Synthesis and Crystal Structure of Bis(tricobalt enneacarbonyl)acetone. An Application of a New Method for Sign Determination

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THE synthesis and properties of tricobalt enneacarbonyl methane and some of its derivatives [$Co_3(CO)_9CX$, (I)—see Fig. 1] have been investigated by one of us,[1] and by other authors.[2,3]

By thermal decomposition at about 90°C of $Co_3(CO)_9CBr$ in an anhydrous toluene solution, a mixture of $CoBr_2$, $Co_6(CO)_{18}C_2$ (II), $Co_6(CO)_{19}C_2$ (III), and CO was obtained; separation of (II) and (III) has been effected by chromatographic techniques. While (II) is very sparingly soluble in most solvents, and decomposes at about 200°, (III) is more soluble in toluene, heptane, and cyclohexane, and melts at 125° with decomposition, (II) being the final product. Further details on the stoicheiometry of the reactions, as well as on the i.r. characterization of the products will be given in a separate communication.

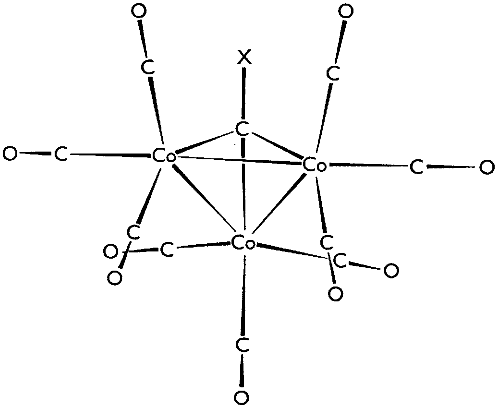

FIGURE 1

While (II) probably corresponds to the dimer obtained by condensation of two molecules of (I) *via* elimination of X_2,[3] the molecular structure of (III) has been assessed by us in the course of a three-dimensional *X*-ray investigation, as corresponding to bis(tricobalt enneacarbonyl)acetone; it is represented in Fig. 2. (III) is probably formed through a carbonyl-insertion mechanism, analogous to that which operates[1] when $Co_3(CO)_9CBr$ is

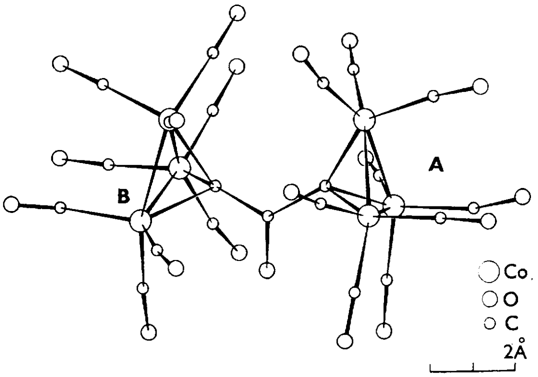

FIGURE 2

transformed into $Co_3(CO)_9CO_2Me$ by warming with methanol.

The following crystal data were determined photographically by the usual Weissenberg technique, using Co-K_α radiation:

$Co_6C_{21}O_{19}$, formula weight = 909·8

Orthorhombic, $a = 31{\cdot}35\ (\pm 0{\cdot}13)$ $b = 9{\cdot}87\ (\pm 0{\cdot}04)$ $c = 9{\cdot}87\ (\pm 0{\cdot}04)$ Å, $V = 3054\ (\pm 31)$ Å^3, $D_{\text{calc}} = 1{\cdot}98$ g./cm.^{3}, $D_{\text{exp}} = 1{\cdot}95$ g./cm.^{3}, $Z = 4$;

Space group, $P2_12_12_1$ (No. 19).

Attempts to locate the six cobalt atoms from Patterson projections failed, but application of a new method of sign-determination[4] to the centrosymmetric *b*- and *c*-axial projections was successful. The structure was then elucidated by electron-density synthesis; the refinement by the least-squares method is in progress: at the present stage, the *R*-value is 0·136 for 1653 observed reflections.

As may be seen from inspection of Figs. 1 and 2, (III) may be considered as consisting of two radicals A and B, obtained from (I) through elimination of X_2, joined together by a (>CO) bridge. In full agreement with the i.r. data, no bridge carbonyl group between cobalt atoms has been found, contrary to what should have been expected by analogy with other cobalt carbonyls.[5,6] The Co–Co bond distances are 2·47 ± 0·02Å as expected;[7] the average Co–C (carbonylic) and (Co–)C–O distances are 1·81 and 1·11 Å respectively, while the Co–C distances to the skeletal carbon atoms are 1·92 Å on the average.

These carbon atoms show a considerably distorted tetrahedral co-ordination: while the Co–C–Co bond angles are 80·7 ± 2·0°, two of the Co–C–C angles are about 120°, while the third one is about 149°. This result seems to be a compromise between the steric requirements of the oxygen atoms belonging to opposite molecular sides, which tend to keep apart at more than 2·90 Å, and of the C–C–C central bond angle which does not exceed 123° (found value). The C–CO–C group is planar within experimental error. A more detailed description of the structure will be published as soon as possible.

As for the cobalt atoms, their octahedral co-ordination is also severely distorted: the C–Co–C bond angles with carbonylic atoms are 98·8° on the average, while Co–Co–Co = 60°, and Co–Co–C (skeletal atoms) = 50·3° (av.).

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