Synthesis and Structural Characterization of the Nitrido—Carbonyl Cluster Anion

\([\text{Co}_{10}N_2(\text{CO})_{19}]\) Having an Unprecedented Metal Cage Built of Three Condensed Trigonal Prisms

Alessandro Fumagalli,*,† Secondo Martinengo,‡ Massimo Tasselli,§ Gianfranco Ciani,§ Piero Macchi,§ and Angelo Sironi*‡

CNR—Centro di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Dipartimento di Chimica Inorganica Metallorganica e Analitica, and Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy

Introduction

Intersitial main group atoms (C, N, P, etc.) play an essential role in the buildup of high-nucleity metal carbonyl clusters because, unlike conventional ligands, they can contribute to the number of cluster valence electrons with no sterical requirements on the cluster surface.\(^1\) In this respect, nitrido species are particularly interesting, since nitrogen atoms may donate up to five electrons, and also show a distinctive aptitude toward unusual stereochimies and coordination numbers within the interstitial cavity; this results in singular cluster shapes. Several examples of nitrido and polynitrido clusters have been reported, most of rhodium, from the precursor of them all, \([\text{Rh}_{28}N_4(\text{CO})_{41}H]\).\(^4\) Not so many are interstitial nitrido species of cobalt; to date only four compounds, \([\text{Co}_4N(\text{CO})_{15}]^{-4}\) \([\text{Co}_2N(\text{CO})_{15}]^{-5}\) \([\text{Co}_2N(\text{CO})_{15}]^{2-}\) and \([\text{Co}_2N(\text{CO})_2]^{-1}\) have been reported.\(^5\) To uncover similarities and peculiarities of cobalt chemistry compared to rhodium chemistry, we reinvestigated the reactivity of \([\text{Co}_2N(\text{CO})_{15}]^{-}\) which afforded the presently reported dinitrido cluster \([\text{Co}_2N_2(\text{CO})_{19}]^{-4}\)\(^4\)

<table>
<thead>
<tr>
<th>Notes</th>
</tr>
</thead>
</table>

**Table 1.** Crystallographic Data for \([\text{Co}_{10}N_2(\text{CO})_{19}]\) fw 3586.99

| chemical formula \([\text{Co}_{10}N_2(\text{CO})_{19}][\text{NMe}_3\text{CH}_2\text{Ph}]_{4}\) |
| 3586.99 |
| a | 14.095(1) Å | μ | 2.340 mm\(^-1\) |
| b | 40.112(1) Å | ρ\(_{\text{calc}}\) | 1.675 g/cm\(^3\) |
| c | 14.297(1) Å | T | 170 K |
| β | 118.38(1)° | λ | 0.7107 Å |
| V | 7111.4(2) Å\(^3\) | R\(_1\) (F\(_0\)) | 0.0321 |
| Z | 2 | R\(_2\) (F\(_2\)) | 0.0532 |
| space group | P\(_2_1\) (No. 4) | wR (F\(_2\)) | 0.0532 |

\(\sum(F_0 - F_2) / \sum(F_0)\)\(^2\) Weighting: w = \(1/(σ(F_2)^2 + (0.0188P)^2)\), where P = (F\(_2\) + 2F\(_1\))/3.

**Experimental Section**

**General Procedures and Materials.** All operations were carried out under N\(_2\) or CO as specified, with standard Schlenk-tube apparatus. Tetrahydrofuran (THF) was distilled from Na-benzophenone and 2-propanol from Al isopropoxide. All other analytical grade solvents were degassed and stored under N\(_2\). K[Co\(_6N(\text{CO})_{15}\)] was prepared by the published method.\(^3\) Infrared spectra were recorded in solution with CaF\(_2\) cells (0.1 mm; 0.075 mm for water solutions) previously purged with nitrogen, on a Perkin-Elmer 16 PC FT-IR spectrophotometer. \(^1\)C NMR spectra were recorded at 50.3 MHz on a Varian instrument. Synthesis of \([\text{NMe}_3\text{CH}_2\text{Ph}]_4[\text{Co}_2N(\text{CO})_{19}].\) K[Co\(_2N(\text{CO})_{15}\)] (0.378 g, 0.457 mmol) was treated with an aqueous solution of NaOH (1.3 M, 15 mL) and the resulting suspension was stirred at room temperature for ca. 30 min, up to formation of a brown solution. After filtration of some insoluble material, the clear solution was treated dropwise, while stirring, with an aqueous solution of \([\text{NMe}_3\text{CH}_2\text{Ph}]\text{Cl}\) (0.5 g in 5 mL); this caused immediate formation of a brown precipitate, which after a few minutes of stirring, was filtered, thoroughly washed with water (4 × 5 mL), and vacuum-dried. The crude product contained some \([\text{Co}(\text{CO})_5]^{-}\) which was mostly extracted with a few THF washings; the residue was dissolved in acetone (6 mL) and after addition of some MeCN, was cautiously layered with 2-propanol (25 mL). When the diffusion of the solvents was complete (about a week), the slightly brown mother liquor was syringed off and the black crystals were washed with 2-propanol and vacuum-dried. Yield: 0.212 g, 50%. The crystals suitable for the X-ray analysis contained one MeCN and one acetone molecule for every 2 mol of product. Anal. Found (calcld) for \([\text{NMe}_3\text{CH}_2\text{Ph}]_4[\text{Co}_2N(\text{CO})_{19}].\) C, 44.03 (41.04); H, 4.13 (3.84); N, 5.51 (5.06). The presence of \([\text{NMe}_3\text{CH}_2\text{Ph}]\text{Cl}\) as an impurity may be checked by the strong IR band at 1893 cm\(^{-1}\) in; in that case a recrystallization is suggested.

The Cs\(^+\) salt is a useful starting material and may be obtained with comparable yields by addition of excess CsCl to the aqueous solution, filtration, washing with 25% MeCN, and vacuum-drying. It can be converted by metathesis in several derivatives of different cations such as the \([\text{NMe}_4]^+\) salt. Anal. Found (calcld) for \([\text{NMe}_4][\text{Co}_{10}N_2(\text{CO})_{19}]\) C, 29.0 (29.7); H, 4.36 (3.35); N, 5.61 (5.81).

**X-ray Structure Determination.** A crystal sample of dimensions 0.12 × 0.16 × 0.30 mm was mounted on a glass fiber in air\(^8\) and collected at T = 170 K on a Siemens SMART CCD area-detector diffractometer. Crystal data are reported in Table 1. Graphite-monochromated Mo Kα (λ = 0.7107 3 Å) radiation was used with the generator working at 50 kV and 35 mA. The cell parameters and

\(^{(*)}\) Although I is air-sensitive in solution and as a powder, its crystals can be mounted in air; during the data-collection, carried out at 170 K, the sample was protected by the cooling N\(_2\) stream.
the orientation matrix were obtained from least-squares refinement on 302 reflections measured in three different sets of 15 frames each, in the range $0 < \theta < 23^\circ$. The intensity data were collected within the limits $8 < 2\theta < 50^\circ$ in the full sphere (ω scan method), with the sample–detector distance fixed at 7 cm, thus avoiding the possible overlap of spots due to the great cell volume. In all, 2100 frames (20 s per frame; $\omega_0 = 0.3^\circ$) were collected; the first 100 frames, containing 859 reflections, were recollected to have a monitoring of crystal decay, which was not observed; an absorption correction was applied (SADABS\textsuperscript{10}). A total of 46 254 reflections were collected (24 238 unique, $R_{int} = 0.0284$; $R_e = 0.0540$\textsuperscript{11}). The structure was solved by direct methods (SIR97\textsuperscript{12}) and refined with full-matrix-block least squares (SHELX93\textsuperscript{13}) on the basis of 21 254 independent reflections with $I > 2\sigma(I)$. Anisotropic temperature factors were assigned to all non-hydrogen atoms. Hydrogens were riding on their carbon atoms.

$[\text{Co}_6\text{N}_2\text{(CO)}_{15}]^+$ is, at least in the solid state, chiral. However, its $[\text{NMe}_3\text{CH}_2\text{Ph}]^+$ salt crystallizes as a racemate in the noncentric space group $P2_1$ with two independent (enantiomeric) anions in the asymmetric unit (which contains also eight cations and two different clathrated solvent molecules). We have carefully checked for the presence of some “missing” symmetry element eventually affording a centrosymmetric group, but we did not find it: the two enantiomeric molecules are not correlated by any extra crystallographic symmetry operation; moreover, the intensities statistic suggests the lack of a center of symmetry.

The final conventional agreement indexes $R_1$ and $wR_2$ for the “best” structural enantiomer were 0.0321 and 0.0532 ($F_o > 4\sigma(F_o)$) and 0.0415 and 0.0588 (all data), respectively, while the “worst” structural enantiomer gave 0.0418 and 0.0776 ($F_o > 4\sigma(F_o)$) and 0.0513 and 0.0797 for all data ($R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|; wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$).

### Results and Discussion

Treatment of $K[\text{Co}_6\text{N(CO)}_{15}]$ with aqueous NaOH (1.3 M) yields within minutes at room temperature a solution from which the anion $[\text{Co}_{10}\text{N}_2\text{(CO)}_{19}]^3-$ (1) can be isolated as the $\text{Cs}^+$, $\text{[NMMe}_4]^+$, or $\text{[NMe}_3\text{CH}_2\text{Ph}]^+$ salts. The side formation of $[\text{Co}_6\text{N(CO)}_{14}\text{H}]^2+$ (ellipsoids are drawn at 50% probability level). The two long Co–Co bond distances are represented as white sticks; all carbonyl labels but the three quoted in the text (indicated by their oxygen atom only) are omitted. Co–Co bond distances in Å (averaged over the two enantiomers: $\alpha_{n-1}$ in parentheses) are as follows: 1–2, 2.628(4); 1–3, 2.553(7); 1–4, 2.518(6); 1–7, 2.572(8); 1–9, 2.666(8); 2–3, 2.547(30); 2–5, 2.469(3); 2–8, 2.610(7); 2–10, 2.603(13); 3–6, 2.511(3); 4–5, 2.792(44); 4–6, 2.540(13); 4–9, 2.580(40); 5–6, 2.531(16); 5–10, 2.922(72); 7–8, 2.490(5); 7–9, 2.593(30); 8–10, 2.530(4); 1–3, 2.553(7); 9–10, 2.524(2). Average Co–Co_{terminal} distance: 1.754(9) Å. Average Co–Co_{bridging} distance: 1.924(24) Å. Individual ESDs are less than 0.001 Å.

1 is very air-sensitive both in solid (as a powder) and in solution (MeCN and acetone) and also very reactive toward CO, which induces a multistep reaction. A solution of 1 in MeCN was treated at room temperature with several small amounts of CO (injected with a gas-tight syringe trough a rubber septum). IR spectra, taken after each addition (allowing a few minutes of stirring for equilibration), showed that ca. 2 mol of CO per mole of 1 is required for complete reaction, yielding $[\text{Co(CO)}_{12}]^-$ and an unknown intermediate anion (IR absorptions at 1974 s, 1938 m, 1893 m, 1889 m, 1798 m, 1775 ms, 1730 w ± 2 cm$^{-1}$).

In the same conditions $[\text{Rhn}_6\text{N(CO)}_{15}]^{-}$ yields $[\text{Rhn}_6\text{N(CO)}_{14}\text{H}]^2+$, which only at considerably higher concentrations of base (> 10 M) gives what has been identified as $[\text{Rh}_6]\text{N(CO)}_{14}\text{H}]^2+$.

All the salts of 1 show the same IR spectrum in MeCN: (1987 w, 1934 s, 1890 mw, 1798 m, 1775 ms, 1730 w ± 2 cm$^{-1}$).

NMR spectra were done on both the $[\text{NMMe}_4]^+$ and $[\text{NMe}_3\text{CH}_2\text{Ph}]^+$ salts in $d_7$-MeCN at 295 and 238 K, close to the freezing point of the solution. $^1H$ spectra (200 and 300 MHz) did not show any resonance due to the presence of hydrate(s) in the range $\delta = +38$ to $-50$ ppm. Natural abundance $^{13}C$ spectra showed at room-temperature two broad peaks at 244.4 and 236.2 ppm whose relative intensities fit for 2 and 17 carboxyls, respectively; this is consistent with a fluctuational behavior that does not involve the whole molecule. When the temperature is lowered, the peak at 236.2 ppm coalesces without evidence of a static structure.

(10) Sheldrick, G. M. SADABS; University of Göttingen: Germany, to be published.

(11) $R_{int} = \Sigma|F_o^2 - F_c|/\Sigma|F_o^2|; R_e = \Sigma|w(F_o^2 - 2F_c^2)|/\Sigma wF_o^4.$


(15) S. Martinengo and A. Fumagalli, unpublished results.
however, the actual carbonyl disposition, of $C_1$ symmetry, promotes significant distortions of otherwise equivalent Co—Co interactions, thus reducing also the cage symmetry to $C_1$.

$[\text{Co}_{10}N_2(\text{CO})_{19}]^{4-}$, with 142 cluster valence electrons, conforms to the EAN rule if the two moderately long Co4—Co5 and Co5—Co10 interactions (average 2.79 and 2.92 Å, respectively) are also considered as bonds. As for the local electron count, Co1 and Co2 can be considered to be more electron rich than Co4, Co5, Co9, and Co10 which on the other hand, are more electron rich than Co3, Co6, Co7, and Co8. Carbonyls bridging “electron rich” and “electron poor” metal atoms are expected to be distorted toward the poor ones, and this holds for all but CO(13), CO(14), and CO(20) which are symmetric or have the opposite behavior. Indeed, the localization of some anionic charge on Co5 and Co10 would explain both the “anomalous” behavior of these same CO ligands and the long Co4—Co5 and Co5—Co10 distances.

Finally, we would like to comment on the overall size and distortion of the three prismatic cavities which, given the nonuniform distribution of the bridging COs, are all rather distorted. However, the cavity containing N1 is clearly more regular than that containing N2 because in the former all the interbasal edges are bridged. Moreover, the empty cavity which, lacking the interstitial nitride, could be the smallest, is clearly the biggest, at least judging from the average Co—Co bond distance (2.565 and 2.579 for units 1 and 2 respectively, 2.633 Å for the empty cavity) or from the fact that the interprismatic bonds are the longest metal—metal interactions within their classes (Co4—Co9 among the bridged and Co5—Co10 among the unbridged).

Acknowledgment. Dr. Silvia Ferranti is gratefully acknowledged for her experimental contributions.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles (15 pages). Ordering information is given to any current masthead page.