Grdenić, D. (1965). *Quart. Rev.* **19**, 303–328.
Howells, R. G. (1950). *Acta Cryst.* **3**, 366–369.
Kitaigorodsky, A. I. (1973). *Molecular Crystals and Molecules*, pp. 11–13. New York, London: Academic Press.
Kitaigorodsky, A. I. & Grdenić, D. (1948). *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, p. 262.
Kunchur, N. R. & Mathew, M. (1966). *Chem. Commun.* pp. 71–73.
Kuz'mina, L. G., Bokij, N. G. & Struchkov, Yu. T. (1975). *Usp. Khim.* **44**, 134–155.
Mathew, M. & Kunchur, N. R. (1970). *Canad. J. Chem.* **48**, 429–434.
Vilkov, L. V., Anashkin, M. G. & Mamaeva, G. I. (1968). *Zh. Strukt. Khim.* **9**, 372–378.
Ziółkowska, B. (1962). *Roczn. Chem.* **36**, 1341–1347.
Ziółkowska, B., Myasnikova, R. M. & Kitaigorodsky, A. I. (1964). *Zh. Strukt. Khim.* **5**, 737–742.

Acta Cryst. (1977). B**33**, 589–591

1-Cyclopentadienyl-2,3-dimethylcobalta-2,3-dicarbaheptaborane

By R. Weiss and R. F. Bryan*

Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901, *USA*

(*Received* 7 *July* 1976; *accepted* 1 *October* 1976)

Abstract. $C_9H_{15}B_4Co$, monoclinic, $P2_1/m$, a = 8·284 (1), b = 10·096 (2), c = 6·836 (1) Å, β = 104·95 (5)° (λ = 0·7107 Å), U = 552 Å^3, Z = 2, D_x = 1·355, D_m = 1·33 g cm^{-3}. The structure was solved by the heavy-atom method, and least-squares refinement gave R = 0·050 for 1498 unique significant reflections measured by counter diffractometry. The molecule has a crystallographic mirror plane of symmetry, and the basal plane of the polyhedron and the cyclopentadienyl plane are inclined at 7·5° to one another. The C–C bond in the polyhedron is 1·461 (2) Å and Co–C [2·031 (1) Å] is close to the average Co–C bond length involving the cyclopentadiene residue, 2·036 Å. Co–B lengths are 2·086 (3) and 2·104 (4) Å.

Introduction. The title compound is a cobaltacenium analog with one of the cyclopentadienyl groups of that compound replaced by the doubly charged dimethylcarborane anion to yield a neutral species. The synthesis, spectral characteristics, and other properties of the compound have been previously described (Grimes, Beer, Sneddon, Miller & Weiss, 1974) and we report here its crystal structure.

Crystallization of the compound from a heptane–dichloromethane mixture afforded a needle (0·75 × 0·25 × 0·12 mm) suited to X-ray study. Systematic absences are 0k0 with k odd, indicating space groups $P2_1$ or $P2_1/m$. The latter was chosen, and with Z = 2 requires the molecule to have a mirror plane of symmetry. The correctness of the choice is confirmed by the results of the analysis. Intensity measurements were made by automatic single-crystal diffractometry for a quadrant of reciprocal space ($2\theta \leq 60°$). The θ–2θ scan method was used with monochromatic (HOG) Mo $K\alpha$ radiation, scintillation counting, and pulse-height analysis. Scattered intensity significantly above back-

Table 1. *Heavy-atom parameters and their standard deviations*

Values have been multiplied by 10^4. The temperature factor has the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. E.s.d.'s in parentheses are applicable to the least significant figures given.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	4080 (1)	2500 (–)	2280 (1)	47 (1)	49 (–)	92 (1)	0 (–)	26 (1)	0 (–)
C(2)	1762 (2)	1776 (2)	2120 (3)	67 (2)	57 (2)	121 (4)	–6 (2)	9 (2)	–1 (2)
B(4)	2454 (3)	1177 (3)	402 (4)	108 (3)	98 (3)	164 (5)	–2 (2)	29 (3)	–48 (3)
B(5)	2930 (6)	2500 (–)	–849 (6)	136 (6)	139 (6)	117 (7)	0 (–)	49 (5)	0 (–)
B(7)	980 (5)	2500 (–)	–305 (6)	97 (4)	119 (5)	116 (7)	0 (–)	1 (4)	0 (–)
C(21)	963 (3)	992 (3)	3501 (4)	93 (3)	88 (2)	206 (6)	–20 (2)	33 (3)	33 (3)
C(3*a*)	6436 (4)	2500 (–)	2019 (6)	80 (4)	99 (4)	189 (8)	0 (–)	57 (4)	0 (–)
C(4*a*)	6168 (3)	1365 (3)	3114 (4)	86 (3)	80 (2)	215 (5)	23 (2)	39 (3)	–4 (3)
C(5*a*)	5734 (3)	1800 (3)	4890 (4)	89 (3)	89 (2)	161 (5)	7 (2)	22 (3)	20 (3)

---

* To whom correspondence should be addressed.

Table 2. *Positional parameters* ($\times 10^3$) *for the hydrogen atoms, and isotropic thermal parameters*

	x	y	z	B (Å^2)
H(4)	243 (5)	15 (5)	9 (7)	5·0 (9)
H(5)	349 (6)	250 (–)	–218 (8)	3·3 (10)
H(7)	–40 (6)	250 (–)	–129 (7)	3·0 (9)
H(3*a*)	681 (5)	250 (–)	97 (7)	2·7 (8)
H(4*a*)	634 (5)	48 (5)	271 (6)	4·5 (8)
H(5*a*)	546 (4)	116 (4)	588 (5)	3·4 (7)
H(21)	135 (5)	126 (5)	488 (7)	4·9 (9)
H(21′)	114 (5)	10 (6)	356 (9)	6·0 (10)
H(21″)	–22 (5)	111 (5)	321 (7)	5·2 (9)

ground [$I > 3\sigma(I)$] was recorded at 1498 of the reciprocal-lattice points surveyed, and structure amplitudes derived from these measurements were used in the analysis. The absorption coefficient for the radiation used is 16 cm^{-1}. No correction for absorption was made and, despite the almost 3 : 1 ratio possible in transmission along the minimum and maximum path lengths in the crystal used, errors from this source do not seem too serious.

The heavy-atom method was used in the solution of the structure and the parameters were refined by block-diagonal least squares (3 × 3, 6 × 6 blocks) minimizing

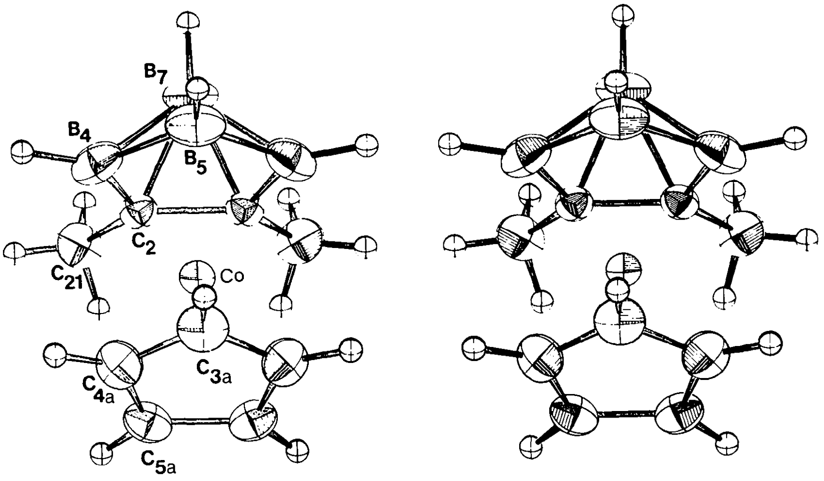

Fig. 1. Stereoscopic view of the molecular structure (*ORTEP*). The mirror plane of symmetry is perpendicular to the plane of the paper. For Co, C and B the thermal ellipsoids are drawn with the 50% probability level as the boundary surface. H atoms are represented by spheres of arbitrary radius.

Table 3. *Selected bond lengths* (Å) *and angles* (°) *with their e.s.d.'s*

Co–C(2)	2·031 (1)	C(2)–C(2′)	1·461 (2)	C(3*a*)–C(4*a*)	1·417 (3)	C(21)–H(21)	0·95 (5)
Co–B(4)	2·086 (3)	C(2)–C(21)	1·510 (3)	C(4*a*)–C(5*a*)	1·421 (3)	C(21)–H(21′)	0·91 (6)
Co–B(5)	2·104 (4)	C(2)–B(4)	1·556 (3)	C(5*a*)–C(5*a*′)	1·414 (3)	C(21)–H(21″)	0·96 (4)
Co–C(3*a*)	2·006 (3)	C(2)–B(7)	1·774 (3)	B(4)–H(4)	1·06 (5)	C(3*a*)–H(3*a*)	0·85 (5)
Co–C(4*a*)	2·030 (2)	B(4)–B(5)	1·686 (4)	B(5)–H(5)	1·12 (5)	C(4*a*)–H(4*a*)	0·96 (5)
Co–C(5*a*)	2·073 (2)	B(4)–B(7)	1·790 (4)	B(7)–H(7)	1·17 (5)	C(5*a*)–H(5*a*)	1·00 (4)
		B(5)–B(7)	1·749 (5)				

Co–C(2)–C(21)	135·8 (2)	C(2)–B(4)–B(5)	104·7 (2)	Co–C(2)–C(2′)	68·9 (1)
C(2)–Co–C(2′)	42·2 (1)	B(4)–B(5)–B(4′)	104·8 (2)	Co–C(2)–B(4)	69·7 (1)
C(2)–Co–B(4)	44·4 (1)	B(7)–B(5)–B(4)	62·8 (2)	Co–B(4)–C(2)	65·9 (1)
B(4)–Co–B(5)	47·5 (1)	B(7)–B(4)–C(2)	63·6 (2)	Co–B(4)–B(5)	66·8 (2)
C(3*a*)–Co–C(4*a*)	41·1 (1)	B(7)–B(4)–B(5)	60·3 (2)	Co–B(5)–B(4)	65·7 (2)
C(4*a*)–Co–C(5*a*)	40·5 (1)	B(7)–C(2)–C(2′)	65·7 (1)	Co–C(3*a*)–C(4*a*)	70·4 (2)
C(5*a*)–Co–C(5*a*′)	39·9 (1)	B(7)–C(2)–B(4)	64·6 (2)	Co–C(4*a*)–C(5*a*)	71·4 (1)
C(2)–B(7)–B(4)	51·8 (2)	B(7)–C(2)–C(21)	133·4 (2)	Co–C(4*a*)–C(3*a*)	68·5 (2)
C(2)–B(7)–C(2′)	48·6 (2)	C(3*a*)–C(4*a*)–C(5*a*)	108·1 (2)	Co–C(5*a*)–C(5*a*′)	70·1 (2)
B(4)–B(7)–B(5)	56·9 (2)	C(4*a*)–C(5*a*)–C(5*a*′)	108·0 (2)	C(21)–C(2)–B(4)	125·1 (2)
C(2′)–C(2)–B(4)	112·9 (2)	C(4*a*)–C(3*a*)–C(4*a*′)	107·8 (2)	C(21)–C(2)–C(2′)	121·6 (2)

the function $\Sigma w(kF_o - F_c)^2$ with a Hughes (1941) weighting scheme being adopted. H atoms were found from a three-dimensional difference electron-density map and their positional and isotropic thermal parameters were refined. At convergence [$\Delta(p) < 0.1\ \sigma(p)$] the conventional weighted and unweighted residuals were 0·061 and 0·050.* Scattering functions were for the neutral atoms (Hanson, Herman, Lea & Skillman, 1964; Stewart, Davidson & Simpson, 1965). All calculations were performed on an XDS Sigma 2 computer with programs written in this laboratory.

Discussion. A stereoscopic view of the molecular structure found in the crystal is shown in Fig. 1. Atomic parameters are given in Tables 1 and 2, and selected bond distances and angles in Table 3. The Co atom is 1·647 Å from the plane of the cyclopentadienyl ring ($\Delta_{\max}$ 0·0001 Å) and 1·566 Å from the basal plane of the carborane moiety ($\Delta_{\max}$ 0·006 Å). The normals to these two planes from the Co atom are inclined at an angle of 172·5°. This non-parallelism does not seem to be steric in origin although the C(21) methyl group is displaced from the basal plane of the carborane in a direction away from the plane of the cyclopentadienyl ring. There are, however, no particularly close contacts between the atoms of the methyl group and those of the cyclopentadienyl ring [C(21)···C(5*a*) 3·91, H(21)···C(5*a*) 3·67, H(21)···H(5*a*) 3·30 Å] and the non-collinearity of the normals is ascribed to *d*-orbital participation in the bonding of the metal atom to the face of the carborane, destroying the psuedo fivefold symmetry and hence removing the degeneracy of the carborane molecular orbitals (Grimes, Rademaker, Denniston, Bryan & Greene, 1972).

The C—C bond distance in the carborane is 1·461 (2) Å, short by comparison with C—C distances in larger metallocarboranes (Greene & Bryan, 1970) but normal for pentagonal pyramidal and bipyramidal carborane structures (Beer, Miller, Sneddon, Grimes, Mathew & Palenik, 1973; Grimes *et al.*, 1974). In $B_4H_6C_2(CH_3)_2$, from which this compound may be regarded as derived by replacement of two bridging hydrogens by a cyclopentadienyl Co moiety, the C—C distance is 1·431 (6), and in $B_4H_6C_2H_2$ 1·419 (6) Å (Boer, Streib & Lipscomb, 1964). Theoretical calculations for the latter compound (Marynick & Lipscomb, 1972) point to the two carbons constituting an ethylenic fragment with π donation to the apex B. The result of replacement of the bridging hydrogens by the cyclopentadienyl Co system is then much as expected with a modest increase in the length of the C—C bond, a change in C(2)—B(4) from 1·520 to 1·556 Å, and a marked contraction of B(4)—B(5) from 1·778 to 1·686 Å on removal of the bridging H. There is no significant change in the lengths of either C(2)—B(7) or the C(2)—methyl bond, but B(5)—B(7) is 1·749 Å in the present compound, 1·705 Å in $B_4H_6C_2(CH_3)_2$.

References

BEER, D. C., MILLER, V. R., SNEDDON, L. G., GRIMES, R. N., MATHEW, M. & PALENIK, G. J. (1973). *J. Amer. Chem. Soc.* **95**, 3046–3048.

BOER, F. P., STREIB, W. E. & LIPSCOMB, W. N. (1964). *Inorg. Chem.* **3**, 1666–1673.

GREENE, P. T. & BRYAN, R. F. (1970). *Inorg. Chem.* **9**, 1464–1471.

GRIMES, R. N., BEER, D. C., SNEDDON, L. G., MILLER, V. R. & WEISS, R. (1974). *Inorg. Chem.* **13**, 1138–1146.

GRIMES, R. N., RADEMAKER, W. J., DENNISTON, M. L., BRYAN, R. F. & GREENE, P. T. (1972). *J. Amer. Chem. Soc.* **94**, 1865–1869.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.

MARYNICK, D. S. & LIPSCOMB, W. N. (1972). *J. Amer. Chem. Soc.* **94**, 8699–8706.

STEWART, R. F., DAVIDSON, E. R., SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32191 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.