sup>19</sup>F{<sup>1</sup>H} NMR spectra were referenced externally to neat trifluoroacetic acid, F<sub>3</sub>CC(O)OH ( $\delta$  = -78.5 ppm versus CFCl<sub>3</sub> = 0.0 ppm). Room temperature FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as Nujol mulls between KBr plates. The following abbreviations were used for the intensities of the IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak and sh = shoulder. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, New Jersey (USA).

# 2.1. Preparation of $CoI_2(CNAr^{Mes2})_3$

A 100 mL Schlenk tube was charged with Col<sub>2</sub> (0.808 g, 0.245 mmol and 1 equiv.) and CNAr<sup>Mes2</sup> (2.500 g, 0.735 mmol and 3 equiv.) and 25 mL of THF were added to the mixture of the starting materials. The resultant suspension was stirred at ambient temperature to afford a dark brown solution within 1 h. The solution was filtered through Celite and all volatiles were then removed in vacuo. The resulting residue was then subjected to three cycles of stirring in 10 mL Et<sub>2</sub>O for 15 min, followed by evaporation to dryness. Upon the last cycle, a purple-brown powder was obtained and collected. Yield: 3.378 g (0.240 mmol, 98%). Xray quality crystals of CoI2(CNArMes2)3. Et2O were obtained from slow evaporation of a saturated Et<sub>2</sub>O solution at room temperature. Anal. Calc. for C<sub>79</sub>H<sub>85</sub>CoI<sub>2</sub>N<sub>3</sub>O: C, 67.52; H, 6.10; N, 2.99. Found: C, 67.30; H, 5.89; N, 3.11%. FTIR (Nujol/KBr plates, cm<sup>-1</sup>): v = 3109 (vw), 2726 (w), 2168 (m) [v(CN)], 2127 (s) [v(CN)], 1733 (vw), 1613 (m) [v(C=C)], 1575 (w) [v(C=C)], 1414 (m), 1274 (w), 1189 (w), 1123 (w), 1071 (vw), 1031 (w), 851 (s), 810 (w), 803 (m), 783 (w), 761 (w), 755 (m), 736 (w), 723 (w), 603 (w), 563 (w), 542 (vw), 529 (w), 517 (w) 474 (vw) and 462 (w). <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  = 2.14 (s br, 18H, 6 × p-CH<sub>3</sub>, Mes), 2.58 (s vbr, 36H,  $12 \times 0$ -CH<sub>3</sub>, Mes) and 6.76 (s vbr, 21H,  $21 \times$ CH,  $C_6H_3$  + Mes) ppm.  $\mu_{eff}$  (Evans Method,  $C_6D_6$  with O(SiMe<sub>3</sub>)<sub>2</sub>, 400.1 MHz, 20 °C) = 1.9(±0.1)  $\mu_B$  (average of three independent measurements).

# 2.2. Preparation of $Col_3(CNAr^{Mes2})_3$

A mixture of  $CoI_2(CNAr^{Mes2})_3$  (0.250 g, 0.188 mmol) and  $I_2$ (0.024 g, 0.095 mmol and 0.5 equiv.) was suspended in 5 mL of Et<sub>2</sub>O and the reaction mixture was stirred at room temperature for 3 h while gradually producing a purple precipitate. The mixture was then concentrated to ca. 2.5 mL and a light brown supernatant was decanted off. The resulting purple solid was washed with Et<sub>2</sub>O  $(4 \times 2.5 \text{ mL each})$ , dried in vacuo and collected. Yield: 0.248 g (0.170 mmol, 90%). X-ray quality crystals of CoI<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> -0.5C<sub>7</sub>H<sub>8</sub> were obtained upon diffusion of *n*-pentane into a concentrated solution in toluene at room temperature. Anal. Calc. for C<sub>75</sub>H<sub>75</sub>CoI<sub>2</sub>N<sub>3</sub>: C. 61.78: H. 5.19: N. 2.88. Found: C. 60.73: H. 5.29: N, 2.82% (Repeated combustion analysis attempts did not produce more accurate results. We suspect this results from the formation of a small amount of the triiodide complex, CoI<sub>2</sub>(I<sub>3</sub>)(CNAr<sup>Mes2</sup>)<sub>3</sub> during oxidation of Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>). FTIR (Nujol/KBr plates, cm<sup>-1</sup>): v = 2727 (w), 2188 (w) [v(CN)], 2164 (vs) [v(CN)], 1614 (m) [v(C=C)], 1575 (w) [v(C=C)], 1488 (w), 1414 (m), 1274 (w), 1192 (vw), 1186 (w), 1160 (vw), 1122 (m), 1073 (w), 1067 (w), 1033 (m), 977 (vw), 916 (vw), 882 (vw), 845 (s), 805 (m), 781 (w), 757 (m), 736 (w), 722 (w), 669 (vw), 603 (w), 561 (w), 543 (vw), 538 (vw), 533 (vw), 520 (w), 481 (w) and 472 (w). <sup>1</sup>H NMR (499.8 MHz,  $C_6D_6$ , 20 °C):  $\delta$  = 2.00 (s, 6H, 2 × o-CH<sub>3</sub>, Mes, *cis*-CNR), 2.21 (s, 12H,  $4 \times 0$ -CH<sub>3</sub>, Mes, trans-CNR), 2.45 (s, 6H,  $2 \times p$ -CH<sub>3</sub>, Mes, trans-CNR), 2.52 (s, 3H,  $1 \times p$ -CH<sub>3</sub>, Mes, cis-CNR), 6.74 (d,  ${}^{3}J(H,H) = 8.0 \text{ Hz}, 2H, 2 \times m\text{-}CH, C_{6}H_{3}, cis\text{-}CNR), 6.77 (d, {}^{3}J(H,H) =$ 7.0 Hz, 4H,  $4 \times m$ -CH, C<sub>6</sub>H<sub>3</sub>, trans-CNR), 6.86 (t, <sup>3</sup>J(H,H) = 7.7 Hz, 2H, 2 × p-CH, C<sub>6</sub>H<sub>3</sub>, trans-CNR), 6.88 (t,  ${}^{3}J$ (H,H) = 7.5 Hz, 1H, 1 × p-CH, C<sub>6</sub>H<sub>3</sub>, trans-CNR), 6.94 (s, 8H, 8 × m-CH, Mes, trans-CNR), 6.96 (s, 4H,  $4 \times m$ -CH, Mes, *cis*-CNR) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz,  $C_6D_6$ , 20 °C:  $\delta$  = 20.5 (s, 4 × o-CH<sub>3</sub>, Mes, *cis*-CNR), 21.3 (s, 8 × o-CH<sub>3</sub>, Mes, trans-CNR), 21.8 (s,  $4 \times p$ -CH<sub>3</sub>, Mes, trans-CNR), 21.9 (s, 2 × p-CH<sub>3</sub>, Mes, *cis*-CNR), 126.8 (s), 127.3 (s), 129.46 (s), 129.52 (s), 129.7 (s), 129.8 (s), 130.1 (s), 130.6 (s), 133.9 (s), 134.3 (s), 135.3(s), 135.7 (s), 137.2 (s), 137.3 (s), 140.98 (s), 141.02 (s), 153.1 (s,  $2 \times iso$ -C, trans-CNR) and 161.0 (s,  $1 \times iso$ -C, cis-CNR) ppm.

# 2.3. Preparation of $[CoI_2(CNAr^{Mes2})_4]BAr_4^F$

#### 2.3.1. Method A

A suspension of CoI<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> (0.100 g, 0.0686 mmol) and CNAr<sup>Mes2</sup> (0.023 g, 0.069 mmol and 1 equiv.) in 5 mL Et<sub>2</sub>O was treated dropwise with a colorless Et<sub>2</sub>O solution of Na[BAr<sup>F</sup><sub>4</sub>] (0.060 g, 0.069 mmol and 1 equiv., 5 mL). The reaction mixture was allowed to stir for 24 h and then filtered to remove liberated NaI. Evaporation of the filtrate afforded [CoI<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>4</sub>]BAr<sup>F</sup><sub>4</sub> as purple powder, which was washed (Et<sub>2</sub>O, 3 × 2.5 mL), dried *in vacuo*, and collected. Yield: 0.074 g (0.029 mmol, 43%).

#### 2.3.2. Method B

To an Et<sub>2</sub>O solution of  $[Co(CNAr^{Mes2})_4]BAr_4^F$  (0.100 g, 0.044 mmol and 5 mL) was added solid I<sub>2</sub> (0.011 g, 0.044 mmol and 1 equiv.) and resulted in a the rapid formation of a vibrant purple precipitate. The reaction mixture was stirred for 2 h and then allowed to settle. A light brown supernatant was then decanted from the purple solid. The latter was washed with Et<sub>2</sub>O (3 × 2.5 mL), dried *in vacuo* and collected. Yield: 0.082 g (0.031 mmol, 71%). X-ray quality crystals of  $[CoI_2(CNAr^{Mes2})_4]BAr_4^F \cdot 2C_6H_{14}$  were obtained upon diffusion of *n*-hexane into a concentrated solution in fluorobenzene at room temperature. *Anal.* Calc. for C<sub>138</sub>H<sub>127</sub>COB- F<sub>24</sub>I<sub>2</sub>N<sub>4</sub>O<sub>1.5</sub>: C, 62.66; H, 4.84; N, 2.12. Found: C, 62.91; H, 4.56; N, 2.17%. FTIR (Nujol/KBr plates,  $cm^{-1}$ ): v = 2731 (w), 2167 (vs) [v(CN)], 2131 (s) [v(CN)], 1614 (m) [v(C=C)], 1587 (w) [v(C=C)], 1570 (w) [v(C=C)], 1490 (vw), 1403 (w), 1354 (s), 1276 (vs), 1192 (vw), 1176 (m), 1158 (s), 1142 (s), 1126 (vs), 1107 (m), 1098 (w), 1076 (vw), 1033 (w), 954 (vw), 943 (vw), 935 (vw), 930 (vw), 895 (w), 885 (m), 855 (m), 839 (w), 813 (w), 808 (w), 794 (vw), 779 (w), 759 (m), 744 (w), 736 (w), 722 (vw), 717 (vw), 712 (m), 683 (m), 671 (m), 626 (vw), 619 (vw), 603 (w), 578 (vw), 563 (w), 553 (vw), 532 (w), 492 (w) and 449 (vw). <sup>1</sup>H NMR (300.1 MHz, THF- $d_8$ , 20 °C):  $\delta$  = 1.11 (t, 9H, <sup>3</sup>J(H,H) = 7.0 Hz,  $3 \times CH_3$ ,  $Et_2O$ ), 1.86 (s, 48H,  $16 \times o\text{-}CH_3$ , Mes), 2.51 (s, 24H,  $8 \times p$ -CH<sub>3</sub>, Mes), 3.38 (q, 6H, <sup>3</sup>J(H,H) = 7.0 Hz,  $3 \times CH_2$ , Et<sub>2</sub>O), 6.91 (s, 32H, 32 × *m*-CH, Mes), 7.21 (d, 8H,  ${}^{3}J(H,H) = 8.00$  Hz, 8 × *m*-CH, C<sub>6</sub>H<sub>3</sub>), 7.57 (s br, 4H,  $4 \times p$ -CH, C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub>), 7.59 (t, 4H,  $^{3}J(H,H) = 7.6 \text{ Hz}, 4 \times p\text{-CH}, C_{6}H_{3}), 7.80 \text{ (m br, 8H, 8 } \times o\text{-CH}, C_{6}H_{3}\text{-}$ 3,5-(CF<sub>3</sub>)<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H{}$  NMR (125.7 MHz, THF- $d_8$ , 20 °C):  $\delta$  = 15.6 (s, 3 × CH<sub>3</sub>, Et<sub>2</sub>O), 21.1 (s, 16 × o-CH<sub>3</sub>, Mes), 21.8 (s,  $8 \times p$ -CH<sub>3</sub>, Mes), 66.2 (s,  $3 \times CH_2$ , Et<sub>2</sub>O), 118.1 (sept, <sup>3</sup>J(F,C) = 4 Hz,  $4 \times p$ -C, C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub>), 125.4 (q, <sup>1</sup>J(F,C) = 273 Hz, 8 × CF<sub>3</sub>, C<sub>6</sub>H<sub>3</sub>- $3,5-(CF_3)_2$ ), 126.0 (s), 129.0 (s br,  $4 \times iso-C$ , CNR), 129.9 (qq,  $^{2}J(F,C) = 32$  Hz,  $^{4}J(F,C) = 3$  Hz,  $8 \times m$ -C,  $C_{6}H_{3}$ -3,5-(CF<sub>3</sub>)<sub>2</sub>), 130.7 (s), 132.1 (s), 133.3 (s), 133.9 (s), 135.5 (s), 136.4 (s), 138.0 (s), 141.4, 162.7 (q,  ${}^{1}J({}^{13}C, {}^{11}B) = 50 \text{ Hz}$ ; sept,  ${}^{1}J({}^{13}C, {}^{10}B) = 17 \text{ Hz}$ ; 4 ipso-C,  $C_6H_3$ -3,5-( $CF_3$ )<sub>2</sub>) ppm.

# 2.4. Preparation of $Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$

A mixture of CoBr<sub>2</sub> (0.043 g, 0.20 mmol) and CNAr<sup>Mes2</sup> (0.100 g, 0.295 mmol and 1.5 equiv.) was dissolved in 5 mL THF, allowed to stir for 24 h and filtered from insoluble components. All volatiles were removed under reduced pressure. The resulting residue was then subjected to three cycles of *n*-pentane (2 mL) wash, followed by drying *in vacuo*. After the last cycle,  $Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$ was obtained as a pale green powder. Yield: 0.128 g (0.0879 mmol, 89%). X-ray quality crystals of  $Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$  were obtained from slow evaporation of a saturated C<sub>6</sub>D<sub>6</sub> solution at room temperature. Anal. Calc. for C75H75Co2Br4N3: C, 61.87; H, 5.19; N, 2.89. Found: C, 61.66; H, 5.07; N, 2.87%. FTIR (Nujol/KBr plates, cm<sup>-1</sup>): v = 2731 (w), 2191 (w) [v(CN)], 2176 (vs) [v(CN)], 2155 (m) [v(CN)], 2085 (w) [v(CN)], 1612 (m) [v(C=C)], 1580 (w) [v(C=C)], 1572 (w) [v(C=C)], 1402 (w), 1275 (m), 1190 (w), 1162 (vw), 1070 (w), 1032 (m br), 919 (vw), 855 (m), 848 (m), 808 (m), 785 (w), 778 (w), 756 (/m), 737 (w), 722 (w), 607 (w), 563 (w), 543 (vw) and 525 (w). <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  = -3.22 (s br, 3H, 3 × p-CH, C<sub>6</sub>H<sub>3</sub>), -0.01 (s vbr, 36H, 12 × o-CH<sub>3</sub>, Mes), 3.54 (s br, 18H,  $6 \times p$ -CH<sub>3</sub>, Mes), 5.17 (s vbr, 6H,  $6 \times m$ -CH, C<sub>6</sub>H<sub>3</sub>), 7.03 (s br, 12H, 12  $\times m$ -CH, Mes) ppm.

# 2.5. Preparation of ICo(CNAr<sup>Mes2</sup>)<sub>3</sub>

A mixture of CoI<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> (0.650 g, 0.488 mmol) and granulated zinc metal (0.160 g, 2.45 mmol and 5.4 equiv.) was suspended in 10 mL of THF and allowed to stir for 48 h. The reaction mixture gradually changed in color from purple-brown to greenbrown. The reaction mixture was then filtered and all volatiles were removed *in vacuo*. The resultant green-brown residue was extracted with an Et<sub>2</sub>O/*n*-pentane mixture (10:1, 15 mL), filtered through Celite and evaporated to dryness. The resulting olivegreen solid was washed with *n*-pentane (3 × 1 mL), dried *in vacuo* and collected. Yield: 0.578 g (0.452 mmol, 93%). X-ray quality crystals of ICo(CNAr<sup>Mes2</sup>)<sub>3</sub>·Et<sub>2</sub>O were obtained from a saturated Et<sub>2</sub>O solution stored at -35 °C. *Anal.* Calc. for C<sub>79</sub>H<sub>85</sub>CoIN<sub>3</sub>O: C, 74.22; H, 6.70; N, 3.29. Found: C, 74.01; H, 6.89; N, 3.20. FTIR (Nujol/ KBr plates, cm<sup>-1</sup>): v = 2730 (w), 2048 (vs) [v(CN)], 1991 (m sh) [v(CN)], 1613 (m) [v(C=C)], 1575 (w) [v(C=C)], 1489 (w), 1415 (m), 1351 (w), 1272 (w), 1186 (w), 1152 (vw), 1120 (m), 1076 (w br), 1031 (m br), 857 (m), 849 (m), 804 (m), 785 (w), 757 (s), 737 (w), 722 (vw), 619 (vw), 603 (w), 564 (w), 519 (m), 514 (m) and 496 (vw). <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  = 2.24 (s br, 18H, 6 × *p*-CH<sub>3</sub>, Mes), 2.70 (s vbr, 36H, 12 × *o*-CH<sub>3</sub>, Mes), 4.47 (s br, 6H, 6 × *m*-CH, C<sub>6</sub>H<sub>3</sub>), 6.54 (s br, 12H, 12 × *m*-CH, Mes), 13.90 (s br, 3H, 3 × *p*-CH, C<sub>6</sub>H<sub>3</sub>) ppm.  $\mu_{eff}$  (Evans Method, C<sub>6</sub>D<sub>6</sub> with O(SiMe<sub>3</sub>)<sub>2</sub>, 400.1 MHz, 20 °C) = 3.0(±0.1)  $\mu_{B}$  (average of three independent measurements).

# 2.6. Preparation of $ClCo(CNAr^{Mes2})_3$

A mixture of  $CoCl_2$  (0.064 g, 0.491 mmol) and  $CNAr^{Mes2}$  (0.500 g, 1.473 mmol and 3 equiv.) was suspended in THF (10 mL) and allowed to stir for 2 h. Granular Zn (0.322 g, 4.91 mmol and 10 equiv.) was then added and resulted in a color change from blue to brown. The reaction mixture was allowed to stir for 3 h and then decanted from the excess Zn metal. All volatiles were removed in vacuo and the resulting residue was extracted with an  $Et_2O/n$ -pentane mixture (9:1, 20 mL) and filtered through Celite. Evaporation of the solvent resulted in an olive-green powder, which was collected. Yield: 0.384 g (0.324 mmol, 66%). X-ray quality crystals of ClCo(CNAr-Mes2)3. Et2O were obtained from a saturated Et2O solution stored at -35 °C. Anal. Calc. for C<sub>79</sub>H<sub>85</sub>ClCoN<sub>3</sub>O: C, 79.94; H, 7.22; N, 3.54. Found: C, 79.27; H, 7.44; N, 3.46%. FTIR (Nujol/KBr plates, cm<sup>-1</sup>): v = 2730 (w), 2045 (vs) [v(CN)], 1995 (s sh) [v(CN)], 1613 (m) [v(C=C)], 1582 (w) [v(C=C)], 1572 (w) [v(C=C)], 1487 (vw sh), 1415 (m), 1300 (vw), 1288 (vw), 1272 (w), 1161 (w), 1105 (vw), 1088 (vw), 1072 (vw), 1301 (m br), 1011 (w sh), 919 (w), 877 (w), 853 (s), 846 (s), 809 (m), 805 (s), 784 (m), 758 (s), 735 (m), 722 (w), 687 (vw), 620 (w), 603 (m), 556 (m), 564 (w), 524 (m), 514 (m) and 496 (vw). <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  = 1.12 (t,  $^{3}J(H,H) = 7.0$  Hz, 6H, 2 × CH<sub>3</sub>, Et<sub>2</sub>O), 2.10 (s br, 18H, 6 × p-CH<sub>3</sub>, Mes), 2.58 (s vbr, 36H,  $12 \times o-CH_3$ , Mes), 3.27 (q, <sup>3</sup>J(H,H) = 7.0 Hz, 4H, 2 × CH<sub>2</sub>, Et<sub>2</sub>O), 3.65 (s br, 6H, 6 × *m*-CH, C<sub>6</sub>H<sub>3</sub>), 6.40 (s br, 12H,  $12 \times m$ -CH, Mes) and 15.50 (s br, 3H,  $3 \times p$ -CH, C<sub>6</sub>H<sub>3</sub>) ppm.  $\mu_{eff}$ (Evans Method,  $C_6D_6$  with  $O(SiMe_3)_2$ , 400.1 MHz, 20 °C) = 3.1(±0.1)  $\mu_{\rm B}$  (average of three independent measurements).

# 2.7. Preparation of $BrCo(CNAr^{Mes2})_3$

This tan-green complex was prepared in analogous fashion to ClCo(CNAr<sup>Mes2</sup>)<sub>3</sub> employing 0.124 g (0.567 mmol) of CoBr<sub>2</sub> and 0.500 g (1.473 mmol, 2.6 equiv.) of CNAr<sup>Mes2</sup> Yield: 0.343 g (0.279 mmol, 57%). X-ray quality crystals of BrCo(CNAr<sup>Mes2</sup>)<sub>3</sub>·Et<sub>2</sub>O were obtained from a saturated  $Et_2O$  solution stored at -35 °C. Anal. Calc. for C<sub>79</sub>H<sub>85</sub>BrCoN<sub>3</sub>O: C, 77.05; H, 6.96; N, 3.41. Found: C, 76.84; H, 6.77; N, 3.29%. FTIR (Nujol/KBr plates, cm<sup>-1</sup>): v = 2729 (w), 2037 (vs) [v(CN)], 1990 (s sh) [v(CN)], 1612 (m) [v(C=C)], 1574 (w) [v(C=C)], 1414 (m), 1351 (vw), 1299 (vw), 1289 (vw), 1271 (w), 1186 (w), 1160 (w), 1152 (w), 1120 (m br), 1074 (w), 1066 (w), 1030 (m br), 971 (vw), 937 (vw), 916 (vw), 890 (vw), 849 (s br), 804 (m), 785 (m), 756 (s), 736 (m), 723 (w sh), 669 (vw), 654 (vw), 620 (w) 603 (w), 564 (w), 553 (vw sh), 513 (m) and 495 (w). <sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 20 °C):  $\delta$  = 1.12 (t, <sup>3</sup>J(H,H) = 7.0 Hz, 6H,  $2 \times CH_3$ , Et<sub>2</sub>O), 2.17 (s br, 18H,  $6 \times p$ -CH<sub>3</sub>, Mes), 2.63 (s vbr, 36H,  $12 \times \text{o-CH}_3$ , Mes), 3.27 (q,  ${}^{3}J(H,H) = 6.9$  Hz, 4H,  $2 \times CH_2$ , Et<sub>2</sub>O), 3.95 (s br, 6H,  $6 \times m$ -CH, C<sub>6</sub>H<sub>3</sub>), 6.43 (s br, 12H, 12 × m-CH, Mes) and 14.95 (s br, 3H, 3  $\times$  *p*-CH, C<sub>6</sub>H<sub>3</sub>) ppm.  $\mu_{eff}$  (Evans Method, C<sub>6</sub>D<sub>6</sub> with  $O(SiMe_3)_2$ , 400.1 MHz, 20 °C) = 3.2(±0.1)  $\mu_B$  (average of three independent measurements).

#### 2.8. Crystallographic structure determinations

Single crystal X-ray structure determinations were carried out at low temperature on a Bruker P4 or Platform Diffractometer equipped with a Bruker APEX II detector. All structures were solved by direct methods with SIR 2004 [28] and refined by full-matrix least-squares procedures utilizing SHELXL-97 [29]. Crystallographic data collection and refinement information is listed in Table 3. CIF files for all structures have been deposited with the Cambridge Crystallographic Data Center (CCDC) (See Supplementary material).

# 3. Results and discussion

To access low-valent, trisisocvanide cobalt complexes, we envisioned that simple pre-coordination of three CNAr<sup>Mes2</sup> ligands to Co(II) halides would suffice as a suitable synthetic entry point. Surprisingly however, we found that treatment of commercially available CoCl<sub>2</sub> with 3.0 equiv of CNAr<sup>Mes2</sup> in THF solution did not lead to an isolable complex of the formulation CoCl<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>. Instead, <sup>1</sup>H NMR and FTIR analysis of 3:1 CNAr<sup>Mes2</sup>/CoCl<sub>2</sub> mixtures in C<sub>6</sub>D<sub>6</sub> solution revealed a complex speciation pattern indicative of rapid exchange between free and coordinated CNAr<sup>Mes2</sup>. While cobalt dichloride complexes of less encumbering isocyanides are known, the [CoCl<sub>2</sub>] fragment presumably lacks sufficient Lewis acidity to tightly bind three CNAr<sup>Mes2</sup> ligands. Notably, we have previously observed similar behavior for the interaction of CNAr<sup>Mes2</sup> and Cu(I) halide salts [22]. In this latter work, it was found that both the [CuI] and [CuOTf] (OTf = triflate, OSO<sub>2</sub>CF<sub>3</sub>) fragments readily bound three CNAr<sup>Mes2</sup> ligands, whereas only two were accommodated by the relatively less Lewis acidic [CuCl] unit [30,31].

Gratifyingly, a similar trend is observed in the case of cobalt. Thus, simple addition of 3.0 equiv of CNAr<sup>Mes2</sup> to Col<sub>2</sub> in THF solution readily provided the trisisocyanide complex Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> as an isolable purple-brown crystalline solid (Scheme 1). Crystallographic structure determination on crystals grown from Et<sub>2</sub>O revealed a square pyramidal, mononuclear complex with the CNAr<sup>Mes2</sup> ligands occupying the axial and two basal positions (Fig. 1). Evans method magnetic moment determination (C<sub>6</sub>D<sub>6</sub>/(Me<sub>3</sub>Si)<sub>2</sub>O, 20 °C) resulted in a  $\mu_{eff}$  value of 1.9(1)  $\mu_{B}$ , which is con-



Scheme 1.



**Fig. 1.** Molecular Structure of Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>. Selected bond lengths (Å) and angles (°): Co1–I1 2.5555(14), Co1–I2 2.5741(16), Co1–C1 1.844(3), Co1–C2 1.894(3), Co1–C3 1.869(3), C1–N1 1.153(4), C2–N2 1.150(4), C3–N3 1.158(4), I1–Co1–I2 149.15(2), I1–Co1–C2 103.75(10), C1–Co1–C3 168.16(12), C1–Co1–C2 93.53(14).

C3

N3

sistent with a mononuclear,  $d^7$  Co(II) center possessing an  $S = \frac{1}{2}$  ground state. Interestingly, the <sup>1</sup>H NMR spectrum of Col<sub>2</sub>(C-NAr<sup>Mes2</sup>)<sub>3</sub> in C<sub>6</sub>D<sub>6</sub>, exhibited a single set of paramagnetically shifted resonances, thus indicating that the five-coordinate complex is likely fluxional in solution. FTIR analysis (Nujol) on Col<sub>2</sub>(C-NAr<sup>Mes2</sup>)<sub>3</sub> revealed the presence of two  $\nu$ (CN) bands centered at 2168 and 2127 cm<sup>-1</sup>. Notably, these  $\nu$ (CN) stretches are shifted to higher energy relative to free CNAr<sup>Mes2</sup> ( $\nu$ (CN) = 2118 cm<sup>-1</sup>) [22], thereby indicating significantly limited  $\pi$  backbonding between the  $d^7$  center and the isocyanide units [32–35].

Despite the presence of three encumbering CNAr<sup>Mes2</sup> ligands. a notable structural feature of Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> is the seeming availability of a sixth coordination site. To access this site and probe the redox behavior of the system, we sought to chemically oxidize  $CoI_2(CNAr^{Mes2})_3$  to d<sup>6</sup> Co(III) species. Accordingly, treatment of  $CoI_2(CNAr^{Mes2})_3$  with 0.5 equiv of  $I_2$  in Et<sub>2</sub>O solution readily provided the diamagnetic complex mer-CoI<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> as determined by X-ray crystallography (Fig. 2, Scheme 1). Notably, the *mer*-configuration of  $Col_3(CNAr^{Mes2})_3$  is retained in solution as indicated by the 2:1 ratio of CNAr<sup>Mes2</sup> resonances in its <sup>1</sup>H NMR spectrum ( $C_6D_6$ ). The FTIR spectrum (Nujol) of  $CoI_3(CNAr^{Mes2})_3$ showed two v(CN) bands at 2188 and 2164 cm<sup>-1</sup>, which are further shifted to higher energy relative to Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> (Table 1). Thus, despite the low-spin d<sup>6</sup> configuration,  $\pi$ -backbonding interactions to the CNAr<sup>Mes2</sup> ligands are significantly attenuated by oxidized nature of the Co center in CoI<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>. Notably however, the molecular orbital structure pertaining to the  $C_{2v}$  mer-configuration of d<sup>6</sup> octahedral complexes does not maximize  $\pi$ -backbonding interactions, especially when compared to the analogous fac-isomers [36].

Other six-coordinate Co(III) complexes are also available from  $CoI_3(CNAr^{Mes2})_3$ . Treatment of  $CoI_3(CNAr^{Mes2})_3$  with NaBAr<sup>F</sup><sub>4</sub> (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) in the presence of an additional equivalent of CNAr<sup>Mes2</sup> cleanly provides the tetraisocyanide salt [CoI<sub>2</sub>(CNAr<sup>-Mes2</sup>)<sub>4</sub>]BAr<sup>F</sup><sub>4</sub>, which possesses a *trans* diiodide configuration (Fig. 3, Scheme 1). As an alternative synthesis, [CoI<sub>2</sub>(CNAr<sup>-Mes2</sup>)<sub>4</sub>]BAr<sup>F</sup><sub>4</sub> can be readily generated by treatment of the salt [Co(CNAr<sup>-Mes2</sup>)<sub>4</sub>]BAr<sup>F</sup><sub>4</sub> with one equiv of I<sub>2</sub> [25]. Tetraisocyanide [CoI<sub>2</sub>(CNAr<sup>-Mes2</sup>)<sub>4</sub>]BAr<sup>F</sup><sub>4</sub> gives rise to v(CN) bands (2167 and 2131 cm<sup>-1</sup>) that are slightly lower in energy relative to its six-coordinate counterpart



**Fig. 2.** Molecular structure of CoI<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>. Selected bond lengths (Å) and angles (°): Co1–I1 2.6017(10), Co1–I2 2.6021(10), Co1–I3 2.6035(10), Co1–C1 1.870(6), Co1–C2 1.866(6), Co1–C3 1.847(6), C1–N1 1.151(8), C2–N2 1.154(8), C3–N3 1.158(8), I1–Co1–I1 172.65(4), I1–Co1–I3 91.87(3), I3–Co1–C3 177.46(18), I3–Co1–C1 87.92(18), C1–Co1–C2 172.3(3), C1–Co1–C3 94.5(2).

#### Table 1

Solid-state v(CN) stretching frequencies for cobalt halide complexes of CNAr<sup>Mes2</sup> (Nujol/KBr plates). Sh = Shoulder.

Compound	$v(CN) (cm^{-1})$
$CoI_2(CNAr^{Mes2})_3$	2168(m), 2127(s)
CoI <sub>3</sub> (CNAr <sup>Mes2</sup> ) <sub>3</sub>	2188(w), 2164(vs)
$[CoI_2(CNAr^{Mes2})_4]BAr_4^F$	2167(vs), 2131(s)
$Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$	2191(w), 2176(vs), 2155(m), 2085(w)
ClCo(CNAr <sup>Mes2</sup> ) <sub>3</sub>	2045(vs), 1995(s, sh)
BrCo(CNAr <sup>Mes2</sup> ) <sub>3</sub>	2037(vs), 1990(s, sh)
ICo(CNAr <sup>Mes2</sup> ) <sub>3</sub>	2048(vs), 1991(m, sh)

# Table 2

Selected bond lengths and angles for  $XCo(CNAr^{Mes2})_3$  complexes (X = Cl, Br and I).

Complex	$ClCo(CNAr^{Mes2})_3$	BrCo(CNAr <sup>Mes2</sup> ) <sub>3</sub>	$ICo(CNAr^{Mes2})_3$
Bond lengths (	Å)		
Co1-X1	2.2062(8)	2.3470(3)	2.5327(5)
Co1-C1	1.913(2)	1.914(2)	1.903(3)
Co1-C2	1.920(2)	1.919(2)	1.918(4)
Co1-C3	1.902(2)	1.906(1)	1.912(3)
C1-N1	1.167(3)	1.168(2)	1.170(4)
C2-N2	1.165(3)	1.168(2)	1.163(5)
C3-N3	1.169(2)	1.166(2)	1.167(4)
Bond angles (°	)		
X1-Co1-C1	116.42(6)	116.57(5)	116.61(9)
X1-Co1-C2	109.42(6)	108.11(5)	107.5(1)
X1-Co1-C3	118.62(6)	118.10(5)	119.26(9)
C1-Co1-C2	106.76(9)	107.23(7)	103.9(1)
C1-Co1-C3	98.82(9)	99.47(7)	99.1(1)
C2-Co1-C3	105.80(9)	106.44(7)	109.3(1)

 $CoI_3(CNAr^{Mes2})_3$  (Table 1). Presumably, this fact reflects the increased electron density on the Co(III) center provided by the fourth  $\sigma$ -donating  $CNAr^{Mes2}$  ligand.

Whereas the reaction between three CNAr<sup>Mes2</sup> ligands and Col<sub>2</sub> proceeded smoothly and completely to a single mononuclear product, the reaction between CNAr<sup>Mes2</sup> and CoBr<sub>2</sub> proved to be more complicated. Combination of CNAr<sup>Mes2</sup> and CoBr<sub>2</sub> in a 3:1 ratio in

<b>Table 3</b> Crystallographic data and <i>r</i>	efinement information.						
	$Col_2(CNAr^{Mes2})_3\cdot Et_2O$	$CoI_3(CNAr^{Mes2})_3 \cdot 0.5C_7H_8$	$[\text{Col}_2(\text{CNAr}^{\text{Mes2}})_4]\text{BAr}_4^F.2\text{C}_6\text{H}_{14}$	$Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$	$ICo(CNAr^{Mes2})_3 \cdot Et_2O$	$CICo(CNAr^{Mes2})_{3}\cdot Et_{2}O$	$BrCo(CNAr^{Mes2})_{3}\cdot Et_{2}O$
Formula	C <sub>79</sub> H <sub>85</sub> Col <sub>2</sub> N <sub>3</sub> O	C <sub>78.5</sub> H <sub>79</sub> Col <sub>3</sub> N <sub>3</sub>	$C_{144}H_{140}BC0F_{24}I_2N_4$	$C_{75}H_{75}Br_4Co_2N_3$	C <sub>79</sub> H <sub>85</sub> CoIN <sub>3</sub> O	C <sub>79</sub> H <sub>85</sub> ClCoN <sub>3</sub> O	C <sub>79</sub> H <sub>85</sub> BrCoN <sub>3</sub> O
Crystal system	triclinic	triclinic	monoclinic	qriclinic	monoclinic	monoclinic	monoclinic
Space group	Pī	$P\overline{1}$	C2/c	$P\overline{1}$	P21/c	P21/c	P2 <sub>1</sub> /c
a (Å)	13.687(10)	15.202(3)	26.981(2)	13.0684(7)	14.1721(9)	14.192(4)	14.1811(9)
p (Å)	14.250(11)	15.255(3)	15.2008(12)	13.2302(7)	20.7613(12)	19.916(5)	20.0416(13)
c (Å)	19.860(14)	17.957(4)	31.876(2)	22.1489(11)	23.2375(14)	23.921(7)	23.8762(16)
α (°)	98.587(10)	69.373(2)	06	84.0770(10)	06	06	06
β (°)	108.406(10)	71.971(3)	103.9920(10)	88.2100(10)	94.301(2)	97.743(4)	97.1100(10)
γ (°)	91.367(11)	64.761(2)	06	61.5680(10)	06	06	06
V (Å <sup>3</sup> )	3624(5)	3462.5(13)	12685.5(17)	3348.9(3)	6817.9(7)	6699(3)	6733.7(8)
Ζ	2	2	4	2	4	4	4
Radiation (2, Å)	Mo Ko, 0.71073	Mo Ka, 0.71073	Mo Ka, 0.71073	Mo Ka, 0.71073	Mo Ka, 0.71073	Mo Ko, 0.71073	Mo Ka, 0.71073
$\rho$ (calcd.) (g/cm <sup>3</sup> )	1.288	1.443	1.417	1.444	1.245	1.177	1.215
$\mu$ (Mo K $lpha$ ) (mm <sup>-1</sup> )	1.133	1.630	0.711	2.926	0.751	0.343	0.895
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$\theta \max(\circ)$	27.70	25.74	27.93	28.29	25.35	26.57	28.35
Data/parameters	16495/796	12315/757	14839/744	15117/775	12397/786	13717/786	15645/786
$R_{1}$	0.0427	0.0496	0.0427	0.0410	0.0454	0.0471	0.0346
$wR_2$	0.0985	0.1538	0.1168	0.0849	0.1118	0.1327	0.0898
Goodness-of-fit (GOF)	1.053	1.382	1.051	1.021	1.061	1.030	1.047



Scheme 2.



**Fig. 3.** Molecular structure of the cation in  $[Col_2(CNAr^{Mes2})_4]BAr_4^F$ . Selected bond lengths (Å) and angles (°): Co1–I1 2.5765(2), Co1–C1 1.907(2), Co1–C2 1.898(2), C1–N1 1.148(3), C2–N2 1.154(3), I1–Co1–C1 91.53(7), I1–Co1–C2 90.04(7), C1–Co1–C2 89.73(9).



**Fig. 4.** Molecular structure of  $Br_2Co(\mu_2-Br)_2Co(CNAr^{Mes2})_3$ . Selected bond lengths (Å) and angles (°): Co1-Br1 2.4096(5), Co1-Br2 2.5599(5), Co2-Br1 2.5205(6), Co2-Br2 2.4468(5), Co2-Br3 2.3598(6), Co2-Br4 2.3632(6), Co1-C1 1.871(3), Co1-C2 1.901(3), Co1-C3 1.879(3), C1-N1 1.152(4), C2-N2 1.154(4), C3-N3 1.152(4), Br1-Co1-Br2 91.127(18), Br1-Co1-C1 167.50(9), Br1-Co1-C2 92.92(9), C2-Co1-C3 172.29(13), Br1-Co1-Br2-Co2 -0.66(2).

THF solution afforded the green dinuclear complex Br<sub>2</sub>Co( $\mu_2$ -Br)<sub>2</sub> Co(CNAr<sup>Mes2</sup>)<sub>3</sub> as determined by X-ray crystallography (Fig. 4). While its formation under these conditions is unclear, it is important to note that Br<sub>2</sub>Co( $\mu_2$ -Br)<sub>2</sub>Co(CNAr<sup>Mes2</sup>)<sub>3</sub> is obtained exclusively in this reaction irrespective of the equivalency of either CNAr<sup>Mes2</sup> or CoBr<sub>2</sub> employed. However, the highest yields of Br<sub>2</sub>Co( $\mu_2$ -Br)<sub>2</sub>Co(CNAr<sup>Mes2</sup>)<sub>3</sub> are obtained when a 3:2 CNAr<sup>Mes2</sup>/ CoBr<sub>2</sub> ratio is used (Scheme 2). Interestingly, the square pyramidal/tetrahedral edge-sharing motif in dinuclear Br<sub>2</sub>Co( $\mu_2$ -Br)<sub>2</sub>Co(C-NAr<sup>Mes2</sup>)<sub>3</sub> has only been observed in one other cobalt halide coordination complex, namely Cl<sub>2</sub>Co( $\mu_2$ -Cl<sub>2</sub>Co(triphos) (triphos = MeC(CH<sub>2</sub>PPh<sub>2</sub>)<sub>3</sub>) [37,38]. The FTIR spectrum of Br<sub>2</sub>Co( $\mu_2$ -Br)<sub>2</sub>Co(C-NAr<sup>Mes2</sup>)<sub>3</sub> exhibits two main *v*(CN) bands at 2176 and 2155 cm<sup>-1</sup>, again reflecting insignificant  $\pi$ -backdonation to the CNAr<sup>Mes</sup> ligands.





Fig. 5. Molecular structure of  $ClCo(CNAr^{Mes2})_3$ . See Table 2 for selected bond lengths and angles.

Despite the differing speciation patterns for CNAr<sup>Mes2</sup> complexes of the divalent cobalt halides, each system can be readily converted into a stable monovalent, trisisocyanide halide complex upon the addition of granulated Zn (Scheme 3). Thus, treatment of pre-formed Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> with Zn granules in THF solution readily provides the four-coordinate complex ICo(CNAr<sup>Mes2</sup>)<sub>3</sub> as a green-brown solid. The monochloro and monobromo complexes, ClCo(CNAr<sup>Mes2</sup>)<sub>3</sub> and BrCo(CNAr<sup>Mes2</sup>)<sub>3</sub>, are obtained in high yields by a similar manner, but without the need for pre-coordination of three CNAr<sup>Mes2</sup> ligands to the Co center (Scheme 3). Notably, this protocol mirrors that used for the formation of the classic tris(triphenylphosphine) monohalides of cobalt (*i.e.* XCo(PPh<sub>3</sub>)<sub>3</sub>; X = Cl, Br and I), which were the first reported tetrahedral cobalt complexes [39].

Structural characterization of the XCo(CNAr<sup>Mes2</sup>)<sub>3</sub> complexes (X = Cl. Br and I. Figs. 5–7, respectively) confirmed that each exists



Fig. 6. Molecular structure of BrCo(CNAr<sup>Mes2</sup>)<sub>3</sub>. See Table 2 for selected bond lengths and angles.



Fig. 7. Molecular structure of  $ICo(CNAr^{Mes2})_3$ . See Table 2 for selected bond lengths and angles.

as a pseudo-tetrahedral monomer in the solid state. Furthermore, Evans Method magnetic moment determination  $(C_6D_6/(Me_3Si)_2O_1)$ 20 °C) confirmed that each complex possesses an S = 1 ground state consistent with a d<sup>8</sup> metal center in a  $C_{3\nu}$ -symmetric ligand field  $(X = Cl, \mu_{eff} = 3.1(1) \mu_{B}; X = Br, \mu_{eff} = 3.2(1) \mu_{B}; X = I, \mu_{eff} = 3.0(1)$  $\mu_{\rm B}$ ). The FTIR spectrum of each complex exhibits two v(CN) bands (Table 1), which are shifted to lower energy relative to free  $CNAr^{Mes2}$  ( $\nu(CN) = 2118 \text{ cm}^{-1}$ ) [22]. Thus, reduction to the monovalent state is apparently necessary for the Co center in these complexes to more efficiently necessary for the co-center in these confi-plexes to more efficiently engage in  $\pi$ -backbonding interactions to three CNAr<sup>Mes2</sup> ligands. Accordingly, isolation of monoiodide ICo(CNAr<sup>Mes2</sup>)<sub>3</sub> is particularly gratifying in that it, along with Col<sub>2</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub> and Col<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>, allow for a systematic assess-ment of both oxidation state and coordination number on  $\pi$ -basicity properties of cobalt toward three CNAr<sup>Mes2</sup> ligands.

# 4. Summary and conclusions

As detailed above, differing speciation patterns are encountered upon addition of the encumbering *m*-terphenyl isocyanide ligand CNAr<sup>Mes2</sup> to cobalt dihalide salts. In the case of the cobalt dichloride fragment, productive isocyanide binding leading to a stable complex does not take place. However, treatment of the more Lewis acidic CoI<sub>2</sub> and CoBr<sub>2</sub> fragments with three CNAr<sup>Mes2</sup> ligands results in the formation of stable mono- and dinuclear Co trisisocyanide complexes, respectively. The diiodide complex, CoI<sub>2</sub>(C- $NAr^{Mes2}$ )<sub>3</sub>, can be further oxidized with I<sub>2</sub> to the six-coordinate, octahedral complex CoI<sub>3</sub>(CNAr<sup>Mes2</sup>)<sub>3</sub>, which retains all three isocyanide ligands. FTIR analysis of these Co(II) and Co(III) complexes revealed that minimal  $\pi$ -backbonding interactions to the CNAr<sup>Mes2</sup> ligands are present. In contrast, FTIR analysis of the Co(I), monohalide complexes XCo(CNAr<sup>Mes2</sup>)<sub>3</sub> revealed that significant  $\pi$ -backbonding interactions are present. These monovalent, monohalide CoX(CNAr<sup>Mes2</sup>)<sub>3</sub> complexes can be conveniently prepared by treatment of cobalt dihalide salts with three equivalents of CNAr<sup>Mes2</sup> followed by addition of zinc. We are currently probing the ability of these  $CoX(CNAr^{Mes2})_3$  complexes to serve as precursors to lowcoordinate and hydrido trisisocyanide complexes such as the [Co(CNAr<sup>Mes2</sup>)<sub>3</sub>]<sup>-</sup> anion and HCo(CNAr<sup>Mes2</sup>)<sub>3</sub>.

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#### Appendix A. Supplementary material

CCDC 779035, 779036, 779037, 779038, 779039, 779040 and 779041 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010. 08.024.

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