

## Bismuth–Cobalt Heteronuclear Carbonyl Cluster Compounds. Synthesis and X-Ray Characterization of the Neutral $[\text{BiCo}_3(\text{CO})_9]$ and of the Paramagnetic Anion $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$

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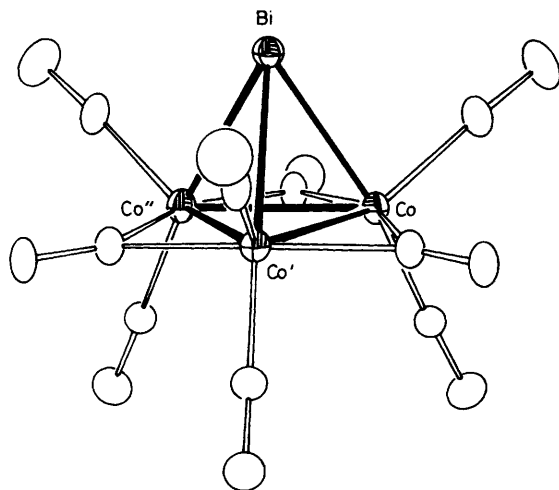
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Reactions between  $\text{BiCl}_3$  and the anion  $[\text{Co}(\text{CO})_4]^-$  under various conditions afford some new products: the anion  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$ , the neutral tetrahedral cluster  $[\text{BiCo}_3(\text{CO})_9]$ , and the paramagnetic cluster  $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$  containing a  $\text{Bi}_2\text{Co}_4$  array formed by three face-to-face condensed tetrahedral units.

Heteronuclear clusters have been studied extensively, and a variety of carbonyl complexes containing transition metals and bare main group elements have been reported.<sup>1</sup> We have previously investigated the reactions of the anion  $[\text{Co}(\text{CO})_4]^-$  with  $\text{PCl}_3$ , giving *inter alia* the anion  $[\text{Co}_6\text{P}(\text{CO})_{16}]^-$  which contains a semi-interstitial phosphorus atom.<sup>2</sup> We have now begun the study of the reactivity of the tetracarbonylcobaltate anion with the halides of the heavier elements of Group 5.

With  $\text{BiCl}_3$  some new products have been characterized, which are reported here.

The reaction of  $\text{BiCl}_3$  with  $[\text{Co}(\text{CO})_4]^-$  in tetrahydrofuran (THF) under nitrogen has been tested at molar ratios from 1:4 to 1:6. At a ratio of 1:4 a dark red anionic compound is formed,<sup>†</sup> which has been formulated as  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_4]^-$  (1) on the basis of chemical evidence (the reaction of



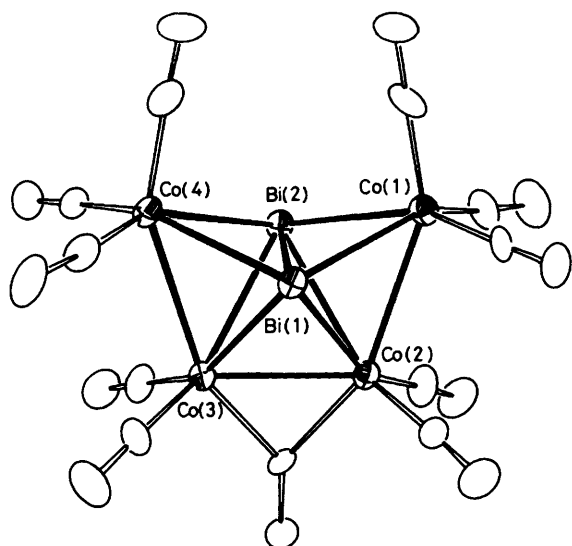
**Figure 1.** A view of the neutral species  $[\text{BiCo}_3(\text{CO})_9]$  (2), which lies on a crystallographic  $3m-C_{3v}$  position; main bond distances (Å): Bi–Co 2.623(2), Co–Co 2.550(2), Co–C(terminal) 1.80 (mean), Co–C(bridging) 1.96(1).

<sup>†</sup> *Syntheses.* All operations were carried out under nitrogen.

(a) A stirred solution of  $\text{Na}[\text{Co}(\text{CO})_4]$  (1.26 g) in THF (25 ml) was treated dropwise with a solution of  $\text{BiCl}_3$  (0.5 g) in THF (15 ml) to give a dark red solution from which (1) was isolated as the  $[\text{NMe}_4]^+$  salt by addition of aqueous  $[\text{NMe}_4]\text{Cl}$ , evaporation of the THF in vacuum, filtration, washing with water, and vacuum drying; crystals were obtained from  $\text{CH}_2\text{Cl}_2/n$ -hexane, leaving in the mother liquor some  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$  and (2). The same product was obtained from the reaction in THF of equimolar amounts of  $[\text{Co}(\text{CO})_4][\text{NMe}_4]$  and  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ ; i.r. (THF) 2065vw, 2030vs, 1985sh, and 1970vs  $\text{cm}^{-1}$ .

(b) A stirred solution of  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$  (0.1 g) in THF (10 ml) was heated on an oil bath at  $60^\circ\text{C}$  for 2 h. The solution was evaporated to dryness in vacuum and the residue dissolved in *n*-hexane, from which crystals of (2) were obtained by slowly cooling the hot saturated solution to room temperature; i.r. (*n*-hexane) 2084m, 2042vs, 2024s, 2015m, and 1882ms  $\text{cm}^{-1}$ .

(c) A solution of (1), obtained as in (a) was heated at reflux in an oil bath at  $75^\circ\text{C}$  until the i.r. bands above  $2010\text{ cm}^{-1}$  had disappeared (2–3 h). The dark brown solution containing (3) and  $[\text{Co}(\text{CO})_4]^-$  was filtered from some black material and evaporated to dryness in vacuum; the residue was redissolved in MeOH (20 ml) and treated with a solution of  $[\text{NMe}_4]\text{Cl}$  (0.5 g) in water (15 ml) to give the  $[\text{NMe}_4]^+$  salt of (3), which was filtered off, washed with water, and vacuum dried. Crystals were obtained from THF/*n*-hexane; i.r. (THF) 1998vs, 1985s, 1965ms, 1938vw, and 1795m  $\text{cm}^{-1}$ .



**Figure 2.** A view of the anion  $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$  (3); metal-metal bond distances ( $\text{\AA}$ ): Bi(1)–Bi(2) 3.088(1), Bi(1)–Co(1) 2.704(2), Bi(1)–Co(2) 2.784(2), Bi(1)–Co(3) 2.758(2), Bi(1)–Co(4) 2.719(2), Bi(2)–Co(1) 2.718(2), Bi(2)–Co(2) 2.767(2), Bi(2)–Co(3) 2.792(3), Bi(2)–Co(4) 2.707(2), Co(1)–Co(2) 2.733(4), Co(2)–Co(3) 2.538(3), Co(3)–Co(4) 2.741(4).

$[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$  with  $[\text{Co}(\text{CO})_4]^-$  in 1:1 molar ratio gives (1) as the unique product, and of the i.r. spectrum, which is similar to those for  $[\text{M}\{\text{Co}(\text{CO})_4\}_4]$  ( $\text{M} = \text{Sn}$  or  $\text{Pb}$ ),<sup>4</sup> but shifted to lower frequencies due to the presence of the negative charge. This formulation is consistent with elemental analyses and preliminary results of an X-ray analysis of the tetramethylammonium salt.

At  $[\text{Co}(\text{CO})_4]^- : \text{BiCl}_3$  ratios higher than 4:1 no other products except (1) are formed, and the excess of  $[\text{Co}(\text{CO})_4]^-$  remains unchanged.

Heating solutions of (1) in THF causes decomposition to different mixtures of products depending on reaction time; by stopping the reaction at an early stage we could isolate from the mixture, by evaporation to dryness and extraction with hexane, a neutral species which has been characterized as the new tetrahedral  $[\text{BiCo}_3(\text{CO})_9]$  (2), the existence of which was previously questioned for steric reasons.<sup>5</sup> We also found that this compound can be obtained in nearly quantitative yield by heating solutions of  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$  in THF or hexane,<sup>†</sup> which causes loss of CO and closure of the tetrahedral frame. Surprisingly, compound (2), in contrast with the open  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$  which easily affords (1), seems unreactive towards  $[\text{Co}(\text{CO})_4]^-$ , and no derivatives isostructural with the known  $[(\text{CO})_9\text{Co}_3\text{X}-\text{Co}(\text{CO})_4]$  ( $\text{X} = \text{Si}$  or  $\text{Ge}$ )<sup>6</sup> have been isolated so far. Another unexpected feature of (2) is that it has no tendency, in contrast with the P and As analogues, to give cyclic trimers.<sup>7</sup>

When heating the solutions of (1) is continued for a long time, further reactions occur to give eventually a mixture of  $[\text{Co}(\text{CO})_4]^-$  with the new anion  $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$  (3).<sup>†</sup> This compound is paramagnetic (e.s.r. signal at  $g$  2.099 at  $-150^\circ\text{C}$ ) and reacts with CO to give a mixture of (1),  $[\text{Co}(\text{CO})_4]^-$ , and a new species under investigation.

Both compounds (2) and (3) have been obtained crystalline and structurally characterized.

Only a few carbonyl clusters containing bismuth and transition metals have previously been fully characterized previously, namely  $[\text{Bi}\{\text{Mn}(\text{CO})_5\}_3]$ ,<sup>8</sup>  $[\text{BiIr}_3(\text{CO})_9]$ ,<sup>9</sup>

$[\text{Bi}_2\text{W}_3(\text{CO})_{15}]$ ,<sup>10</sup> and a series of Bi–Fe derivatives including  $[\text{BiFe}_3(\text{CO})_{10}]^-$ ,<sup>11a</sup>  $[\text{Bi}_2\text{Fe}_3(\text{CO})_9]$ ,<sup>11b</sup>  $[\text{BiFe}_4(\text{CO})_{16}]^{3-}$ ,<sup>11c</sup>  $[\text{Bi}_4\text{Fe}_4(\text{CO})_{13}]^{2-}$ ,<sup>11d</sup>  $[\text{BiFe}_3\text{H}_3(\text{CO})_9]$ ,<sup>11e</sup>  $[\text{BiFe}_3(\text{CO})_9(\mu_3\text{-COMe}_3)]$ ,<sup>11e</sup>  $[\text{Bi}_2\text{Fe}_4(\text{CO})_{13}]^{2-}$ ,<sup>11f</sup> and the mixed species  $[\text{Bi}_2\text{Fe}_2\text{Co}(\text{CO})_{10}]^-$ .<sup>11f</sup> In the case of the Bi–Co system, only the open species  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$ <sup>3</sup> was reported. However none of these compounds has the same stereochemistry as compounds (2) and (3). The structure<sup>‡</sup> of (2) is shown in Figure 1. It has crystallographic  $C_{3v}$  symmetry and contains a tetrahedral  $\text{BiCo}_3$  cluster, with two terminal CO groups for each cobalt atom and three bridging ligands on the Co–Co edges. The structure can be derived from that of  $[\text{Co}_4(\text{CO})_{12}]$  by replacement of the apical  $\text{Co}(\text{CO})_3$  moiety with a Bi atom.

The Bi–Co bond lengths are significantly shorter than in the related open species  $[\text{Bi}\{\text{Co}(\text{CO})_4\}_3]$  [2.623(2) *vs.* (mean) 2.766  $\text{\AA}$ ] and the Co–Bi–Co angles are considerably narrower [58.16(5) *vs.* (mean) 106.8 $^\circ$ ]. The Co–Co bonds are normal [2.550(2)  $\text{\AA}$ ].

The presence of bridging CO groups is unexpected,<sup>5</sup> the only other example of such a stereochemistry in a  $[\text{MCo}_3(\text{CO})_9]$  species ( $\text{M} = \text{main group element}$ ) possibly being present in  $[\text{AlCo}_3(\text{CO})_9]$  (characterized by spectroscopy).<sup>12</sup>

The structure<sup>‡</sup> of the paramagnetic anion  $[\text{Bi}_2\text{Co}_4(\text{CO})_{11}]^-$  (3) is illustrated in Figure 2. It shows an overall idealized  $C_{2v}$  symmetry and contains a  $\text{Bi}_2\text{Co}_4$  mixed-metal array consisting of three face-to-face condensed tetrahedral units, having as common edge Bi(1)–Bi(2). This cluster geometry was previously found for the homonuclear  $[\text{Os}_6(\text{CO})_{18}]$ ,<sup>13</sup> but the two species are not isoelectronic. The metallic skeleton can alternatively be described as an incomplete pentagonal bipyramid, with the ideal five-fold axis passing through the two Bi atoms, missing a metal atom of the pentagon (mean Co–Co–Co angle of 108.2 *vs.* the ideal value of 108 $^\circ$ ). Of the eleven carbonyl groups ten are terminally bonded: three to each of Co(1) and Co(4) and two to each of the other two Co atoms (mean Co–C and C–O 1.76 and 1.15  $\text{\AA}$ , respectively). One carbonyl ligand bridges the Co(2)–Co(3) edge [Co–C 1.87 (mean), C–O 1.18(2)  $\text{\AA}$ ].

The Bi–Bi interaction, 3.088(1)  $\text{\AA}$ , is similar to that in the bulk metal (3.07  $\text{\AA}$  for the nearest neighbours),<sup>14</sup> to the mean value for the bare  $\text{Bi}_8^{2+}$  cluster cation (3.100  $\text{\AA}$ ),<sup>15</sup> to the lower values found for the bare  $\text{Bi}_9^{5+}$  cation,<sup>16</sup> and to other Bi–Bi single bonds.<sup>11d,f</sup> It is greater than the Bi–Bi contact in

<sup>‡</sup> Crystal data for compound (2):  $\text{C}_9\text{BiCo}_3\text{O}_9$ ,  $M = 637.9$ , hexagonal, space group  $P6_3mc$  (No. 186),  $a = b = 11.094(4)$ ,  $c = 7.301(3)$   $\text{\AA}$ ,  $U = 778.2$   $\text{\AA}^3$ ,  $Z = 2$ ,  $D_c = 2.72$   $\text{g cm}^{-3}$ ,  $\mu$  ( $\text{Mo-K}\alpha$ ) = 144.2  $\text{cm}^{-1}$ . Compound (3):  $\text{C}_{15}\text{H}_{12}\text{Bi}_2\text{Co}_4\text{NO}_{11}$ ,  $M = 1035.9$ , monoclinic, space group  $P2_1/c$  (No. 14),  $a = 6.979(2)$ ,  $b = 30.592(8)$ ,  $c = 13.264(4)$   $\text{\AA}$ ,  $\beta = 96.29(3)^\circ$ ,  $U = 2814.8$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 2.44$   $\text{g cm}^{-3}$ ,  $\mu$  ( $\text{Mo-K}\alpha$ ) = 147.7  $\text{cm}^{-1}$ .  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073$   $\text{\AA}$ ). The intensity data for both species were collected with an Enraf-Nonius CAD4 automated diffractometer by the  $\omega$ -scan method, within the limits  $3 < \theta < 25^\circ$  for (2) and  $3 < \theta < 24.5^\circ$  for (3). In the case of (2), owing to the rapid decay of the sample upon X-ray exposure, a fast collection was performed only of the independent part of the sphere. An empirical absorption correction was applied to both data sets [normalized transmission factors in the range 0.59–1.00 (2) and 0.17–1.00 (3)]. The structures were solved by conventional Patterson and Fourier methods. The molecules of (2) were found in special positions  $3m-C_{3v}$  ( $b$  in Wyckoff notation). The refinements were carried out by full-matrix least-squares techniques, on the basis of 255 (2) and 2025 (3) independent significant reflections [ $I > 3\sigma(I)$ ], up to current values of  $R$  and  $R_w$  of 0.025 and 0.030 for the correct enantiomorph of (2) and of 0.040 and 0.049 for (3). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn [for (2)] or at the Cambridge Crystallographic Data Centre [for (3)]. See Notice to Authors, Issue No. 1.

[Bi<sub>2</sub>W<sub>3</sub>(CO)<sub>15</sub>] [2.818(3) Å],<sup>10</sup> which is considered to have considerable multiple-bond character.

The Bi atoms also exhibit long contacts with Bi atoms of anions in adjacent cells [4.106(1) Å].

The Bi-Co bonds (overall mean 2.744 Å) are closer to those found in [Bi{Co(CO)<sub>4</sub>}]<sub>3</sub> than those in compound (2). They belong, however, to two classes: the shorter Bi-Co(1,4) (mean 2.712 Å) and the longer Bi-Co(2,3) (mean 2.775 Å).

Finally, the Co-Co edge bridged by the carbonyl ligand is significantly shorter [2.538(3) Å] than the other two (mean 2.737 Å).

*Note added in proof:* While this work was in the press, an independent synthesis and characterisation of (2) has been reported, see K. H. Whitmire, J. S. Leigh, and M. E. Gross, *J. Chem. Soc., Chem. Commun.*, 1987, 926. Some new Bi-Ru and Bi-Os carbonyl clusters have been described, H. G. Ang, C. M. Hay, B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. J. Whitton, *J. Organomet. Chem.*, 1987, 330, C5.

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