An Example of a Facial Hydrogen Atom Attempting to Bridge All Five Atoms of an Open Pentagonal B_3C_2 Face. The Crystal and Molecular Structure of $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$, Including the Location and Refinement of All Hydrogen Atoms

Melvyn Rowen Churchill* and Barry G. DeBoer

Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. Received April 24, 1974

Abstract: The species $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$, with $a = 10.0216$ (9) Å, $b = 10.9913$ (11) Å, $c = 14.5535$ (13) Å, $\beta = 98.57$ (1)°, $V = 1585.2$ (3) Å, ρ(obsd) = 1.347 (5), ρ(calcd) = 1.343 g cm⁻³, and $Z = 4$. X-Ray diffraction data complete to $2\theta = 62.5°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved using a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms (including the 20 hydrogen atoms) were accurately located, the final discrepancy indices being $R_F = 4.60\%$ and $R_{wF} = 3.36\%$ for the 5197 independent reflections. The molecule is zwitterionic and may be regarded as formed from a cobaltocenium cation and a $[B_9C_2H_{12}^-]$ anion, which are linked *via* a carbon–carbon bond with concomitant loss of a terminal hydrogen atom from each species, thereby yielding the molecular formula $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$. The cobaltocenium residue is fairly regular, with cobalt–carbon distances ranging from 2.0207 (17) to 2.0666 (12) Å and carbon–carbon bond lengths ranging from 1.387 (3) to 1.428 (2) Å. The carborane anion is linked to the cobaltocenium cation *via* atom C(1), with C(1)–CP(1) = 1.480 (2) Å. The remaining ten atoms of the icosahedral B_9C_2 "nest" bear apical hydrogen atoms, with C(2)–H = 0.991 (14) Å and B–H(terminal) = 1.045 (14)–1.152 (15) Å. The "extra" (facial) hydrogen atom, H(FAC), lies asymmetrically above the open pentagonal face defined by C(1)–B(4)–B(8)–B(7)–C(2). Its bonding is principally to atom B(8) (H(FAC)–B(8) = 1.331 (22) Å), but it clearly interacts appreciably with atoms B(4) and B(7) (H(FAC)⋯B(4) = 1.631 (22) and H(FAC)⋯B(7) = 1.636 (22) Å) and interacts weakly with atoms C(1) and C(2) (H(FAC)⋯C(1) = 2.009 (22) Å and H(FAC)⋯C(2) = 1.976 (22) Å).

The reaction of the $[B_{10}C_2H_{12}^{2-}]$ ion with excess $Na^+C_5H_5^-$ and excess $CoCl_2$ has been shown[1,2] to yield a species of molecular formula $(\pi\text{-}C_5H_5)Co(\pi\text{-}B_{10}C_2H_{12})$, the structure of which has been reported previously.[3,4] The complex presently under consideration, $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$, occurs as a side product in the above reaction.[5] Its stoichiometry and stereochemistry were elucidated only by the present structural analysis.

As outlined below, the observed structure is of considerable interest because it reveals an unusual zwitterionic cobaltocenium derivative and it is (to our knowledge) the first reported for a (substituted) $[B_9C_2H_{12}^-]$ ion. Apart from a presumed association with the open face, the "extra" hydrogen atom of the $[B_9C_2H_{12}^-]$ anion has not previously been located nor has a definitive location been assigned. The present study show this "extra" hydrogen atom to be present in a unique, multiply bridging environment.

Collection and Reduction of the X-Ray Diffraction Data

Orange crystals of $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ were provided by Professor M. F. Hawthorne of the University of California at Los Angeles. The crystal used during the diffraction study was a rather irregular truncated wedge ($\sim0.47 \times 0.48 \times 0.54$ mm) which

had been cut from a much larger crystal ($\sim$(4 mm)³). The crystal was sealed inside a thin-walled Lindemann glass capillary, which was fixed into a brass pin on a eucentric goniometer. Preliminary precession and cone-axis photographs gave approximate cell dimensions, indicated C_{2h} (2/m) Laue symmetry, and exhibited the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with the centrosymmetric space group $P2_1/c$ (C_{2h}^5; No. 14).[6]

The crystal was transferred to a Picker FACS-1 computer-controlled diffractometer, was accurately centered, and was orientated so as to place [011] precisely coincident with the instrumental ϕ axis. The apparatus and experimental technique were as described previously.[7] Details specific to the present analysis are given in Table I. The validity of the applied absorption correction was checked by measuring the strong 022 reflection (by a θ–2θ scan) at $\chi = 90°$ and at 10° intervals of ϕ from $\phi = 0°$ to $\phi = 350°$. The observed variation of $\sim11\%$ was reduced to $\sim2\%$ after correcting these data for absorption.

Solution and Refinement of the Structure

Programs used in determining the structure included FORDAP (Fourier Synthesis, by A. Zalkin), LSHF (a version of C. T. Prewitt's SFLS5, highly modified by B. G. DeBoer,) STAN1 (distances and angles, with estimated standard deviations, by B. G. DeBoer), PLOD (least-squares planes, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral cobalt, carbon, and boron were taken from the compilation of Cromer and Waber.[8] Both the real and the imaginary components of anomalous dispersion were included in the calculated structure factor, using the values of Cromer and Liberman.[9] The scattering factors of Stewart, Davidson, and

(1) G. B. Dunks, M. M. McKown, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 2541 (1971).

(2) D. F. Dustin, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **95**, 1109 (1973).

(3) M. R. Churchill and B. G. DeBoer, *J. Chem. Soc., Chem. Commun.*, 1326 (1972).

(4) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **13**, 1411 (1974).

(5) Personal communication from Professor M. F. Hawthorne and Dr. D. F. Dustin.

(6) "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 99.

(7) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973).

(8) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(9) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

Table I. Experimental Data for X-Ray Diffraction Study of $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$

(A) Crystal Parameters (at 24°)[a]

$a = 10.0216 (9)$ Å
$b = 10.9913 (11)$ Å
$c = 14.5535 (13)$ Å
$\cos \beta = -0.14904 (15)$
$\beta = 98.57 (1)°$
$V = 1585.2 (3)$ Å³
Space group, $P2_1/c$
$Z = 4$[b]
Mol wt = 320.53
$\rho(\text{calcd}) = 1.343$ g cm⁻³
$\rho(\text{obsd}) = 1.347 (5)$ g cm⁻³ [c]

(B) Intensity Measurements

Crystal orientation, ϕ axis = [011]
Reflections measured, hkl for $h, k \geq 0$; $0kl$ for $l \geq 0$
Maximum 2θ, 62.5°
Radiation, Mo $K\alpha$, Nb foil post-filter
Attenuators, Cu foil; used if $I > 10^4$ counts sec⁻¹
Takeoff angle, 4.0°
Detector aperture: 4.5×4.5 mm; 330 mm from crystal
Scan type, θ(crystal)–2θ(counter)
Scan speed, 2.0°/min
Scan length, $\Delta(2\theta) = (1.50 + 0.692 \tan \theta)°$, starting 0.75° below the Mo $K\alpha_1$ peak.
Background counts, stationary, 20 sec each at beginning and end of 2θ scan
Standard reflections, three remeasured after every 48 reflections; rms deviations were 0.68% for 400, 0.75% for 048, 0.77% for 033. No decay correction applied
Reflections collected, 5199 independent measurements, plus 270 systematic absences

(C) Data Treatment

Conversion to $|F_o|$ and $\sigma(|F_o|)$ as in ref 7, using $p = 0.02$. Corrected for β-filter absorption as in ref 7. Corrected for absorption[d]: $\mu = 11.065$ cm⁻¹; max and min transmission factors were 0.720 and 0.614.

[a] Unit cell parameters are from a least-squares fit to the setting angles of the resolved Mo $K\alpha_1$ peaks (λ 0.70926 Å) of 12 reflections ($2\theta = 46–65°$). Maximum and root-mean-square disagreements were 0.022 and 0.010°, respectively. See ref 7. [b] No crystallographic symmetry is imposed upon the molecule. [c] Neutral buoyancy in aqueous BaI₂. [d] Using the Fortran IV program DRAB, by B. G. DeBoer.

Simpson[10] were used for hydrogen. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(|F_o|)$. Discrepancy indices used below are defined as follows

$$R_F = \left[\frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}\right] \times 100 \ (\%)$$

$$R_{wF} = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w|F_o|^2}\right]^{1/2} \times 100 \ (\%)$$

The analysis was begun using only data with $(\sin \theta/\lambda) < 0.5$ (1652 independent reflections). The position of the cobalt atom was determined from a three-dimensional Patterson map; an observed Fourier synthesis, phased only by this one atom, led to the location of all nonhydrogen atoms. Refinement of all positional parameters, anisotropic thermal parameters for the cobalt atom, and isotropic thermal parameters for the other nonhydrogen atoms, led to convergence with $R_F = 8.3\%$ and $R_{wF} = 11.3\%$. A difference Fourier at this stage yielded the approximate locations of all hydrogen atoms (19 terminal, 1 "facial"). Terminal hydrogen atoms were included in calculated positions (using $d(\text{C–H}) = 0.95$ Å[11] and

$d(\text{B–H}) = 1.12$ Å[12]), but the "facial" hydrogen atom was deliberately omitted. Refinement of all positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms led to convergence with $R_F = 3.38\%$ and $R_{wF} = 4.24\%$. A difference Fourier synthesis revealed the "facial" hydrogen, H(FAC), as its largest feature ($\rho = 0.45$ e Å⁻³), in essentially the same position as before; the other features of this map were (in order) a peak of 0.31 e Å⁻³ between CP(7) and HCP(7) and peaks of 0.25 and 0.23 e Å⁻³ close to the position of the cobalt atom; all other features were less than 0.20 e Å⁻³. Inclusion of H(FAC) and refinement led to convergence at $R_F = 3.13\%$ and $R_{wF} = 3.83\%$ for the low angle data.

All 5199 data were now included; several cycles of full-matrix least-squares refinement led to $R_F = 4.63\%$ and $R_{wF} = 3.97\%$ (or $R_F = 4.60\%$ and $R_{wF} = 3.36\%$ upon omission of the (presumably unreliable) $20\bar{2}$ and 510 reflections for which $\Delta F/\sigma(F) > 15$). Final shifts were as follows: $<0.09 \ \sigma$ for all nonhydrogen atoms' positional parameters, $<0.35\sigma$ for all hydrogen atoms' positional parameters, $<0.37\sigma$ for all anisotropic thermal parameters, $<0.92\sigma$ for all isotropic thermal parameters. The final value of the "goodness-of-fit," defined as $[\Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, was 1.521. The number of data (n) was 5197, and the number of parameters (m) was 279 ($n/m = 18.63$). The function $\Sigma w(|F_o| - |F_c|)^2$ was not appreciably dependent either upon $\sin \theta$ or on $|F_o|$, thereby indicating a correctly assigned weighting scheme.

It should be noted that *no reflections were rejected on the basis of being "not significantly above background"* (cf. ref 7). Thus, ca. 25.2% of the data had $I < 3\sigma(I)$ and ca. 13.4% had $I < \sigma(I)$. The advantage of retaining these data is, of course, the increased $n:m$ ratio (*vide supra*) and concomitantly lower esd's; the single disadvantage is an unimportant, but cosmetically displeasing, higher value for R_F.

The largest peaks on a final difference Fourier synthesis (based on all 5199 data) were of height 0.44 and 0.41 e Å⁻³. (Both these and the next five most significant features are close to the π-cyclopentadienyl rings or to the cobalt atom.) Note that the residual peaks on *this* difference Fourier map are larger than those on the map synthesized only from data with $\sin \theta/\lambda < 0.5$. We refer the reader to a discussion by Cruickshank.[13] "The "error" in ρ [the electron density] evidently increases with the number of observations, contrary to one's natural instinct that a result ought to become more accurate as the number of observations increases. The resolution of this paradox is that…[the so-called "error"]…is not strictly the error in the electron density, which would need an infinite number of terms, but [is] the error in a particular truncated series."

In other words, the error formula referred to[13] neglects the error contributions represented by the omitted (larger $\sin \theta/\lambda$) terms. In the case of an "observed" Fourier synthesis an omitted term contributes an error equal to its $|F|$, leading to the much-discussed "series-termination errors." Conversely, omitting a term from a difference $(|F_o| - F_c|)$ synthesis is equivalent to assuming *perfect* agreement of $|F_o|$ and $|F_c|$, leading to an under-estimation of the "difference density" obtainable from real experimental measurements. Thus, the magnitude of the features in a difference synthesis is *expected* to increase with an increasing number of included terms, consistent with our observation above. (Presumably the increase is an asymptotic approach to a limit so long as it is statistically true that each $|F_o|$ is a better approximation to the true $|F|$ than would be, say, a value assigned from the extrapolation of a Wilson plot; *i.e.*, so long as the variation or width of the distribution of $|F_o|$'s is greater than $\sim\sigma(|F_o|)$.)

A table of observed and calculated structure factor amplitudes is available.[14] Atomic coordinates and isotropic thermal parameters, with their estimated standard deviations (esd's), are shown in Table II. Anisotropic thermal parameters (with esd's) are collected in Table III.

Description of the Molecular Structure

Interatomic distances and their esd's are given in Table IV; bond angles, with esd's, are shown in Table

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965). The "best floated spherical H atom" values of Table II, p 3178, were used.

(11) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

(12) M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 2674 (1973).

(13) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, Oxford, England, 1965; see Chapter 13, pp 107–111.

(14) See paragraph at end of paper regarding supplementary material.

Table II. Atomic Coordinates and Isotropic Thermal Parameters, with Esd's, for $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})^{a,b}$

Atom	x	y	z	B, Å^2
Co	0.788277 (17)	0.230669 (16)	0.188563 (11)	2.320
CP(1)	0.62198 (12)	0.18673 (12)	0.09249 (8)	2.31
CP(2)	0.72574 (13)	0.24236 (14)	0.04955 (8)	2.89
CP(3)	0.84365 (14)	0.16961 (16)	0.06842 (10)	3.38
CP(4)	0.81539 (15)	0.07148 (14)	0.12415 (11)	3.52
CP(5)	0.67955 (14)	0.08147 (12)	0.13984 (10)	2.96
CP(6)	0.85683 (18)	0.21979 (19)	0.32681 (10)	4.51
CP(7)	0.95121 (17)	0.28049 (23)	0.28026 (13)	5.36
CP(8)	0.88956 (25)	0.38234 (20)	0.23640 (14)	5.97
CP(9)	0.75614 (23)	0.38707 (18)	0.25583 (13)	5.44
CP(10)	0.73710 (16)	0.28631 (18)	0.31125 (11)	4.40
C(1)	0.48190 (12)	0.22984 (11)	0.09181 (8)	2.24
C(2)	0.44637 (14)	0.35827 (13)	0.05086 (11)	3.28
B(4)	0.39917 (15)	0.19937 (14)	0.17737 (10)	2.59
B(5)	0.35058 (15)	0.13003 (14)	0.06642 (11)	2.69
B(6)	0.38880 (17)	0.23505 (17)	−0.01789 (11)	3.35
B(7)	0.33658 (19)	0.43132 (15)	0.09971 (15)	3.71
B(8)	0.28779 (17)	0.32930 (16)	0.18661 (13)	3.29
B(9)	0.22818 (15)	0.19473 (15)	0.12661 (11)	2.87
B(10)	0.22045 (17)	0.21824 (17)	0.00395 (12)	3.45
B(11)	0.28796 (19)	0.36535 (18)	−0.01199 (14)	3.96
B(12)	0.18855 (17)	0.34388 (16)	0.07629 (13)	3.53
HCP(2)	0.7191 (14)	0.3211 (14)	0.0146 (10)	2.9 (3)
HCP(3)	0.9187 (17)	0.1907 (15)	0.0514 (11)	3.8 (4)
HCP(4)	0.8722 (16)	0.0115 (15)	0.1505 (11)	4.0 (4)
HCP(5)	0.6353 (15)	0.0270 (14)	0.1785 (11)	3.5 (3)
HCP (6)	0.8744 (21)	0.1427 (20)	0.3598 (14)	7.5 (6)
HCP(7)	1.0135 (21)	0.2545 (17)	0.2746 (14)	5.6 (7)
HCP(8)	0.9198 (20)	0.4356 (19)	0.1968 (14)	6.9 (6)
HCP(9)	0.6886 (26)	0.4471 (24)	0.2372 (17)	10.2 (8)
HCP(10)	0.6519 (22)	0.2659 (16)	0.3284 (14)	5.4 (5)
H(FAC)	0.4181 (22)	0.3468 (20)	0.1820 (15)	8.1 (6)
HC(2)	0.5208 (14)	0.4049 (13)	0.0298 (9)	2.9 (3)
HB(4)	0.4464 (15)	0.1394 (14)	0.2387 (11)	3.9 (4)
HB(5)	0.3683 (14)	0.0375 (13)	0.0567 (10)	3.0 (3)
HB(6)	0.4251 (18)	0.2106 (15)	−0.0817 (13)	4.9 (4)
HB(7)	0.3338 (17)	0.5264 (17)	0.1064 (12)	5.2 (4)
HB(8)	0.2453 (15)	0.3521 (14)	0.2517 (10)	3.6 (3)
HB(9)	0.1533 (14)	0.1373 (14)	0.1553 (10)	3.2 (3)
HB(10)	0.1374 (17)	0.1762 (16)	−0.0449 (12)	4.7 (4)
HB(11)	0.2616 (19)	0.4212 (20)	−0.0743 (14)	6.9 (5)
HB(12)	0.0867 (16)	0.3813 (14)	0.0734 (11)	3.9 (4)

^{a} Estimated standard deviations, shown in parentheses, are right-adjusted to the last digit of the preceding number and are those derived from the inverse of the least-squares matrix. ^{b} For nonhydrogen atoms, the "equivalent isotropic thermal parameters" are listed. They correspond to the average of the mean-square displacements along the three principal axes of the anisotropic thermal ellipsoid.

Table III. Anisotropic Thermal Parameters,^{a} with Esd's,^{b} for Nonhydrogen Atoms in the $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ Molecule

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U \rangle^c$
Co	2.233 (7)	2.685 (7)	2.004 (7)	−0.173 (6)	0.185 (5)	−0.267 (6)	0.153, 0.171, 0.188
CP(1)	2.33 (5)	2.41 (5)	2.09 (4)	0.06 (4)	0.03 (4)	−0.27 (4)	0.153, 0.171, 0.187
CP(2)	2.67 (5)	4.03 (7)	1.99 (5)	0.28 (5)	0.43 (4)	−0.01 (4)	0.158, 0.182, 0.227
CP(3)	2.45 (5)	4.95 (8)	2.78 (6)	0.56 (5)	0.47 (4)	−0.97 (5)	0.161, 0.183, 0.263
CP(4)	2.86 (6)	3.31 (6)	4.09 (7)	0.97 (5)	−0.49 (5)	−1.03 (5)	0.163, 0.186, 0.270
CP(5)	2.75 (5)	2.27 (5)	3.65 (6)	0.12 (4)	−0.25 (5)	−0.18 (4)	0.168, 0.176, 0.231
CP(6)	4.31 (8)	6.69 (11)	2.30 (6)	−0.23 (7)	−0.28 (5)	−0.47 (6)	0.163, 0.244, 0.292
CP(7)	2.74 (7)	9.35 (16)	3.88 (8)	−1.35 (8)	0.12 (6)	−2.71 (9)	0.159, 0.212, 0.365
CP(8)	8.26 (14)	5.40 (11)	4.38 (9)	−3.90 (11)	1.34 (9)	−1.90 (8)	0.165, 0.243, 0.375
CP(9)	7.37 (13)	4.27 (9)	4.49 (9)	0.71 (9)	0.29 (8)	−2.22 (7)	0.164, 0.275, 0.323
CP(10)	3.57 (7)	6.92 (11)	2.86 (6)	−0.49 (7)	0.91 (5)	−1.72 (7)	0.164, 0.211, 0.310
C(1)	2.22 (4)	2.18 (4)	2.27 (4)	−0.01 (4)	0.18 (3)	0.09 (4)	0.162, 0.166, 0.176
C(2)	2.94 (6)	2.63 (6)	4.39 (7)	0.43 (5)	0.93 (5)	0.90 (5)	0.167, 0.188, 0.248
B(4)	2.43 (5)	2.80 (6)	2.48 (6)	−0.32 (4)	0.18 (4)	0.11 (4)	0.168, 0.177, 0.198
B(5)	2.45 (6)	2.42 (6)	3.02 (6)	0.02 (5)	−0.21 (5)	−0.31 (5)	0.162, 0.175, 0.213
B(6)	3.11 (6)	4.35 (8)	2.49 (6)	0.90 (6)	0.05 (5)	0.20 (6)	0.167, 0.196, 0.247
B(7)	3.67 (8)	2.16 (6)	5.56 (10)	0.30 (5)	1.49 (7)	0.07 (6)	0.163, 0.204, 0.270
B(8)	2.89 (6)	3.30 (7)	3.87 (7)	−0.23 (6)	1.14 (5)	−0.88 (6)	0.173, 0.190, 0.243
B(9)	2.26 (5)	2.86 (6)	3.46 (7)	−0.30 (5)	0.30 (5)	0.07 (5)	0.165, 0.193, 0.211
B(10)	2.69 (6)	4.18 (8)	3.19 (7)	0.48 (6)	−0.55 (5)	−0.22 (6)	0.160, 0.215, 0.243
B(11)	3.49 (7)	4.26 (9)	4.09 (8)	1.32 (6)	0.44 (6)	1.70 (7)	0.157, 0.221, 0.277
B(12)	2.63 (6)	3.41 (8)	4.62 (9)	0.85 (5)	0.73 (6)	0.34 (6)	0.162, 0.219, 0.245

^{a} These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å^2. They enter the expression for the structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}\cdot klb^*c^*)]$. ^{b} See footnote a to Table II. ^{c} These values correspond to the root-mean-square amplitudes of vibration (in A) of the atom along the three principal axes (minor, median, major, respectively) of its vibration ellipsoid. For relative orientations, see figures.

Table IV. Distances (in Å) and Esd's within the $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ Molecule[a,b]

Atoms	Distance	Atoms	Distance
(a) Distances from Cobalt Atoms			
Co–CP(1)	2.0666 (12)	Co–CP(6)	2.0303 (15)
Co–CP(2)	2.0309 (12)	Co–CP(7)	2.0242 (16)
Co–CP(3)	2.0260 (13)	Co–CP(8)	2.0207 (17)
Co–CP(4)	2.0223 (14)	Co–CP(9)	2.0277 (16)
Co–CP(5)	2.0369 (13)	Co–CP(10)	2.0244 (15)
Co⋯C(1)	3.1815 (12)	Co⋯HCP(6)	2.692 (21)
Co⋯HCP(2)	2.712 (15)	Co⋯HCP(7)	2.427 (21)
Co⋯HCP(3)	2.581 (16)	Co⋯HCP(8)	2.604 (21)
Co⋯HCP(4)	2.638 (17)	Co⋯HCP(9)	2.714 (26)
Co⋯HCP(5)	2.705 (16)	Co⋯HCP(10)	2.643 (21)
(b) Carbon–Carbon Distances within C_5 Rings			
CP(1)–CP(2)	1.4281 (17)	CP(6)–CP(7)	1.4106 (27)
CP(2)–CP(3)	1.4193 (19)	CP(7)–CP(8)	1.3874 (32)
CP(3)–CP(4)	1.4035 (23)	CP(8)–CP(9)	1.4083 (29)
CP(4)–CP(5)	1.4178 (20)	CP(9)–CP(10)	1.3997 (27)
CP(5)–CP(1)	1.4239 (18)	CP(10)–CP(6)	1.3945 (25)
CP(1)–C(1)	1.4803 (16)		
(c) Carbon–Hydrogen Distances in π-Cyclopentadienyl Rings			
		CP(6)–HCP(6)	0.976 (22)
CP(2)–HCP(2)	1.001 (15)	CP(7)–HCP(7)	0.703 (20)
CP(3)–HCP(3)	0.858 (16)	CP(8)–HCP(8)	0.905 (20)
CP(4)–HCP(4)	0.917 (17)	CP(9)–HCP(9)	0.955 (25)
CP(5)–HCP(5)	0.973 (15)	CP(10)–HCP(10)	0.951 (22)
(d) Distances within B_9C_2 Cage			
C(1)–C(2)	1.553 (2)	B(6)–B(10)	1.772 (3)
C(1)–B(4)	1.630 (2)	B(6)–B(11)	1.762 (3)
C(1)–B(5)	1.711 (2)	B(7)–B(8)	1.811 (3)
C(1)–B(6)	1.726 (2)	B(7)–B(11)	1.780 (3)
C(2)–B(6)	1.731 (2)	B(7)–B(12)	1.758 (3)
C(2)–B(7)	1.611 (2)	B(8)–B(9)	1.775 (2)
C(2)–B(11)	1.712 (2)	B(8)–B(12)	1.765 (3)
B(4)–B(5)	1.786 (2)	B(9)–B(10)	1.794 (2)
B(4)–B(8)	1.830 (2)	B(9)–B(12)	1.815 (2)
B(4)–B(9)	1.763 (2)	B(10)–B(11)	1.781 (3)
B(5)–B(6)	1.768 (2)	B(10)–B(12)	1.794 (3)
B(5)–B(9)	1.760 (2)	B(11)–B(12)	1.755 (3)
B(5)–B(10)	1.765 (2)		
(e) Terminal C–H Distance within $B_9C_2H_{11}$ Cage			
C(2)–HC(2)	0.991 (14)		
(f) Terminal B–H Distances within $B_9C_2H_{11}$ Cage			
B(4)–HB(4)	1.152 (15)	B(9)–HB(9)	1.110 (15)
B(5)–HB(5)	1.045 (14)	B(10)–HB(10)	1.112 (17)
B(6)–HB(6)	1.081 (18)	B(11)–HB(11)	1.094 (21)
B(7)–HB(7)	1.050 (18)	B(12)–HB(12)	1.096 (15)
B(8)–HB(8)	1.123 (14)		
(g) Distances Involving H(FAC), the Facial Hydrogen Atom			
H(FAC)–B(8)	1.331 (22)	H(FAC)⋯HB(8)	2.134 (26)
H(FAC)⋯B(4)	1.631 (22)	H(FAC)⋯HB(4)	2.426 (27)
H(FAC)⋯B(7)	1.636 (22)	H(FAC)⋯HB(7)	2.355 (29)
H(FAC)⋯C(2)	1.976 (22)	H(FAC)⋯HC(2)	2.657 (27)
H(FAC)⋯C(1)	2.009 (22)		
(h) Some Nonbonded Distances involving B(8)			
B(8)⋯C(1)	2.772 (2)	B(8)⋯C(2)	2.732 (2)

[a] See footnote a to Table II and ref 16. [b] Esd's are calculated by considering all elements of the positional covariance matrix of the last cycle of refinement. The calculation was performed using the Fortran IV program STAN1, by B. G. DeBoer. Contributions from errors in the unit cell dimensions are included. No distances have been corrected for the effects of thermal motion.

V.[15] The overall molecular geometry and labeling of

(15) The reader will notice that, here and elsewhere, the esd's are given to two significant figures. This is clearly necessary for statistical purposes when the first digit is "1." Consider the following example. Two independent bond lengths are written as 1.30 (1) and 1.35 (1) Å; are they statistically different? Using the normally accepted criterion that a 3σ difference is meaningful, and using $\sigma(\text{diff}) = [\sigma_1^2 + \sigma_2^2]^{1/2}$, the difference of 0.05 Å represents $\sim 3.5\,\sigma$ and the difference may be judged meaningful. However, we are neglecting both the error in-
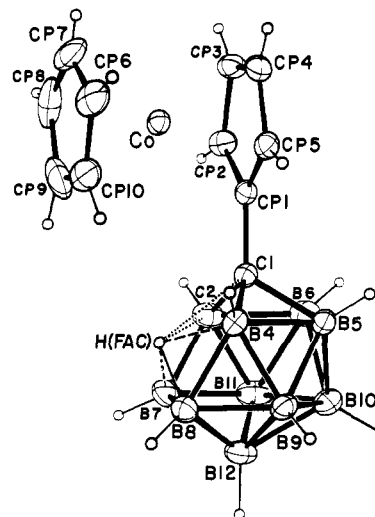

Figure 1. A general view of the $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ molecule, showing the scheme used for labeling atoms. (ORTEP diagram, 30% ellipsoids; hydrogen atoms are artificially reduced to spheres of radius 0.07 Å).

atoms is shown in Figure 1. The molecule is a zwitterionic species in which the positive charge on the cobaltocenium moiety is balanced by the negative charge on the C-bonded $B_9C_2H_{11}$ substituent.

The Cobaltocenium Cation. As shown in Figure 2, the cobaltocenium ion has a staggered conformation. The individual cobalt–carbon distances within this system range from 2.0207 (17) to 2.0666 (12) Å. A close inspection, however, reveals that CP(1) (the carbon atom involved in the bonding to the carborane substituent) is significantly farther from the cobalt atom (2.0666 (12) Å) than are the remaining four carbon atoms within this substituted π-cyclopentadienyl ring (range: 2.0223 (14)–2.0369 (13) Å: av 2.0290 ± 0.0064 Å[16]). Cobalt–carbon distances for the unsubstituted π-cyclopentadienyl ligand range from 2.0207 (17) to 2.0303 (15) Å, with an average of 2.0255 ± 0.0037 Å.[16]

As expected, the carbon atoms of the unsubstituted π-cyclopentadienyl ligand are coplanar within the limits of experimental error (root-mean-square (rms) deviation $\sim$0.002 Å: see Table VI), while those of the substituted π-cyclopentadienyl ligand show small, but significant, deviations from planarity (rms deviation $\sim$0.007 Å). The cobalt atom lies +1.641 Å from the plane defined by CP(1)–CP(5) and −1.638 Å from that defined by CP(6)–CP(10).

Carbon–carbon distances within the substituted (and hence "well-anchored") π-cyclopentadienyl ligand range from 1.4035 (23) to 1.4281 (17) Å, averaging 1.4185 ± 0.0093 Å;[16] those within the unsubstituted π-cyclopentadienyl ligand range from 1.3874 (32) to 1.4106 (27)

volved in rounding the esd and the error involved in rounding the bond lengths (the former, perhaps surprisingly, being the most important), and to three decimal places these same bond lengths and esd's might range from 1.295 (5) and 1.354 (5) Å (diff = 0.059 Å or 8.3 σ) to 1.304 (14) and 1.345 (14) Å (diff = 0.041 Å or 2.1 σ).

(16) Throughout the text esd's on individual parameters appear in parentheses, right adjusted to the least significant digit of the preceding number. Esd's of average values are given in the form "±X.XXXÅ" and are calculated via the expression

$$\sigma = \left[\sum_{i=1}^{i=N} (\chi_i - \bar{\chi})^2/(N-1) \right]^{1/2}$$

where χ_i is the ith value and $\bar{\chi}$ is the mean of N equivalent measurements.

Table V. Angles (in deg) and Esd's within the $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ Molecule[a]

Atoms	Angle	Atoms	Angle
	(a) Angles Involving the Cobalt Atom		
CP(1)–Co–CP(2)	40.78 (5)	CP(6)–Co–CP(7)	40.72 (8)
CP(2)–Co–CP(3)	40.96 (5)	CP(7)–Co–CP(8)	40.12 (9)
CP(3)–Co–CP(4)	40.57 (7)	CP(8)–Co–CP(9)	40.71 (9)
CP(4)–Co–CP(5)	40.88 (7)	CP(9)–Co–CP(10)	40.42 (8)
CP(5)–Co–CP(1)	40.60 (5)	CP(10)–Co–CP(6)	40.23 (7)
CP(1)···Co···CP(7)	177.67 (8)	CP(4)...Co···CP(9)	177.84 (8)
CP(2)···Co···CP(6)	178.21 (6)	CP(5)...Co···CP(8)	177.83 (9)
CP(3)···Co···CP(10)	177.77 (7)		
	(b) C–C–C Angles within the π-Cyclopentadienyl Rings		
CP(5)–CP(1)–CP(2)	106.90 (11)	CP(10)–CP(6)–CP(7)	107.24 (18)
CP(1)–CP(2)–CP(3)	108.28 (13)	CP(6)–CP(7)–CP(8)	108.55 (17)
CP(2)–CP(3)–CP(4)	108.11 (13)	CP(7)–CP(8)–CP(9)	107.97 (18)
CP(3)–CP(4)–CP(5)	108.35 (13)	CP(8)–CP(9)–CP(10)	107.55 (18)
CP(4)–CP(5)–CP(1)	108.33 (13)	CP(9)–CP(10)–CP(6)	108.70 (17)
	(c) External Angles of Carbocyclic Rings		
C(1)–CP(1)–CP(5)	125.37 (11)	HCP(6)–CP(6)–CP(10)	128.5 (13)
C(1)–CP(1)–CP(2)	127.71 (12)	HCP(6)–CP(6)–CP(7)	124.1 (13)
HCP(2)–CP(2)–CP(1)	126.5 (8)	HCP(7)–CP(7)–CP(6)	122.4 (18)
HCP(2)–CP(2)–CP(3)	125.1 (8)	HCP(7)–CP(7)–CP(8)	128.1 (18)
HCP(3)–CP(3)–CP(2)	122.2 (11)	HCP(8)–CP(8)–CP(7)	130.3 (14)
HCP(3)–CP(3)–CP(4)	129.5 (11)	HCP(8)–CP(8)–CP(9)	121.5 (14)
HCP(4)–CP(4)–CP(3)	128.9 (10)	HCP(9)–CP(9)–CP(8)	128.5 (17)
HCP(4)–CP(4)–CP(5)	122.6 (10)	HCP(9)–CP(9)–CP(10)	124.0 (16)
HCP(5)–CP(5)–CP(4)	125.2 (9)	HCP(10)–CP(10)–CP(9)	122.9 (12)
HCP(5)–CP(5)–CP(1)	126.4 (9)	HCP(10) CP(10)–CP(6)	128.2 (12)
	(d) Angles within Triangular Faces of the B_9C_2 Cage		
C(2)–C(1)–B(6)	63.47 (9)	B(9)–B(8)–B(12)	61.68 (10)
B(6)–C(1)–B(5)	61.91 (9)	B(12)–B(8)–B(7)	58.86 (10)
B(5)–C(1)–B(4)	64.59 (9)	B(4)–B(9)–B(5)	60.94 (8)
C(1)–C(2)–B(6)	63.14 (9)	B(5)–B(9)–B(10)	59.53 (9)
B(6)–C(2)–B(11)	61.58 (10)	B(10)–B(9)–B(12)	59.60 (10)
B(11)–C(2)–B(7)	64.72 (11)	B(12)–B(9)–B(8)	58.89 (10)
C(1)–B(4)–B(5)	59.89 (8)	B(8)–B(9)–B(4)	62.28 (9)
B(5)–B(4)–B(9)	59.46 (9)	B(5)–B(10)–B(6)	59.97 (9)
B(9)–B(4)–B(8)	59.19 (9)	B(6)–B(10)–B(11)	59.46 (10)
C(1)–B(5)–B(4)	55.52 (8)	B(11)–B(10)–B(12)	58.80 (11)
B(4)–B(5)–B(9)	59.61 (8)	B(12)–B(10)–B(9)	60.78 (10)
B(9)–B(5)–B(10)	61.19 (9)	B(9)–B(10)–B(5)	59.28 (9)
B(10)–B(5)–B(6)	60.23 (9)	C(2)–B(11)–B(6)	59.75 (9)
B(6)–B(5)–C(1)	59.46 (8)	B(6)–B(11)–B(10)	60.02 (10)
C(1)–B(6)–C(2)	53.39 (8)	B(10)–B(11)–B(12)	60.96 (11)
C(2)–B(6)–B(11)	58.68 (10)	B(12)–B(11)–B(7)	59.62 (10)
B(11)–B(6)–B(10)	60.52 (10)	B(7)–B(11)–C(2)	54.89 (10)
B(10)–B(6)–B(5)	59.80 (9)	B(7)–B(12)–B(8)	61.87 (11)
B(5)–B(6)–C(1)	58.63 (8)	B(8)–B(12)–B(9)	59.43 (9)
C(2)–B(7)–B(11)	60.39 (10)	B(9)–B(12)–B(10)	59.61 (9)
B(11)–B(7)–B(12)	59.47 (11)	B(10)–B(12)–B(11)	60.24 (11)
B(12)–B(7)–B(8)	59.27 (10)	B(11)–B(12)–B(7)	60.90 (11)
B(4)–B(8)–B(9)	58.53 (8)		
	(e) Angles within Pentagonal Equatorial Belts of the B_9C_2 Cage		
B(4)–C(1)–C(2)	111.48 (11)	B(9)–B(5)–B(6)	108.71 (11)
C(1)–C(2)–B(7)	114.61 (12)	B(5)–B(6)–B(11)	108.16 (12)
C(2)–B(7)–B(8)	105.83 (12)	B(6)–B(11)–B(12)	108.58 (12)
B(7)–B(8)–B(4)	101.58 (11)	B(11)–B(12)–B(9)	107.63 (11)
B(8)–B(4)–C(1)	106.33 (11)	B(12)–B(9)–B(5)	106.91 (11)
	(f) (Substituent)–(Cage Atom)–(Cage Atom) Angles for the Open Pentagonal Face		
Cp(1)–C(1)–C(2)	117.17 (10)	HB(4)–B(4)–B(8)	125.0 (8)
Cp(1)–C(1)–B(4)	121.25 (10)	HB(4)–B(4)–B(9)	124.7 (8)
Cp(1)–C(1)–B(5)	119.63 (10)	HB(7)–B(7)–C(2)	124.5 (10)
Cp(1)–C(1)–B(6)	113.47 (10)	HB(7)–B(7)–B(8)	122.5 (10)
HC(2)–C(2)–C(1)	116.7 (8)	HB(7)–B(7)–B(11)	118.9 (10)
HC(2)–C(2)–B(6)	115.3 (8)	HB(7)–B(7)–B(12)	121.9 (10)
HC(2)–C(2)–B(7)	118.3 (8)	HB(8)–B(8)–B(4)	123.3 (8)
HC(2)–C(2)–B(11)	119.5 (8)	HB(8)–B(8)–B(7)	128.8 (8)
HB(4)–B(4)–C(1)	120.8 (8)	HB(8)–B(8)–B(9)	117.3 (8)
HB(4)–B(4)–B(5)	118.7 (8)	HB(8)–B(8)–B(12)	120.9 (8)
	(g) H–B–B Angles for Lower Pentagonal Belt		
HB(5)–B(5)–C(1)	120.8 (8)	HB(9)–B(9)–B(10)	121.7 (7)
HB(5)–B(5)–B(4)	120.5 (8)	HB(9)–B(9)–B(12)	123.1 (8)
HB(5)–B(5)–B(6)	118.9 (8)	HB(11)–B(11)–C(2)	123.9 (11)
HB(5)–B(5)–B(9)	127.2 (8)	HB(11)–B(11)–B(6)	119.0 (11)
HB(5)–B(5)–B(10)	126.3 (8)	HB(11)–B(11)–B(7)	121.9 (11)

Table V (*Continued*)

Atoms	Angle	Atoms	Angle
HB(6)–B(6)–C(1)	125.6 (10)	HB(11)–B(11)–B(10)	124.6 (11)
HB(6)–B(6)–C(2)	124.4 (10)	HB(11)–B(11)–B(12)	126.1 (10)
HB(6)–B(6)–B(5)	124.7 (9)	HB(12)–B(12)–B(7)	123.9 (8)
HB(6)–B(6)–B(10)	125.4 (10)	HB(12)–B(12)–B(8)	117.7 (8)
HB(6)–B(6)–B(11)	120.8 (10)	HB(12)–B(12)–B(9)	120.1 (8)
HB(9)–B(9)–B(4)	121.9 (8)	HB(12)–B(12)–B(10)	120.9 (8)
HB(9)–B(9)–B(5)	121.2 (8)	HB(12)–B(12)–B(11)	123.3 (8)
HB(9)–B(9)–B(8)	119.1 (8)		

(h) H–B–B Angles for Basal Boron Atom

Atoms	Angle	Atoms	Angle
HB(10)–B(10)–B(5)	121.8 (10)	HB(10)–B(10)–B(11)	123.9 (9)
HB(10)–B(10)–B(6)	124.8 (9)	HB(10)–B(10)–B(12)	120.9 (9)
HB(10)–B(10)–B(9)	119.6 (9)		

(i) All Angles Involving the "Facial" Hydrogen Atom, H(FAC)

Atoms	Angle	Atoms	Angle
H(FAC)–B(8)–B(4)	59.7 (10)	H(FAC)···B(4)–C(1)	76.0 (8)
H(FAC)–B(8)–B(7)	60.5 (10)	H(FAC)···B(4)–B(8)	44.9 (8)
H(FAC)–B(8)–B(9)	110.9 (10)	H(FAC)···B(7)–C(2)	75.0 (8)
H(FAC)–B(8)–B(12)	111.4 (10)	H(FAC)···B(7)–B(8)	45.1 (8)
H(FAC)–B(8)–HB(8)	120.5 (13)		
B(4)···H(FAC)–B(8)	75.5 (11)	B(4)···H(FAC)···B(7)	119.4 (14)
B(7)···H(FAC)–B(8)	74.5 (11)		

a See footnotes to Table IV.

Å, averaging 1.4001 ± 0.0096 Å.[16] The smaller value for the unsubstituted π-cyclopentadienyl ligand may be attributed to its larger amplitude of libration (see Figure 2), rather than to any subtle electronic effect.

Angles within the planar carbocyclic rings necessarily average 108.00°. However, the angle CP(5)–CP(1)–CP(2) is only 106.90 (11)°, whereas the other angles within this substituted ligand range from 108.11 (13) to 108.35 (13)°, averaging 108.27 ± 0.11°.[16] Clearly this perturbation must result from the substituent on CP(1), since angles within the unsubstituted π-cyclopentadienyl system show a more random variation, *i.e.*, from 107.24 (18) to 108.55 (17)°, averaging 108.00 ± 0.56°.[16]

Carbon–hydrogen distances within the cobaltocenium ion range from CP(7)–HP(7) = 0.703 (20) to CP(2)–HCP(2) = 1.001 (15) Å.[17] As may be seen in Table VI, the hydrogen atoms do not lie in the planes of the carbocyclic rings but are (on average) displaced toward the cobalt atom (by an average of 0.053 Å for HCP(2)–HCP(5) and 0.059 Å for HCP(6)–HCP(10)).

We note at this point that X-ray studies on the cobaltocenium derivatives [(π-C₅H₅)₂Co⁺][ClO₄⁻],[18] [(π-C₅H₅)₂Co⁺][Co(PPh₃)I₃⁻],[19] [(π-C₅H₅)₂Co⁺]₂[CoCl₄²⁻],[20] and [(π-C₅H₅)₂Co⁺]₂[ZnCl₄²⁻][20] have been reported; the precision of these studies is sufficiently low that a comparison of their molecular parameters with those of the current structure is unwarranted.

The Carborane Anion. The carborane anion is a C-substituted derivative of the parent [B₉C₂H₁₂⁻] anion. The present structural determination is, to the best of our knowledge, the first on such an anion, although many derivatives of the [B₉C₂H₁₁²⁻] anion have been examined.

The "heavy-atom" (*i.e.*, B₉C₂) framework of the ligand defines an icosahedron from which one apex has been removed.

(17) The expected C–H distance from an X-ray study is ~0.95 Å; see ref 11.
(18) E. Frasson, G. Bombieri, and C. Panattoni, *Acta Crystallogr., Sect. A*, **16**, 68 (1963).
(19) M. van den Akker, R. Olthof, F. van Bolhius, and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, **91**, 75 (1972).
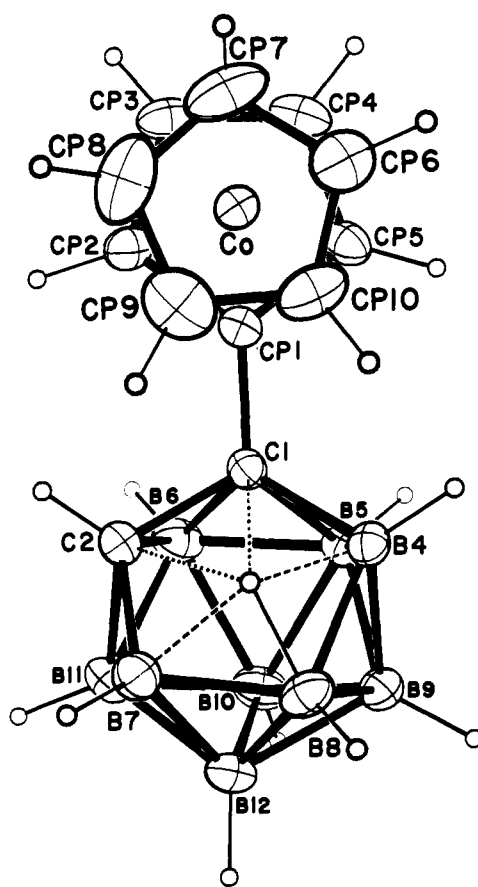(20) J. R. Guenter, G. Mattman, and H. Werner, *J. Organometal. Chem.*, **25**, 475 (1970).

Figure 2. The (π-C₅H₅)Co(π-C₅H₄·B₉C₂H₁₁) molecule, showing the staggered conformation of the cobaltocenium fragment (ORTEP diagram, 30% ellipsoids; hydrogen atoms shown as spheres of radius 0.07 Å).

The carbon–carbon distance, C(1)–C(2) = 1.553 (2) Å, is similar to that found in other B₉C₂-containing systems *in which the C₂ fragment is not bound to a metal atom*, *viz.*, 1.528 (19) Å for B₉C₂H₁₂AlMe₂[21] and values

(21) M. R. Churchill and A. H. Reis, *J. Chem. Soc., Dalton Trans.*, 1314 (1972).

Table VI. Least-Squares Planes (and Deviations of Atoms from Those Planes) within the $(\pi\text{-}C_5H_5)Co(\pi\text{-}C_5H_4\cdot B_9C_2H_{11})$ Molecule[a,b]

Atom	Dev, Å	Atom	Dev, Å
Plane I:	$0.17166X + 0.54226Y + 0.82249Z = 3.2522$		
CP(1)*	−0.009	C(1)	−0.001
CP(2)*	0.009	HCP(2)	0.067
CP(3)*	−0.006	HCP(3)	0.054
CP(4)*	−0.000	HCP(4)	0.042
CP(5)*	0.006	HCP(5)	0.048
Co	1.641		
Plane II:	$0.18257X + 0.54237Y + 0.82007Z = 6.6063$		
CP(6)*	−0.001	HCP(6)	−0.052
CP(7)*	0.003	HCP(7)	−0.103
CP(8)*	−0.003	HCP(8)	−0.082
CP(9)*	0.003	HCP(9)	0.024
CP(10)*	−0.001	HCP(10)	−0.083
Co	−1.638		
Plane III:	$0.63106X + 0.40247Y + 0.66316Z = 4.8297$		
C(1)*	−0.015	CP(1)	0.686
C(2)*	−0.006	HC(2)	0.499
B(4)*	0.027	HB(4)	0.561
B(7)*	0.022	HB(7)	0.480
B(8)*	−0.028	HB(8)	0.337
		H(FAC)	0.836
Plane IIIa:	$0.64863X + 0.39910Y + 0.64807Z = 4.8718$		
C(1)*	−0.004	CP(1)	0.723
C(2)*	0.004	HC(2)	0.526
B(4)*	0.002	HB(4)	0.531
B(7)*	−0.002	HB(7)	0.450
		H(FAC)	0.809
Plane IIIb:	$0.59606X + 0.40995Y + 0.69040Z = 4.8157$		
B(4)*	0.000	HB(4)	0.541
B(7)*	0.000	HB(7)	0.470
B(8)*	0.000	HB(8)	0.411
		H(FAC)	0.817
Plane IV:	$0.62847X + 0.40238Y + 0.66567Z = 3.3350$		
B(5)*	−0.006	HB(5)	−0.383
B(6)*	0.006	HB(6)	−0.398
B(9)*	0.004	HB(9)	−0.487
B(11)*	−0.004	HB(11)	−0.435
B(12)*	0.000	HB(12)	−0.500
B(10)	−0.950		

Dihedral Angles (deg)

I/II	0.64	I/III	29.31
IIIa/IIIb	3.92	III/IV	0.21

[a] Planes are in Cartesian coordinates such that $[X,Y,Z] = [xa + zc \cos\beta, yb, zc \sin\beta]$. [b] Planes are derived using unit weights for atoms marked with an asterisk and zero weight for all other atoms.

of 1.53 (1) and 1.49 (3) Å (respectively) for the "slipped" bis(η^3-1,2-dicarbollyl)metal species $[(B_9C_2H_{11})_2Cu^{2-}]^{22}$ and $[(B_9C_2H_{11})_2Cu^-]$.[23] In contrast to this, it should be noted that carbon–carbon distances within η^5-dicarbollyl ligands are typically ∼1.60–1.63 Å in length.[24]

Carbon–boron bond lengths fall into two sets. Within the open pentagonal face of the icosahedral fragment, C(1)–B(4) is 1.630 (2) Å and C(2)–B(7) is 1.611 (2) Å in length; within the body of the B_9C_2 "nest" carbon–boron distances are considerably longer, individual values being C(1)–B(5) = 1.711 (2) Å, C(1)–B(6) = 1.726 (2) Å, C(2)–B(6) = 1.731 (2) Å, and C(2)–B(11) = 1.712 (2) Å. The shorter carbon–boron bonds within the open pentagonal face presumably

(22) R. M. Wing, *J. Amer. Chem. Soc.*, **89**, 5599 (1967).
(23) R. M. Wing, *J. Amer. Chem. Soc.*, **90**, 4828 (1968).
(24) M. R. Churchill and A. H. Reis, *J. Chem. Soc., Dalton Trans.*, 1317 (1972); see, especially, Table 6 on p 1320.

reflect a greater bond order due to the lower connectivity of the atoms involved.

Boron–boron bond distances range from 1.755 (3) to 1.830 (2) Å; two of the three longest distances (*i.e.*, B(4)–B(8) = 1.830 (2) Å and B(7)–B(8) = 1.811 (3) Å) are associated with B(8), the central boron atom of the open pentagonal B_3C_2 face. As outlined below, this atom [B(8)] is the most strongly involved with the "facial" hydrogen atom, H(FAC).

As may be seen from Table VI, the lower pentagonal belt of the "nest-like" $[B_9C_2H_{11}R^-]$ (R = $C_5H_5CoC_5H_4^+$) ligand, defined by B(5)–B(6)–B(11)–B(12)–B(9), is planar within the limits of experimental error (rms deviation of boron atoms from the least-squares plane = 0.005 Å). In contrast to this, the rms deviation of constituent atoms from the open pentagonal face is ∼0.024 Å (plane III, Table VI). The dihedral angle between the system B(4)–C(1)–C(2)–B(7) (rms deviation ∼0.004 Å) and the strictly planar system B(4)–B(8)–B(7) is 3.92°.

All hydrogen atoms of the $[B_9C_2H_{11}R^-]$ anion have been located. The carbon–hydrogen bond, C(2)–HC(2), is 0.991 (14) Å in length, while individual terminal boron–hydrogen bond lengths range from B(5)–HB(5) = 1.045 (14) Å to B(4)–HB(4) = 1.152 (15) Å, averaging 1.096 ± 0.034 Å. (This may be compared with the average B–H bond distance of 1.116 ± 0.018 Å found in $[Me_4N^+][Me_2B_{10}C_2H_{11}^-]$.[12]) These distances are, however, X-ray determined distances (*i.e.*, from centroid of electron density to centroid of electron density) and are thus systematically reduced from the accepted *internuclear* distances.

As shown in Table V, H–B(10)–B angles range from 119.6 (9) to 124.8 (9)°, H–B–B angles centered on the lower pentagonal belt range from 117.7 (8) to 127.2 (8)°, and H(terminal)–B–(B or C) angles centered on the open pentagonal face range from 117.3 (8) to 128.8 (8)°. (The expected exterior angle for a regular icosahedron is 121.71°, *i.e.*, 90° + cos^{-1}(1/(2 sin 36°)).)

Hydrogen atoms associated with the belt B(5)–B(6)–B(11)–B(12)–B(9) are all displaced from that plane toward B(10), by amounts ranging from −0.383 to −0.500 Å (plane IV of Table VI): terminal hydrogen atoms associated with the open pentagonal face, C(1)–C(2)–B(7)–B(8)–B(4), are displaced by 0.499 Å (HC(2)), 0.561 Å (HB(4)), and 0.480 (HB(7)): HB(8) is only 0.337 Å from this plane, while CP(1) lies 0.686 Å above the plane.

All the preceding evidence is presented to assure the reader that hydrogen atoms have been located with reasonable precision, and that each terminal hydrogen atom is in a position very close to that expected for an external substituent of a regular icosahedral fragment. We now come to a consideration of the unique "facial" hydrogen atom, designated H(FAC).

The position of H(FAC) relative to the open pentagonal face is shown in Figures 3a and 3b. It lies *on* the *pseudo*-mirror plane of the anion, 0.836 Å above the open B_3C_2 face; its X-ray crystallographically determined distances to the five atoms in this plane are (in order): H(FAC)–B(8) = 1.331 (22) Å, H(FAC)···B(4) = 1.631 (22) Å, H(FAC)···B(7) = 1.636 (22) Å, H(FAC)···C(2) = 1.976 (22) Å, and H(FAC)···C(1) = 2.009 (22) Å. Thus, while the atom H(FAC) is principally involved in bonding to B(8), there are clearly significant interactions with B(4) and B(7) and
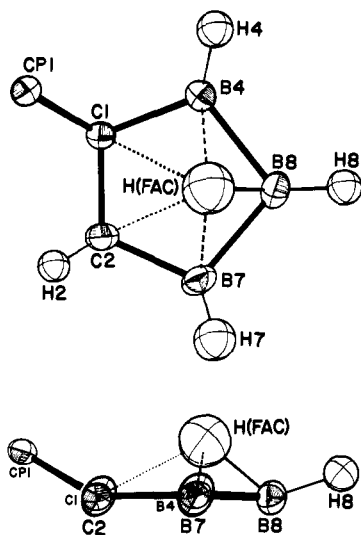
Figure 3. The environment of the "facial" hydrogen atom. (a) Projection on to the least-squares plane of the open pentagonal face (ORTEP diagram; 30% ellipsoids for all atoms; carbon and boron atoms shaded). (b) "Side-on" view of the facial hydrogen over the B_3C_2 face; only substituents C(1), HB(8), and H(FAC) are shown (ORTEP diagram; 30% ellipsoids).
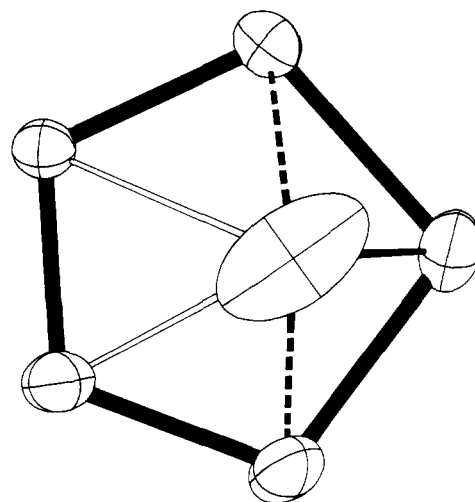

Figure 4. The C(1)–C(2)–B(7)–B(8)–B(4) face, showing the orientation of the vibration ellipsoid associated with atom H(FAC). (This diagram has the same perspective as Figure 3a.) Details of the thermal parameters of H(FAC) are as follows: $B_{11} = 7.3$ (10), $B_{22} = 5.3$ (8), $B_{33} = 10.6$ (11), $B_{12} = -0.4$ (8), $B_{13} = -4.6$ (9), $B_{23} = -6.0$ (7) $Å^2$. The rms amplitudes of vibration along the principal axes of the ellipsoid are 0.03, 0.29, and 0.48 Å, the "thin" direction being perpendicular to the plane of projection of this figure.

weak, but finite, interactions with C(1) and C(2), as is indicated by the following evidence.

(1) The B(8)–H(FAC) distance of 1.331 (22) Å is about 0.2 Å longer than that found for a normal terminal B–H bond. (B(4)–HB(4), the longest *terminal* bond in the present structure, is 1.152 (15) Å in length.)

(2) H(FAC) lies in a position tending toward (*i.e.*, within 0.5 Å of) that which would be occupied by the 12th particle of the idealized completed regular icosahedron.

(3) The angle H(FAC)–B(8)–HB(8) is 120.5(13)°, *i.e.*, larger than a regular tetrahedral angle. One would expect a reduction in this angle if such contacts as H(FAC)···B(4) and H(FAC)···B(7) (1.631 (22) and 1.636 (22) Å) were repulsive.

(4) Normal van der Waals distances for B···H and C···H contacts are ~2.9 and ~2.8 Å.[25,26] The observed distances between H(FAC) and atoms B(4), B(7), C(1), and C(2) are all substantially lower than these van der Waals distances.

(5) As pointed out by Hawthorne,[27] the bonding orbitals within the open pentagonal face of the B_9C_2-$H_{11}{}^{2-}$ ion closely resemble those of the cyclopentadienide $(C_5H_5{}^-)$ ion.[28] As such, the lowest lying orbital is cylindrically symmetric (in the approximation that boron and carbon are equivalent). The introduction of H$^+$ above the open pentagonal face (to produce $B_9C_2H_{12}{}^-$) therefore leads to a situation where all atoms of the open pentagonal face must have some finite bonding interaction with the H$^+$ (since the hydrogen's 1s orbital is spherically symmetric).

(6) The open pentagonal face is, in fact, heteronuclear, with the carbon atoms being the most positive.

(25) These are *very approximate*. The van der Waals radius for hydrogen (1.2 Å) is taken directly from ref 26a. Values of ~1.7 Å for boron and ~1.6 Å for carbon are calculated by adding 0.8 Å to the appropriate *covalent* radii (see ref 26b).

(26) L. Pauling, "Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N. Y.: (a) Table 7–20, p 260; (b) p 263.

(27) M. F. Hawthorne, *Accounts Chem. Res.*, 1, 281 (1968).

(28) W. Moffitt, *J. Amer. Chem. Soc.*, 76, 3386 (1954).

Electrophilic attack (*e.g.*, H$^+$) on the open pentagonal face of a $B_9C_2H_{11}{}^{2-}$ ion would preferentially occur at B(8)—the position furthest from C(1) and C(2).

In summary, then, H(FAC) has bonding interactions with all atoms in the open pentagonal face but is most strongly linked to B(8).

A further point which must be considered carefully is the possibility that H(FAC) represents the net result of either static disorder or dynamic tautomerism between normal μ_2 bridging hydrogen atoms between B(8)–B(4) and B(8)–B(7). Concerning this problem we make the following observations. (a) The idealized positions of such μ_2 bridges would be on planes perpendicular to, and passing through the midpoints of, B(8)–B(4) and B(8)–B(7) and directed over the open pentagonal face. From the available structural information, we cannot, on any *a priori* grounds, reject the possibilities of a double (or multiple) potential minimum or disorder. However, disorder of, or tautomerism between, such μ_2-hydrido bridges would lead to the electron density associated with H(FAC) being elongated in a direction parallel to the B(4)···B(7) vector. This is simply *not* observed. (See (b) and (c).) (b) An electron density map of H(FAC) (*i.e.*, a difference Fourier map of the structure using F_c values based on all atoms other than H(FAC)) shows pronounced elongation of this peak in the direction B(8)···(midpoint of C(1)–C(2)), *i.e.*, perpendicular to that expected for disordered μ_2 bridges. (c) We have also refined anisotropically the thermal parameters associated with H(FAC),[29] the resulting discrepancy indices being $R_F = 4.56\%$ and $R_{wF} = 3.31\%$. The results of this procedure, while not entirely satisfactory, show the major axis of the vibration ellipsoid to lie at

(29) Parameters for *all* atoms were refined (three cycles). At the termination of this phase, the anisotropic thermal parameters for H(FAC) were still shifting by about 0.5 σ, but refinement was declared complete. No atomic parameter, except those associated with H(FAC), shifted by more than 0.1 σ, and all results in this article are based on the isotropic refinement of H(FAC). Note, however, that the positional parameters of H(FAC) only moved by *ca.* 1.0 σ.

an angle of *ca.* 60° to that expected for disordered μ_2-hydrido bridges. (See Figure 4.)

We should add that the systematic error between X-ray determined $H\cdots X$ distances and true internuclear distances will act in such a way that the true (*internuclear*) separation for H(FAC)–B(8) will be greater than 1.331 (22) Å, and perhaps as great as ~1.43 Å. Other H(FAC)–B and H(FAC)–C distances will not be so drastically affected.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-6310.

A New Type of Metalloborane. Structural and Spectroscopic Characterization of Tricarbonylmanganese Tridecahydrooctaborate, $(CO)_3MnB_8H_{13}$

Joseph C. Calabrese, Mark B. Fischer, Donald F. Gaines,* and John W. Lott

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received May 16, 1974

Abstract: The title compound is the first structurally characterized example of a new type of metalloborane. It contains a tridentate B_8 ligand bound to manganese by two M–H–B bridge hydrogen bonds from borons bordering the open face of the borane cage and one M–H–B bond from an adjacent boron in the base of the borane cage. Crystals of the complex form in the orthorhombic space group *Pmcn* with unit cell parameters $a = 11.549$ (2) Å, $b = 5.506$ (1) Å, $c = 19.260$ (3) Å, $V = 1224.7$ (3) Å³, and $Z = 4$; $d_{calcd} = 1.294$ and $d_{measd} = 1.289$ (6) g/cm³. The X-ray crystal structure was solved by conventional heavy atom techniques and refined to $R_1 = 0.033$ and $R_2 = 0.041$ for 928 independent nonzero reflections on a Syntex P1 autodiffractometer. The molecule has crystallographic site symmetry C_s-*m*. The bond angles about the manganese indicate nearly perfect octahedral coordination.

The reaction of $Mn(CO)_5Br$ with KB_9H_{14} in ethereal solvents has produced several metalloboranes in which the $Mn(CO)_3$ moiety replaces the 6 (or 9) B–H unit in a decaborane-like framework; bonding to the rest of the cage is *via* a σ bond and two bridging hydrogen bonds.[1–3] Examples of these metalloboranes include $6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{12}L$ (L = $2\text{-}OC_4H_8$, $5\text{-}OC_4H_8$, $2\text{-}O(C_2H_5)_2$, and $8\text{-}O(CH_2)_4N\text{-}(C_2H_5)_3$) and salts of $6\text{-}(CO)_3\text{-}6\text{-}MnB_9H_{13}{}^-$. An additional compound, $(CO)_3MnB_8H_{13}$, is produced in small yields. It appears to be an elision product, in which the $(CO)_3Mn$ moiety is bonded to the borane cage in a novel and unprecedented manner. We report here the synthesis, characterization, structure, and bonding of this compound.

Experimental Section

Reagents and Solvents. Potassium tetradecahydrononaborate(−1), KB_9H_{14}, was made by a modification[1] of the method of Benjamin, Stafiej. and Takacs.[4] Manganese pentacarbonyl bromide was prepared from the parent metal pentacarbonyl dimer, $Mn_2(CO)_{10}$, and bromine. All other reagents and solvents were reagent grade and were used as received.

Compound Preparation. $(CO)_3MnB_8H_{13}$ was prepared according to the method of Lott and Gaines.[1] In a typical reaction a solution of 0.9308 g of KB_9H_{14} (6.2 mmol) and 1.4357 g of $Mn(CO)_5Br$ (5.2 mmol) in diethyl ether was refluxed for 3–6 hr. The reaction mixture was then stripped of solvent by evaporation under vacuum. The remaining oily red material was dissolved in a minimum of dichloromethane and placed on a Florisil-packed liquid chromatography column. Elution with heptane gave a bright yellow band, containing the $(CO)_3MnB_8H_{13}$. If these yellow solutions were allowed to stand for several hours, definite signs of decomposition were observed. To minimize this decomposition the solution was quickly evaporated under vacuum immediately after its removal from the chromatography column. The solid material was then transferred to the bottom of a long (35–40 cm) Pyrex glass tube having a reasonably wide cross section (25–28 mm diameter) and equipped with a vacuum stopcock. The tube was then enclosed in two halves of a copper tubing heat sink and an outer glass tube for insulation. This assemblage was clamped vertically so that the bottom of the sample tube and several centimeters of the copper jacket were submerged in an oil bath. The tube was then evacuated continuously while the temperature was slowly raised to 45–52° overnight. The desired product was then separated from impurities (generally $Mn_2(CO)_{10}$ and $Mn_2(CO)_3Br_2$) by cutting the tube into sections and checking the golden yellow crystals which had grown on the walls of each section by infrared spectroscopy. Very pure $(CO)_3MnB_8H_{13}$ was obtained in this manner. The yield from a

(1) (a) J. W. Lott and D. F. Gaines, *Inorg. Chem.*, in press; (b) J. W. Lott, Ph.D. Thesis, University of Wisconsin, Madison, Wisc., 1973.

(2) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, 95, 3042 (1973).

(3) (a) D. F. Gaines, J. W. Lott, and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 295 (1973); (b) D. F. Gaines, J. W. Lott, and J. C. Calabrese, *Inorg. Chem.*, in press.

(4) L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, 85, 2674 (1963).