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

Nils Weidemann, Grant W. Margulieux, Curtis E. Moore, Arnold L. Rheingold, Joshua S. Figueroa *

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, Mail Code 0358, La Jolla, CA 92093-0358, United States

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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-$Me_3C_6H_3$). Addition of $CNAr^{Mes2}$ to CoI_2 in a 3:1 molar ratio provides the mononuclear complex, $CoI_2(CNAr^{Mes2})_3$, which can be oxidized to six-coordinate $CoI_3(CNAr^{Mes2})_3$ upon treatment with 0.5 equivalents of I_2. Contrastingly, addition of $CNAr^{Mes2}$ to $CoBr_2$ provided the dinuclear complex $Br_2Co(\mu_2\text{-}Br)_2Co(CNAr^{Mes2})_3$ irrespective of the molar ratios employed. FTIR analysis on these Co(II) and Co(III) complexes is used to assess the relative π-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 π-basicities of these complexes.

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 $Co_2(CO)_8$ and H_2 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 $Co(CO)_4$ molecules prior to the H_2 activation step [10,11]. Once formed however, carbon monoxide dissociation from $HCo(CO)_4$ 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 $Co(CO)_4$ or $HCo(CO)_3$ 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, encumbering 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 $[Co(CNR)_5]^+$ cations [16,18–20], whereas the analogous pentacarbonyl cobalt cation, $[Co(CO)_5]^+$ 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 $Na[Co(CNAr^{Mes2})_4]$ is accessible from Na/Hg reduction of $CoCl_2$ in the presence of $CNAr^{Mes2}$. Interestingly, optimization of the reaction conditions predicated that only three equivalents of $CNAr^{Mes2}$ were necessary to achieve both reasonable yields (ca. 60%) of $Na[Co(CNAr^{Mes2})_4]$ and full consumption of the isocyanide. Indeed, when greater than three equivalents of $CNAr^{Mes2}$ are employed, no increase in the yield of $Na[Co(CNAr^{Mes2})_4]$ was achieved. Furthermore, significant quantities of free $CNAr^{Mes2}$ 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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* Corresponding author. Tel.: +1 858 822 7478.
E-mail address: jsfig@ucsd.edu (J.S. Figueroa).

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(n = +1, 0 and −1). Accordingly, herein we present synthetic details for tris-CNAr^{Mes2} cobalt halide complexes which may serve this purpose. Most importantly, the complexes reported here exhibit spectroscopic and structural features which provide insight into π-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_6 (Cambridge Isotope Laboratories) was degassed and stored over 4 Å molecular sieves for 2 d prior to use. THF-d_8 (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^{Mes2}, [Co(CNAr^{Mes2})$_4$]BAr$^F_4$ and NaBAr$^F_4$ (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) 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. Nujol 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 ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian Mercury 300 and 400 spectrometers and a Varian VNMRS 500 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to SiMe$_4$ (^{1}H and ^{13}C δ = 0.0 ppm) with reference to the residual proton resonances of 7.16 ppm (^{1}H) and 128.06 ppm (^{13}C) for benzene-d_6 and 1.73 ppm (^{1}H) and 25.3 ppm (^{13}C) for THF-d_8, respectively [27]. ^{19}F{^{1}H} NMR spectra were referenced externally to neat trifluoroacetic acid, F$_3$CC(O)OH (δ = −78.5 ppm versus CFCl$_3$ = 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 CoI$_2$ (0.808 g, 0.245 mmol and 1 equiv.) and CNAr^{Mes2} (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$_2$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%). X-ray quality crystals of CoI$_2$(CNAr^{Mes2})$_3$·Et$_2$O were obtained from slow evaporation of a saturated Et$_2$O solution at room temperature. *Anal.* Calc. for C$_{79}$H$_{85}$CoI$_2$N$_3$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^{-1}): ν = 3109 (vw), 2726 (w), 2168 (m) [ν(CN)], 2127 (s) [ν(CN)], 1733 (vw), 1613 (m) [ν(C=C)], 1575 (w) [ν(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). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, 20 °C): δ = 2.14 (s br, 18H, 6 × p-C*H*$_3$, Mes), 2.58 (s vbr, 36H, 12 × o-C*H*$_3$, Mes) and 6.76 (s vbr, 21H, 21 × C*H*, C$_6$H$_3$ + Mes) ppm. μ_{eff} (Evans Method, C$_6$D$_6$ with O(SiMe$_3$)$_2$, 400.1 MHz, 20 °C) = 1.9(±0.1) μ_B (average of three independent measurements).

2.2. Preparation of CoI$_3$(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$_2$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$_2$O (4 × 2.5 mL each), dried *in vacuo* and collected. Yield: 0.248 g (0.170 mmol, 90%). X-ray quality crystals of CoI$_3$(CNAr^{Mes2})$_3$ ·0.5C$_7$H$_8$ were obtained upon diffusion of n-pentane into a concentrated solution in toluene at room temperature. *Anal.* Calc. for C$_{75}$H$_{75}$CoI$_3$N$_3$: 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$_2$(I$_3$)(CNAr^{Mes2})$_3$ during oxidation of CoI$_2$(CNAr^{Mes2})$_3$). FTIR (Nujol/KBr plates, cm^{-1}): ν = 2727 (w), 2188 (w) [ν(CN)], 2164 (vs) [ν(CN)], 1614 (m) [ν(C=C)], 1575 (w) [ν(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). ^{1}H NMR (499.8 MHz, C$_6$D$_6$, 20 °C): δ = 2.00 (s, 6H, 2 × o-C*H*$_3$, Mes, *cis*-CNR), 2.21 (s, 12H, 4 × o-C*H*$_3$, Mes, *trans*-CNR), 2.45 (s, 6H, 2 × p-C*H*$_3$, Mes, *trans*-CNR), 2.52 (s, 3H, 1 × p-C*H*$_3$, Mes, *cis*-CNR), 6.74 (d, ^3J(H,H) = 8.0 Hz, 2H, 2 × m-C*H*, C$_6$H$_3$, *cis*-CNR), 6.77 (d, ^3J(H,H) = 7.0 Hz, 4H, 4 × m-C*H*, C$_6$H$_3$, *trans*-CNR), 6.86 (t, ^3J(H,H) = 7.7 Hz, 2H, 2 × p-C*H*, C$_6$H$_3$, *trans*-CNR), 6.88 (t, ^3J(H,H) = 7.5 Hz, 1H, 1 × p-C*H*, C$_6$H$_3$, *trans*-CNR), 6.94 (s, 8H, 8 × m-C*H*, Mes, *trans*-CNR), 6.96 (s, 4H, 4 × m-C*H*, Mes, *cis*-CNR) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C$_6$D$_6$, 20 °C: δ = 20.5 (s, 4 × o-*C*H$_3$, Mes, *cis*-CNR), 21.3 (s, 8 × o-*C*H$_3$, Mes, *trans*-CNR), 21.8 (s, 4 × p-*C*H$_3$, Mes, *trans*-CNR), 21.9 (s, 2 × p-*C*H$_3$, 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 × *iso*-C, *trans*-CNR) and 161.0 (s, 1 × *iso*-C, *cis*-CNR) ppm.

2.3. Preparation of [CoI$_2$(CNAr^{Mes2})$_4$]BAr$^F_4$

2.3.1. Method A

A suspension of CoI$_3$(CNAr^{Mes2})$_3$ (0.100 g, 0.0686 mmol) and CNAr^{Mes2} (0.023 g, 0.069 mmol and 1 equiv.) in 5 mL Et$_2$O was treated dropwise with a colorless Et$_2$O solution of Na[BAr^F$_4$] (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$_2$(CNAr^{Mes2})$_4$]BAr$^F_4$ as purple powder, which was washed (Et$_2$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$_2$O solution of [Co(CNAr^{Mes2})$_4$]BAr$^F_4$ (0.100 g, 0.044 mmol and 5 mL) was added solid I$_2$ (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$_2$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$^F_4$·2C$_6$H$_{14}$ were obtained upon diffusion of n-hexane into a concentrated solution in fluorobenzene at room temperature. *Anal.* Calc. for C$_{138}$H$_{127}$CoB-