

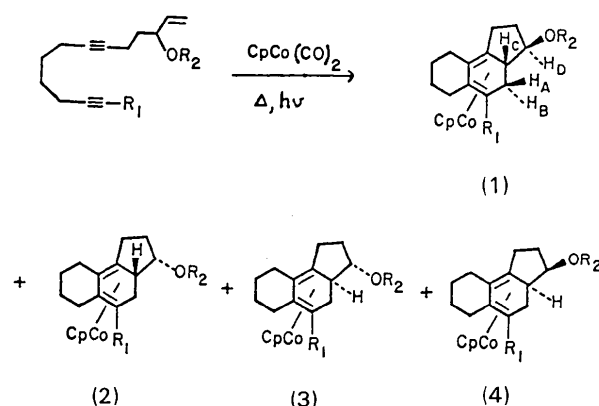
## Structure of ( $\eta$ -Cyclopentadienyl){(3*R*\*,3*aR*\*)-5-5*a*-9*a*-9*b*- $\eta$ -3-methoxy-5-trimethylsilyl-2,3,3*a*,4,6,7,8,9-octahydro-1*H*-benz[*e*]indene}cobalt, [Co(C<sub>5</sub>H<sub>5</sub>)(C<sub>17</sub>H<sub>28</sub>OSi)]

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**Abstract.**  $M_r = 400.53$ , monoclinic,  $P2_1/n$ ,  $a = 14.514$  (4),  $b = 8.332$  (3),  $c = 18.007$  (5) Å,  $\beta = 106.19$  (2)°,  $V = 2091$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.265$  (7),  $D_x = 1.272$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 8.81$  cm<sup>-1</sup>,  $F(000) = 692$ ,  $T = 295$  K,  $wR = 3.91$  and  $R = 3.72\%$  for 3332 observed reflections [ $F^2 > 3\sigma(F^2)$ ] with 226 variables. The cobalt is coordinated by the cyclopentadienyl ring and the two double bonds of the tricyclic organic fragment. Of special interest is the relative orientation of the methoxy group and the unique hydrogen atom on the adjacent carbon atom, both of which are *exo* with respect to the cobalt atom.

**Introduction.** Cobalt-mediated cyclization of linear achiral enediyne to form complexed chiral polycycles in a one-step process has recently been reported (Sternberg & Vollhardt, 1980) and may be of great utility in the synthesis of biologically interesting organic molecules such as antibiotics and other natural products. The [2 + 2 + 2] cyclizations have proven to be mechanistically controversial and a recent study (Clinet, Duñach & Vollhardt, 1983) reported the first results of diastereoselectivity experiments employing chiral substrates with a variety of substituents (see scheme below). The structure analysis reported here was undertaken to determine the relative stereochemistry [from (1)–(4)] resulting from the reaction shown in the equation when  $R_1 = \text{Si}(\text{CH}_3)_3$  and  $R_2 = \text{CH}_3$ .



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**Experimental.** Several orange needle-like crystals (obtained from Dr J. C. Clinet and Professor K. P. C. Vollhardt) were cleaved and mounted in glass capillaries, which were then flushed with dry nitrogen and flame sealed.  $D_m$  by flotation. Preliminary precession photographs yielded rough cell dimensions and showed monoclinic ( $2/m$ ) Laue symmetry with systematic absences that uniquely defined space group  $P2_1/n$  (reflections observed:  $0k0$ ,  $k = 2n$ ;  $h0l$ ,  $h + l = 2n$ ). Crystal  $0.23 \times 0.36 \times 0.53$  mm, Enraf–Nonius CAD-4 diffractometer, cell parameters from setting angles of 6 sets of 4 symmetry-related reflections with  $2\theta$  25–30°. Intensity data for  $h = 0$  to 17,  $k = 0$  to 9,  $l = -21$  to 21,  $\theta$ – $2\theta$  scan,  $2\theta$  range 3–55°, correction for scan speed, background and Lorentz–polarization effects. All calculations with locally-modified Enraf–Nonius SDP software (*Structure Determination Package User's Guide*, 1980). Three intensity standards (413, 040, 004) measured every 2 h of X-ray exposure time, no decay observed. Orientation checked after every 250 reflections and redetermined twice when angles  $> 0.15\%$  off. Azimuthal scan data collected for several reflections near  $\chi = 90^\circ$ , which were measured at  $10^\circ$  increments of rotation about diffraction vector. These showed average variation of relative intensity of  $\pm 5\%$ . Absorption correction based on measured faces of crystal and  $10 \times 14 \times 6$  Gaussian grid of internal points; max. and min. transmission 0.874 and 0.739. 4468 unique data; three-dimensional Patterson map gave positions of Co and Si atoms. Standard Fourier and least-squares techniques located all other atoms. Hydrogen atoms included (in idealized positions) in structure-factor calculations for final cycles of least squares, but not refined.  $\sum w(|F_o| - |F_c|)^2$  minimized,  $w = 4F_o^2/\sigma^2(F_o^2)$ ,  $\sigma^2(F_o^2) = \sigma_o^2(F_o^2) + (\rho F^2)^2$ .  $\rho$ , used to reduce weight of intense reflections, was 0.03. Analytical forms for scattering factors for neutral atoms, all non-hydrogen scattering factors corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). Positional and anisotropic thermal parameters refined for each non-hydrogen atom. Isotropic  $B$  values for H atoms set between 5 and 9 Å<sup>2</sup> depending on  $B_{ij}$ 's for associated

Table 1. Final atomic parameters and e.s.d.'s

$$B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Co	0.44702 (2)	0.10986 (4)	0.22706 (2)	3.224 (6)
Si	0.54680 (5)	0.34661 (9)	0.38499 (4)	3.40 (1)
O	0.4082 (2)	0.6043 (2)	0.0696 (1)	5.74 (5)
C(1)	0.3735 (2)	-0.1064 (4)	0.2076 (2)	6.17 (8)
C(2)	0.3995 (2)	-0.0764 (4)	0.2850 (2)	6.88 (9)
C(3)	0.3605 (2)	0.0655 (5)	0.2974 (2)	7.69 (9)
C(4)	0.3066 (2)	0.1273 (5)	0.2266 (3)	7.8 (1)
C(5)	0.3165 (2)	0.0188 (5)	0.1704 (2)	6.59 (9)
C(11)	0.5579 (2)	0.1054 (3)	0.1838 (1)	3.17 (5)
C(12)	0.5952 (2)	-0.0444 (4)	0.1539 (2)	4.55 (6)
C(13)	0.6446 (3)	-0.1556 (4)	0.2166 (2)	5.53 (9)
C(14)	0.7101 (3)	-0.0722 (5)	0.2816 (3)	5.9 (1)
C(15)	0.6589 (2)	0.0472 (3)	0.3214 (2)	3.74 (5)
C(16)	0.5864 (2)	0.1493 (3)	0.2632 (1)	2.76 (4)
C(17)	0.5371 (1)	0.2858 (3)	0.2832 (1)	2.72 (4)
C(18)	0.5179 (2)	0.4328 (3)	0.2303 (1)	3.64 (6)
C(19)	0.4947 (2)	0.3862 (3)	0.1453 (1)	3.58 (5)
C(20)	0.4876 (2)	0.2060 (3)	0.1364 (1)	3.52 (5)
C(21)	0.4381 (2)	0.1746 (4)	0.0521 (2)	5.29 (7)
C(22)	0.3813 (3)	0.3246 (4)	0.0234 (2)	6.93 (9)
C(23)	0.4003 (2)	0.4415 (3)	0.0915 (2)	4.54 (7)
C(24)	0.3203 (3)	0.6684 (5)	0.0245 (2)	8.5 (1)
C(25)	0.5622 (3)	0.1829 (5)	0.4586 (2)	6.21 (9)
C(26)	0.4382 (2)	0.4629 (5)	0.3860 (2)	6.07 (8)
C(27)	0.6527 (2)	0.4818 (4)	0.4185 (2)	5.24 (7)

carbon atoms. Max.  $\Delta/\sigma = 0.03$ ,  $S = 2.21$ , max. peak height in final difference Fourier synthesis  $0.49 \text{ e \AA}^{-3}$ . Inspection of residuals in ranges of  $\sin\theta/\lambda$ , ( $|F_o|$ ) and parity and value of individual indices showed no unusual features or trends. No evidence for secondary extinction in low-angle high-intensity data. The final positional and thermal parameters of the non-hydrogen atoms are given in Table 1.\*

**Discussion.** The numbering scheme used in this study is shown in Fig. 1, and the bond lengths and angles are given in Table 2. The C(13)–C(14) distance is shortened owing to high thermal motion. During the final stages of refinement, the two largest peaks in the difference Fourier synthesis appeared close to these two carbon atoms. This was interpreted as disorder and the two peaks were modeled as minor components C(13') and C(14'). Subsequent refinement of the occupancies for C(13), C(14), C(13'), C(14') showed major and minor components to have approximate occupancies of 0.85 and 0.15, respectively. The occupancies were fixed at the above values and refinement of the positional and thermal parameters was attempted. The positional parameters of the minor components refined poorly. Consequently, both the positional and thermal parameters of the minor components were fixed before the final refinement was done.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39777 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

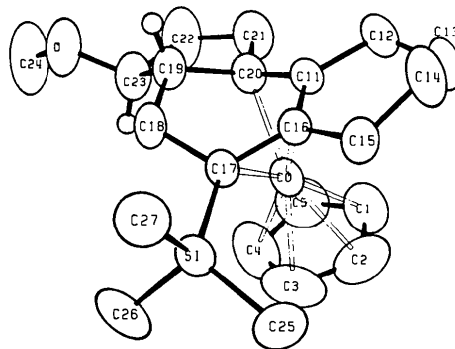


Fig. 1. ORTEP (Johnson, 1965) drawing of the molecule showing the atomic numbering scheme.

Table 2. Bond lengths (Å) and inter-bond angles (°)

The e.s.d.'s given in parentheses, right-adjusted to the least significant digit(s) shown, are calculated including the correlation terms derived from the inverted least-squares matrix. Distances and angles are uncorrected for thermal motion.

Co–C(11)	1.974 (2)	C(14)–C(15)	1.534 (3)
Co–C(16)	1.973 (2)	C(15)–C(16)	1.520 (2)
Co–C(17)	2.035 (1)	C(16)–C(17)	1.442 (2)
Co–C(20)	2.047 (2)	C(17)–C(18)	1.528 (2)
Co–C(1)	2.074 (2)	C(18)–C(19)	1.523 (2)
Co–C(2)	2.091 (2)	C(19)–C(20)	1.510 (2)
Co–C(3)	2.051 (2)	C(19)–C(23)	1.512 (3)
Co–C(4)	2.041 (2)	C(20)–C(21)	1.510 (3)
Co–C(5)	2.031 (2)	C(21)–C(22)	1.507 (3)
		C(22)–C(23)	1.530 (3)
Si–C(17)	1.869 (2)	C(23)–O	1.426 (2)
Si–C(25)	1.871 (2)	O–C(24)	1.412 (3)
Si–C(26)	1.855 (2)		
Si–C(27)	1.865 (2)	C(1)–C(2)	1.362 (4)
		C(2)–C(3)	1.357 (4)
		C(3)–C(4)	1.396 (5)
		C(4)–C(5)	1.394 (4)
		C(5)–C(1)	1.383 (4)
C(11)–C(12)	1.518 (2)		
C(11)–C(16)	1.421 (2)		
C(11)–C(20)	1.410 (2)		
C(12)–C(13)	1.482 (3)		
C(13)–C(14)	1.462 (4)		
Co–C(16)–C(15)	125.65 (12)	C(15)–C(16)–C(17)	124.49 (15)
Co–C(11)–C(12)	124.47 (13)	C(12)–C(11)–C(20)	122.93 (16)
Co–C(17)–Si	123.02 (8)	C(16)–C(11)–C(20)	114.48 (14)
Co–C(17)–C(18)	106.73 (10)	C(11)–C(16)–C(17)	115.35 (14)
Co–C(20)–C(21)	124.88 (14)	C(11)–C(20)–C(19)	120.68 (16)
Co–C(20)–C(19)	109.33 (12)	C(16)–C(17)–C(18)	119.58 (14)
		C(17)–C(18)–C(19)	111.88 (14)
C(17)–Si–C(25)	117.29 (9)	C(18)–C(19)–C(20)	110.45 (15)
C(17)–Si–C(26)	108.58 (9)		
C(17)–Si–C(27)	108.15 (8)	C(11)–C(20)–C(21)	124.49 (16)
C(25)–Si–C(26)	107.95 (12)	C(19)–C(20)–C(21)	106.17 (16)
C(25)–Si–C(27)	106.62 (11)	C(18)–C(19)–C(23)	118.25 (16)
C(26)–Si–C(27)	107.90 (12)	C(20)–C(19)–C(23)	102.28 (15)
Si–C(17)–C(16)	123.44 (12)	C(20)–C(21)–C(22)	105.19 (17)
Si–C(17)–C(18)	110.17 (11)	C(21)–C(22)–C(23)	107.10 (17)
		C(22)–C(23)–C(19)	104.36 (17)
C(16)–C(11)–C(12)	122.45 (16)		
C(11)–C(12)–C(13)	112.80 (17)	C(19)–C(23)–O	109.86 (17)
C(12)–C(13)–C(14)	112.43 (22)	C(22)–C(23)–O	113.22 (18)
C(13)–C(14)–C(15)	112.92 (21)	C(23)–O–C(24)	112.96 (20)
C(14)–C(15)–C(16)	111.95 (17)		
C(15)–C(16)–C(11)	120.00 (15)	C(1)–C(2)–C(3)	108.6 (3)
		C(2)–C(3)–C(4)	108.9 (3)
		C(3)–C(4)–C(5)	106.2 (3)
		C(4)–C(5)–C(1)	107.9 (3)
		C(5)–C(1)–C(2)	108.40 (24)

The bonding of the cyclopentadienyl ring to the cobalt atom is essentially symmetrical. Given the relatively large thermal parameters of the carbon atoms in the cyclopentadienyl ring, the variation in the cobalt-carbon bond lengths is not significant. Two of the butadiene carbon atoms [C(11), C(16)] are about 0.05 Å closer to the cobalt atom than are the other two [C(17), C(20)]. The four atoms are coplanar and the bond lengths between them indicate a delocalized  $\pi$  system. There is also a plane consisting of these four carbon atoms plus C(12) and C(15), and all six atoms are within 0.040 (2) Å of the plane. The atoms C(17) to C(20) are also coplanar to within 0.030 (3) Å. The adjacent six-membered ring [C(11) to C(16)] is twisted with C(14) and C(13) approximately equidistant [0.310 (4) and 0.49 (4) Å] above and below the plane of the other four atoms. The five-membered ring [C(19)-C(23)] is in an envelope conformation with C(19) 0.573 (3) Å out of the plane defined by the other four carbon atoms.

The disposition of the methoxy group [O-C(24)] relative to the rest of the tricyclic ligand was the reason for this study. In this compound, the oxygen and cobalt atoms are on opposite sides of the tricycle (*i.e. exo* with respect to each other) as in structure (1) in the scheme. In a related structure (Clinet, Duñach & Vollhardt, 1983) where the methoxy group is replaced by a benzyloxy substituent (OCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), the oxygen and cobalt atoms are on the same side of the tricycle, as in structure (2) in the scheme. This structure provides a piece of the puzzle regarding the mechanism of cobalt-mediated enediyne cyclizations, and shows that stereochemical control of such cyclizations can be obtained by changing the alkyl substituent of the alkoxy group.

Fig. 2 shows the unit-cell packing.

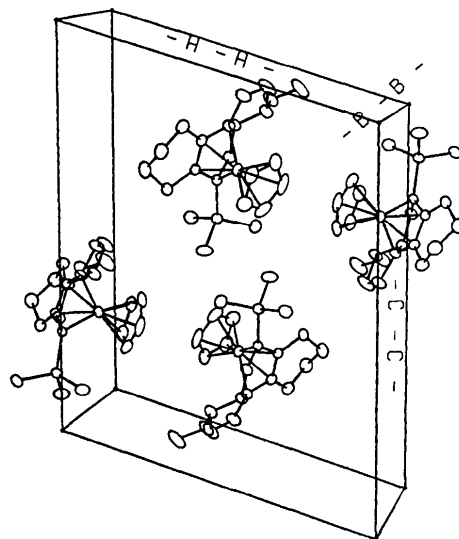


Fig. 2. Arrangement of the molecules in the unit cell.

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### Structure of *trans*-Dichloro[dimethyl(phenyl)phosphine] (*trans*-2,3-dimethylpyrrolidine)platinum(II), [PtCl<sub>2</sub>(C<sub>6</sub>H<sub>13</sub>N)(C<sub>8</sub>H<sub>11</sub>P)]

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**Abstract.**  $M_r = 503.3$ , orthorhombic,  $P2_12_1$ ,  $a = 11.295$  (4),  $b = 11.964$  (3),  $c = 13.200$  (4) Å,  $V = 1783.8$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.874$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 83.3$  cm<sup>-1</sup>,  $F(000) = 968$ , room tem-

perature,  $R = 0.036$  for 2213 observed counter reflections. The coordination sphere of the Pt<sup>II</sup> atom is square-planar with a geometry very similar to that of the studied complexes of the type [PtCl<sub>2</sub>(R<sub>3</sub>P)L] where L is