

## Crystal Structure of Tetracarbonylcobalt-diphenyltin-pentacarbonylmanganese, (CO)<sub>4</sub>CoSnPh<sub>2</sub>Mn(CO)<sub>5</sub>

By B. P. BIR'YUKOV, YU. T. STRUCHKOV, K. N. ANISIMOV, N. E. KOLOBOVA, O. P. OSIPOVA,  
and M. YA. ZAKHAROV

(Institute of Organo-element Compounds, Academy of Sciences of the U.S.S.R., Moscow)

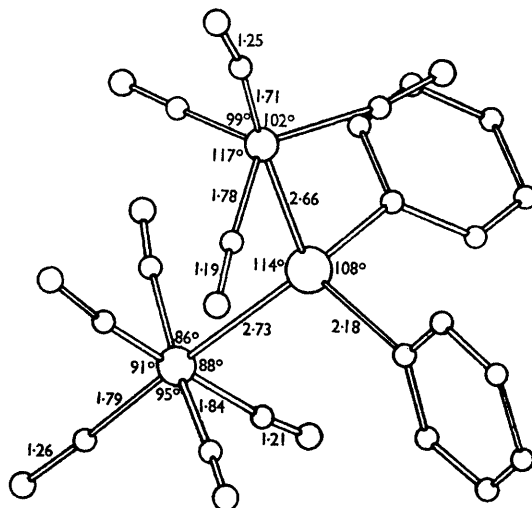
SOME time ago we undertook a preliminary X-ray study of a series of bimetallic carbonyl derivatives and determined their metal-to-metal bond lengths.<sup>1</sup> We are now determining the detailed structure of some termetallic derivatives containing in their molecules fragments of transition-metal  $\pi$ -complexes and of  $\sigma$ -carbon-metal compounds. We now report some basic structural data on tetracarbonylcobalt-diphenyltin-pentacarbonylmanganese, (CO)<sub>4</sub>CoSnPh<sub>2</sub>Mn(CO)<sub>5</sub> (I), which we have recently synthesized.<sup>2</sup> There are literature data on the structures of triphenyltin-triphenylphosphine-tetracarbonylmanganese Ph<sub>3</sub>SnMn(CO)<sub>4</sub>PPh<sub>3</sub> (II),<sup>3</sup> diphenyltin-bis(pentacarbonylmanganese) Ph<sub>2</sub>Sn[Mn(CO)<sub>5</sub>]<sub>2</sub> (III),<sup>4</sup> triphenyltin-pentacarbonylmanganese Ph<sub>3</sub>SnMn(CO)<sub>5</sub> (IV),<sup>5</sup> and trimethyltin-pentacarbonylmanganese Me<sub>3</sub>SnMn(CO)<sub>5</sub> (V),<sup>6</sup> all of which molecules contain the Sn-Mn bond. Structures of compounds containing the Sn-Co bond, as far as we know, have not been investigated previously.

**Crystal data.** Lamellar, pale yellow crystals of (I) are orthorhombic. Space group is *Pbca*,  $a = 8.38$ ,  $b = 17.25$ ,  $c = 33.47$  Å,  $V = 4838$  Å<sup>3</sup>,  $D_m = 1.71$ ,  $D_c = 1.76$  g.cm.<sup>-3</sup> for  $Z = 8$ ,  $M = 638.89$ .

From Weissenberg photographs taken with Cu-K radiation the intensities of *ca.* 1250 nonzero independent reflexions were estimated visually, neglecting absorption. The structure was solved by the standard heavy-atom method, and refined by the least-squares full-matrix method (with individual isotropic temperature-factors). At the present stage of refinement (which is being pursued further) the discrepancy index is  $R = 0.17$ , with the mean overall temperature-factor  $B = 3.8$  Å<sup>2</sup>.

The geometry of the molecule shown in the Figure is characterized by the Sn-Mn bond length  $2.73 \pm 0.01$  Å, which is somewhat shorter than the sum of Sn tetrahedral and Mn metallic radii (2.78 Å),<sup>7</sup> but distinctly greater than bond lengths found earlier in analogous compounds: 2.627 in (II), 2.70 in (III), 2.674 Å in (IV) and (V). The Sn-Co bond distance is  $2.66 \pm 0.01$  Å and coincides with the analogous radii sum of 2.66 Å. The mean Sn-C bond-length  $2.18 \pm 0.02$  Å does not differ from the values found earlier in similar compounds

[2.17 in (II) and 2.15 Å in (IV)] and is equal to the tetrahedral radii sum of 2.18 Å. The phenyl rings are planar, with the mean values; C-C 1.40 Å and C-C-C 120°.



FIGURE

The equatorial carbonyl groups of the Mn(CO)<sub>5</sub> fragment have mean bond-distances Mn-C 1.84 and C-O 1.21 Å, and for the axial group they are 1.79 and 1.26 Å respectively. This shortening of the axial Mn-C bond while the overall Mn...O distance remains constant is usual for metal carbonyls in general; it has been observed in Mn<sub>2</sub>(CO)<sub>10</sub> (VI),<sup>8</sup> [BrMn(CO)<sub>4</sub>]<sub>2</sub>,<sup>9</sup> and (CO)<sub>5</sub>MnH.<sup>10</sup> axial Mn-C 1.79, 1.76, and 1.82 Å; equatorial Mn-C 1.83, 1.87, and 1.84 Å respectively. It may be noted that in (II), which is rather similar to (I) in the Mn-Sn fragment of the structure, the mean Mn-C (1.758 Å) and C-O bond distances (1.184 Å) are considerably shorter. The mean equatorial bond distances are Co-C 1.78 and C-O 1.19 Å. The distances for the axial carbonyl group are 1.71 and 1.25 Å, so that in this case the difference is much more pronounced. Published data (for instance<sup>11</sup>) on Co-C bond distances show large discrepancies (1.70—1.89 Å);

the mean C-O distance in cobalt carbonyls is 1.16—1.18 Å.

The Sn atom co-ordination is distorted tetrahedral with the angle Mn-Sn-Co increased to  $114^\circ$  [Mn-Sn-Mn angle in (III) is  $117^\circ$ ]. Accordingly, the angle C-Sn-C is decreased to  $107.5^\circ$  [ $100^\circ$  in (III),  $106.0^\circ$  in (IV)]. The Mn co-ordination is distorted octahedral (C-Mn-C angles range from  $86$  to  $98^\circ$ ). As in (VI), the equatorial CO groups are bent from the axial one in the direction of the metal-to-metal bond. The Co atom co-ordination found here is of a rarely observed type: strongly distorted trigonal-bipyramidal. Such co-ordination was found recently, for instance, in the structure of heptacarbonylperfluorocyclopentadienedicobalt.<sup>11</sup> In our case the mean C-Co-C

angle in the equatorial plane of the bipyramid is  $118 \pm 5^\circ$ , while the other angles C-Co-C are in the range  $78$ — $102^\circ$  (instead of  $90^\circ$ ).

The mean angles Mn-C-O ( $170^\circ$ ) and Co-C-O ( $172^\circ$ ) are typical of the flexibility of metal-C-O groups. These deformations and measurable distortions of the metal-atom co-ordination polyhedra are imposed by intra- and inter-molecular (steric overcrowding) non-valence interactions. In this connection we mention our intention to embark on the conformational analysis of these polymetallic ("cluster") molecules with, as main interest, the potential barriers to rotation around metal-to-metal bonds.

(Received, June 12th, 1967; Com. 586.)

<sup>1</sup> K. N. Anisimov, Yu. T. Struchkov, O. P. Osipova, N. E. Kolobova, and A. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, 1967, **172**, 107.

<sup>2</sup> A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and M. Ya. Zakharova, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1965, 1122.

<sup>3</sup> R. F. Bryan, *J. Chem. Soc. (A)*, 1967, 172.

<sup>4</sup> B. T. Kilbourn and H. M. Powell, *Chem. and Ind.*, 1964, 1578.

<sup>5</sup> H. P. Weber and R. F. Bryan, *Chem. Comm.*, 1966, 443.

<sup>6</sup> R. F. Bryan, *Chem. Comm.*, 1967, 355.

<sup>7</sup> L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N.Y., 3rd end., 1960.

<sup>8</sup> L. F. Dahl and R. E. Rundle, *Acta Cryst.*, 1963, **16**, 419.

<sup>9</sup> L. F. Dahl and Chin-Hsuan Wei, *Acta Cryst.*, 1963, **16**, 611.

<sup>10</sup> S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Amer. Chem. Soc.*, 1964, **86**, 2288.

<sup>11</sup> P. B. Hitchcock and R. Mason, *Chem. Comm.*, 1966, 503.