Journal of Organometallic Chemistry, 358 (1988) C23–C25
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A new high nuclearity cobalt nitrido-carbonyl cluster. Synthesis and crystal structure of the anion $[Co_{14}N_3(CO)_{26}]^{3-}$

Secondo Martinengo *

Centro del C.N.R. di Studio della Sintesi e Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione, Via G. Venezian 21, 20133 Milano (Italy)

Gianfranco Ciani * **and Angelo Sironi**

Istituto di Chimica Strutturistica Inorganica and Centro del C.N.R., Via G. Venezian 21, 20133 Milano (Italy)

(Received June 6th, 1988)

Abstract

The high nuclearity anion $[Co_{14}N_3(CO)_{26}]^{3-}$, obtained by pyrolysis in diglyme of the trigonal prismatic $[Co_6N(CO)_{15}]^-$, contains a large metallic cluster formed by two superimposed rather folded centered-hexagons of cobalt atoms, with three interstitial nitrogen atoms located at the centres of three non adjacent distorted trigonal prismatic cavities.

Few carbonyl cluster compounds containing fully encapsulated nitrogen atoms are known. In 1979 we described the synthesis and structural characterization of the first such compounds, namely the trigonal prismatic species $[M_6N(CO)_{15}]^-$ (M = Co [1], Rh [1,2]). We have subsequently described other species with interstitial nitrides, namely the large mixed-metal anion $[PtRh_{10}N(CO)_{21}]^{3-}$ [3] and the anions $[Rh_6MN(CO)_{15}]^{2-}$ (M = Co, Rh, Ir) [4]. An octahedral cluster containing a fully encapsulated N atom has also been reported, i.e. the anion $[Ru_6N(CO)_{16}]^-$, but, to our knowledge, not characterized by a structural determination [5]. In the case of rhodium, gentle pyrolysis of the $[M_6N(CO)_{15}]^-$ anions gave rise to larger clusters such as the dinitride $[Rh_{12}HN_2(CO)_{23}]^{3-}$ [6], while in the case of cobalt only rearrangement of the metal framework to the octahedral $[Co_6N(CO)_{13}]^-$ was observed [7].

We have now investigated the pyrolysis of the cobalt species under more drastic conditions, and this has afforded the novel large species $[Co_{14}N_3(CO)_{26}]^{3-}$, the first example of a trinitride cluster and, at present, the cobalt cluster of highest nuclearity.

The $[Co_{14}N_3(CO)_{26}]^{3-}$ anion was prepared by heating a solution of the potas-

0022-328X/88/$03.50

sium salt of $[Co_6N(CO)_{15}]^-$ in diglyme at 140–150°C under nitrogen. During the reaction carbon monoxide was evolved, and some Co metal separated out. Close IR monitoring showed that after the initial decarbonylation to $[Co_6N(CO)_{13}]^-$, further transformation takes place. After 2–3 hours, when the spectrum mainly showed bands at 1991vs, 1820ms and 1792m cm^{-1} (sometimes a small band at 1987 cm^{-1} of the $[Co(CO)_4]^-$ anion is also present), the pyrolysis was stopped and the $[Co_{14}N_3(CO)_{26}]^{3-}$ anion isolated by evaporation of the solvent in vacuum and extraction of the residue with methanol, to give a solution from which the bulky cation salts were obtained by metathesis. The IR spectrum of the benzyltriphenylphosphonium salt in acetonitrile shows bands at 1995vs, 1953vw, 1821ms and 1790m cm^{-1}.

Crystals suitable for the X-ray analysis were obtained by slow diffusion of $[Ph_3PCH_2Ph]Cl$ dissolved in 2-propanol into a methanol solution of the potassium salt.

The structure * of the anion is shown in the Fig. 1. The unprecedented metal atom cluster, of idealized D_3 symmetry, consists of two superimposed rather folded centered hexagons of cobalt atoms. It can be derived by distortion of a fragment of simple hexagonal packing (2 layers, 7/7 metals). Three non-adjacent distorted trigonal prismatic cavities are occupied by interstitial nitrogen atoms. The $Co_{14}N_3$ moiety is reminiscent of the groupings present in bulk binary phases of some metal carbides and nitrides. However, the three empty cavities are quite irregular.

There are 14 terminal CO ligands, one for each metal atom, and 12 edge-bridging carbonyls, spanning all the edges of the external square faces of the irregular trigonal prisms containing the nitrides.

The metal atoms are of three kinds: the two central Co atoms are 7-connected to other metals and exhibit the shortest Co–Co bond; of the other 12 Co atoms, 6 are five, and 6 are four metal–metal connected, with a regular alternation.

The Co–Co bond lengths are scattered over the range 2.411(2)–2.949(3) Å. The 12 carbonyl bridged edges have a mean value of 2.507 Å. Within each of the two centered-hexagonal layers the central metals show, with respect to the external Co atoms, alternation of three shorter (mean 2.498 Å) and three longer (mean 2.793 Å) Co–Co bonds. The remaining 9 peripheral metal–metal interactions are particularly long (mean 2.918 Å).

The Co–N bond lengths are significantly longer for the central metals (mean 1.995 Å) than for the other cobalt atoms (mean 1.911 Å). For comparison the mean value of the Co–N bonds in $[Co_6N(CO)_{15}]^-$ is 1.938 Å.

Finally, the mean values of the Co–C and C–O bond lengths are 1.70 and 1.18 Å

---

* Crystal data: $C_{101}H_{66}Co_{14}N_3O_{26}P_3$, $M = 2655.6$, monoclinic, space group $P2_1/n$ (non-standard No. 14), with a 21.619(6), b 21.273(6), c 23.920(7) Å, β 96.12(2)°, D_c 1.613 g cm^{-3} for $Z = 4$. The structure was solved by direct methods and Fourier methods and refined by least-squares on the basis of 5602 significant $[I > 3\sigma(I)]$ absorption corrected counter data, up to a current R value of 0.062. (The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.)

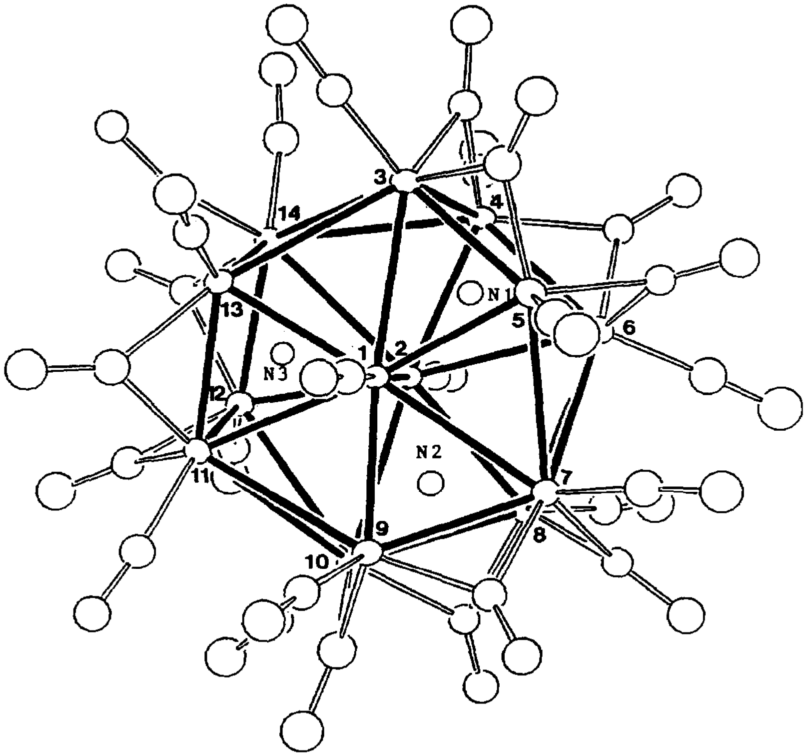

Fig. 1. A view of the anion $[Co_{14}N_3(CO)_{26}]^{3-}$. The Co–Co bond distances are as follows: 1–2 2.411, 1–3 2.815, 1–5 2.485, 1–7 2.790, 1–9 2.490, 1–11 2.767, 1–13 2.503, 2–4 2.506, 2–6 2.820, 2–8 2.496, 2–10 2.790, 2–12 2.508, 2–14 2.775, 3–4 2.486, 3–5 2.527, 3–13 2.906, 3–14 2.914, 4–6 2.528, 4–14 2.935, 5–6 2.477, 5–7 2.903, 6–7 2.859, 6–8 2.925, 7–8 2.488, 7–9 2.531, 8–10 2.532, 9–10 2.492, 9–11 2.949, 10–11 2.939, 10–12 2.936, 11–12 2.480, 11–13 2.531, 12–14 2.530, 13–14 2.487 Å, e.s.d.s 0.002–0.003 Å.

for the terminal and 1.88 and 1.19 Å for the bridging carbonyl groups, respectively.

Further work on this class of nitride compounds in the cobalt triad is in progress.

Acknowledgments. We thank the Italian C.N.R. for financial support.

References

1 S. Martinengo, G. Ciani, A. Sironi, B.T. Heaton and J. Mason, J. Am. Chem. Soc., 101 (1979) 7095.
2 R. Bonfichi, G. Ciani, A. Sironi and S. Martinengo, J. Chem. Soc., Dalton Trans., (1983) 253.
3 S. Martinengo, G. Ciani and A. Sironi, J. Am. Chem. Soc., 104 (1982) 328.
4 S. Martinengo, G. Ciani and A. Sironi, J. Chem. Soc., Chem. Commun., (1984) 1577.
5 M.L. Blohm, D.E. Fjare and W.L. Gladfelter, Inorg. Chem., 22 (1983) 1004.
6 S. Martinengo, G. Ciani and A. Sironi, J. Chem. Soc., Chem. Commun., (1986) 1742.
7 G. Ciani and S. Martinengo, J. Organomet. Chem., 306 (1986) C49.