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Synthesis and Structural Characterization of $[Co\{CN(2,6\text{-}C_6H_3Me_2)\}_4]^-$, the First Transition Metal Isonitrilate

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Abstract: The homoleptic Co(–I) isonitrile complex $[Co(CNPh^*)_4]^-$ (1^-, Ph* = $2,6\text{-}C_6H_3Me_2$), the first example of an isonitrilate complex, can be prepared by ethylene substitution within the Co(–I) complex $[Co(C_2H_4)_4]^-$ or by potassium naphthalenide (K(Nap)) reduction of Co(0), Co(I), and Co(II) substrates. Reductions of the isonitrile-containing precursors $[Co(CNPh^*)_4I_2]$ (**3**) and $[Co(CNPh^*)_5]^+$ (4^+) proceed via $[Co_2(CNPh^*)_8]$ (**2**), which is then reduced further to 1^-. Complex 1^- can be prepared in one pot by K(Nap) reduction of cobaltocene followed by addition of CNPh* or by potassium reduction of a mixture of CoI_2 and CNPh* to give **2**, which is then further reduced to 1^-. The anion 1^- can be isolated as K^+, $[K(DME)]^+$, $[K(crypt\text{-}2,2,2)]^+$, and $[K(18\text{-}C\text{-}6)]^+$ salts and has been characterized spectroscopically and analytically. Oxidation of 1^- gives **2**, which is the only observable product from the reaction of 1^- with many simple electrophiles. The only electrophilic adduct of 1^- isolated to date is $[Co(CNPh^*)_4(SnPh_3)]$ (**5**), the product of reaction with Ph_3SnCl. Single-crystal X-ray diffraction has confirmed that [K(DME)]**1** contains discrete, approximately tetrahedral cobalt anions held together as loose dimers through interactions with the $[K(DME)]^+$ counterions (space group $P\bar{1}$, with $a = 11.160(2)$ Å, $b = 14.204(3)$ Å, $c = 14.339(3)$ Å, $\alpha = 102.91(1)°$, $\beta = 111.88(1)°$, $\gamma = 102.78(1)°$, $D_c = 1.223$ g/mL, $Z = 2$, and $R_F = 5.93\%$). Crystallography has also established that **2** is a dimer with two bridging isonitrile groups (space group $P\bar{1}$, with $a = 12.239(4)$ Å, $b = 13.985(4)$ Å, $c = 21.609(6)$ Å, $\alpha = 98.87(2)°$, $\beta = 99.19(2)°$, $\gamma = 112.72(2)°$, $D_c = 1.185$ g/mL, $Z = 2$, and $R_F = 6.10\%$), and examination of molecular parameters for 1^- and **2** suggest that increased back-donation of electron density from the metal results in significant lengthening of the C≡N triple bond in 1^- but has no consistent effect on the CNC bend angles of the ligands. Decreases in the CNC angles correlate instead with close approaches between the carbon atoms of the ligands and the $[K(DME)]^+$ counterions, which are also responsible for the major distortions of the metal geometry away from that of an ideal tetrahedron.

Introduction

Isonitriles are isoelectronic with CO, and it has been recognized for many years that they form stable transition metal complexes analogous to metal carbonyls.[1] Early examples of homoleptic isonitrile complexes, however, generally contained metals in positive oxidation states, in sharp contrast with the ubiquity of zerovalent metals in carbonyl chemistry.[2] In the case of cobalt, for example, Malatesta and Sacco first reported the syntheses of homoleptic Co(I) complexes of the type $[Co(CNR)_5]^+$ (R = aryl or alkyl) in 1953[3] and of Co(II) complexes of the type $[Co(CNR)_5]^{2+}$ (R = aryl or alkyl) shortly thereafter,[3c,4] but it was not until 1979 that the groups of Yamamoto and of Stone independently reported syntheses of the zero valent complexes $[Co_2(CNPh^*)_8]$ (Ph* = $2,6\text{-}C_6H_3Me_2$)[5] and $[Co_2(CN^tBu)_8]$.[6]

This synthetic history has been rationalized in terms of the electronic character of isonitrile ligands, which are generally accepted to be stronger σ-donors and poorer π-acceptors than CO. This model is well supported by early spectroscopic[7] and electrochemical[8] studies and would not encourage efforts to prepare isocyanide complexes of metals in negative oxidation states. We recently, however, realized that the Co(I) isonitrile complexes $[Co(CNR)_5]^+$ are remarkably air stable, and this led us to postulate that isonitrile complexes of metals in negative oxidation states might in fact be synthetically accessible and, hence, as outlined in a preliminary communication[9] and described in more detail in the present manuscript, to prepare $K[Co(CNPh^*)_4]$ (K**1**), the first example of a transition metal isonitrilate (a homoleptic isonitrile complex of a metal in a negative oxidation state) by displacement of ethylene from Jonas' labile Co(–I) complex $K[Co(C_2H_4)_4]$[10] (eq 1).

The optimized 72% yield for eq 1 is good, but $K[Co(C_2H_4)_4]$ is not a readily available starting material and developments of the chemistry of $K[Co(CNPh^*)_4]$ demanded a more direct synthesis from readily available starting materials. We now wish

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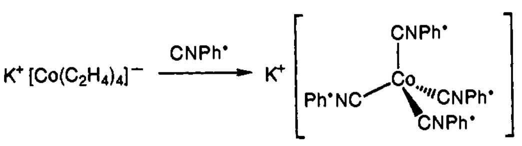


(1)

to report that $[Co(CNPh^*)_4]^-$ is easily prepared by reduction of a range of common Co(0), Co(I), and Co(II) precursors, including $[Co_2(CNPh^*)_8]$, $[Co(CNPh^*)_4I_2]$, $[Co(CNPh^*)_5]^+$, $[Co(\eta^5\text{-}C_5H_5)_2]$, and CoI_2 as summarized in Scheme 1. We have established crystallographically that the DME solvate of $K[Co(CNPh^*)_4]$ contains discrete, approximately tetrahedral anions and propose that the distortions of the isonitrile ligands in the anion away from linear geometries are primarily the result of cation/anion interactions and other crystal packing forces. We have also determined the structure of the Co(0) complex $[Co_2(CNPh^*)_8]$ crystallographically—this dimer is an intermediate in (or the starting material for) many of the routes to 1^-.

Experimental Section

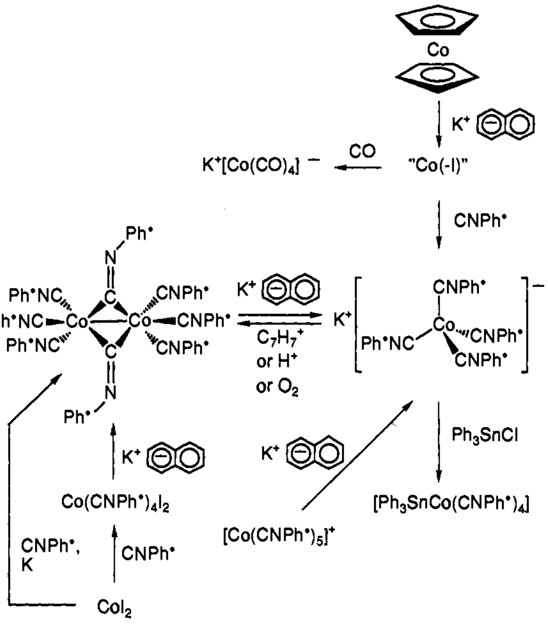
General Procedures. All reactions and manipulations were carried out under an inert atmosphere of nitrogen by means of standard Schlenk techniques[11] or a Vacuum Atmospheres Dry-lab glovebox unless otherwise noted. Glassware was oven dried or flamed under vacuum. Celite 545 (Fisher) was oven dried (24 h) prior to use. Tetrahydrofuran (THF) and diethyl ether were stored over sodium ribbon. THF, 1,2-dimethoxyethane (DME), and diethyl ether were passed through a column of neutral ativity I alumina (Aldrich) prior to distillation from potassium benzophenone ketyl. Pentane was pretreated with 5% nitric acid/sulfuric acid and then potassium carbonate and distilled from calcium hydride. Toluene was distilled from sodium, hexane from potassium benzophenone ketyl, and absolute ethanol from sodium ethoxide/magnesium. All solvents were freshly distilled and deoxygenated immediately prior to use.

The following reagents were purchased from commercial sources and deoxygenated prior to use: cobaltocene (Strem), tropylium tetrafluoroborate (Aldrich), 18-crown-6 (Aldrich), and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt-2,2,2; Aldrich). The ligand 2,6-dimethylphenyl isocyanide (CNPh*) was prepared by standard methodology[12] or purchased from Fluka. Anhydrous CoI_2 was prepared from the dihydrate (Alfa) in an Abderhalden drying pistol (<1 mm Hg/P_2O_5/xylenes, 24 h). $[Co(CNPh^*)_5]BF_4$ was prepared by a variation of the literature method for the preparation of $[Co(CNC_6H_4\text{-}4\text{-}Cl)_5]BF_4$.[13] $[Co(CNPh^*)_4I_2]$ was prepared by a variation of the procedure in the literature.[14]

Potassium naphthalenide (K(Nap)) solutions with concentrations ranging from 0.2 to 0.5 mol L^{-1} were prepared as described previously[15] by dissolution of freshly cut potassium (Fisher) and 1.1 equiv of naphthalene (Aldrich) in either THF or DME at room temperature. The solutions were stirred with a glass-coated stir bar until no solid potassium remained (4 h on average).

Infrared spectra were recorded on a Perkin-Elmer 783 grating spectrophotometer with polystyrene as an external standard. Solutions were loaded via small-bore steel cannula or syringe into 0.1-mm NaCl cells (Teflon seals) fitted with 5-mm septa. Nujol mulls were prepared under an inert atmosphere in a drybox and were loaded on to NaCl plates in air unless otherwise noted. All NMR spectra were recorded on a Bruker AF300 spectrometer (^1H, 300.13 MHz; ^{13}C, 75.46 MHz). Deuterated solvents were purchased from Cambridge Isotopes Laboratory, Merck Sharp and Dohme, or Aldrich and deoxygenated before use; d_6-acetone and d_3-acetonitrile were passed through 2.5 cm of neutral activity I alumina (Aldrich) immediately prior to use. Microanalyses were carried out by Domis und Kolbe, Mulheim a.d. Ruhr, FRG (DK), or Atlantic Microlab, Inc., Norcross, GA (Atl.).

Scheme 1



Preparation of $[K(DME)][Co(CNPh^*)_4]$ from $K[Co(C_2H_4)_4]$. A Schlenk flask was charged with $K[Co(C_2H_4)_4]$[10] (0.4 g, 1.9 mmol) and CNPh* (1.0 g, 7.6 mmol). The flask was immersed in a dry ice/acetone bath, and chilled THF (50 mL) was added. Gas evolution began immediately, and the mixture was then allowed to warm to room temperature. The resulting blood red solution was concentrated to dryness, and the residue was extracted into DME. The DME solution was filtered through 2 cm of Celite and concentrated to ca. 15 mL, and Et_2O (80 mL) was carefully layered over the concentrated DME solution. The layers were gently mixed, and the resulting solution was placed at −78 °C overnight to precipitate 0.98 g (1.38 mmol, 72%) of red crystalline $[K(DME)][Co(CNPh^*)_4]$. IR (Nujol, ν_{CN}): 2005 (w), 1880 (sh), 1815 (vs, br) cm^{-1}. ^1H NMR (d_3-acetonitrile, DME resonances omitted): δ 6.91 (t, $J = 7$ Hz, 4 H, C_6H_2H), 6.79 (d, $J = 7$ Hz, 8 H, C_6H_2H), 2.37 (s, 24 H, CH_3). Anal. Calcd for $C_{40}H_{46}CoKN_4O_2$: C, 67.40; H, 6.50. Found (DK): C, 67.28; H, 6.60.

Preparation of $K[Co(CNPh^*)_4]$ from $[Co_2(CNPh^*)_8]$. A Schlenk flask was charged with a magnetic stir bar and $[Co_2(CNPh^*)_8]$[5] (0.4 g, 0.34 mmol). THF (25 mL) was added and the stirred solution cooled to −78 °C. During dropwise addition of K(Nap) solution (1.4 mL, THF, 0.51 mol L^{-1}), the solution changed from clear orange-red in appearance to a deep blood-red color. The solution was allowed to warm for 15 min and then concentrated to 10 mL under vacuum. Hexane (100 mL) was carefully layered over the concentrated solution. The layers were allowed to mix slowly by diffusion at −80 °C until the solution appeared uniform. This yielded 0.31 g (0.50 mmol, 73%) of the unsolvated potassium salt $K[Co(CNPh^*)_4]$. IR (Nujol, ν_{CN}): 2005 (vw), 1890 (sh), 1815 (vs, br) cm^{-1}. Anal. Calcd for $C_{36}H_{36}CoKN_4$: C, 69.43; H, 5.83. Found (DK): C, 68.78; H, 5.93.

Preparation of $[Co(CNPh^*)_4I_2]$.[14] A 250-mL flask was charged in a drybox with anhydrous CoI_2 (4.4 g, 14.1 mmol), CNPh* (8.0 g, 61.1 mmol), and a Teflon stir bar and fitted with a septum. The flask was removed from the drybox and EtOH (175 mL) added. The resulting brown precipitate was removed by filtration and recrystallized from a cold THF/Et_2O solution (−30 °C). Yield: 9.1 g (10.9 mmol, 78%). IR (Nujo, ν_{CN}): 2170 cm^{-1}. Anal. Calcd: C, 51.63; H, 4.34; N, 6.69. Found (Atl.): C, 51.73; H, 4.39; N, 6.66.

Preparation of $[K(DME)][Co(CNPh^*)_4]$ from $[Co(CNPh^*)_4I_2]$. A Schlenk flask was charged in air with $[Co(CNPh^*)_4I_2]$ (0.9 g, 1.1 mmol) and a Teflon stir bar. Air was removed from the flask via three pump–purge cycles. THF (25 mL) was added and the brown slurry stirred at room temperature during addition of K(Nap) solution (THF, 10 mL, 0.35 mol L^{-1}, 3.5 mmol). The solution became turbid, and the color changed to a deep blood-red. The solvent was removed under vacuum and the naphthalene byproduct sublimed off under vacuum by warming the sides of the Schlenk flask in a bath of warm water. The residue was extracted into THF, and the solution was filtered through Celite (1 cm) on a medium frit and concentrated to dryness under vacuum. The residue

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was dissolved in DME (15 mL), and Et_2O (40 mL) was added. Crimson microcrystals began to form at the interface after addition of a layer of pentane (20 mL) to the homogeneous solution. The mixture was left until completely mixed by diffusion (12 h). A 4:1 Et_2O/DME solution was added to redissolve the crimson microcrystals, and the flask was placed at −80 °C for several days. The supernatant was removed and the crop of X-ray-quality crystals washed with hexane (3 × 30 mL) and dried under vacuum. Yield 0.59 g (0.83 mmol, 77%). IR (Nujol, ν_{CN}): 2008 (vw), 1880 (sh), 1815 (vs, br) cm^{-1}.

Preparation of [K(crypt-2,2,2)][Co(CNPh*)$_4$] from [Co(CNPh*)$_5$]BF$_4$. A yellow/orange solution of $[Co(CNPh^*)_5]BF_4$ (0.37 g, 0.46 mmol) in THF (30 mL) was reduced by dropwise addition of 2.1 molar equiv of a 0.39 mol L^{-1} solution of K(Nap) in THF (2.5 mL) at −78 °C to give a deep blood red solution. To this stirred solution was added via cannula crypt-2,2,2 (0.17 g, 0.46 mmol) in THF (10 mL). The solution was allowed to stir for 15 min at −78 °C and then slowly warmed to room temperature. A red microcrystalline solid began to precipitate from solution. After 1 h at room temperature Et_2O (125 mL) was carefully layered on top of the red solution and the mixture left to stand overnight to give a black crystalline solid. The Et_2O layer had not completely mixed, so the mother liquor was removed via a cannula. A second crop of a red/black solid began to precipitate. An additional 100 mL of Et_2O was added, and the mixture was placed at −78 °C overnight. The first crop of black crystals was washed with Et_2O (3 × 25 mL) and dried under vacuum overnight. The second crop of crystals was collected, washed, and dried similarly. The combined yield of $[K(crypt\text{-}2,2,2)][Co(CNPh^*)_4]$ was 0.38 g (0.37 mmol, 82%). IR (THF, ν_{CN}): 2005 (vw), 1900 (sh), 1815 (vs, br) cm^{-1}.

Preparation of K[Co(CNPh*)$_4$] from [Co(η^5-C$_5$H$_5$)$_2$]. A Schlenk flask was charged with cobaltocene (0.4 g, 2.12 mmol) and a magnetic stir bar, and the atmosphere was replaced with argon. THF (40 mL) was added, and the resulting solution was stirred. K(Nap) (THF, 13 mL, 0.5 mol L^{-1}, 6.5 mmol) was added dropwise at room temperature. The clear red solution was stirred at room temperature for 20 min and cooled to −78 °C. A solution of CNPh* (1.2 g, 9.3 mmol) in THF (30 mL) was added to the cold solution, which turned deep red immediately. The solution was concentrated to dryness under vacuum. The residue was extracted into THF and the resulting solution filtered through Celite (1.5 cm) and concentrated. A red-brown powder precipitated upon the addition of Et_2O. After removal of the supernatant, the product was washed with pentanes (3 × 20 mL) and dried under vacuum. This yielded 0.92 g (1.48 mmol, 70%) of $K[Co(CNPh^*)_4]$.

Preparation of [K(18-C-6)][CNPh*)$_4$] from [K(DME)][Co(CNPh*)$_4$]. A sample of $[K(DME)][Co(CNPh^*)_4]$ (0.50 g, 0.70 mmol) in THF was mixed with 18-C-6 (0.37 g, 1.41 mmol) in THF. The mixture was concentrated to ca. 10 mL under reduced pressure, and ca. 30 mL of diethyl ether was added. After 12 h at −30 °C dark red crystals had formed, and these were collected by decantation after the mixture had been cooled to −78 °C. The crystals were washed with diethyl ether and pentene and dried under vacuum. Yield: 0.50 g (0.56 mmol, 80%). Anal. Calcd: C, 65.00; H, 6.82; N, 6.32. Found (DK): C, 64.78; H, 6.65; N, 6.18.

Preparation of [K(18-C-6)][Co(CNPh*)$_4$] from CoI$_2$. Potassium (0.055 g, 1.4 mmol), CNPh* (0.43 g, 3.3 mmol), and CoI_2 (0.22 g, 0.70 mmol) were placed in a Schlenk flask, and THF (50 mL) was added to give a brown solution and a brown precipitate. The mixture was stirred at 0 °C until $[Co_2(CNPh^*)_8]$ was the only isonitrile-containing complex detectable by IR (ca. 6 h). The orange solution was cooled to −78 °C, and 2.4 mL of a 0.37 mol L^{-1} solution of potassium naphthalenide was added. The solution became blood red, and $[Co(CNPh^*)_4]^-$ was the only isonitrile species identifiable by IR. The cold reaction mixture was filtered through a medium frit which was washed with 2 × 20 mL of THF. The filtrate and washings were collected, and 18-C-6 (0.20 g, 0.76 mmol) dissolved in 10 mL of THF was added. The solution was allowed to warm to ambient temperature and stirred for 1 h. It was then concentrated under vacuum to 40 mL, and 200 mL of Et_2O was added carefully to form two layers which were allowed to mix by diffusion at −30 °C over 12 days. The red microcrystalline solid was separated by filtration, washing with 2 × 30 mL Et_2O, and dried under vacuum to yield 0.50 g (0.56 mmol, 81%) of $[K(18\text{-}C\text{-}6)][Co(CNPh^*)_4]$.

[Co(CNPh*)$_4$(SnPh$_3$)]. A solution of Ph_3SnCl (0.62 g, 1.61 mmol) in THF (30 mL) was added dropwise to a solution of $K[Co(CNPh^*)_4]$ (1.0 g, 1.61 mmol) in THF (35 mL) at −78 °C. The mixture was allowed to warm to room temperature, and the solvent was removed from the bright yellow solution under reduced pressure. The product was extracted into diethyl ether (20 mL), the solution was filtered, and the solvent was again removed under reduced pressure. The crude yield of 1.20 g (1.2 mmol, 80%) was recrystallized from ether (0.8 g in 8 mL) by addition of pentane (24 mL) and cooling to −30 °C to give two crops of analytically pure $[Co(CNPh^*)_4(SnPh_3)]$ (0.55 g, 0.59 mmol, 69%). IR (Nujol mull, ν_{CN}): 2110 (w), 2035 (sh), 1992 (s, br) cm^{-1}. ^1H NMR (CD_3OCD_2-CD_2OCD_3): δ 7.9–6.7 (m, 27 H, C_6H_3+C_6H_5), 2.12 (s, 24 H, CH_3). Anal. Calcd for $C_{54}H_{51}CoN_4Sn$: C, 69.47; H, 5.51; N, 6.00. Found (DK): C, 69.32; H, 5.46; N, 5.91.

Table 1. Summary of Crystallographic Data

	[K(DME)]- [Co(CNPh*)$_4$]	[Co$_2$(CNPh*)$_8$]
	Crystal Data	
formula	$C_{40}H_{46}CoKN_4O_2$	$C_{72}H_{72}Co_2N_8$
cryst size (mm)	0.20 × 0.25 × 0.38	0.38 × 0.35 × 0.25
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.160(2)	12.239(4)
b (Å)	14.204(3)	13.985(4)
c (Å)	14.339(3)	21.609(6)
α (deg)	102.91(1)	98.87(2)
β (deg)	111.88(1)	99.19(2)
γ (deg)	102.78(1)	112.72(2)
V (Å^3)	1936(1)	3272(2)
Z	2	2
μ (cm^{-1})	5.84	5.49
fw	712.8	1167.2
D_c (g/mL)	1.223	1.185
T (°C)	23	23
	Data Collection	
radiation	Nb-filtered Mo Kα (λ = 0.710 73 Å)	
scan type	Wyckoff	
2θ range (deg)	4.0–45.0	4.0–45.0
scan range (ω), deg	1.10	1.10
scan speed (deg/min)	variable; 8.00–20.00 in ω	variable; 7.00–20.00 in ω
index ranges	$-12 \le h \le 10$; $-15 \le k \le 14$; $0 \le l \le 15$	$-14 \le h \le 13$, $-16 \le k \le 15$, $0 \le l \le 24$
no. of reflcns collcd	5392	10 579
no. of indpt reflcns	5062 (R_{int} = 1.73%)	10 274 (R_{int} = 2.44%)
no. of obsd reflcns $F > 5.0\sigma(F)$	2102	4564
abs corr	N/A	semi-empirical
min/max transm	N/A	0.7390/0.9118
	Refinement	
no. of params refined	433	739
data to param ratio	4.9:1	6.2:1
R_F (%)[a]	5.93	6.10
R_w (%)[b]	6.96	7.63
goodness-of-fit (GOF)[c]	1.10	1.18
largest diff peak (e Å^{-3})	0.49	0.64
largest diff hole (e Å^{-3})	−0.29	−0.32

[a] $R_F = \sum|F_o - F_c|/\sum|F_o|$. [b] $R_w = \sum|(w)^{1/2}(F_o - F_c)|/\sum|(w)^{1/2}F_o$; $w^{-1} = \sigma^2(F_o) + 0.002F_o^2$. [c] $GOF = [\sum w(|F_o| - F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Oxidation of [K(DME)][Co(CNPh*)$_4$] with Tropylium Tetrafluoroborate. A Schlenk flask was charged with $[K(DME)][Co(CNPh^*)_4]$ (0.3 g, 0.42 mmol) and Teflon stir bar. A slurry of tropylium tetrafluoroborate (0.09 g, 0.51 mmol) in THF (40 mL) was added via cannula. The reaction was complete in 10 min (solution IR). The solution was concentrated to dryness under vacuum and the residue extracted with toluene. The resulting solution was filtered and concentrated to 8 mL. Hexane (25 mL) was carefully layered over the toluene solution. When the layers had completely mixed, the supernatant was removed to leave orange crystals of $[Co_2(CNPh^*)_8]$, which were washed with pentane and dried under vacuum. The product was identified by comparison of IR and ^1H NMR spectra with those of an authentic sample. Yield: 0.12 g (0.10 mmol, 49%).

X-ray Diffraction Studies of [K(DME)][Co(CNPH*)$_4$] and [Co$_2$(CNPh*)$_8$]. Crystals of $[K(DME)][(Co(CNPh^*)_4]$ ([K(DME)]**1**) and $[Co_2(CNPh^*)_8]$ (**2**) were encased in epoxy cement and attached to fine glass fibers. In both cases axial photographs confirmed the crystal quality, and systematic absences did not reveal any crystal summetry higher than triclinic. The centrosymmetric space group $P\bar{1}$ was chosen for [K(DME)]-**1** and for **2** on the basis of E-values and confirmed in each case by the

Table 2. Fractional Atomic Coordinates (×10^4) and Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[K(DME)][Co(CNPh^*)_4]$

atom	*x*	*y*	*z*	*U*(eq)[a]
K	8106(2)	9905(2)	–998(2)	60(2)
Co	9876(1)	11198(1)	1821(1)	39(1)
C(1)	8703(10)	9948(9)	1347(8)	46(6)
N(1)	7910(9)	9072(8)	1055(8)	59(6)
C(2)	11383(12)	11270(8)	2910(10)	47(7)
N(2)	12317(12)	11312(8)	3686(10)	64(7)
C(3)	9307(9)	12088(8)	2539(9)	45(6)
N(3)	9031(9)	12706(7)	3034(8)	63(6)
C(4)	10139(9)	11784(8)	905(8)	40(5)
C(5)	5332(21)	10539(14)	–1049(16)	131(16)
C(6)	4541(14)	9577(17)	–2026(16)	129(14)
C(7)	6901(17)	12138(14)	–362(14)	153(14)
C(8)	4748(16)	8185(13)	–3120(12)	144(12)
O(1)	6369(11)	11156(10)	–1143(8)	108(7)
O(2)	5381(9)	9048(8)	–2187(9)	105(6)
N(4)	10202(9)	12167(7)	240(7)	51(5)
C(11)	6419(12)	7340(9)	347(12)	63(8)
C(12)	5789(14)	6481(11)	527(15)	87(10)
C(13)	6037(17)	6504(13)	1523(18)	103(13)
C(14)	6899(17)	7350(13)	2390(15)	88(11)
C(15)	7567(13)	8241(11)	2270(13)	63(9)
C(16)	7297(12)	8207(9)	1226(13)	58(8)
C(17)	6098(12)	7337(9)	–763(11)	84(8)
C(18)	8489(13)	9172(11)	3194(11)	85(9)
C(21)	13861(14)	11120(11)	5238(12)	65(9)
C(22)	14992(18)	11540(16)	6212(14)	99(11)
C(23)	15667(16)	12570(20)	6647(12)	118(13)
C(24)	15190(18)	13184(14)	6099(17)	105(12)
C(25)	14094(15)	12789(12)	5110(12)	66(9)
C(26)	13413(14)	11747(11)	4664(12)	57(9)
C(27)	13125(15)	9969(11)	4754(11)	100(10)
C(28)	13599(16)	13473(11)	4491(13)	122(12)
C(31)	8959(11)	13081(10)	4719(10)	58(7)
C(32)	8576(14)	13651(13)	5436(10)	85(9)
C(33)	8063(16)	14384(12)	5154(14)	98(11)
C(34)	7908(13)	14610(10)	4262(12)	77(9)
C(35)	8229(11)	14030(9)	3545(9)	52(7)
C(36)	8742(10)	13276(9)	3778(9)	46(7)
C(37)	9578(15)	12264(11)	4958(11)	111(11)
C(38)	8020(14)	14263(10)	2538(10)	92(10)
C(41)	11372(13)	13982(11)	834(9)	62(7)
C(42)	11778(16)	14835(11)	544(13)	98(10)
C(43)	11428(18)	14735(12)	–499(15)	111(12)
C(44)	10627(15)	13820(13)	–1297(11)	82(9)
C(45)	10166(12)	12953(10)	–1080(10)	50(7)
C(46)	10599(11)	13064(10)	12(10)	48(7)
C(47)	11778(15)	14097(10)	1966(9)	109(10)
C(48)	9296(12)	11951(9)	–1948(9)	70(8)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

successful solution and refinement of the structure. Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 18° ≤ 2θ ≤ 25°. Diffraction data were collected on a Siemens R3M/E diffractometer. Data collection parameters and other crystallographic data are summarized in Table 1. A semiempirical absorption correction was applied to the diffraction data for **2** using the program XABS. No decay was observed for either crystal in three standard reflections during the data collection. The structures were solved using the direct methods program SOLV which located the Co atom in [K(DME)]**1** and the two Co atoms in **2**. All remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses and were refined anisotropically. Idealized atomic positions were calculated for all hydrogen atoms (d(C–H) = 0.96 Å, $U = 1.2U$ of the attached carbon atom). The final difference Fourier syntheses showed only a diffuse background (maximum contour 0.64 e/Å^3 for [K(DME)]**1** and 0.49 e/Å^3 for **1**). Inspections of F_o vs F_c values and trends based upon sin θ, the Miller index, and parity groups failed to reveal any systematic errors in the X-ray data for either compound. Atomic coordinates for [K(DME)]**1** are listed in Table 2, with selected bond lengths and angles in Table 3. Atomic coordinates for **2** are listed in Table 4, with selected bond distances and angles in Table 5. All the computer programs used in the data collection and refinement are contained in the Siemens programs packages P3 and SHELXTL PLUS.[16]

Table 3. Selected Bond Lengths (Å) and Angles (deg) within $[K(DME)][Co(CNPh^*)_4]$

K–O(1)	2.890(15)	K–O(2)	2.685(8)
Co–C(1)	1.760(11)	Co–C(2)	1.781(12)
Co–C(3)	1.824(13)	Co–C(4)	1.780(13)
C(1)–N(1)	1.228(15)	N(1)–C(16)	1.389(19)
C(2)–N(2)	1.186(16)	N(2)–C(26)	1.358(16)
C(3)–N(3)	1.172(17)	N(3)–C(36)	1.373(18)
C(4)–N(4)	1.215(17)	C(5)–C(6)	1.517(24)
C(5)–O(1)	1.358(27)	C(6)–O(2)	1.375(25)
C(7)–O(1)	1.411(20)	C(8)–O(2)	1.404(17)
N(4)–C(46)	1.403(18)		
O(1)–K–O(2)	59.7(3)	C(1)–Co–C(2)	107.3(5)
C(1)–Co–C(3)	109.2(6)	C(2)–Co–C(3)	99.3(6)
C(1)–Co–C(4)	120.2(5)	C(2)–Co–C(4)	116.1(6)
C(3)–Co–C(4)	102.3(6)	Co–C(1)–N(1)	177.5(11)
C(1)–N(1)–C(16)	153.8(12)	Co–C(2)–N(2)	173.9(15)
C(2)–N(2)–C(26)	157.5(13)	Co–C(3)–N(3)	175.5(8)
C(3)–N(3)–C(36)	165.2(14)	Co–C(4)–N(4)	174.6(9)
C(4)–N(4)–C(46)	147.7(9)		

Results and Discussion

Synthesis of $[Co(CNPh^*)_4]^-$. The Co(0) complex $[Co_2(CNPh^*)_8]$[5] is the most obvious alternative to the Co(-I) complex $[Co(C_2H_4)_4]^-$ [10] as a starting material from the preparation of **1**$^-$, but the literature indicates that the Co(0) complexes $[Co_2(CNR)_8]$ (R = Ph*, ^{t}Bu) cannot be reduced by means of alkali-metal amalgams.[5,6] We have confirmed this, but, since we[15,17] and others[18] have previously found polyaromatic radical anions such as the naphthalenide anion to be powerful reducing agents which are effective in many unusual organometallic reductions, we reinvestigated the reduction of $[Co_2(CNPh^*)_8]$ with potassium naphthalenide (KNap). After some initial failures[9] we have found that addition of 2 equiv of K(Nap) to orange-red THF solutions of the dimer at –78 °C leads to formation of the deep blood red solutions characteristic of the isonitrilate anion. Solution IR spectra have confirmed that **1**$^-$ is the only observable isonitrile-containing product, and **1**$^-$ can be isolated as the K$^+$ salt in good yield (73%).

Yamamoto reports that $[Co_2(CNPh^*)_8]$ (**2**) can itself be prepared by reduction of $[Co(CNPh^*)_4Cl_2]$ with sodium amalgam,[5] and this led us to examine reduction of $[Co(CNPh^*)_4X_2]$ complexes of Co(II) with 3 equiv of naphthalenide, in the expectation that this might result in direct formation of **1**$^-$ without requiring the isolation of intermediate $[Co_2(CNPh^*)_8]$.

Reduction of $[Co(CNPh^*)_4I_2]$ (**3**)[14] with K(Nap) gives **1**$^-$ as the only isonitrile-containing product as indicated by solution IR. The reduction does, as anticipated, involve intermediate formation of $[Co_2(CNPh^*)_8]$, since the absorptions characteristic of the terminal (2010 cm^{-1}) and bridging (1680 cm^{-1}) CN stretches of $[Co_2(CNPh^*)_8]$ can be observed during the course of the K(Nap) addition. This would suggest that naphthalenide reduction offers a convenient route to **2**, and we have confirmed this by the quantitative isolation of **2** from the naphthalenide reduction of **3**. It is not, however, necessary to isolate **2** en route to **1**$^-$, and upon continued in situ addition of K(Nap), the IR bands of **2** are replaced by the broad absorption at 1815 cm^{-1} characteristic of the isonitrilate anion. Yields of **1** from **3** were somewhat variable and ranged from 50 to 80%.

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Table 4. Fractional Atomic Coordinates (×10^4) and Isotropic Displacement Coefficients (Å^2 × 10^3) for $[Co_2(CNPh^*)_8]$

atom	*x*	*y*	*z*	*U*(eq)^a	atom	*x*	*y*	*z*	*U*(eq)^a
Co(1)	6275(1)	1632(1)	1968(1)	40(1)	C(38)	6623(11)	848(9)	–198(5)	99(7)
Co(2)	7366(1)	2917(1)	3020(1)	39(1)	C(41)	9021(14)	6675(10)	3128(5)	78(7)
C(1)	5492(8)	2254(7)	1473(4)	47(4)	C(42)	9516(17)	7774(11)	3224(7)	132(10)
N(1)	4988(6)	2636(8)	1166(4)	57(4)	C(43)	8754(22)	8295(14)	3219(9)	145(13)
C(2)	4858(9)	576(8)	2035(4)	51(5)	C(44)	7516(22)	7734(13)	3097(8)	139(13)
N(2)	3998(7)	–168(7)	2065(4)	63(4)	C(45)	7020(16)	6624(11)	3000(6)	96(8)
C(3)	6728(7)	872(7)	1389(4)	47(4)	C(46)	7775(13)	6128(9)	3031(5)	73(7)
N(3)	7001(7)	356(6)	1012(4)	59(4)	C(47)	9878(11)	6117(9)	3148(6)	100(7)
C(4)	7255(8)	4175(7)	2986(4)	48(4)	C(48)	5670(18)	5999(13)	2886(7)	147(13)
N(4)	7280(8)	5019(6)	2958(4)	66(4)	C(51)	12108(11)	4549(8)	3963(6)	76(6)
C(7)	7032(7)	1420(6)	2743(4)	40(4)	C(52)	13258(10)	4923(9)	4433(9)	102(7)
C(5)	8926(9)	3401(6)	3487(4)	42(4)	C(53)	13297(19)	4863(14)	5036(11)	146(12)
N(5)	9939(7)	3764(6)	3778(3)	54(4)	C(54)	12270(19)	4448(13)	5236(7)	123(11)
C(6)	6463(9)	2656(7)	3625(5)	52(5)	C(55)	11129(12)	4068(8)	4829(6)	76(6)
N(6)	5946(8)	2548(6)	4049(4)	69(5)	C(56)	11090(9)	4154(7)	4202(4)	49(4)
N(7)	7196(6)	684(5)	2928(3)	52(4)	C(57)	12047(12)	4632(10)	3293(7)	123(9)
C(8)	7775(8)	2938(6)	2207(4)	43(4)	C(58)	9973(14)	3604(10)	5059(5)	108(9)
N(8)	8592(6)	3530(5)	1995(3)	47(3)	C(61)	5487(12)	2373(8)	5064(6)	72(6)
C(11)	4345(9)	3374(8)	319(6)	76(6)	C(62)	4661(15)	2323(9)	5457(6)	96(8)
C(12)	3650(12)	3934(10)	130(7)	97(7)	C(63)	3559(15)	2332(10)	5204(8)	105(9)
C(13)	2988(13)	4199(11)	527(9)	116(10)	C(64)	3236(12)	2403(10)	4598(8)	104(8)
C(14)	2951(11)	3963(10)	1106(7)	99(8)	C(65)	4008(11)	2444(8)	4194(5)	73(6)
C(15)	3615(9)	3436(8)	1321(6)	71(6)	C(66)	5146(10)	2457(7)	4449(5)	62(5)
C(16)	4320(8)	3163(7)	935(5)	56(5)	C(67)	6725(13)	2435(10)	5320(6)	111(9)
C(17)	5070(10)	3044(9)	–73(5)	91(6)	C(68)	3689(12)	2550(11)	3515(6)	115(9)
C(18)	3570(11)	3100(10)	1953(6)	104(8)	C(71)	9043(11)	974(7)	3699(5)	65(6)
C(21)	3524(12)	–2043(9)	1835(5)	78(6)	C(72)	9576(11)	933(8)	4314(6)	78(6)
C(22)	2644(15)	–3074(10)	1721(6)	114(8)	C(73)	8883(14)	608(9)	4751(6)	90(7)
C(23)	1463(16)	–3259(12)	1757(7)	132(9)	C(74)	7643(13)	312(8)	4599(5)	80(7)
C(24)	1145(13)	–2460(12)	1921(7)	122(8)	C(75)	7073(10)	346(7)	3998(6)	66(5)
C(25)	1969(11)	–1405(11)	2032(6)	91(7)	C(76)	7779(10)	694(7)	3558(5)	54(5)
C(26)	3141(9)	–1214(9)	1981(5)	69(5)	C(77)	9759(9)	1253(8)	3210(6)	82(6)
C(27)	4791(12)	–1800(9)	1780(6)	101(8)	C(78)	5713(11)	–22(9)	3813(6)	96(7)
C(28)	1622(12)	–512(13)	2203(7)	135(10)	C(81)	8494(9)	4089(8)	990(5)	64(5)
C(31)	8039(10)	–703(9)	699(6)	75(6)	C(82)	8763(10)	4033(10)	382(6)	82(6)
C(32)	8504(12)	–1093(10)	220(9)	111(8)	C(83)	9331(11)	3431(11)	173(6)	89(7)
C(33)	8376(14)	–830(14)	–374(10)	126(10)	C(84)	9662(9)	2852(9)	555(5)	76(6)
C(34)	7765(13)	–229(11)	–512(6)	110(8)	C(85)	9432(8)	2863(7)	1171(4)	52(4)
C(35)	7276(9)	167(9)	–59(5)	71(5)	C(86)	8803(7)	3458(7)	1369(4)	47(4)
C(36)	7431(8)	–72(7)	543(5)	59(5)	C(87)	7908(9)	4773(7)	1234(5)	65(5)
C(37)	8131(12)	–980(9)	1336(7)	113(8)	C(88)	9848(9)	2268(8)	1608(5)	74(6)

^{a} Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The variable yields of **1**$^-$ from the reduction of $[Co(CNPh^*)_4I_2]$ led us to examine the synthesis of **1**$^-$ by reduction of $[Co(CNPh^*)_5]^+$ (**4**$^+$), a homoleptic Co(I) isonitrile complex readily prepared as a BF_4^- salt from the reaction of $Co(BF_4)_2{\cdot}6H_2O$ with CNPh* in ethanol.[19] Reduction of a solution of $[Co(CNPh^*)_5]BF_4$ in THF by dropwise addition of 2.1 molar equiv of a K(Nap) solution in THF at –78 °C resulted in a color change from yellow/orange to deep blood red, and the absence of the characteristic IR absorptions of **4**$^+$ at 2150 and 2115 cm^{-1} confirmed that **4**$^+$ had been consumed, while the appearance of a band at 1815 (vs, br) cm^{-1} indicated that **1**$^-$ had again been formed. In this case **1**$^-$ was isolated as the [K(crypt-2,2,2)]$^+$ salt (crypt-2,2,2 = the cryptand 4,7,13,16,21,24-hexaoxo-1,10-diazabicyclo[8.8.8]hexacosane) in 82% yield, and IR established that the reduction proceeded through the intermediacy of **2**.

At this point it appeared that **1**$^-$ could be prepared by reduction of virtually any reasonable substrate, and we turned our attention to "one-pot" syntheses using "off-the-shelf" reagents which do not contain CNPh* ligands.

The Co(-I) salt $K[Co(C_2H_4)_4]$ is prepared by potassium reduction of cobaltocene under ethylene,[10] and this suggested that naphthalenide reduction of cobaltocene should provide direct access to Co(-I). This was confirmed by a series of experiments involving naphthalenide reduction of cobaltocene in THF by dropwise addition of 3 equiv of K(Nap) at room temperature. We initially explored the course of the reduction under Ar to avoid the formation of N_2 complexes such as the $[Co(1,5\text{-cyclooctadiene})(N_2)_2]$ species reported by Jonas as a product of cobaltocene reduction in the presence of cyclooctadiene under nitrogen[20] and discovered that the reaction resulted in formation of solutions demonstrated to contain Co(-I) by addition of CO to give $K[Co(CO)_4]$.[21] The reduced solution reacted as anticipated with CNPh* at –78 °C to give a 70% yield of K**1**.

The nature of the reduced solution obtained following naphthalenide reduction of cobaltocene has not been established, but the solution is surprisingly stable and can, for example, be stored for days at –80 °C without apparent deterioration. The Co(-I) in the solution must be stabilized by a π-acceptor ligand, and naphthalene is the only obvious candidate for such a role. Reasonable stoichiometries include $[Co(\eta^6\text{-}C_{10}H_8)(THF)]^-$ and $[Co(\eta^4\text{-}C_{10}H_8)_2]^-$, and literature precedents for the intermediacy of naphthalene complexes of metals in negative oxidation studies are provided by Wreford's proposal that naphthalenide reduction of $[TaCl_4(dmpe)_2]$ generates $[Ta(\eta^4\text{-}C_{10}H_8)(dmpe)_2]^-$ [22] and by Ellis's synthesis of $[Ti(C_{10}H_8)_2]^{2-}$ and of a number of related complexes (probably including the Zr and Hf analogs).[18]

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(19) (a) This procedure is based on the detailed description provided by Becker for the preparation of unsolvated $[Co(CNC_6H_4\text{-}4\text{-}Cl)_5]BF_4$.[13] The $[Co(CNPh^*)_5]^+$ cation has been previously reported,[5,19b] but there are no complete descriptions of a rational synthesis. (b) Becker, C. A. L.; Cooper, J. C. *Inorg. Chim. Acta* **1989**, *158*, 141.

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Table 5. Selected Bond Lengths (Å) and Angles (deg) within $[Co_2(CNPh^*)_8]$

Co(1)–Co(2)	2.468(1)	Co(1)–C(1)	1.851(10)
Co(1)–C(2)	1.837(9)	Co(1)–C(3)	1.808(10)
Co(1)–C(7)	1.902(9)	Co(1)–C(8)	1.947(7)
Co(2)–C(4)	1.829(11)	Co(2)–C(7)	1.944(9)
Co(2)–C(5)	1.816(9)	Co(2)–C(6)	1.834(11)
Co(2)–C(8)	1.903(9)	C(1)–N(1)	1.157(14)
N(1)–C(16)	1.382(15)	C(2)–N(2)	1.180(12)
N(2)–C(26)	1.394(13)	C(3)–N(3)	1.179(14)
N(3)–C(36)	1.374(15)	C(4)–N(4)	1.179(14)
N(4)–C(46)	1.402(14)	C(7)–N(7)	1.233(13)
C(5)–N(5)	1.165(11)	N(5)–C(56)	1.401(11)
C(6)–N(6)	1.191(14)	N(6)–C(66)	1.389(16)
N(7)–C(76)	1.428(12)	C(8)–N(8)	1.232(11)
N(8)–C(86)	1.412(12)		
Co(2)–Co(1)–C(1)	107.4(2)	Co(2)–Co(1)–C(2)	110.7(3)
C(1)–Co(1)–C(2)	94.7(4)	Co(2)–Co(1)–C(3)	133.3(3)
C(1)–Co(1)–C(3)	103.8(4)	C(2)–Co(1)–C(3)	100.2(4)
Co(2)–Co(1)–C(7)	50.8(3)	C(1)–Co(1)–C(7)	156.1(4)
C(2)–Co(1)–C(7)	86.2(4)	C(3)–Co(1)–C(7)	99.5(4)
Co(2)–Co(1)–C(8)	49.3(3)	C(1)–Co(1)–C(8)	90.6(4)
C(2)–Co(1)–C(8)	159.9(4)	C(3)–Co(1)–C(8)	97.3(4)
C(7)–Co(1)–C(8)	81.2(3)	Co(1)–Co(2)–C(4)	109.0(2)
Co(1)–Co(2)–C(7)	49.3(2)	C(4)–Co(2)–C(7)	157.9(3)
Co(1)–Co(2)–C(5)	131.4(3)	C(4)–Co(2)–C(5)	100.9(4)
C(7)–Co(2)–C(5)	98.4(4)	Co(1)–Co(2)–C(6)	111.8(2)
C(4)–Co(2)–C(6)	93.4(4)	C(7)–Co(2)–C(6)	92.4(4)
C(5)–Co(2)–C(6)	103.5(4)	Co(1)–Co(2)–C(8)	50.9(2)
C(4)–Co(2)–C(8)	86.4(4)	C(7)–Co(2)–C(8)	81.3(4)
C(5)–Co(2)–C(8)	95.3(4)	C(6)–Co(2)–C(8)	160.9(3)
Co(1)–C(1)–N(1)	179.0(9)	C(1)–N(1)–C(16)	166.5(10)
Co(1)–C(2)–N(2)	173.6(11)	C(2)–N(2)–C(26)	161.9(12)
Co(1)–C(3)–N(3)	178.5(7)	C(3)–N(3)–C(36)	169.5(9)
Co(2)–C(4)–N(4)	174.5(9)	C(4)–N(4)–C(46)	158.2(11)
Co(1)–C(7)–Co(2)	79.8(4)	Co(1)–C(7)–N(7)	137.3(6)
Co(2)–C(7)–N(7)	142.9(6)	Co(2)–C(5)–N(5)	176.3(8)
C(5)–N(5)–C(56)	171.7(9)	Co(2)–C(6)–N(6)	175.2(7)
C(6)–N(6)–C(66)	167.0(11)	C(7)–N(7)–C(76)	127.9(7)
Co(1)–C(8)–Co(2)	79.7(3)	Co(1)–C(8)–N(8)	143.7(6)
Co(2)–C(8)–N(8)	136.6(6)	C(8)–N(8)–C(86)	131.5(6)

Attempts to derivitize the intermediate Co(-I) complex by addition of simple electrophiles like HPF_6, CH_3I, $PhCH_2Cl$, and CO_2 have been unsuccessful to date.

Napthalenide reduction of cobaltocene under nitrogen gave a turbid solution which differed somewhat in appearance from the clear, deep red solution obtained under argon, but the solution cleared on stirring at ambient temperatures and reacted with added CNPh* to give K**1** in yields comparable to those obtained under argon, establishing that it is *not* essential to carry out the reduction under argon.

The second one-pot approach to $\mathbf{1}^-$ which we have developed begins with reduction of anhydrous CoI_2 with 2 equiv of potassium in the presence of excess CNPh* in THF. The first product observed in this reaction is a brown precipitate similar in appearance to $[Co(CNPh^*)_4I_2]$, which then redissolves and reacts with potassium to give a solution in which the only isonitrile-containing compound is $[Co_2(CNPh^*)_8]$ (IR). These solutions can then be further reduced by the addition of 1 equiv of naphthalenide (per Co) to give $\mathbf{1}^-$ in good yield.

Isolation of $[Co(CNPh^*)_4]^-$ Salts—Choice of Counterion. To facilitate comparison between synthetic procedures we have worked exclusively with K^+ cations. Even with this restriction, however, we have obtained $\mathbf{1}^-$ as a variety of salts which differ in solvation or complexation of the K^+ counterion and hence in their solubility, ease of crystallization and handling, and cost.

The easiest salt of $\mathbf{1}^-$ to isolate contains a $[K(crypt\text{-}2,2,2)]^+$ counterion. This is obtained by addition of the cryptand to a solution of K**1**, and the salt has little solubility in THF. This salt is not one with which we have worked extensively because of the high cost of the cryptand.

The $[K(18\text{-}C\text{-}6)]^+$ (18-C-6 = 18-crown-6) salt is similarly convenient to isolate and is moderately soluble in THF, facilitating recrystallization by concentration and cooling or by addition of Et_2O or pentane to a concentrated solution at room temperature. The crown ether does, however, again render this a moderately expensive material with which to work.

The "naked" K^+ salt is the least expensive and the simplest to obtain, and we have prepared analytically pure samples by concentration of THF solutions. The main disadvantage of this salt is that the material is microcrystalline at best, and this renders it extremely air sensitive and inconvenient to store and to manipulate.

The best overall compromise between cost, accessibility, and storage properties are offered by the DME solvate [K(DME)]**1**, but this does require some care in its isolation. Simple addition of Et_2O to concentrated DME solutions of K**1** sometimes gave good yields of [K(DME)]**1**, but it is often necessary to induce nucleation by one of a number of methods: pumping on a supersaturated DME/Et_2O solution; seeding a solution with fully formed crystals; or adding pentanes or hexanes to a DME solution to precipitate the product rapidly in a microcrystalline form followed by readjustment of the solvent composition to redissolve the bulk of the product while leaving microcrystalline nucleation sites for crystal growth following subsequent addition of pentane or hexanes. Crystallization of K[(DME)]**1** is highly dependent on the purity of the solvents, but the difficulty experienced in reproducibly crystallizing the DME solvate is probably related to its surprisingly high solubility—the presence of material of limited solubility seems to inhibit nucleation.

Formulation of [K(DME)]**1** as a monosolvate is based on three complementary lines of evidence: excellent agreement between calculated and experimental combustion analysis data for the salt; the observation of 1.0 ± 0.1 equiv of DME per $\mathbf{1}^-$ anion in ^1H NMR spectra recorded in CD_3CN; crystallographic characterization of the $[K(DME)]^+$ counterion in a single-crystal diffraction study (see below).

Attempts to use metathetical procedures to obtain $\mathbf{1}^-$ with noncoordinating counterions such as tetraalkylammonium ions or $[Ph_3PNPPh_3]^+$ (PPN^+) have been unsuccessful to date.

The ^1H NMR characteristics of the $\mathbf{1}^-$ anion in CD_3CN are independent of the counterion present, as are IR spectra of $\mathbf{1}^-$ in THF. IR spectra of $\mathbf{1}^-$ salts in Nujol mulls are only slightly dependent on the nature of the counterion, the most noticeable effect being that the ν_{CN} absorptions of $\mathbf{1}^-$ are broader with the K^+ counterion than with the complex counterions.

Oxidation of $[Co(CNPh^*)_4]^-$. Solutions and solid samples of $[Co(CNPh^*)_4]^-$ with K^+, $[K(DME)]^+$, $[K(18\text{-}C\text{-}6)]^+$, and $[K(crypt\text{-}2,2,2)]^+$ counterions are indefinitely stable thermally, but as might be anticipated, solutions and finely divided solid samples are extremely air sensitive and readily oxidize to give, in the first instance, $[Co_2(CNPh^*)_8]$ (solution IR). Synthetic oxidation of $[Co(CNPh^*)_4]^-$ to pure, isolated $[Co_2(CNPh^*)_8]$ was surprisingly difficult as a consequence of purification problems, but we eventually established that oxidation of [K(DME)]**1** with tropylium tetrafluorobate provided a reproducible route to isolated **2** in ca. 50% yield.

Electrophile Addition to $[Co(CNPh^*)_4]^-$. We indicated in our preliminary communication that addition of Ph_3SnCl to K**1** leads to formation of the triphenyltin adduct $[Co(CNPH^*)_4(SnPh_3)]$ (**5**) in good yield, and details of this procedure are given in the Experimental Section.

Attempts to prepare other derivatives of $\mathbf{1}^-$ by electrophilic addition have been unsuccessful to date. Protonic acids, for example, oxidize $\mathbf{1}^-$ to **2** (IR), suggesting that initial formation of a hydride $[Co(CNPh^*)_4H]$ is followed by H_2 evolution and dimerization. This would be precisely analogous to the formation of $[Co_2(CO)_8]$ by protonation of $[Co(CO)_4]^-$ to give the unstable

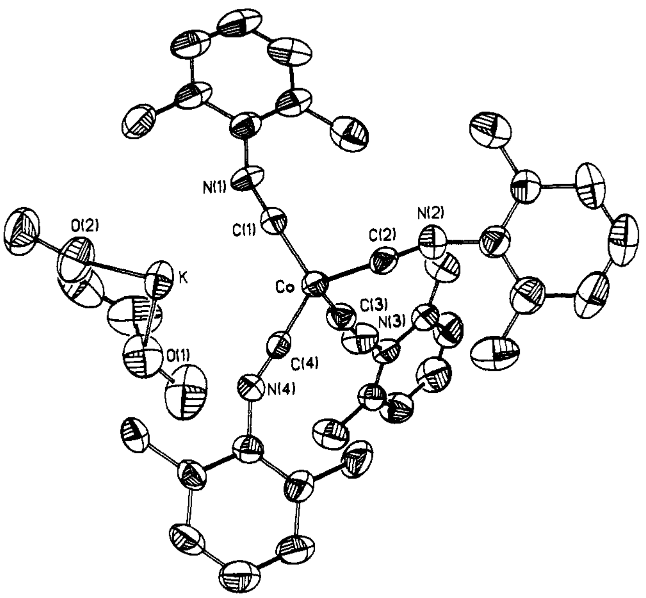

Figure 1. Molecular structure of [K(DME)][Co(CNPh*)$_4$] (35% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

hydride [Co(CO)$_4$H][23] (a key intermediate in early cobalt carbonyl based catalytic hydroformylation systems[24]). No tractable products other than **2** have been obtained to date from the addition of other simple electrophiles like CH_3I, $(CH_3)_3O^+$, $Me_3SiOSO_2CF_3$, PhCOCl, or $PhCH_2Cl$ to solutions of [Co(CNPh*)$_4$]$^-$.

Structure of [K(DME)][Co(CNPh*)$_4$]. The structure of [K(DME)]**1** was determined by the X-ray diffraction study described in the Experimental Section, which established (Figure 1) that the complex contains [K(DME)]$^+$ cations and discrete [Co(CNPh*)$_4$]$^-$ anions (with the molecular parameters reported in Table 3) in which the isonitrile ligands form an appproximately tetrahedral array about cobalt analogous to the arrangement of the carbonyl ligands in [Co(CO)$_4$]$^-$ [25] and in [Fe(CO)$_4$]$^{2-}$.[26]

Determining experimentally that [K(DME)]**1** contains discrete [Co(CNPh*)$_4$]$^-$ anions is important in part because of the elegant body of work by Lippard in which he has demonstrate that isonitrile ligands in early transition metal complexes undergo facile reductive copuling to give *N,N'*-dialkyldiaminoalkyne ligands.[27] While it is no longer believed that steric crowding in seven-coordinate envuironments is as critical a factor in the conditions required to induce such reactions as once accepted,[27,28] the observation that isonitrile ligands in a tetrahedrally coordinated complex of Co(-I) do *not* undergo a reductive coupling reaction does emphasize that extremely high electron density is not sufficient by itself to drive such coupling.

The existence of discrete [Co(CNPh*)$_4$]$^-$ anions in [K(DME)]**1** is consistent with the observation that solutions containing **1**$^-$ react with Ph_3SnCl to give [Co(CNPh*)$_4$(SnPh$_3$)], which also contains discrete, uncoupled isonitrile ligands.

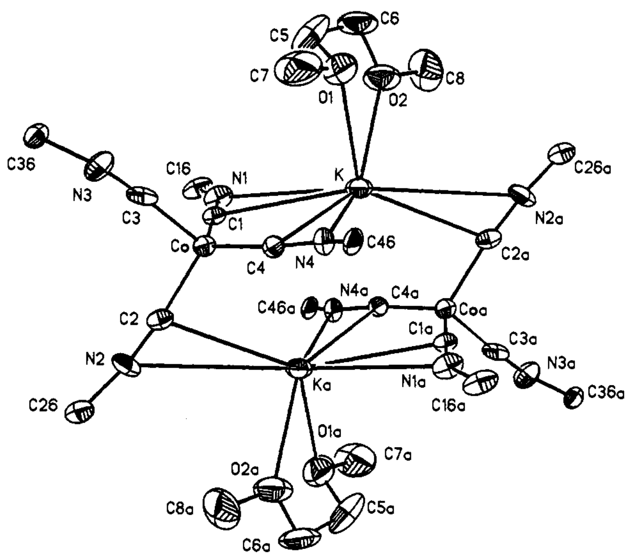

Figure 2. View of the two molecules of [K(DME)][Co(CNPh*)$_4$] in the unit cell illustrating the principal close approaches and bonds (25% probability ellipsoids). Atoms with an "a" suffix are generated from the original atoms by inversion through the center of symmetry. Hydrogen atoms and all but the ipso carbon atom of the aryl rings have been omitted for clarity.

Table 6. Selected Close Contacts within [K(DME)][Co(CNPh*)$_4$]

K–Co	3.568(3)	K–C(1)	3.158(13)
K–N(1)	3.469(12)	K–C(4)	3.028(8)
K–N(4)	3.159(8)	Co–K$_a$	3.410(4)
C(2)–K$_a$	3.189(15)	N(2)–K$_a$	3.657(15)

It is clear from inspection of Figure 1 and the data in Table 3 that, although the coordinated DME might be expected to reduce the Lewis acidity of the K$^+$ cation, interactions with the [K(DME)]$^+$ counterion significantly affect the structure of the [Co(CNPh*)$_4$]$^-$ anion. This is not surprising given the established ability of alkali-metal counterions to interact with and distort the structures of carbonylmetalate anions,[29] but interpreting these counterion effects requires consideration of *all* the close contacts within and between unit cells of [K(DME)]**1**.

The unit cell contains two molecules of [K(DME)]**1** related by an inversion center such that the two [K(DME)]$^+$ cations essentially bridge the two anions, forming a loose dimer (Figure 2). The K$_a$–Co distance of 3.410(4) Å in this dimer is somewhat less than the K–Co distance of 3.568(3) Å, but this difference is unlikely to be significant given that both distances are too long to correspond to other than a weak K$^+$/Co$^-$ interaction. The observation of close contacts between **1**$^-$ and both K and K$_a$ does, however, emphasize that the depiction of K rather than K$_a$ in Figure 1 is arbitrary. We have examined potential interunit cell close contacts, and none are as significant as the close contacts shown in Figure 2 and tabulated in Table 6.

The simplest counterion effects on the geometry of **1**$^-$ are the distortions of the **1**$^-$ anion away from the ideal tetrahedral interligand angles of 109°—since K$^+$ is located between the C(1) and C(4) isonitriles, interaction with the cation would appear to be responsible for the widening of the C(1)–Co–C(4) angle to 120.2(5)° while the C(2)–Co–C(3) angle, on the opposite side from the metal, closes to 99.3(6)°. This distortion is quite similar to the distortions from ideal tetrahedral geometries observed in the structure of the isoelectronic carbonylmetalate [Fe(CO)$_4$]$^{2-}$ with some counterions, as in Na$_2$[Fe(CO)$_4$]·1.5dioxane.[26a]

It is apparent from Figure 2 that, in addition to the close approach between the [K(DME)]$^+$ counterion and the C(1) and C(4) isonitrile ligands, there is an equally significant close approach between K$_a$ and the C(2) isonitrile in **1**$^-$. This leaves

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Table 7. Potential Correlations between Isonitrile Bend Angles and Other Molecular Parameters in $[K(DME)][Co(CNPh^*)_4]$

isonitrile bend (deg)		closest K–C contact (Å)		C≡N dist (Å)		Co–C dist (Å)	
C(4)–N(4)–C(46)	147.7(9)	K–C(4)	3.028(8)	C(4)–N(4)	1.215(17)	Co–C(4)	1.780(13)
C(1)–N(1)–C(16)	153.8(12)	K–C(1)	3.158(13)	C(1)–N(1)	1.228(15)	Co–C(1)	1.760(11)
C(2)–N(2)–C(26)	157.5(13)	K_a–C(2)	3.189(15)	C(2)–N(2)	1.186(16)	Co–C(2)	1.781(12)
C(3)–N(3)–C(36)	165.2(14)	none		C(3)–N(3)	1.172(17)	Co–C(3)	1.824(13)

the C(3) isonitrile as the only isonitrile *without* a close ounterion approach—the CNC bend angle of this isonitrile (165.2(14)°) is close to 180° and is within the range appropriate for classification as a "linear" isonitrile ligand.[30]

The bending observed in the C(1), C(2), and C(4) isonitrile ligands is superficially consistent with our earlier suggestion that the low C≡N stretching frequencies of ca. 1815 cm^{-1} observed for 1^- in THF reflect marked bending of the isonitrile ligands as a consequence of extensive π back-donation from the metal.[9] The variability of the bend angles and the relatively linear geometry of the C(3) isonitrile argue against this simplistic interpretation, however, and comparison of the bend angles for the isonitrile ligands with other molecular parameters of $[K(DME)][Co(CNPh^*)_4]$ (Table 7) suggests instead that bending of the ligands correlates best with close approaches between the carbon atoms of the ligands and the $[K(DME)]^+$ counterions. There is no correlation between the isonitrile bend angle and the Co–C distance (which might itself be expected to indicate the extent of back-bonding) and only a weak correlation with the C≡N distances (which are lengthened, particularly in the two most bent isonitrile ligands). All that we can conclude at this point is that while the low C≡N stretching frequencies of 1^- do suggest that the isonitrile ligands are weakened by back-donation of electron density from Co(–I), this weakening does not correlate with changes in the CNC bend angle.

The evidence for counterion effects on structural parameters for 1^- raises intriguing questions as to the nature of the $[K(DME)]^+$ interactions with 1^-, which the structural evidence suggests primarily involve interactions between the potassium centers and the carbon atoms of the isonitrile ligands. Thus, while the similarity between the K–C(4) and K–N(4) distances of 3.028(8) and 3.159(8) Å might be taken as indicative of an interaction with a π-component of the C≡N π bond, the K–C distances for the C(1) and C(2) isonitrile are both much shorter than the corresponding K–N distances (Table 6) and hence inconsistent with such a description. This counterion interaction can be usefully compared with that observed between the $[Fe(CO)_4]^{2-}$ anions and the bridging Na^+ counterions in $Na_2[Fe(CO)_4]\cdot 1.5$dioxane,[26a] in which the counterion has a close approach to both the carbon atoms *and* the iron atom of a "$Fe(CO)_2$" fragment. In the iron system this leads to a description in terms of a Na^+/C–Fe–C interaction, in sharp contrast with any reasonable description of interactions within [K(DME)]1, in which the K^+/Co distance is much longer than the K^+/C distance. This particular contrast between the two systems reflects the different counterion orientations with respect to the ligand–M–ligand groups, but the comparison broadly suggests that the interactions in these systems lack directionality, indicating that they are probably primarily ionic in nature.

Structure of $[Co_2(CNPh^*)_8]$. Although the discussion above would suggest that deviations of the CNC angles of isonitrile ligands from 180° are not of much electronic significance when discussing the bonding of isonitrile ligands to low-valent transition metals, it would obviously be valuable to compare the ligand geometry in 1^- with that of isonitrile ligands in related isonitrile complexes of Co in other oxidation states. The molecular strucure of the Co(0) complex $[Co_2(CN^tBu)_8]$ has reported,[6b] but the marked differences between the CN^tBu ligand in this dimer and the $CNPh^*$ ligand in 1^- suggested that we should take advantage of the availability of crystalline complexes of **2** to determine the molecular geometry of the $CNPh^*$ complex by X-ray diffraction methods. This seemed particularly appropriate given the key role of **2** as an intermediate in the routes to 1^- involving reduction of $[Co(CNPh^*)_4I_2]$, $[Co(CNPh^*)_5]^+$, and CoI_2, and the diffraction study was carried out as described in the Experimental Section.

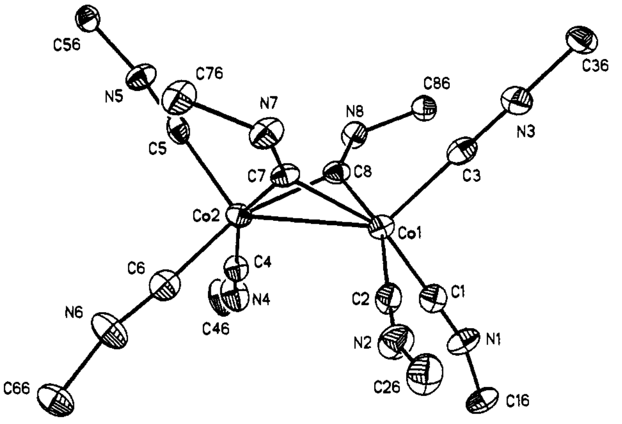

Figure 3. Molecular structure of $[Co_2(CNPh^*)_8]$ (40% probability ellipsoids). Hydrogen atoms and all except the ipso carbons of the aryl rings have been omitted for clarity.

As anticipated, **2** has a dimeric structure (Figure 3; selected molecular parameters are listed in Table 5) analogous to those of $[Co_2(CN^tBu)_8]$[6b] and of $[Co_2(CO)_8]$[31] in which each Co has three terminal isonitrile ligands while two isonitriles bridge the metal centers. The Co–Co distance of 2.468(1) Å is consistent with the presence of the Co–Co bond anticipated on electron-counting grounds. The carbon to nitrogen bonds of the bridging isonitriles (1.232(11) and 1.233(13) Å) are somewhat longer than those of the terminal isonitriles (average 1.175 Å) but markedly shorter than a C(sp^2)═N bond (ca. 1.376 Å),[32] but the bond lengths and the marked bending observed (CNC angles = 127.9(7) and 131.5(6)°) are consistent with a significant contribution to the bonding by a canonical in which the bridging isonitriles have a CN double bond.

The average terminal CN bond length of 1.175 Å in **2** is between the typical uncoordinated C≡N isonitrile triple bond length of 1.144 Å[32] and the average C≡N bond length in 1^- of 1.200 Å. This correlates with the higher C≡N stretching frequency of 2010 cm^{-1} observed in **2** and suggests that the C≡N triple bonds in 1^- are indeed weakened by back-donation of electron density from the highly reduced Co(–I) metal center in 1^-.

The terminal isonitrile ligands in **2** exhibit a range of CNC angles from 158.2 to 171.7°, which brackets the 165.2° CNC angle of the isonitrile in 1^- which does not have a close approach to the counterion. The variations in CNC angles within **2** can reasonably be ascribed to varying crystal packing interactions, and this comparison of CNC bond angles for 1^- with those for **2** provides no evidence for a significant correlation between the CNC angles and the oxidation state of cobalt.

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Conclusion

When we first reported the synthesis of $[Co(CNPh^*)_4]^-$, we used a procedure which implied that **1**$^-$ was an exotic species requiring an exotic starting material for its synthesis.[9] The present studies have clearly established, however, that **1**$^-$ can be prepared in good yield from a variety of readily available Co(0), Co(I), and Co(II) precursors, and all of the procedures described in this paper offer practical approaches to the synthesis of **1**$^-$. They have varying strengths and weaknesses, and reduction of $[Co(CNPh^*)_4I_2]$, for example, is straightforward, but has the disadvantage that the yield is somewhat variable. The route to **1**$^-$ involving reduction of isolated **2** is highly reproducible but is unnecessarily circuitous. A very direct route is offered by one-pot potassium reduction of CoI_2 in the presence of CNPh* followed by naphthalenide reduction, but this approach does not offer high yields.

This leaves reduction of $[Co(CNPh^*)_5]BF_4$ or of cobaltocene as our preferred routes to **1**$^-$. Both of these procedures are high-yield, reproducible, and convenient, and the choice between them can be based on the relative availability of the two starting materials.

Our structural studies of **1**$^-$ and **2** have established that $[K(DME)][Co(CNPh^*)_4]$ contains discrete, approximately tetrahedral $[Co(CNPh^*)_4]^-$ anions, in which there is significant lengthening of the C≡N triple bonds relative to the terminal C≡N bonds in $[Co_2(CNPh^*)_8]$, consistent with increased back-donation of electron density in the Co(-I) complex. Interactions with the counterion are probably responsible for the major distortions of the metal geometry away from that of an ideal tetrahedron within **1**$^-$, but a full understanding of the bonding in this complex will require a more detailed analysis of the electronic structure of the complex—such a study, utilizing comparison with isoelectronic complex of Ni(0) and Cu(I), is underway in collaboration with Professor Cliff Kubiak.[33]

The parallels between the structures and reactivities of $[Co(CNPh^*)_4]^-$ and of $[Co(CO)_4]^{-25}$ support the analogy which we have drawn between isonitrilates and carbonylmetalates.[9] The ease with which $[Co(CNPh^*)_4]^-$ can now be prepared, together with our recent report of the application of similar approaches to the synthesis of solutions of ruthenium isonitrilates $[Ru(CNR)_4]^{2-}$,[34] supports our assertion[9] that isonitrilates will constitute a significant class of transition metal complexes, accessible with many transition metals in negative oxidation states. Although the derivative chemistry of $[Co(CNPh^*)_4]^-$ is limited, such limitations parallel those in the chemistry of $[Co(CO)_4]^-$, and the successful preparation of a range of carbon and other group 14 adducts of the ruthenium dianions[34] suggests that isonitrilates may have reaction chemistries comparable in diversity to those of carbonylmetalates.

Acknowledgment. We thank the National Science Foundation for financial support through Grant CHE-9113808 and Professor Cliff Kubiak for valuable discussions.

Supplementary Material Available: Tables of bond lengths and angles, anisotropic displacement coefficients, and H atom positional and displacement parameters for $[K(DME)][Co(CNPh^*)_4]$ and $[Co_2(CNPh^*)_8]$ (11 pages); tables of structure factors for $[K(DME))][Co(CNPh^*)_4]$ and $[Co_2(CNPh^*)_8]$ (54 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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