

# Reactivity of Cyanide and Thiocyanate Towards the Nitrosyl Carbonyl $[\text{Co}(\text{CO})_3(\text{NO})]$

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*Dedicated to Professor Georg Süss-Fink on the Occasion of his 70th Birthday*

**Abstract.** The reaction of equimolar amounts of  $[\text{Co}(\text{CO})_3(\text{NO})]$  and  $[\text{PPN}]\text{CN}$ ,  $\text{PPN}^+ = (\text{PPh}_3)_2\text{N}^+$ , in THF at room temperature resulted in ligand substitution of a carbonyl towards the cyanido ligand presumably affording the complex salt  $\text{PPN}[\text{Co}(\text{CO})_2(\text{NO})(\text{CN})]$  as a reactive intermediate species which could not be isolated. Applying the synthetic protocol using the nitrosyl carbonyl in excess, the title reaction afforded unexpectedly the novel complex salt  $\text{PPN}[\text{Co}_2(\mu\text{-CN})(\text{CO})_4(\text{NO})_2]$  (**1**) in high yield. Because of many disor-

der phenomena in crystals of **1** the corresponding  $\text{NBu}_4^+$  salt of **1** has been prepared and the molecular structure of the dinuclear metal core in  $\text{NBu}_4[\text{Co}_2(\mu\text{-CN})(\text{CO})_4(\text{NO})_2]$  (**2**) was determined by X-ray crystal diffraction in a more satisfactory manner. In contrast to the former result, the reaction of  $[\text{PPN}]\text{SCN}$  with  $[\text{Co}(\text{CO})_3(\text{NO})]$  yielded the mononuclear complex salt  $\text{PPN}[\text{Co}(\text{CO})_2(\text{NO})(\text{SCN-}\kappa\text{N})]$  (**3**) in good yield whose molecular structure in the solid was even determined and its composition additionally confirmed by spectroscopic means.

## Introduction

There is an actual interest in nitrosyl complexes because they play a very important role in biochemical and photochemical processes and thus many investigations in this field are in the focus of current chemical research.<sup>[1]</sup> In the literature it is well established that the nitrite salt of the bis(triphenylphosphane)iminium(1+) cation,  $(\text{PPh}_3)_2\text{N}^+$ , is suitable for introducing the NO ligand into metal carbonyl complexes on the one hand as well as the nitrito ligand on the other hand.<sup>[2]</sup> The formation of the corresponding reaction product is frequently driven by the 18-electron rule. Thus the synthesis of  $\text{PPN}[\text{Co}(\text{CO})_2(\text{NO})(\text{NO}_2\text{-}\kappa\text{N})]$  by the reaction of  $[\text{Co}(\text{CO})_3(\text{NO})]$  with  $[\text{PPN}]\text{NO}_2$  in THF was described.<sup>[2]</sup> This reaction result followed the principle that in nitrosyl carbonyls, especially also in the case of the cobalt complex, the carbonyl ligands were successively substituted at first by the incoming nucleophilic ligands whereas the NO group remained on the metal atom.<sup>[3]</sup>

In this light we were interested in the reaction of cyanide with  $[\text{Co}(\text{CO})_3(\text{NO})]$  and we applied the known synthetic procedure of  $\text{PPN}[\text{Co}(\text{CO})_2(\text{NO})(\text{NO}_2\text{-}\kappa\text{N})]$  to investigate the reaction between  $[\text{PPN}]\text{CN}$ <sup>[4]</sup> and  $[\text{Co}(\text{CO})_3(\text{NO})]$

with the aim of obtaining the hypothetical compound  $\text{PPN}[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]$ . The potassium salt of the latter anionic complex was reported firstly in 1956 by *Nast* and *Rohmer* prepared by the reaction of  $[\text{Co}(\text{CO})_3(\text{NO})]$  with KCN in methanol at room temperature over a period of 18 h.<sup>[5]</sup> In 1966 a synthetic protocol of the same compound  $\text{K}[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]$  was described by *Behrens* and co-workers; however, the salt was prepared under very harsh conditions whereby  $[\text{Co}(\text{CO})_3(\text{NO})]$  reacted with equimolar amounts of sodium cyanide in liquid ammonia at 60 °C under pressure.<sup>[6]</sup> By other authors the use of  $\text{K}[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]$  in nitrosation reactions of benzyl halides was reported,<sup>[7]</sup> whereas the preparation of the potassium salt was undertaken using the preparation method described by *Nast* and *Rohmer*.<sup>[5]</sup> In 1973 *Job* and *Curtis* used the latter method of the preparation of the potassium salt to synthesize heterobimetallic complexes for the purpose to study the photochemistry of germanium compounds derived from reactions with transition metal carbonyl species.<sup>[8]</sup> *Nast* and *Rohmer*<sup>[5]</sup> reported, however, that the  $\text{K}[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]$  was an unstable species and could not be obtained in an analytical pure form indicated by the elemental analysis data. Unfortunately, IR spectroscopic data were also not reported by these authors at that time. In this light, and in the light of the harsh conditions reported by *Behrens* and co-workers,<sup>[6]</sup> we searched for a preparation method of  $[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]^-$  under milder and convenient conditions. Thus we examined the described synthetic protocol in analogy as used for  $\text{PPN}[\text{Co}(\text{CO})_2(\text{NO})(\text{NO}_2\text{-}\kappa\text{N})]$ .<sup>[2]</sup> In that originally reported method,  $[\text{Co}(\text{CO})_3(\text{NO})]$  was used in a large excess. During these adapted investigations we obtained, very unexpectedly, the formation of the novel dinuclear complex  $[\text{Co}_2(\mu\text{-CN})(\text{CO})_4(\text{NO})_2]^-$  formed by a condensation reaction. Furthermore, we investigated the reaction behavior of  $[\text{Co}(\text{CO})_3(\text{NO})]$  towards the ambidentate ligand thiocyanate. The latter followed the reaction pathway as described for the

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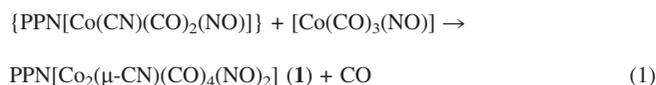
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/zaac.202000182> or from the author.

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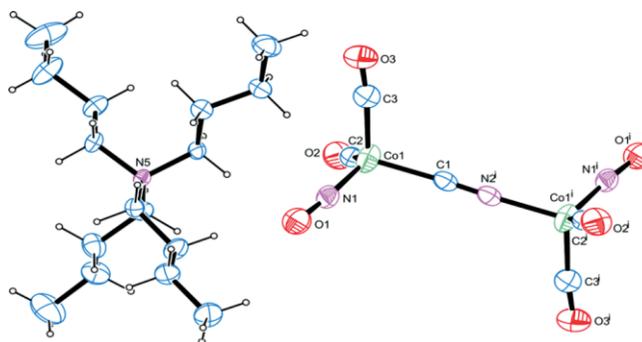
nitrito ligand resulting in the synthesis of mononuclear  $[\text{Co}(\text{CO})_2(\text{NO})(\text{SCN-}\kappa\text{M})]^-$ . On these findings we report in this paper.

## Results and Discussion

As described for the synthesis of the salt  $\text{PPN}[\text{Co}(\text{CO})_2(\text{NO})(\text{NO}_2)]$ ,<sup>[2]</sup> we adopted that procedure to prepare the new hypothetical compound  $\text{PPN}[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]$ . Thus, we reacted  $[\text{PPN}]\text{CN}$  with an excess of  $[\text{Co}(\text{CO})_3(\text{NO})]$  in THF at room temperature for 1 h. The progress of the reaction was accompanied by an immediate gas evolution, and the solution turned quickly from brown to dark red. During that time a clear solution resulted, whereas the  $[\text{PPN}]\text{CN}$  was completely dissolved. The solvent and the excess of  $[\text{Co}(\text{CO})_3(\text{NO})]$  were removed in vacuo, and the crude product was crystallized from dichloromethane/diethyl ether affording dark red crystals. The compound was characterized by IR spectroscopy to compare the data with the related salt  $\text{K}[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]$ , whereas for the latter the following bands were reported: 2097m (CN); 2030s, 1963vs. (CO); 1728s (NO) ( $\text{cm}^{-1}$ ) (KBr).<sup>[6]</sup> [In diglyme solutions for the potassium salt the bands 2019, 1952 (CO) and 1726 (NO) were reported.<sup>[7]</sup>] In contrast to the report,<sup>[6]</sup> for our compound we obtained a significantly different band pattern: 2122m (CN); 2020sh, 2016s, 1941vs., 1938sh (CO); 1704vs., 1700s (NO) ( $\text{cm}^{-1}$ ) (ATR). In light of our observed vibration band for the cyanide ligand at  $2122\text{ cm}^{-1}$ , a value at  $2121\text{ cm}^{-1}$  for the stretching frequency for the bridging cyanide in the fully characterized compound  $\text{PPN}[\text{W}_2(\mu\text{-CN})(\text{CO})_{10}]$  was reported.<sup>[9]</sup> These uncertainties prompted us to investigate the molecular structure of the new compound in the crystal. Single crystals for X-ray diffraction of the new species were grown from dichloromethane/diethyl ether at room temperature overnight. The result of the X-ray diffraction study was unexpected, because we found the structure of the novel dinuclear compound  $\text{PPN}[\text{Co}_2(\mu\text{-CN})(\text{CO})_4(\text{NO})_2]$  (**1**). Obviously, since we worked with an excess of the nitrosyl carbonyl, a condensation of the hypothetical intermediate  $[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]^-$  with the excess  $[\text{Co}(\text{CO})_3(\text{NO})]$  occurred, resulting in the dinuclear complex, according to Equation (1):



Because of the different reaction behavior of  $\text{PPN}[\text{NO}_2]$  with  $[\text{Co}(\text{CO})_3(\text{NO})]$  (in excess) we had to assume that the cyanido ligand is more suitable to function as a bridging ligand in polynuclear complexes, whereas that seems to be lesser the case for the nitrito ligand. Unfortunately, our preliminary result of the X-ray crystal-structure determination of **1** was very unsatisfactory and frustrated because of many disorder phenomena even in the region of the PPN cation. For this reason we changed to another cation and examined the reaction of  $[\text{NnBu}_4]\text{CN}$  with  $[\text{Co}(\text{CO})_3(\text{NO})]$ . During these investigations we observed the same reaction behavior as found for  $[\text{PPN}]\text{CN}$  resulting in the corresponding dinuclear complex salt as dark



**Figure 1.** Selected view of the molecular structure of compound **2** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Only one of the two symmetrically independent cobaltate anions is depicted. C1 and N2 share the same sites with site occupation factors of 0.5. Symmetry code  $i = -x, 1 - y, -z$ . Selected bond lengths /Å and angles /°: Co1–C1, 1.965(3); Co1–C2, 1.794(3); Co1–N1, 1.694(3); Co1–C3, 1.782(3); N1–O1, 1.155(4); C2–O2, 1.132(4); C3–O3, 1.131(4). Co1–N1–O1, 175.0(3); C2–Co1–N1, 114.38(14); C1–Co1–C2, 101.9 (13); C1–Co1–C3, 108.62(13); C2–Co1–C3, 105.10(14); N1–Co1–C3, 114.32(14); N1–Co1–C1, 111.50(12).

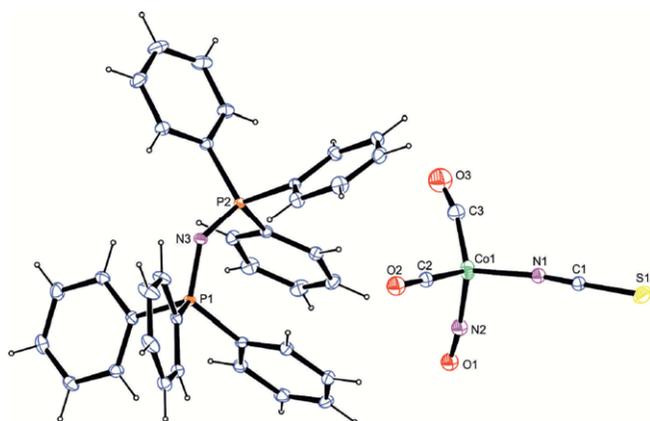
red crystals in comparable yields. Also, in that case, we obtained crystals from dichloromethane/diethyl ether suitable for an X-ray diffraction study. The compound **2** crystallized as red-brown crystals in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell. A selected view of the compound is depicted in Figure 1.

Besides the perfect disorder of the bridging cyanide which is forced by inversion symmetry, the NO and CO ligands are disordered as well (further details are given in the Experimental Section).

To bring more insight into the correct determination of the molecular structure, a mass spectrum (ESI<sup>-</sup>) of **2** showed the molecular ion peak at  $m/z = 315$  ( $\text{M}^-$ ) corresponding to the composition of the proposed dinuclear anion. A proper elemental analysis was even obtained (see Exp. Sect.). Furthermore, the appearance of a doubling of the characteristic CO and NO stretching frequencies in the IR spectra of **1** and **2** supplied a hint that two slightly different  $\text{Co}(\text{CO})_2(\text{NO})$  fragments should be present in the molecules caused by the bridging cyanido ligand. Considering the formation of the dinuclear species **1** and **2** in the title reaction, it should be absolutely noted that the use of equimolar amounts of reactants also resulted in the formation of the dinuclear species however in lower yields related to the  $[\text{Co}(\text{CO})_3(\text{NO})]$ . Therefore, at the moment, we have no indication for the formation of the intermediate species  $\{[\text{Co}(\text{CN})(\text{CO})_2(\text{NO})]^-$  during our examined reaction conditions. A similar spontaneous condensation behavior of related species was reported by other authors during the nitrosation attempt of  $[\text{W}(\text{CN})(\text{CO})_5]^-$  with  $\text{NO}^+$  whereby the trinuclear complex  $[\text{W}_3(\mu\text{-CN})_3(\text{CO})_9(\text{NO})_3]$  was formed.<sup>[10]</sup> Also, in this case, at no stage of the structure analysis and refinement for the latter was it possible to distinguish between nitrosyl and carbonyl ligands in the individual  $\text{W}(\text{CO})_3(\text{NO})$  fragments.

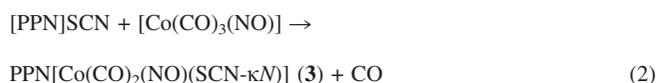
Considering the aspect that thiocyanate as an ambidentate ligand can also open the opportunity to function as the bridging

ligand in multinuclear complexes, we even investigated the reaction of [PPN]SCN with [Co(CO)<sub>3</sub>(NO)]. Thus, as described for the synthesis of PPN[Co(CO)<sub>2</sub>(NO)(NO<sub>2</sub>-κN)],<sup>[12]</sup> we adopted the procedure for preparing the new hypothetical compound PPN[Co(CO)<sub>2</sub>(NO)(SCN-κN)]. First, we reacted [PPN]SCN with an excess of [Co(CO)<sub>3</sub>(NO)] in THF at room temperature for 30 min. The progress of the reaction was visible by an immediate gas evolution and the solution turned from yellowish brown to dark red. During 20 min the [PPN]SCN was completely dissolved and the work-up procedure was analogously performed to the synthetic protocols for the synthesis of compounds **1** and **2**. A new compound (**3**) was obtained as a dark red solid after removing the solvent and crystallization from dichloromethane/diethyl ether. Compound **3** was characterized by microanalysis and IR spectroscopy (see Experimental Section). It should be noted that compound **3** is very air-sensitive in solution resulting in a fast decomposition. Single crystals suitable for an X-ray diffraction study were obtained from dichloromethane/diethyl ether at room temperature. Compound **3** crystallized as dark red crystals in the monoclinic space group *P*2<sub>1</sub>/*n* with four molecules in the unit cell. In the crystal the anion is fully disordered over two sites (further details are given in the Experimental Section). A selected view of the compound is depicted in Figure 2, selected bond lengths and angles are given in the caption.



**Figure 2.** Selected view of the molecular structure of compound **3** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Only one of the two disordered anion moieties was used to create the picture. Selected bond lengths /Å and angles /°: Co1–C2, 1.800(5); Co1–C3, 1.733(8); Co1–N1, 1.960(5); Co1–N2, 1.777(6); N2–O1, 1.136(6); C2–O2, 1.143(6); C3–O3, 1.078(10); N1–C1, 1.118(8); C1–S1, 1.733(10). Co1–C2–O2, 174.2(4); Co1–C3–O3, 167.0(6); Co1–N2–O1, 172.9(5); Co1–N1–C1, 173.4(5); N1–C1–S1, 177.7(7).

The result of the structure determination showed the formation of a mononuclear complex species as found in the case of nitrite. Thus the reaction pathway followed according to Equation (2). Obviously, the thiocyanate was not able to function as the bridging ligand resulting in a dinuclear framework as observed in the case of cyanide:



Closely related compounds bearing pseudohalide ligands, e.g. PPN[Fe(NO)<sub>2</sub>(XCN)<sub>2</sub>] (X = O, S) were reported by *Darensbourg* and co-workers.<sup>[11]</sup> The latter were prepared by the reaction of [Fe(CO)<sub>2</sub>(NO)<sub>2</sub>] with cyanate and thiocyanate, respectively, in THF at room temperature and their molecular structures in the crystal were confirmed by X-ray diffraction. The bonding parameters concerning the Co–NCS unit of **3** are comparable to the ones found for PPN[Fe(NO)<sub>2</sub>(SCN-κN)<sub>2</sub>]. Thus for the latter the distances Fe–NO(av.) were found as to be 1.701(2) Å, and Fe–NCS(av.) = 1.970(2) Å, N–O(av.) = 1.169(2) Å as well as the angles Fe–N–O(av.) = 161.9(2)°, Fe–N–C(av.) = 177.2(2)° and N–C–S(av.) = 178.9(2)°.<sup>[11]</sup> Beside the characteristic CO and NO vibration bands in the IR spectrum of **3**, which are comparable to the corresponding pattern of **1** and **2**, a strong band at 2097 cm<sup>-1</sup> was found. This vibration we assigned to the C≡N moiety of the thiocyanato ligand which is in good agreement with the reported data of PPN[Fe(NO)<sub>2</sub>(SCN-κN)<sub>2</sub>] (2076sh, 2056vs, THF).<sup>[11]</sup> In light of the simple hard/soft interaction of the ambidentate ligand SCN<sup>-</sup>, we first expected a coordination of that ligand by the sulfur to the low-valent cobalt in our case. However, our crystal-structure result of **3** afforded the bonding mode SCN-κN. In fact, searching in the CCDC data base indicated the latter linkage isomer as the most predominant form in many deposited structures, even in many cases of soft, zerovalent metal carbonyls.<sup>[11]</sup>

## Conclusions

In summary, we have investigated the reaction behavior of [Co(CO)<sub>3</sub>(NO)] towards the ligands cyanide and thiocyanate. For the thiocyanate, a simple substitution of one carbonyl group towards the incoming ligand was observed, resulting in species [Co(CO)<sub>2</sub>(NO)X]<sup>-</sup> (X = NO<sub>2</sub> and SCN<sup>-</sup>), whereas the reaction with the nitrite had been already reported in the literature.<sup>[2]</sup> In the case of cyanide, the analogous species with X = CN seemed to be only an intermediate immediately reacting with a second molecule of [Co(CO)<sub>3</sub>(NO)] in a condensation reaction affording the novel complex [Co<sub>2</sub>(μ-CN)(CO)<sub>4</sub>(NO)<sub>2</sub>]<sup>-</sup>. The molecular structure of the latter in its corresponding tetra-*n*-butylammonium salt (**2**) and of PPN[Co(CO)<sub>2</sub>(NO)(SCN-κN)] (**3**), respectively, were established by X-ray single-crystal diffraction and their composition further confirmed by spectroscopic methods.

## Experimental Section

**General:** All reactions were carried out in an atmosphere of dry nitrogen using standard Schlenk techniques. THF and diethyl ether were dried with sodium-benzophenone ketyl and freshly distilled prior to use. Reagents were purchased commercially from ABCR and used without further purification. [PPN]CN and [PPN]SCN were prepared following the known literature procedures.<sup>[4]</sup> IR spectra were recorded from solids with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. Mass spectra were recorded using a MAT 95 spectrometer. Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

**PPN[Co<sub>2</sub>(μ-CN)(CO)<sub>4</sub>(NO)<sub>2</sub>] (1):** To a stirred solution of [Co(CO)<sub>3</sub>(NO)] (0.40 mL, 3.40 mmol) in THF (15 mL) [PPN]CN (226 mg, 0.40 mmol) was added at room temperature. The solution turned quickly to red-brown whereas a strong gas evolution was observed. After stirring for 1 h the solvent was evaporated in vacuo. **CAUTION:** During this procedure the excess of the volatile and toxic [Co(CO)<sub>3</sub>(NO)] was distilled in the condensation trap! The remaining residue was crystallized from dichloromethane/diethyl ether affording **1** as dark red crystal plates. Yield: 237 mg (70% related to [PPN]CN). C<sub>41</sub>H<sub>30</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>6</sub>P<sub>2</sub> (854.53): calcd. C, 57.63; H, 3.54; N, 6.56%; found: C, 57.98; H, 3.23; N, 6.83%. **IR** (solid, ATR):  $\tilde{\nu}$  = 2125m (μ-CN); 2020sh, 2018vs, 1946vs, 1940sh (CO); 1723vs, 1720sh (NO) cm<sup>-1</sup>. **MS** (ESI<sup>-</sup>): 316 (anion, C<sub>5</sub>Co<sub>2</sub>N<sub>3</sub>O<sub>6</sub>).

**NnBu<sub>4</sub>[Co<sub>2</sub>(μ-CN)(CO)<sub>4</sub>(NO)<sub>2</sub>] (2):** To a stirred solution of [Co(CO)<sub>3</sub>(NO)] (0.40 mL, 3.40 mmol) in THF (15 mL) [NnBu<sub>4</sub>]CN (107 mg, 0.40 mmol) was added at room temperature. The solution turned quickly to red-brown whereas a strong gas evolution was observed. After stirring for 1 h the solvent was evaporated in vacuo. **CAUTION:** During this procedure the excess of the volatile and toxic [Co(CO)<sub>3</sub>(NO)] was distilled in the condensation trap! The remaining residue was crystallized from dichloromethane/diethyl ether affording **2** as dark red rhombus-like crystal plates. Yield: 190 mg (85% related to [NnBu<sub>4</sub>]CN). C<sub>21</sub>H<sub>36</sub>Co<sub>2</sub>N<sub>4</sub>O<sub>6</sub> (558.41): calcd. C, 45.17; H, 6.50; N, 10.03%; found: C, 45.21; H, 6.13; N, 9.83%. **IR** (solid, ATR):  $\tilde{\nu}$  = 2122m (μ-CN); 2020sh, 2016s, 1941vs, 1938sh (CO); 1704vs, 1700sh (NO) cm<sup>-1</sup>. **MS** (ESI<sup>-</sup>): 316 (anion, C<sub>5</sub>Co<sub>2</sub>N<sub>3</sub>O<sub>6</sub>).

**PPN[Co(CO)<sub>2</sub>(NO)(SCN-κN)] (3):** To a solution of [Co(CO)<sub>3</sub>(NO)] (0.40 mL, 3.40 mmol) in THF (20 mL) [PPN]SCN (238 mg, 0.40 mmol) was added and the mixture stirred at room temperature. During an initial time of 20 min (some gas evolution) a red-brown solution resulted. After further stirring for 10 min the solvent was evaporated in vacuo. **CAUTION:** During this procedure the excess of the volatile and toxic [Co(CO)<sub>3</sub>(NO)] was distilled in the condensation trap! The remaining residue was crystallized from dichloromethane/diethyl ether affording **3** as red-brown needles. The solid was filtered off, washed with cold diethyl ether (5 mL), and dried in vacuo. Yield: 211 mg (71%, related to thiocyanate). C<sub>39</sub>H<sub>30</sub>CoN<sub>3</sub>O<sub>3</sub>P<sub>2</sub>S (741.63): calcd. C, 63.16; H, 4.08; N, 5.67%; found: C, 62.74; H, 4.29; N, 5.69%. **IR** (solid, ATR):  $\tilde{\nu}$  = 2097s (SCN); 2018s, 1941vs. (CO); 1717vs. (NO) cm<sup>-1</sup>.

**Crystal Structure Determination and Refinement:** Crystals suitable for X-ray crystallography of **2** and **3**, respectively, were obtained as described above. Crystals were selected by means of a polarization microscope, mounted on a MiTeGen MicroLoop, and investigated with a Bruker D8 Venture TXS diffractometer using Mo-K<sub>α</sub> radiation ( $\lambda$  = 0.71073 Å). The structures were solved by direct methods and refined employing SHELXT.<sup>[12]</sup> Anisotropic displacement parameters were refined for all non-hydrogen atoms with the exception of the C, N and O atoms of the anion in **3**, which had to be refined isotropically. All hydrogen atoms were calculated in ideal geometry riding on their parent atoms. Split model refinements revealed that the C and N coordination sites of the CO and NO ligands are occupied by N and C. According to the refinement of the site occupation factors, the anion in Figure 1 is the most abundant one (67%). Less abundant are the moieties with N located at the site of C2 (3%) and C3 (30%). For the other symmetrically independent cobaltate, the split model refinement led to corresponding values of 46%, 34% and 20%. This kind of disorders, as well as that of the bridging cyanide, was also present in the various attempts to refine the structure of **2** in lower-symmetry space groups. In **3**, there are two kinds of disorder in the cobaltate anion: Firstly, the whole anion is slightly disordered (see the SI for a Figure visualizing

the disorder). The refinement of the ratio of site occupation factors of the two moieties led to 0.506/0.494. The SIMU restraint had to be applied in order to improve the (an)isotropic displacement parameters of atoms located within a distance of 0.7 Å or closer that. The second type of disorder in this anion is formed by CO and NO. Each C- or N-site of CO/NO has been occupied with 1/3 N and 2/3 C which represents a perfect disorder over all three CO and NO sites within one anion. Finally, the solvent had to be squeezed out. There are two voids with a volume of 172 Å<sup>3</sup> each bearing 27 electrons according to PLATONS SQUEEZE routine.<sup>[13]</sup> This corresponds to about 0.6 diethyl ether in each of the voids. ORTEP has been used to create Figure 1 and Figure 2.<sup>[14]</sup> Details of the crystal data, data collection and structure refinement parameters of compounds **2** and **3** are summarized in Table 1.

**Table 1.** Details of the X-ray crystal data collection and structure refinement for compounds **2** and **3**.

	<b>2</b>	<b>3</b>
Empirical formula	C <sub>21</sub> H <sub>36</sub> Co <sub>2</sub> N <sub>4</sub> O <sub>6</sub>	C <sub>39</sub> H <sub>30</sub> CoN <sub>3</sub> O <sub>3</sub> P <sub>2</sub> S
<i>M<sub>r</sub></i>	558.40	741.59
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / Å	15.4326(11)	9.8319(3)
<i>b</i> / Å	11.6987(8)	17.3319(4)
<i>c</i> / Å	15.7650(12)	22.1862(12)
$\beta$ / °	102.228(3)	95.4680(10)
<i>V</i> / Å <sup>3</sup>	2781.7(3)	3763.45(18)
<i>Z</i>	4	4
<i>T</i> / K	102(2)	102(2)
$\rho_{\text{calcd.}}$ / g·cm <sup>-3</sup>	1.333	1.309
$\mu$ [mm <sup>-1</sup> ]	1.231	0.636
$\theta$ range for data collection (°)	2.701 to 30.508	3.006 to 27.103
Reflections collected	52018	66722
Independent reflections	8482	8293
<i>R</i> <sub>int</sub>	0.0768	0.0554
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0642	0.0404
<i>wR</i> <sub>2</sub> (all data)	0.1550	0.1084
Parameters	308	453
Goodness of fit on <i>F</i> <sup>2</sup>	1.058	1.064
Largest diff. peak/hole / e <sup>-</sup> ·Å <sup>-3</sup>	1.161 / -1.498	0.593 / -0.448

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1993133 (**2**) and CCDC-1993134 (**3**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

**Supporting Information** (see footnote on the first page of this article): Crystallographic data of compounds **2** and **3** (packing of **2** and **3** in the crystal as well as the illustration of the disorder in the anion of **3**).

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