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**THE STRUCTURE OF (1—2 : 5—6- $\eta$ -CYCLOOCTA-1,5-DIENE)-( $\eta^5$ -CYCLOPENTADIENYL)COBALT(I)**

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The structure of the title complex, C<sub>13</sub>H<sub>17</sub>Co (232.2), was determined by the heavy-atom method and anisotropically refined to the value  $R = 0.029$  for 1 558 observed reflections ( $I > 1.96\sigma(I)$ ). The substance crystallizes in the monoclinic space group  $P2_1/c$ ;  $a = 12.6744(6)$ ,  $b = 7.3887(5)$ ,  $c = 11.4519(8)$  Å,  $\beta = 102.91(1)^\circ$ ,  $Z = 4$ . The molecule has the sandwich-arrangement, in which cycloocta-1,5-diene ring assumes the boat conformation. The bond distances to the Co atom, in the range of 2.010–2.025 Å, are short. The relatively strong interactions of the  $\pi$ -orbitals of the diolefin with the cyclopentadienyl-Co fragment is manifested in the elongation of the C=C bonds (1.411 and 1.412 Å).

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Although some cpCo-diolefin (cp means cyclopentadienyl) complexes are described in the literature, to our best knowledge no crystallographic data are published for a cpCo complex with an coordinated unconjugated diolefin. Concerning the remarkable stability and usefulness of [Co(cp)(cod)] (cod means cycloocta-1,5-diene) as a homogenous catalyst for oligomerization of acetylenes at higher temperatures in the absence of carbon monoxide, the structure of the title compound is reported now.

## EXPERIMENTAL

### Preparation of Compound Studied

To obtain [Co(cp)(cod)] in good yield from commercially available [Co(cp)(CO)<sub>2</sub>] a method described by King, Treichel and Stone<sup>1</sup> was modified. To a degassed solution of 15 g (142 mmol) of cycloocta-1,5-diene in 100 ml decalin was added 3 g (16.7 mmol) of [Co(cp)(CO)<sub>2</sub>]. Under a slow argon stream the solution was stirred 60 h at 145°C. Afterwards the volatile compounds of the reaction mixture were removed under reduced pressure. The dark orange residue crystal-

lized and after sublimation 2.75 g (11.8 mmol) of analytically pure [Co(cp)(cod)] was isolated (71% yield). The density was measured by the flotation method.

#### Crystal Structure Determination

Monoclinic, space group  $P2_1/c$ ,  $a = 12.6744(6)$ ,  $b = 7.3887(5)$ ,  $c = 11.4519(8)$  Å,  $\beta = 102.91(1)^\circ$ ,  $V = 1.045.3(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.476$  Mg m<sup>-3</sup>,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å,  $\mu = 1.59$  mm<sup>-1</sup>,  $F(000) = 488$ .

The single crystal with the dimensions 0.20 × 0.35 × 0.40 mm was measured on an Enraf-Nonius CAD4 diffractometer at 23°C. Graphite-monochromated MoK $\alpha$  radiation was employed. The lattice parameters were refined from the positions of 25 centred reflections ( $38^\circ < 2\theta < 40^\circ$ ). A total of 8 054 intensities were measured in the range  $h: -20 \rightarrow 20$ ,  $k: -12 \rightarrow 12$ ,  $l: 0 \rightarrow 14$ . During the data collection ( $\omega/2\theta$  mode,  $2\theta < 50^\circ$ ) three intensity-control reflections ( $-10\ 0\ -4$ ,  $-10\ 1\ -2$ ,  $-7\ 4\ -8$ ) monitored after every 200 reflections showed no significant fluctuation. After averaging of the equivalent reflections only 1 558 intensities were considered as observed on the basis of the  $I > 1.96\sigma(I)$  condition. The phase problem was solved using the heavy-atom method, H-atom positions were calculated from the expected ideal geometry and isotropically refined. The structure was refined by minimizing of  $\sum w(|F_o| - |F_c|)^2$  using the block-diagonal least-squares procedure. A total of 195 parameters were refined in two blocks. In the last refinement cycle the maximal value of  $(\Delta/\sigma)$  was 0.002 and the weighting scheme had the  $w = [\sigma^2(F_o) + 0.0009F_o^2]^{-1}$  form. Refinement yielded the  $R = 0.029$ ,  $wR = 0.026$ ,  $S = 1.034$  values for 1 558 observed intensities, absorption and extinction effects were neglected. The maximum and minimum heights in the final  $\Delta\rho$  map were 0.24 and  $-0.62$  e Å<sup>-3</sup>. Atomic scattering factors for neutral atoms were taken from literature<sup>2</sup>. The following crystallographic programs were employed: SDP (ref.<sup>3</sup>), SHELX-76 (ref.<sup>4</sup>), PARST (ref.<sup>5</sup>). Calculations were carried out on PDP 11/73 and EC 1033 computers.

#### RESULTS AND DISCUSSION

The molecular structure of [Co(cp)(cod)] with the numbering of atoms is illustrated in Fig. 1. Final atomic coordinates for non-hydrogen atoms and their equivalent isotropic thermal parameters are listed in Table I\*. Bond lengths and angles are given in Table II.

For the discussion of the geometric arrangement it might be useful to compare the data obtained with already known bond angles and lengths of similar [M(cod)L<sub>n</sub>] complexes. Regarding the arrangement of two coordinated carbocyclic  $\pi$ -systems no unusual features are obvious. The atoms of the cp cycle (C9, C10, C11, C12, and C13) are situated nearly in one plane with a maximum deviation of  $-0.011(3)$  Å for C13. Cycloocta-1,5-diene adopts the expected boat conformation. The displacements of the C3, C4, C7 and C8 atoms from the C1, C2, C5 and C6 plane are 1.228(3) Å, 0.952(3) Å, 1.220(3) Å and 0.974(3) Å, respectively. The dihedral angle between the C1, C2, C5, C6 plane and the plane of the cp cycle is  $178.7(1)^\circ$ . The

\* Lists of structure factors, anisotropic thermal parameters, H-atom positions, bond distances and angles involving H atoms and least-squares plane details are available on request from the author (B.K.).

bond distances to the cobalt, in the range of 2.010–2.025 Å, are relatively short. Compared, for example to  $[\text{Fe}(\text{cod})(\text{CO})_3]$  (ref.<sup>6</sup>), where the olefin–metal distance lies between 2.16 and 2.18 Å, the force constant of the Co–olefin bond must be stronger. In  $[\text{Ni}(\text{cod})_2]$  the analogous bond length is 2.11 Å (ref.<sup>7</sup>), also clearly longer than in  $[\text{Co}(\text{cp})(\text{cod})]$ . The situation is a somewhat different in the paramagnetic 17-electron species  $[\text{Fe}(\text{cp})(\text{cod})]$  (ref.<sup>8</sup>), where the Fe atom tries to satisfy its electron deficiency by shortening the corresponding bond lengths, so that a metal–olefin distances of about 2.04 Å results.

The relatively strong interaction of the  $\pi$ -orbitals of the diolefin with the cpCo-fragment can also be verified by looking at the elongation of the C=C bond. The value for this bond length is 1.334 Å in the uncoordinated cycloocta-1,5-diene<sup>9</sup> and 1.411 and 1.412 Å respectively, in  $[\text{Co}(\text{cp})(\text{cod})]$ . The analogous distances in  $[\text{Ni}(\text{cod})_2]$  are between 1.38 and 1.39 Å, and 1.37 Å in  $[\text{Fe}(\text{cod})(\text{CO})_3]$ . The bond angles are quite normal and are more similar to those found in  $[\text{Fe}(\text{cp})(\text{cod})]$  than to those in  $[\text{Ni}(\text{cod})_2]$ .

An examination of intermolecular distances between non-hydrogen atoms shows that the crystal is stabilized by van der Waals interactions only (Fig. 2); the shortest distances are  $\text{C10} \cdots \text{C13}^i = 3.578(4)$  Å and  $\text{C10} \cdots \text{C1}^{ii} = 3.578(3)$  Å, where i:  $1 - x, y - 1/2, 1/2 - z$  and ii:  $x, y - 1, z$ .

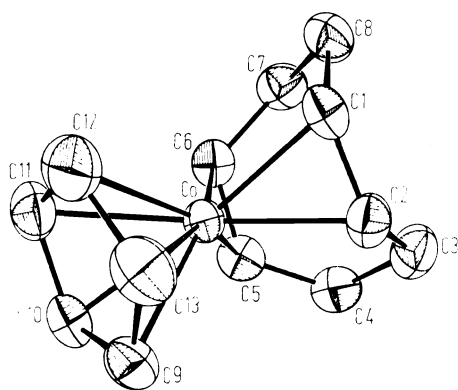


FIG. 1

View of the  $[\text{Co}(\text{cp})(\text{cod})]$  molecule with atom numbering. The displacement ellipsoids are drawn at the 50% probability level

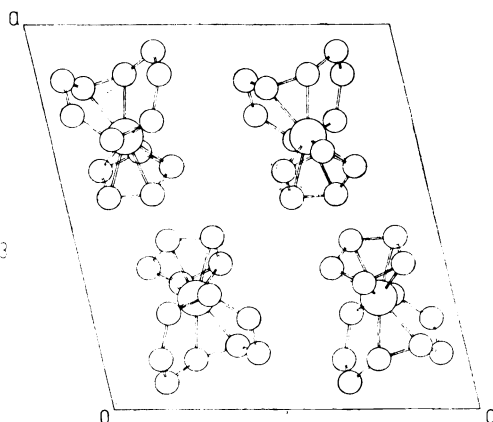


FIG. 2

The crystal packing projected into the  $XZ$  plane

TABLE I

The final coordinates for non-hydrogen atoms ( $\cdot 10^4$ ) and their isotropic equivalent displacement parameters ( $\cdot 10^4$ ) defined as  $U_{\text{eq}} = (1/3) [U_{22} + 1/\sin^2 \beta (U_{11} + U_{33} + 2U_{13} \cos \beta)]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{Å}^2$
Co	2 898·6(2)	3 206·4(4)	2 943·4(2)	264(2)
C1	2 979(2)	5 866(3)	3 328(2)	376(13)
C2	2 497(2)	5 595(3)	2 105(2)	377(13)
C3	1 292(2)	5 825(4)	1 602(3)	516(16)
C4	697(2)	4 048(4)	1 614(3)	489(15)
C5	1 292(2)	2 777(4)	2 555(3)	399(14)
C6	1 650(2)	3 212(3)	3 780(3)	398(14)
C7	1 454(2)	5 049(4)	4 297(2)	491(16)
C8	2 361(3)	6 377(4)	4 256(3)	489(16)
C9	3 680(2)	1 665(3)	1 853(3)	402(15)
C10	3 287(2)	533(3)	2 639(2)	423(14)
C11	3 792(2)	1 006(4)	3 832(3)	510(16)
C12	4 484(2)	2 439(5)	3 783(3)	551(17)
C13	4 400(2)	2 871(4)	2 553(3)	478(16)

TABLE II

Interatomic distances (in Å) and angles (in °)

Atoms	Value	Atoms	Value
Distances			
Co—C1	2·011(2)	C3—C4	1·516(4)
Co—C2	2·020(2)	C4—C5	1·500(4)
Co—C5	2·010(2)	C5—C6	1·411(4)
Co—C6	2·025(3)	C6—C7	1·524(4)
Co—C9	2·095(3)	C7—C8	1·521(4)
Co—C10	2·084(3)	C1—C8	1·504(5)
Co—C11	2·109(3)	C9—C10	1·399(4)
Co—C12	2·102(3)	C10—C11	1·417(4)
Co—C13	2·064(3)	C11—C12	1·384(4)
C1—C2	1·412(4)	C12—C13	1·425(5)
C2—C3	1·516(4)	C9—C13	1·394(4)

TABLE II  
(Continued)

Angles			
C6—Co—C5	40.9(1)	C9—Co—C11	66.0(1)
C1—Co—C5	101.7(1)	C9—Co—C12	66.1(1)
C1—Co—C6	84.4(1)	C9—Co—C13	39.2(1)
C2—Co—C5	84.1(1)	Co—C9—C10	70.0(2)
C2—Co—C6	94.7(1)	Co—C9—C13	69.2(2)
C2—Co—C1	41.0(1)	C13—C9—C10	107.1(2)
C10—Co—C5	94.5(1)	Co—C13—C9	71.6(2)
C10—Co—C6	108.7(1)	C9—C13—C12	108.7(3)
C10—Co—C1	163.8(1)	Co—C13—C3	71.4(2)
C10—Co—C2	142.5(1)	Co—C12—C13	68.6(2)
C11—Co—C5	113.2(1)	C13—C12—C11	107.6(3)
C11—Co—C6	99.5(1)	Co—C12—C11	71.1(2)
C11—Co—C1	130.7(1)	Co—C11—C12	70.6(2)
C11—Co—C2	162.7(1)	C12—C11—C10	107.7(3)
C11—Co—C10	39.5(1)	Co—C12—C10	69.3(2)
C12—Co—C5	151.2(2)	C9—C10—C11	108.9(2)
C12—Co—C6	123.5(1)	Co—C10—C11	71.2(2)
C12—Co—C1	99.6(1)	Co—C10—C9	70.9(1)
C12—Co—C2	124.5(1)	Co—C2—C3	113.8(2)
C12—Co—C10	65.4(1)	Co—C2—C1	69.2(1)
C12—Co—C11	38.4(1)	C1—C2—C3	122.5(2)
C13—Co—C5	150.5(1)	Co—C1—C2	69.8(1)
C13—Co—C6	163.4(1)	C2—C1—C8	124.0(3)
C13—Co—C1	99.2(1)	Co—C1—C8	113.0(2)
C13—Co—C2	98.6(1)	C1—C8—C7	112.2(2)
C13—Co—C10	65.6(1)	C8—C7—C6	111.9(2)
C13—Co—C11	65.8(1)	Co—C6—C7	113.5(2)
C13—Co—C12	40.0(1)	C7—C6—C5	123.0(2)
C9—Co—C5	111.9(1)	Co—C6—C5	69.0(2)
C9—Co—C6	143.7(1)	Co—C5—C6	70.1(2)
C9—Co—C1	130.8(1)	C6—C5—C4	124.8(3)
C9—Co—C2	107.1(1)	Co—C5—C3	112.5(2)
C9—Co—C10	39.1(1)	C5—C4—C3	122.2(2)
		C2—C3—C4	111.1(2)

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