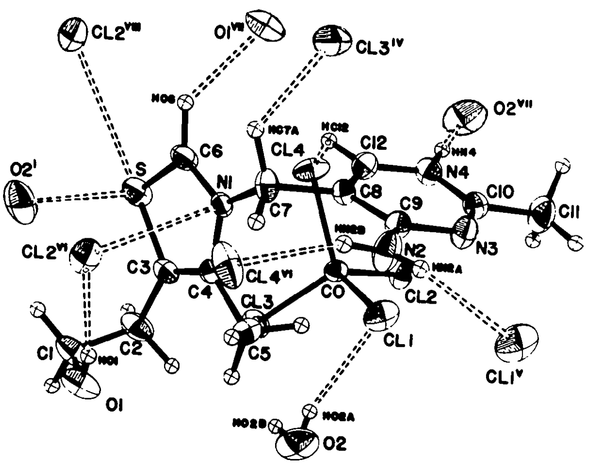

Fig. 1. The $HThi^{2+}$ and $CoCl_4^{2-}$ ions, showing the numbering scheme and thermal ellipsoids. The view is down the x axis. Short contacts other than hydrogen bonds are: N(1)$\cdots$Cl(2^{vi}) 3·265 (3), S$\cdots$Cl(2^{viii}) 3·350 (1), S$\cdots$O(2^{i}) 3·413 (3) Å. Symmetry superscripts (chosen to correspond to $HThiCdCl_4.H_2O$): (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (v) $1-x, -y, -z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vii) $x, y, -1+z$; (viii) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

$HThiCoCl_4.H_2O$ is isostructural with $HThiCdCl_4.H_2O$ (Richardson, Franklin & Thompson, 1975). The main difference between the two structures lies in the locations of the metal and chlorine atoms, since cobalt has a smaller radius than cadmium. The Co—Cl distances range from 2·2563 (8) to 2·2934 (8) Å, compared to Cd—Cl 2·432–2·465 Å in $HThiCdCl_4.H_2O$. Nonetheless, the tetrachlorocobaltate anion is a nearly regular tetrahedron, as is the tetrachlorocadmate anion. Distances and angles other than those involving cobalt and chlorine are essentially the same as in $HThiCdCl_4.H_2O$.

The smaller tetrachlorocobaltate anion has an essentially negligible effect on the thiamine conformation. The C(8)—C(7)—N(1)—C(6) and N(1)—C(7)—C(8)—C(9) torsion angles are 111·6 (2) and 135·6 (2)° respectively, nearly the same as observed for $HThiCdCl_4.H_2O$ (110·4 and 137·3°, respectively). Thus, the extent to which a large anion stabilizes the *S* conformation, and the mechanism by which it effects this stabilization are still uncertain.

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Acta Cryst. (1983). C**39**, 856–858

Structural Characterization of 3-η-Cyclopentadienyl-1,2-dimethyl-1,2-dicarba-3-cobalta-*closo*-octaborane, $1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$

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Abstract. $M_r = 237·22$, monoclinic, $P2_1/n$, $a = 11·534$ (5), $b = 13·618$ (8), $c = 7·754$ (4) Å, $\beta = 103·11$ (1)°, $V = 1187$ (2) Å^3, $Z = 4$, $F(000) = 488$, $D_x = 1·327$ g cm^{-3}, D_m not measured, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 14·549$ cm^{-1}, 298 K. The structure was refined by the full-matrix least-squares method to a final R of 0·040 and R_w of 0·056 for the 1775 reflections with $F_o^2 > 3\sigma(F_o^2)$. In agreement with the structure previously proposed based on the spectroscopic data, the compound is shown to be a cyclopentadienyl substituted cobaltacarborane cage complex in which the

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cage atoms adopt a closed dodecahedral-type geometry with the C and Co atoms occupying adjacent positions.

Introduction. The complex, 1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$, was originally obtained along with a number of other new cobaltacarborane complexes as a product of the reaction of thermally generated cobalt atoms with cyclopentadiene, 2-butyne and hexaborane(10) (Zimmerman, Hall & Sneddon, 1980). We report here the crystal structure of this complex which confirms the structure previously proposed.

Experimental. Red–orange parallelepiped crystal, 0·58 × 0·20 × 0·08 mm, grown by vapor diffusion of heptane into a methylene chloride solution of the compound; preliminary precession photographs indicated systematic absences characteristic of $P2_1/n$; Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, cell parameters determined from least-squares refinement of 25 reflections with $16 < 2\theta < 30°$; coupled $\omega/2\theta$ scan, $2\theta_{max} = 50°$, $-h, k, \pm l$: h 0–$\overline{13}$, k 0–16, l 9–$\overline{9}$; intensities of three standard reflections, 00$\overline{4}$, 04$\overline{2}$, and 3$\overline{1}$0, monitored every 4000 s, showed no significant variations (<5%); 2194 measured intensities, 2084 unique, 1775 with $F_o^2 > 3\sigma(F_o^2)$, Lorentz–polarization and numerical absorption (maximum transmission 89·3%, minimum 65·6%) corrections; position of Co atom obtained from Patterson synthesis, positions of B and C atoms determined from successive Fourier maps; difference Fourier map located 5 hydrogen atoms bonded to boron atoms, the remaining 11 H positions were calculated (C—H = 0·95 Å) but not refined; full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms and isotropic thermal parameters for the H atoms, $R = 0{\cdot}040$ and $R_w = 0{\cdot}056$, greatest parameter shift in the final least-squares cycle was 0·05 its standard deviation, the e.s.d. of an observation of unit weight was 3·38, quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [4F_o/\sigma(F_o^2)]^2$; atomic scattering factors for non-hydrogen atoms from Cromer & Waber (1974), for hydrogen from Stewart, Davidson & Simpson (1965), anomalous-dispersion corrections from Cromer & Ibers (1974), maximum height in the final difference Fourier map was 0·35 e Å^{-3}, all calculations on a PDP 11/60 computer using the Enraf–Nonius structure determination package.

Discussion. The atomic parameters are given in Table 1.* The molecular structure of 1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$ is depicted in the *ORTEP* drawing (Johnson, 1965) shown in Fig. 1, and selected bond distances and angles are presented in Table 2.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Co	0·21174 (4)	0·10020 (3)	0·24385 (5)	2·8
C(11)	0·4849 (4)	0·1489 (4)	0·3115 (6)	5·6
C(21)	0·3049 (3)	0·2728 (3)	0·0369 (5)	4·5
C(31)	0·1550 (4)	0·0548 (3)	0·4564 (5)	7·2
C(32)	0·2318 (5)	0·1309 (5)	0·5073 (6)	8·2
C(33)	0·1878 (6)	0·2094 (4)	0·4193 (6)	9·4
C(34)	0·0897 (5)	0·1899 (5)	0·3108 (6)	10·6
C(35)	0·0615 (4)	0·0925 (5)	0·3307 (6)	9·3
C(1)	0·3739 (3)	0·1072 (3)	0·1970 (4)	3·4
C(2)	0·2890 (3)	0·1646 (3)	0·0691 (4)	3·0
B(4)	0·3569 (4)	0·0707 (3)	−0·0211 (5)	3·6
B(6)	0·1911 (3)	0·0937 (3)	−0·0463 (5)	3·1
B(5)	0·3387 (4)	−0·0062 (3)	0·1766 (5)	3·5
B(7)	0·1779 (4)	−0·0156 (3)	0·0885 (5)	3·5
B(8)	0·2632 (4)	−0·0232 (3)	−0·0502 (5)	3·8
HB(4)	0·426 (3)	0·094 (2)	−0·095 (4)	4·3
HB(6)	0·123 (3)	0·119 (2)	−0·153 (4)	3·5
HB(5)	0·397 (3)	−0·048 (3)	0·262 (4)	4·7
HB(7)	0·104 (3)	−0·067 (3)	0·099 (4)	4·5
HB(8)	0·262 (4)	−0·079 (3)	−0·144 (5)	6·0

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Co—C(31)	2·005 (2)	B(4)—B(6)	1·904 (3)
Co—C(32)	2·046 (3)	B(4)—B(5)	1·907 (3)
Co—C(33)	2·076 (3)	B(4)—B(8)	1·657 (4)
Co—C(34)	2·020 (3)	B(6)—B(7)	1·847 (3)
Co—C(35)	1·999 (3)	B(6)—B(8)	1·801 (3)
Co—C(1)	1·986 (2)	B(5)—B(8)	1·791 (3)
Co—C(2)	1·987 (2)	B(5)—B(7)	1·830 (3)
Co—B(6)	2·210 (2)	B(7)—B(8)	1·617 (3)
Co—B(5)	2·206 (2)	C(31)—C(32)	1·363 (5)
Co—B(7)	1·970 (2)	C(32)—C(33)	1·308 (6)
C(1)—C(2)	1·453 (2)	C(33)—C(34)	1·275 (6)
C(1)—B(4)	1·730 (3)	C(34)—C(35)	1·382 (6)
C(1)—B(5)	1·597 (3)	C(35)—C(31)	1·379 (6)
C(1)—C(11)	1·495 (3)	HB(4)—B(4)	1·13 (2)
C(2)—B(4)	1·728 (3)	HB(6)—B(6)	1·05 (2)
C(2)—B(6)	1·597 (3)	HB(5)—B(5)	1·01 (2)
C(2)—C(21)	1·513 (3)	HB(7)—B(7)	1·12 (2)
		HB(8)—B(8)	1·05 (2)

C(1)—C(2)—B(6)	109·8 (2)	B(7)—Co—C(1)	89·5 (1)
C(2)—B(6)—B(7)	108·0 (2)	B(7)—Co—C(2)	89·6 (1)
B(6)—B(7)—B(5)	87·0 (2)	Co—C(1)—C(11)	128·7 (2)
B(7)—B(5)—C(1)	108·5 (2)	Co—C(2)—C(21)	129·2 (1)
B(5)—C(1)—C(2)	109·7 (2)	C(1)—C(2)—C(21)	123·3 (2)
B(5)—B(8)—B(6)	89·6 (1)	C(2)—C(1)—C(11)	123·7 (2)
B(7)—B(8)—B(4)	109·7 (1)	C(32)—C(31)—C(35)	105·8 (3)
B(8)—B(4)—C(1)	106·3 (2)	C(31)—C(32)—C(33)	108·8 (4)
B(8)—B(4)—C(2)	106·6 (2)	C(32)—C(33)—C(34)	111·0 (4)
B(5)—B(4)—B(6)	83·3 (1)	C(33)—C(34)—C(35)	108·9 (4)
B(5)—Co—B(6)	70·0 (1)	C(34)—C(35)—C(31)	105·8 (3)

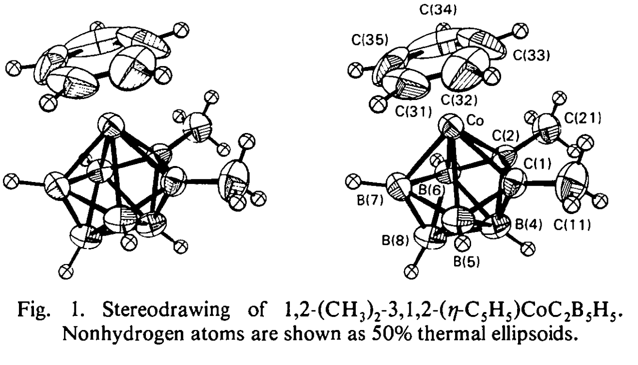

Fig. 1. Stereodrawing of 1,2-$(CH_3)_2$-3,1,2-(η-C_5H_5)$CoC_2B_5H_5$. Nonhydrogen atoms are shown as 50% thermal ellipsoids.

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* Lists of structure factors, anisotropic thermal parameters, calculated hydrogen positions, and mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38471 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The overall cage geometry of the complex is seen to be based on a closed dodecahedral structure in which the Co and C atoms occupy adjacent positions on a triangulated face. Such a cage structure is in agreement with that previously proposed (Zimmerman, Hall & Sneddon, 1980) and is consistent with skeletal electron-counting rules (Wade, 1976) which predict a closed polyhedral cage for such a $2n + 2$ electronic system (8 cage atoms, 18 skeletal electrons). Similar cage geometries have been confirmed for isoelectronic cage systems, $1,7\text{-}(CH_3)_2C_2B_6H_6$ (Hart & Lipscomb, 1968), $B_8H_8^{2-}$ (Guggenberger, 1969), and *commo*-$[\eta\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$ (Finster, Sinn & Grimes, 1981) and proposed based on the NMR data for the isomeric complex, $3,1,7\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_7$ (Miller & Grimes, 1973). In addition, it should be noted that closed dodecahedral cage structures have also been observed for boron clusters with other skeletal electron counts. For example, B_8Cl_8 (Pawley, 1966; Jacobson & Lipscomb, 1958, 1959) and $(\eta\text{-}C_5H_5)_4Co_4B_4H_4$ (Pipal & Grimes, 1979), which are both $2n$ electron cage systems, and $(\eta\text{-}C_5H_5)_4Ni_4B_4H_4$ (Bowser, Bonny, Pipal & Grimes, 1979), which has a $2n + 4$ skeletal electron count, have each been shown to adopt such a cage structure. Thus, as noted previously (Pipal & Grimes, 1979) the dodecahedral cage structure appears to be a favored geometry for eight-vertex boron clusters.

In $1,2\text{-}(CH_3)_2\text{-}3,1,2\text{-}(\eta\text{-}C_5H_5)CoC_2B_5H_5$, the atoms C(1), C(2), B(7) and B(8) occupy four-coordinate positions, while Co and B(4), B(5) and B(6) are in five-coordinate positions in the cage. In general the distances and angles observed in the cage are normal and within the ranges observed for metallacarborane complexes (Grimes, 1982). The B(7)—B(8) distance, 1·617 (3) Å, is somewhat short; however, it is longer than the comparable distance, 1·56 (3) Å, observed between four-coordinate borons in $B_8H_8^{2-}$. Likewise, the B(4)—B(5) and B(4)—B(6) distances are long, 1·907 (3) and 1·904 (3) Å respectively, but are again similar to the distances reported between the five-coordinate borons in $B_8H_8^{2-}$, $1,7\text{-}(CH_3)_2C_2B_6H_6$ and *commo*-$[\eta\text{-}C_5(CH_3)_5]_2Co_3(CH_3)_4C_4B_8H_7$.

The bonding of the Co atom to the cyclopentadienyl ring appears normal, with an average Co—ring carbon distance of 2·029 (3) Å and an average C—C ring distance of 1·341 (6) Å.

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Carbonatobis(triisopropylphosphine)platinum(II), $C_{19}H_{42}O_3P_2Pt$

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Abstract. $M_r = 575\cdot59$, monoclinic, space group $P2/c$, $a = 11\cdot223$ (1), $b = 9\cdot901$ (1), $c = 13\cdot505$ (1) Å, $\beta = 128\cdot67$ (1)°, $U = 1176\cdot0$ Å^3, $Z = 2$, $D_x = 1\cdot63$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0\cdot7093$ Å, $\mu = 5\cdot862$ mm^{-1}, $T = 295$ (2) K. Final $R = 0\cdot014$ for 3158 unique observed reflections. Principal bond lengths and angles are Pt—P 2·263 (1), Pt—O 2·060 (2), —O—C 1·330 (2), C=O 1·212 (4) Å, P—Pt—P 108·04 (4), P—Pt—O 93·98 (5) and O—Pt—O 64·2 (1)°. The molecular geometry is compared with that in the corresponding triphenylphosphine complex.

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