

## X-Ray Crystal and Molecular Structures of Three Methinyl Tricobalt Enneacarbonyl Derivatives

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**Summary** Crystal structures have been determined of three derivatives of  $YCo_3(CO)_9$ , all containing the tetrahedral  $Co_3$  cluster of the parent compound: in  $PhCCo_3(CO)_6 \cdot \pi-C_6H_3Me_3$ , a mesitylene molecule is  $\pi$ -bonded to a single Co atom of the  $Co_3$  triangle, having replaced three CO groups; in  $PhCCo_3(CO)_6 \cdot \pi-C_8H_8$ , a cyclo-octatetraene molecule has replaced the three axial CO groups of the parent molecule and is  $\pi$ -bonded to the  $Co_3$  triangle through three of its double bonds, and in the dimer,  $[CCo_3(CO)_9]_2$  the length of the central formally single C-C bond is 1.37(2) Å.

METHINYL tricobalt enneacarbonyls of general formula  $YCo_3(CO)_9$  (Y = alkyl or aryl) react with polyenes to form  $\pi$ -complexes in which three CO groups are replaced by a  $\pi$ -donor molecule.<sup>1,2</sup>

of the Co atoms, and is oriented so that the normal to the ring plane through its associated Co atom points approximately to the centroid of the  $Co_3C$  tetrahedron. The plane of the terminal phenyl ring is tilted significantly, by  $6.4^\circ$  away from the normal to the  $Co_3$  plane, presumably as a result of crystal packing forces. Important bond lengths are: Co(1)-Co(2), 2.441(5); Co(2)-Co(2'), 2.477(5); Co-C (bridge), 1.89(2) (mean); Co(2)-C (carbonyl), 1.78(2) (mean); Co-C (mesitylene), 2.14(2) (mean); C(4)-C(5), 1.48(2) Å.

The dark-brown crystals of the cyclo-octatetraene complex  $PhCCo_3(CO)_6 \cdot C_8H_8$  are monoclinic (space group  $P2_1/c$ ) with  $a = 17.13$ ,  $b = 15.72$ ,  $c = 16.86$  Å;  $\beta = 115.9^\circ$ ;  $V = 4088$  Å<sup>3</sup>;  $Z = 8$ ;  $D_m = 1.73$ , and  $D_c = 1.75$  g cm<sup>-3</sup>. There are therefore 2 molecules in the asymmetric unit and hence 60 non-hydrogen atoms to be located. The structure was

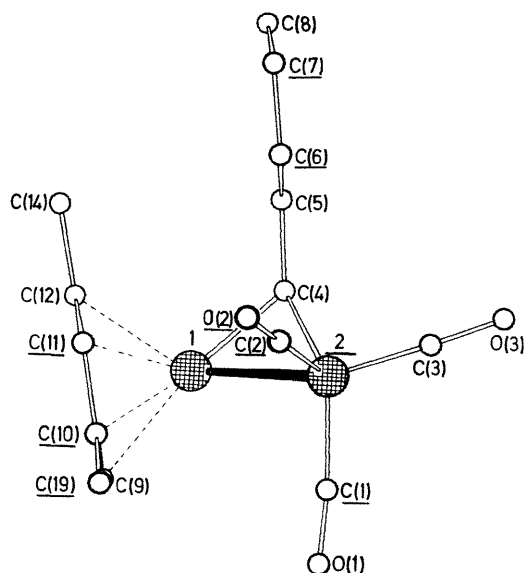


FIGURE 1. The molecule  $PhCCo_3(CO)_6 \cdot \pi-C_6H_3Me_3$  viewed normal to the crystallographic mirror plane. Underlined atoms are related to other atoms in the molecule by the mirror plane.

The dark brown crystals of the mesitylene complex  $PhCCo_3(CO)_6 \cdot C_6H_3Me_3$  are orthorhombic (space group  $Pnma$ ) with  $a = 19.26$ ,  $b = 13.088$ ,  $c = 8.731$  Å;  $V = 2201$  Å<sup>3</sup>;  $Z = 4$ , and  $D_c = 1.67$  g cm<sup>-3</sup>. The required molecular symmetry is  $C_s-m$ . 969 independent reflections were used in the crystal structure determination, by Patterson methods. In the final refinement all atoms were treated anisotropically and the hydrogen atoms were located from difference maps. The  $R$ -factor is 0.057.

The structure is illustrated in Figure 1. The mesitylene molecule has replaced the three CO groups attached to one

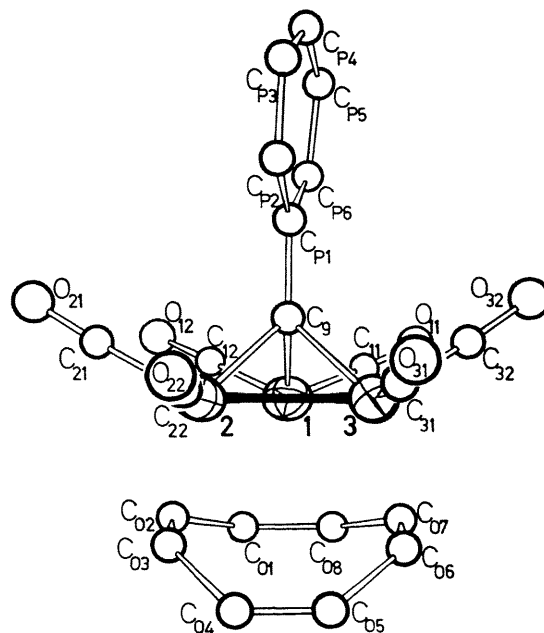


FIGURE 2. One molecule of  $PhCCo_3(CO)_6 \cdot \pi-C_8H_8$  viewed parallel to the  $Co_3$  triangle.

solved by direct phase-determining procedures. In the final refinement, using 1638 independent reflections, Co atoms only were treated anisotropically and no attempt was made to locate hydrogen atoms. The  $R$ -factor is 0.061.

The structure is shown in Figure 2. The cyclo-octatetraene molecule is in the tub conformation and the normal to its central plane {defined by  $Co_1, Co_4, Co_5, Co_8$ } is tilted by  $15^\circ$  from the normal to the  $Co_3$  triangle. In this way the pairs of atoms  $Co_1, Co_8$ ;  $Co_2, Co_3$ ;  $Co_6, Co_7$  are positioned equidistantly from  $Co(1)$ ,  $Co(2)$ , and  $Co(3)$ ,

respectively. In the Table are listed the bond lengths within the cyclo-octatetraene ring and between the Co

*Interatomic distances (Å), involving the cyclo-octatetraene molecule in  $\text{PhCCo}_3(\text{CO})_9 \cdot \pi\text{-C}_8\text{H}_8$*

$\text{Co}_1\text{-Co}_2 \dots$	1.46	$\text{Co}(1)\text{-Co}_1 \dots$	2.18
$\text{Co}_2\text{-Co}_3 \dots$	1.38	$\text{Co}(1)\text{-Co}_8 \dots$	2.16
$\text{Co}_3\text{-Co}_4 \dots$	1.51	$\text{Co}(2)\text{-Co}_2 \dots$	2.19
$\text{Co}_4\text{-Co}_5 \dots$	1.32	$\text{Co}(2)\text{-Co}_3 \dots$	2.21
$\text{Co}_5\text{-Co}_6 \dots$	1.51	$\text{Co}(2)\text{-Co}_4 \dots$	3.17
$\text{Co}_6\text{-Co}_7 \dots$	1.40	$\text{Co}(3)\text{-Co}_6 \dots$	2.22
$\text{Co}_7\text{-Co}_8 \dots$	1.47	$\text{Co}(3)\text{-Co}_7 \dots$	2.18
$\text{Co}_8\text{-Co}_1 \dots$	1.38	$\text{Co}(3)\text{-Co}_8 \dots$	3.17
Mean e.s.d. 0.03 Å		Mean e.s.d. 0.02 Å	

atoms and the ring. (There are no significant differences between the two molecules and the figures quoted are average values.) These bond lengths show clearly that there are three pairs of double-bonded ring carbon atoms associated with the three Co atoms. The fourth double bond  $\text{C}_{04}\text{-C}_{05}$  does not interact with the metal cluster. Although there have been no previous reports of bonding between cyclo-octatetraene and a complete metal cluster (as distinct from one or two atoms of a larger cluster), a similar situation exists in  $\text{Me}_3\text{C}_{10}\text{H}_5\text{Ru}_4(\text{CO})_9$  where a molecule of 4,6,8-trimethylazulene is associated with one face of an  $\text{Ru}_4$  tetrahedron.<sup>3</sup>

The dimer  $[\text{CCo}_3(\text{CO})_9]_2$  which is one product of the reaction between  $\text{XCCo}_3(\text{CO})_9$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) and arenes<sup>1,4,5</sup> also forms very dark crystals which are monoclinic (space

group  $C2/c$ ) with  $a = 16.37$ ,  $b = 9.450$ ,  $c = 18.91$  Å;  $\beta = 106.8^\circ$ ;  $V = 2799$  Å<sup>3</sup>;  $Z = 4$ ;  $D_m = 2.10$ , and  $D_c = 2.09$  g cm<sup>-3</sup>. The required molecular symmetry is therefore  $C_2$ -2. The structure was solved by direct phase-determining procedures and in the refinement, using 1650 independent reflections Co atoms only were treated anisotropically. The  $R$ -factor is 0.054. (For all three of the structure analyses reported here, X-ray intensity data were recorded by a Hilger-Watts four-circle diffractometer using Zr filtered  $\text{Mo-K}_\alpha$  radiation and the technique of moving-crystal-moving-counter scans, backgrounds being measured with crystal and counter stationary.)

The molecular structure is as expected with two  $\text{CCo}_3(\text{CO})_9$  units linked directly through the bridging carbon atoms. Notable dimensional features are the central C-C bond length of 1.37(2) Å and the mean Co-C (bridge) length of 1.96(1) Å. There seems no basis for ascribing multiple bond character to the central C-C bond and we may rationalise the extreme reduction of bond length in terms of the orbitals which are used to form the bond. The very small Co-C-Co angles (mean  $77.5^\circ$ ) suggest that the bridging carbons are using predominantly  $p$ -orbitals in bonding to Co and predominantly  $s$ -orbitals in bonding to each other.

The three structure investigations reported here form part of a general study of derivatives of  $\text{YCCo}_3(\text{CO})_9$ <sup>5,6</sup> and will be discussed later in more detail within their wider setting. We thank Dr. B. H. Robinson, University of Otago, for close collaboration throughout these studies.

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<sup>5</sup> R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, 1970, 9, 2197, 2204.

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