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**COMMUNICATION** Chunhua Hu, Jianfeng Jiang *et al.*  $[Co^{I}(CN)_{\gamma}(CO)_{3}]^{-}$ , a new discovery from an 80-year-old reaction

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## [Co<sup>l</sup>(CN)<sub>2</sub>(CO)<sub>3</sub>]<sup>-</sup>, a new discovery from an 80-year-old reaction<sup>†</sup>

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A systematic study of the 80-year-old simple and fundamental reaction of cobalt( $\Pi$ ) salt with cyanide under one atmosphere CO was carried out and two novel Co( $\Pi$ ) complexes were isolated in the absence of hydroxide. These complexes are the first structurally characterized mixed cobalt CO–CN<sup>-</sup> compounds.

In the early 1930s, the addition of cyanide to a basic aqueous solution of a  $\text{Co}^{2+}$  salt under one atmosphere CO was studied, and the cobalt carbonyl compound  $[\text{Co}(\text{CO})_4]^-$  was isolated.<sup>1</sup> Protonation of  $[\text{Co}(\text{CO})_4]^-$  yields  $[\text{Co}^{\text{I}}(\text{H})(\text{CO})_4]$ , which is a major catalyst for the hydroformylation reaction and one of the first homogeneous catalysts.<sup>2</sup> Both  $[\text{Co}(\text{CO})_4]^-$  and  $[\text{Co}^{\text{I}}(\text{H})(\text{CO})_4]$  have been extensively studied over the last 80 years. The reaction leading to  $[\text{Co}(\text{CO})_4]^-$  is shown in eqn (1). However, cyanide, a very strong ligand, was surprisingly not found in *any* of the cobalt complexes isolated from the reaction system. Cyanide is believed to serve only as a promoting agent according to previous publications.<sup>3</sup>

$$2\text{Co}^{2^+} + 12\text{OH}^- + 11\text{CO} \rightarrow 2[\text{Co}(\text{CO})_4]^- + 3\text{CO}_3^{2^-} + 6\text{H}_2\text{O}$$
(1)

Driven by the recent discovery of other mixed metal cyanide carbonyl complexes  $[M(CN)_x(CO)_y]^{n-4}$  and our curiosity regarding what really happens in such a simple and fundamental reaction system, we decided to systematically study the reactions of aqueous Co<sup>2+</sup> solution with varying amounts of cyanide and hydroxide under one atmosphere CO, just like initially investigated 80 years ago. Astonishingly, we have discovered new cyanide carbonyl compounds of cobalt(1).

The reactions were carried out on a millimolar scale. In the absence of hydroxide, the addition of four equivalents of sodium cyanide to an aqueous cobalt(II) chloride solution under one atmosphere carbon monoxide gave a light yellow solution in 24 hours. By treating the reaction mixture with a solution of PPh<sub>4</sub>Cl in CH<sub>2</sub>Cl<sub>2</sub>, we separated two major products: (PPh<sub>4</sub>)[Co<sup>I</sup>(CN)<sub>2</sub>(CO)<sub>3</sub>] from the organic phase and Na<sub>3</sub>[Co<sup>III</sup>(CN)<sub>6</sub>] from the aqueous phase.<sup>5</sup> Both products were isolated in around 50% yield. Even though other Co–CN–CO complexes have been previously described by Stuhl and Foxman *et al.*,<sup>6</sup> (PPh<sub>4</sub>)[Co<sup>I</sup>(CN)<sub>2</sub>(CO)<sub>3</sub>] represents the first example of a cobalt complex with mixed cyanide–carbonyl ligands determined using single crystal X-ray diffraction.‡

The crystals of  $(PPh_4)[Co^I(CN)_2(CO)_3]$  were grown by diffusing hexane into the  $CH_2Cl_2$  solution, and its crystal structure was established using single crystal X-ray diffraction. The  $[Co^I(CN)_2(CO)_3]^-$  anion was analyzed by dispersion-corrected density-functional calculations.<sup>5,7</sup> In the structure Co<sup>I</sup> takes a trigonal bipyramidal geometry with both CN ligands in the axial position and three CO groups in the equatorial position. The Co-C<sub>CO</sub> bond distances are around 1.8 Å, which are significantly shorter than the Co-C<sub>CN</sub> bond distances (*ca.* 1.9 Å). This observation agrees with the data in other metal cyanide carbonyl complexes.<sup>4</sup> The molecular drawing of the anion  $[Co^I(CN)_2(CO)_3]^$ is depicted in Fig. 1, and selected bond distances and angles



Fig. 1 ORTEP drawing of  $[Co^{l}(CN)_{2}(CO)_{3}]^{-}$  and  $[Co^{l}(CN)_{3}(CO)_{2}]^{2-}$  at the 50% ellipsoid level.

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y, -z + 1.

**Table 1** Structural, IR and NMR data for  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  and  $[Co^{I}(CN)_{3}(CO)_{2}]^{2}$ 

Anion	$[\mathrm{Co}^{\mathrm{I}}(\mathrm{CN})_2(\mathrm{CO})_3]^-$	$[{\rm Co}^{\rm I}({\rm CN})_3({\rm CO})_2]^{2-}$
Selected bond	Co1-C1 1.896(2)	Co1-C1 1.9499(17)
distance (Å)	Co1-C2 1.789(3)	Co1-C2 1.8912(19)
	Co1-C3 1.801(4)	Co1-C3 1.8978(18)
		Co1-C4 1.7781(19)
		Co1-C5 1.7586(18)
Selected bond	C1-Co1-C2 89.35(12)	C2-Co1-C1 91.59(7)
angle (°)	C1-Co1-C3 90.53(11)	C2-Co1-C4 91.47(8)
	$C1-Co1-C2' 90.10(12)^a$	C2-Co1-C5 87.48(8)
	C1-Co1-C1' 178.9(2)	C2-Co1-C3 175.58(7)
	C2-Co1-C3 120.97(10)	C1-Co1-C4 115.25(7)
	C2-Co1-C2' 118.05(19)	C1-Co1-C5 118.49(7)
		C4-Co1-C5 126.25(8)
IR frequency in	$\nu_{\rm CO}$ 2004	ν <sub>CO</sub> 1917
$\operatorname{CH}_2\operatorname{Cl}_2(\operatorname{cm}^{-1})$		1980
	$\nu_{\rm CN}$ 2112	$\nu_{\mathrm{CN}}$ 2074
		2088
		2114
NMR <sup>13</sup> C shift (ppm)	$\delta_{\rm CO}$ 195.0	$\delta_{\rm CO}$ 195.1
	$\delta_{\rm CN}$ 126.0	$\delta_{\rm CN}^{-1}$ 131.0, 123.6
<sup><i>a</i></sup> The primed atoms ar	e generated by the symme	try operation of $-x + 1$ .

are presented in Table 1. In  $CH_2Cl_2$  solution  $[Co^{I}(CN)_2(CO)_3]^{-1}$ has a  $D_{3h}$  symmetry since only one CN and one CO peak were detected by the solution infrared spectrum (IR) at 2112 and 2004 cm<sup>-1</sup>. To assign these peaks, the IR spectrum of the <sup>13</sup>C-labeled cyanide complex was measured. The peak at 2112 cm<sup>-1</sup> shifted to 2067 cm<sup>-1</sup> in the labeled complex, which was assigned to the asymmetric CN stretch; the peak at 2004 cm<sup>-1</sup> remained at the same frequency and was assigned to the CO stretch. Density-functional theory calculations fully support the assignment. Compared to the isostructural and isoelectric iron analog,  $[Fe^{0}(CN)_{2}(CO)_{3}]^{2-}$  ( $\nu_{CO} = 1844 \text{ cm}^{-1}$ ),<sup>4b</sup> the CO vibration frequency has a blue shift of 160  $\text{cm}^{-1}$ . The shift is from the different strength of the metal-to-CO  $\pi$ -back donation bonding caused by the charge and/or electronegativity on the center metal atom. Similar results were recorded for the series of complexes such as  $[Mn(CO)_6]^+$  (2100 cm<sup>-1</sup>),  $[Cr(CO)_6]$  $(2000 \text{ cm}^{-1})$  and  $[V(CO)_6]^-$  (1859 cm<sup>-1</sup>), which were well documented in a textbook contribution.8

 $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  is oxygen-sensitive. A cyclic voltammetry experiment conducted in  $CH_{2}Cl_{2}$  solution showed that the irreversible oxidation of  $Co^{II}/Co^{I}$  occurred at +206 mV vs. Ag/AgCl. Addition of the mild oxidant  $I_{2}$  led to the dissociation of all CO ligands, which was monitored by conducting an infrared study.

Dispersion-corrected density-functional calculations<sup>9</sup> on the crystal structure of  $(PPh_4)[Co^I(CN)_2(CO)_3]$  were carried out in order to elucidate the relative structural stability, which is evaluated by calculating the phonon density of states using the quasi-harmonic approximation,<sup>10,11</sup> as depicted in Fig. S1 (ESI<sup>†</sup>).

Indeed, there are no imaginary phonon frequencies hence this very compound must be a relative minimum on the energy hypersurface. We find the  $C \equiv N$  peak in the range of 2160–2180 cm<sup>-1</sup> and the  $C \equiv O$  peak at 1982–2060 cm<sup>-1</sup>, which is in good agreement with the experimental results.

The electronic structure and its associated charge distribution are easily mirrored from the Bader charges,<sup>12</sup> a byproduct of the DFT calculations. These charges are listed in Table S1 in the ESI,<sup>†</sup> and they do reflect our expectations on the oxidation of cobalt as +1 and the whole  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  anion as -1 charged.

During the preparation of  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$ , the reaction mixtures were continuously monitored using IR spectroscopy. There were additional peaks observed between 1900 and  $2000 \text{ cm}^{-1}$  upon reaction, suggesting that other cobalt carbonyl complexes might exist as reaction intermediates. It could be  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  in accord with Halpern and Pribanić's findings.<sup>13a</sup> However, we were unable to separate the pure product from the reaction mixtures. Varying the amount of cvanide to the reaction system did not help either. We then decided to treat the purified (PPh<sub>4</sub>)[Co<sup>I</sup>(CN)<sub>2</sub>(CO)<sub>3</sub>] with more CN<sup>-</sup> to test the former hypothesis. Indeed, the addition of one equivalent  $CN^{-}$  to  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  in  $CH_{2}Cl_{2}$  resulted in  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$ . Successfully we crystallized its PPh<sub>4</sub><sup>+</sup> salt and then determined the structure using single-crystal X-ray diffraction.<sup>5</sup>  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  prepared in this manner is still trigonal bipyramidal, and in its structure two CO ligands remain in the equatorial plane. The bond angle between two CO ligands is 126.25(8)°. Two apical and one equatorial CN ligands form a T shape. An ORTEP drawing of  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  is depicted in Fig. 1, and selected bond distances and angles are also listed in Table 1 for comparison with  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$ .

In CH<sub>2</sub>Cl<sub>2</sub> solution  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  has  $C_{2v}$  symmetry. All of its CO and CN vibration modes are IR active. The IR peaks observed in CH<sub>2</sub>Cl<sub>2</sub> solution at 1917(vs) and 1980(s) cm<sup>-1</sup> were assigned to the C–O stretches, and peaks at 2074(w), 2088(w) and 2114(w) were assigned to the C–N stretches. The IR frequencies of both  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  and  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  are also listed in Table 1. IR spectra of both compounds in CH<sub>2</sub>Cl<sub>2</sub> solution are shown in Fig. S2 in the ESI.<sup>†</sup> There are significant shifts in CO stretching frequencies in aqueous solution observed at 1960 and 2004 cm<sup>-1</sup>. These shifts caused by the solvent effect have also been observed in many other mixed CN–CO complexes and have been explained by theoretical calculations.<sup>4,14</sup>

 $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  is also oxygen-sensitive. A cyclic voltammetry experiment conducted in  $CH_{2}Cl_{2}$  solution indicates that the irreversible oxidation of  $Co^{II}/Co^{I}$  occurs at +49 mV vs. Ag/AgCl. The negative shift of 157 mV due to the substitution of one CO by one CN is far less than the -550 mV shift observed in  $[[Fe^{0}(CN)(CO)_{4}]^{-}/Fe^{0}(CN)_{2}(CO)_{3}]^{2-}$ ,<sup>4b</sup> suggesting that  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  is just marginally more electron-rich than  $[Co^{I}(CN)_{2}(CO)_{3}]^{1-}$ .

Both  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  and  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  are diamagnetic as observed in NMR experiments. Not too surprisingly, spinpolarized DFT calculations of  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  also arrive at full spin pairing and yield a diamagnetic ground state. No paramagnetic NMR shift is observed in either complex. The <sup>13</sup>C chemical shifts of CN and CO for both complexes are shown in Table 1.

While  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  has been discovered for the first time ever,  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  was previously reported by the carbonylation of  $[Co^{II}(CN)_{5}]^{3-}$  in aqueous solution.<sup>13</sup> Halpern and

Pribanić<sup>13a</sup> suggested that the formation of  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  was from the disproportionation of Co<sup>II</sup>. In fact, the disproportionation of Co<sup>II</sup> to Co<sup>III</sup> and Co<sup>I</sup> is not rare, as some Co<sup>I</sup> vitamin B<sub>12</sub> model compounds were prepared by such disproportionation.<sup>15</sup> Based on the observation of close to 50% yield of both Co<sup>III</sup> hexacyanide and Co<sup>I</sup> dicyanide tricarbonyl in our preparation and the disproportionation of Co<sup>II</sup> pentacyanide under CO, we assume that the formation of  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  is from the disproportionation of Co<sup>II</sup> under one atmosphere CO through the reaction shown in eqn (2):

$$2\text{Co}^{2+} + 8\text{CN}^{-} + 3\text{CO} \rightarrow [\text{Co}^{\text{III}}(\text{CN})_6]^{3-} + [\text{Co}^{\text{I}}(\text{CN})_2(\text{CO})_3]^{-}$$
(2)

In summary,  $[Co^{I}(CN)_{2}(CO)_{3}]^{-}$  and  $[Co^{I}(CN)_{3}(CO)_{2}]^{2-}$  not only represent the first examples of cobalt cyanide carbonyl complexes characterized using single crystal X-ray diffraction, their formation also suggests a comprehensive reaction mechanism for the preparation of  $[Co(CO)_{4}]^{-}$ . These two anions may be the reaction intermediates and might further react with OH<sup>-</sup> to form  $[Co(CO)_{4}]^{-}$ . More work is in progress in order to prove this hypothesis.

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#### Notes and references

<sup>‡</sup> Preparation of PPh<sub>4</sub>[Co<sup>I</sup>(CN)<sub>2</sub>(CO)<sub>3</sub>]: to a pink solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (238 mg, 1.00 mmol) in 20 mL H<sub>2</sub>O under 1 atm CO, a solution of NaCN (196 mg, 4.00 mmol) in 10 mL H<sub>2</sub>O was added dropwise resulting in a light green cloudy mixture. The mixture was stirred under CO for 24 hours to give a clear light yellow solution. A solution of PPh<sub>4</sub>Cl (188 mg, 0.50 mmol) in 30 mL CH<sub>2</sub>Cl<sub>2</sub> was added to the light yellow aqueous solution and stirred under 1 atm CO for another hour. The CH<sub>2</sub>Cl<sub>2</sub> layer was collected under 1 atm CO, and CH<sub>2</sub>Cl<sub>2</sub> was removed by a constant flow of CO gas to afford 251 mg (47% yield) PPh<sub>4</sub>[Co<sup>I</sup>(CN)<sub>2</sub>(CO)<sub>3</sub>] as an off-white solid. Absorption (λ (nm), ε (Lmol<sup>-1</sup>cm<sup>-1</sup>)): (262 nm, 7700; 269 nm, 7500; 276 nm, 6800). <sup>13</sup>C NMR: δ<sub>CO</sub> 195.0 ppm,  $\delta_{\rm CN}$  126.0 ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\rm CO}$  2004 cm<sup>-1</sup>,  $\nu_{\rm CN}$  2112 cm<sup>-1</sup>. Elementary analysis data are inconclusive since this compound is air and light sensitive and only stable under 1 atm CO gas even in the solid state. The 49% yield of Na<sub>3</sub>Co(CN)<sub>6</sub> was measured by a quantitative UV-visible absorption experiment.

Preparation of  $(PPh_4)_2[Co^1(CN)_3(CO)_2]$ : all operations were performed under the protection of a flow of nitrogen gas. To a light yellow solution of  $PPh_4[Co^1(CN)_2(CO)_3]$  (99 mg, 0.19 mmol) in 5 mL  $CH_2Cl_2$ , a solution of  $PPh_4CN^{16}$  (68 mg, 0.19 mmol) in 2 mL  $CH_2Cl_2$  was added and the resulting solution was stirred for 2 hours. 20 mL hexane was added to the reaction mixture and a light green crystalline material was precipitated. The light green crystalline material was filtered and rinsed three times using 3 mL hexane and dried *in vacuo* to afford 122 mg (76% yield)  $(PPh_4)_2[Co^1(CN)_3(CO)_2] \cdot H_2O$  as a light green powder.

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