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Boranometallacarboranes. 2. Crystal and Molecular Structures of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$, $[2,3\text{-}(CH_3)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$, and $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$[1]

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X-ray crystallographic studies were conducted on the title compounds, which were obtained from reactions of $2,3\text{-}R_2C_2B_4H_5^-$ ions (R = CH_3 or C_2H_5) with species formed from $CoCl_2$ and $B_5H_8^-$ or $B_9H_{14}^-$, as described in the preceding article. Each complex incorporates both metallaborane and metallacarborane cages sharing a common metal atom, an arrangement not previously known. In all three species, the borane ligand is formally $[B_9H_{12}O(CH_2)_4]^-$, a derivative of $B_9H_{13}^{2-}$ in which a tetrahydrofuran (THF) substituent displaces a terminal H^-; the CoB_9 cages are analogous to $B_{10}H_{14}$ with cobalt occupying the 5- or 6-position on the open face. The carborane ligands are different in the three compounds, such that the cobalt atom completes a 7-vertex *closo*-CoC_2B_4, a 6-vertex *nido*-CoC_2B_3, and a 10-vertex *closo*-CoC_2B_7 framework, respectively. In each case the borane and carborane ligands are arranged in a mutually twisted, unsymmetrical conformation, which appears to be a consequence of electronic factors rather than steric interaction between the ligands. In the $(R_2C_2B_7H_7)Co(B_9H_{12}\cdot THF)$ complex, the 10-vertex CoC_2B_7 cage contains a long C–B bond [2.192 (9) Å], which creates a quasi-open face which may arise from the presence of electron density beyond the "normal" $(2n + 2)$-electron allotment in the skeletal bonding molecular orbitals of the cobaltacarborane. Crystal data: $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$, mol wt 370.0, space group $P2_1/n$, $Z = 4$, $a = 14.175$ (4) Å, $b = 9.032$ (6) Å, $c = 17.771$ (3) Å, $\beta = 112.12$ (3)°, $V = 2108$ Å^3, $R = 0.038$ for 2543 reflections having $F_o^2 > 3\sigma(F_o^2)$; $[2,3\text{-}(CH_3)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$, mol wt 332.0, space group $P2_1/n$, $Z = 4$, $a = 8.692$ (2) Å, $b = 9.658$ (4) Å, $c = 22.383$ (9) Å, $\beta = 97.51$ (4)°, $V = 1863$ Å^3, $R = 0.053$ for 2370 reflections having $F_o^2 > 3\sigma(F_o^2)$; $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$, mol wt 405.3, space group $P2_1/c$, $Z = 4$, $a = 13.166$ (7) Å, $b = 12.166$ (5) Å, $c = 14.786$ (4) Å, $\beta = 105.99$ (5)°, $V = 2277$ Å^3, $R = 0.065$ for 2426 reflections having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Reactions of $CoCl_2$ with the borane anions $B_5H_8^-$ or $B_9H_{14}^-$, with subsequent addition of the *nido*-carborane anion $2,3\text{-}R_2C_2B_4H_5^-$ (R = CH_3 or C_2H_5), afford a series of mixed-ligand cobaltaborane-*commo*-carboranes consisting of metallaborane and metallacarborane frameworks sharing a common metal atom.[2] The synthesis and spectroscopic characterization of these species, the first examples of this genre, are described in an accompanying report.[2] The structures of the new compounds could not be assigned with confidence from NMR data alone, even at high field strengths, since in each case the spectra are complicated by the presence of both a borane and a carborane ligand. Consequently, X-ray crystallographic studies were conducted on three of the new compounds (labelled II, III, and V in the preceding paper), which contain three different carborane ligands and hence can serve as prototypes for structural assignments on other members of this class. Although the spectroscopically characterized species were all derived from *C,C′*-diethylcarboranes,[2] the X-ray investigation of III reported herein was conducted on the dimethyl homologue.

Table I. Experimental Parameters and Crystal Data

	II	III	V
mol wt	369.86	332.00	405.31
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	14.175 (4)	8.692 (2)	13.166 (7)
b, Å	9.032 (6)	9.658 (4)	12.166 (5)
c, Å	17.771 (3)	22.383 (9)	14.786 (4)
β, deg	112.12 (3)	97.51 (4)	105.99 (5)
V, Å^3	2108	1863	2277
μ, cm^{-1}	8.4	9.4	7.8
D(calcd), g/cm^3	1.165	1.184	1.182
A^a	0.60	0.60	0.60
B^a	0.35	0.35	0.35
max trans coeff	0.89		0.91
min trans coeff	0.83		0.88
2θ range, deg	0.7–25	0.7–25	1.5–52
reflctns obsd	3094	3228	3694
reflctns refined	2543	2370	2426
R	0.038	0.053	0.065
R_w	0.039	0.061	0.068
esd unit wt	1.1	2.2	1.7
Z	4	4	4
cryst dimens (mm from centroid)	110 (0.175), $\bar{1}\bar{1}0$ (0.175), 011 (0.155), $0\bar{1}\bar{1}$ (0.155), $01\bar{1}$ (0.175), $0\bar{1}1$ (0.175)	no regular faces	100 (0.09), $\bar{1}00$ (0.09), 110 (0.10), $\bar{1}\bar{1}0$ (0.10), $1\bar{1}0$ (0.11), $\bar{1}10$ (0.11), 001 (0.26), $00\bar{1}$ (0.26)

^{a} For explanation see ref 3.

Experimental Section

Data Collection and Reduction. Crystals of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (II), $[2,3\text{-}(CH_3)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (III), and $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (V) were grown by slow evaporation in, respectively, 5% CH_2Cl_2 in hexane at 10 °C, CH_2Cl_2 at 23 °C, and hexane at 10 °C. Each crystal was mounted on a glass fiber in an arbitrary orientation and examined by preliminary precession photographs, which indicated acceptable crystal quality.

Relevant parameters for the data collections and structure determinations are given in Table I. The procedures followed in data collection and processing have been described elsewhere.[3] Space groups were chosen on the basis of chemical and spectroscopic information.

The intensities of three standard reflections, monitored at regular intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and then for absorption, except in the case of III where the crystal was too irregular in shape to permit an absorption correction. Only those reflections for which

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(1) Taken in part from: Borodinsky, L. Ph.D. Thesis, University of Virginia, 1982.

(2) Borodinsky, L.; Grimes, R. N., *Inorg. Chem.*, companion paper in this issue.

(3) Finster, D. C.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 1399.

0020-1669/82/1321-1928$01.25/0

Table II. Positional Parameters and Their Estimated Standard Deviations for $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$

atom	x	y	z	atom	x	y	z
Co	0.14280 (3)	0.22525 (5)	−0.11767 (3)	H(7)	0.280 (2)	0.110 (4)	−0.289 (2)
O	0.2952 (2)	−0.0155 (3)	−0.0114 (1)	H(67)	0.225 (2)	0.274 (4)	−0.251 (2)
C(4)	0.2592 (3)	−0.1676 (5)	−0.0341 (2)	H(8)	0.453 (3)	0.269 (5)	−0.172 (2)
C(5)	0.3063 (3)	−0.2547 (5)	0.0434 (2)	H(89)	0.338 (2)	0.386 (4)	−0.164 (2)
C(6)	0.3225 (3)	−0.1397 (5)	0.1090 (2)	H(9)	0.408 (2)	0.479 (4)	−0.066 (2)
C(7)	0.3535 (3)	−0.0033 (5)	0.0771 (2)	H(910)	0.284 (3)	0.401 (4)	−0.084 (2)
C(2′)	0.0152 (3)	0.3477 (5)	−0.1273 (2)	H(10)	0.312 (2)	0.342 (4)	0.022 (2)
C(3′)	−0.0142 (3)	0.1989 (5)	−0.1608 (2)	H(4′)	0.026 (3)	−0.033 (4)	−0.119 (2)
C(2M)	−0.0363 (4)	0.4823 (5)	−0.1764 (3)	H(5′)	0.150 (2)	0.102 (4)	0.039 (2)
C(2E)	0.0137 (6)	0.6194 (7)	−0.1517 (4)	H(6′)	0.116 (2)	0.449 (4)	−0.004 (2)
C(3M)	−0.1000 (3)	0.1791 (6)	−0.2424 (3)	H(7′)	−0.086 (2)	0.235 (4)	−0.049 (2)
C(3E)	−0.1234 (5)	0.0276 (8)	−0.2701 (4)	H(41T)	0.280 (2)	−0.198 (4)	−0.077 (2)
B(1)	0.2785 (3)	0.1099 (5)	−0.0724 (2)	H(42T)	0.192 (2)	−0.163 (4)	−0.053 (2)
B(2)	0.2053 (3)	0.0679 (5)	−0.1752 (2)	H(51T)	0.367 (2)	−0.298 (4)	0.045 (2)
B(3)	0.3419 (3)	0.0829 (5)	−0.1408 (2)	H(52T)	0.262 (3)	−0.337 (4)	0.046 (2)
B(4)	0.3976 (3)	0.2029 (5)	−0.0570 (2)	H(61T)	0.366 (3)	−0.164 (4)	0.157 (2)
B(6)	0.1472 (3)	0.2223 (6)	−0.2340 (2)	H(62T)	0.261 (2)	−0.118 (4)	0.117 (2)
B(7)	0.2662 (3)	0.1558 (6)	−0.2350 (2)	H(71T)	0.419 (2)	0.002 (4)	0.083 (2)
B(8)	0.3880 (3)	0.2574 (6)	−0.1557 (3)	H(72T)	0.334 (2)	0.095 (4)	0.094 (2)
B(9)	0.3732 (3)	0.3849 (6)	−0.0851 (3)	H(21M)	−0.119 (2)	0.526 (4)	−0.177 (2)
B(10)	0.2962 (3)	0.2957 (5)	−0.0374 (2)	H(22M)	−0.050 (3)	0.458 (5)	−0.233 (2)
B(4′)	0.0392 (3)	0.0782 (5)	−0.0980 (3)	H(31M)	−0.170 (2)	0.198 (4)	−0.249 (2)
B(5′)	0.1106 (3)	0.1680 (6)	−0.0140 (3)	H(32M)	−0.084 (2)	0.229 (4)	−0.282 (2)
B(6′)	0.0912 (3)	0.3480 (6)	−0.0383 (3)	H(21E)	−0.024 (3)	0.689 (5)	−0.157 (2)
B(7′)	−0.0131 (3)	0.2252 (7)	−0.0616 (3)	H(22E)	0.051 (3)	0.609 (5)	−0.184 (2)
H(2)	0.180 (2)	−0.049 (4)	−0.189 (2)	H(23E)	0.057 (3)	0.606 (5)	−0.100 (3)
H(3)	0.381 (2)	−0.028 (4)	−0.148 (2)	H(31E)	−0.190 (3)	0.018 (5)	−0.322 (2)
H(4)	0.469 (2)	0.166 (4)	−0.005 (2)	H(32E)	−0.134 (3)	−0.040 (5)	−0.227 (2)
H(56)	0.149 (2)	0.322 (3)	−0.185 (2)	H(33E)	−0.067 (3)	−0.019 (5)	−0.284 (2)
H(6)	0.083 (2)	0.212 (4)	−0.288 (2)				

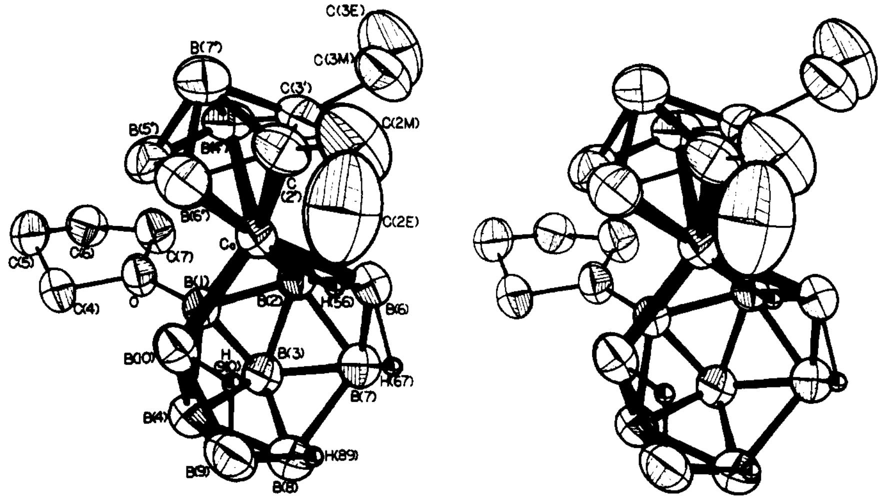

Figure 1. Stereoview of the molecular structure of $[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (II). Hydrogen atoms are omitted for clarity, except for the B–H–B and B–H–Co bridges.

$F_o^2 > 3\sigma(F_o^2)$, where F_o^2 was estimated from counting statistics ($p = 0.03$), were used in the final refinement of the structural parameters, after averaging for equivalent reflections.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[4] and those for hydrogen from Stewart et al.[5] The effects of anomalous dispersion for all nonhydrogen atoms were included in F with use of the values of Cromer and Ibers[6] for $\Delta f'$ and $\Delta f''$.

Solution and Refinement of the Structures. The cobalt atom in each compound was located from a three-dimensional Patterson difference map calculated from all intensity data. The data were phased sufficiently well by these positional parameters so that the nonhydrogen atoms were located from subsequent Fourier difference maps. Anisotropic thermal parameters were then introduced for all nonhydrogen atoms. In the case of III, additional Fourier syntheses disclosed all of the hydrogen positions; for II and V, several hydrogen locations had to be calculated, and these were included in subsequent refinements. For all three structures, all hydrogen positions were allowed to vary for several cycles of refinement and thereafter held fixed. In each case, a final Fourier difference map was essentially featureless.

The models converged to the R and R_w values listed in Table I, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. Tables of observed and calculated structure factors are available (see paragraph on supplementary material at the end of the paper). The principal programs employed in this work have been described elsewhere.[7]

Results and Discussion

Final positional parameters for the three compounds are

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[4] Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[5] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[6] Cromer, D. T.; Ibers, J. A. In ref 4.

[7] Freyberg, D. P.; Mockler, G. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1976**, 447.

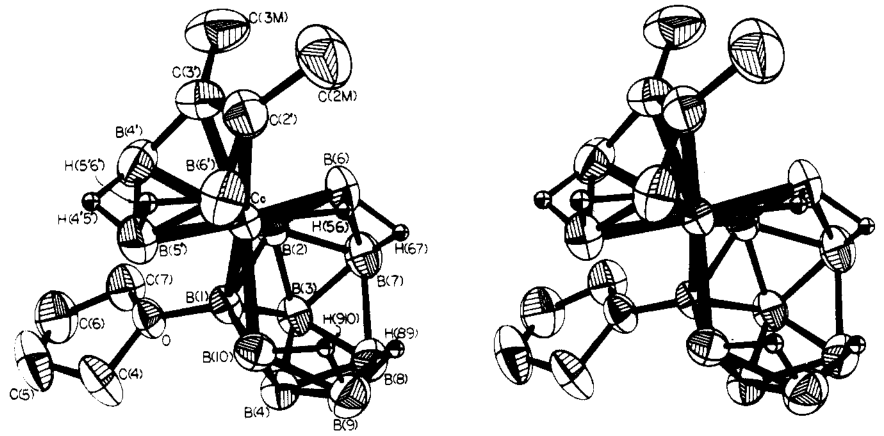

Figure 2. Stereoview of the molecular structure of $[2,3\text{-}(CH_3)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (III).

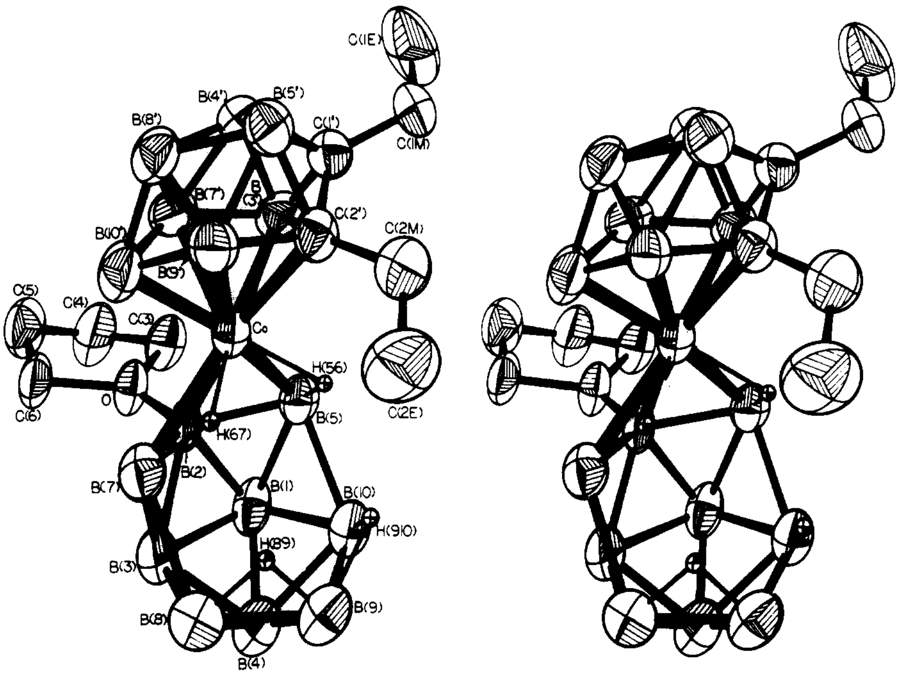

Figure 3. Stereoview of the molecular structure of $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$ (V).

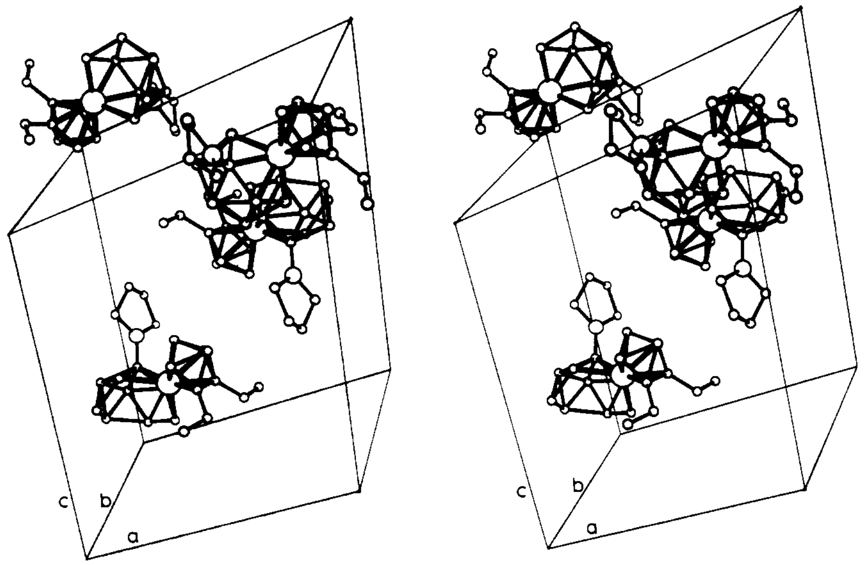

Figure 4. Unit cell packing in II.

given in Tables II–IV, bond distances are listed in Tables V and VI, and Tables VII and VIII contain selected bond angles (in each table, the digits in parentheses are the estimated standard deviations in the least significant figures quoted). Tables of selected mean planes are available as supplementary data.

Table III. Positional Parameters and Their Estimated Standard Deviations for $[2,3\text{-}(CH_3)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	0.19668 (5)	0.21662 (6)	−0.08604 (2)	H(8)	0.619 (4)	−0.086 (4)	−0.135 (2)
O	0.0602 (3)	0.0557 (3)	−0.2012 (1)	H(9)	0.433 (5)	−0.176 (4)	−0.036 (2)
C(3)	0.1060 (5)	0.4208 (4)	−0.0814 (2)	H(10)	0.133 (4)	−0.073 (4)	−0.069 (2)
C(2)	0.1538 (4)	0.3742 (5)	−0.0227 (2)	H(6′)	0.140 (4)	0.184 (4)	0.032 (2)
C(4)	0.0391 (5)	0.1209 (5)	−0.2611 (2)	H(5′)	−0.089 (4)	0.076 (4)	−0.082 (2)
C(5)	−0.1095 (6)	0.0632 (7)	−0.2910 (2)	H(4′)	−0.037 (5)	0.324 (4)	−0.167 (2)
C(6)	−0.1751 (6)	−0.0233 (7)	−0.2464 (2)	H(56)	0.386 (4)	0.233 (4)	−0.058 (2)
C(7)	−0.0470 (6)	−0.0620 (5)	−0.2017 (2)	H(67)	0.543 (5)	0.204 (4)	−0.089 (2)
C(3M)	0.1613 (6)	0.5559 (6)	−0.1064 (3)	H(89)	0.509 (4)	−0.008 (4)	−0.073 (2)
C(2M)	0.2716 (6)	0.4517 (6)	0.0197 (2)	H(910)	0.328 (4)	−0.004 (4)	−0.045 (2)
B(1)	0.2051 (5)	0.0777 (5)	−0.1558 (2)	H(56′)	−0.037 (5)	0.225 (4)	−0.019 (2)
B(2)	0.3187 (5)	0.2251 (5)	−0.1640 (2)	H(45′)	−0.104 (5)	0.247 (4)	−0.100 (2)
B(3)	0.3866 (5)	0.0589 (5)	−0.1843 (2)	H(41T)	0.132 (4)	0.091 (4)	−0.284 (2)
B(4)	0.3151 (5)	−0.0817 (5)	−0.1445 (2)	H(42T)	0.038 (5)	0.210 (4)	−0.258 (2)
B(6)	0.4205 (5)	0.2812 (6)	−0.0965 (2)	H(51T)	−0.103 (6)	0.012 (6)	−0.322 (3)
B(7)	0.5167 (5)	0.1726 (6)	−0.1458 (2)	H(52T)	−0.181 (6)	0.133 (6)	−0.308 (2)
B(8)	0.5104 (5)	−0.0289 (6)	−0.1298 (2)	H(61T)	−0.218 (5)	−0.097 (4)	−0.262 (2)
B(9)	0.4034 (6)	−0.0887 (6)	−0.0718 (2)	H(62T)	−0.241 (6)	0.040 (6)	−0.226 (2)
B(10)	0.2150 (5)	−0.0095 (5)	−0.0865 (2)	H(71T)	−0.060 (4)	−0.079 (4)	−0.164 (2)
B(6′)	0.0965 (6)	0.2330 (6)	−0.0071 (2)	H(72T)	−0.003 (5)	−0.130 (5)	−0.215 (2)
B(5′)	−0.0274 (6)	0.1790 (6)	−0.0735 (3)	H(31M)	0.247 (5)	0.570 (5)	−0.084 (2)
B(4′)	−0.0011 (6)	0.3220 (6)	−0.1201 (2)	H(32M)	0.177 (6)	0.550 (5)	−0.148 (2)
H(2)	0.294 (4)	0.292 (4)	−0.201 (2)	H(33M)	0.091 (5)	0.621 (5)	−0.101 (2)
H(3)	0.410 (4)	0.039 (4)	−0.226 (2)	H(21M)	0.227 (5)	0.514 (5)	0.037 (2)
H(4)	0.282 (4)	−0.180 (4)	−0.167 (2)	H(22M)	0.357 (5)	0.485 (5)	0.006 (2)
H(6)	0.464 (4)	0.393 (4)	−0.086 (2)	H(23M)	0.330 (5)	0.394 (5)	0.045 (2)
H(7)	0.620 (5)	0.201 (4)	−0.166 (2)				

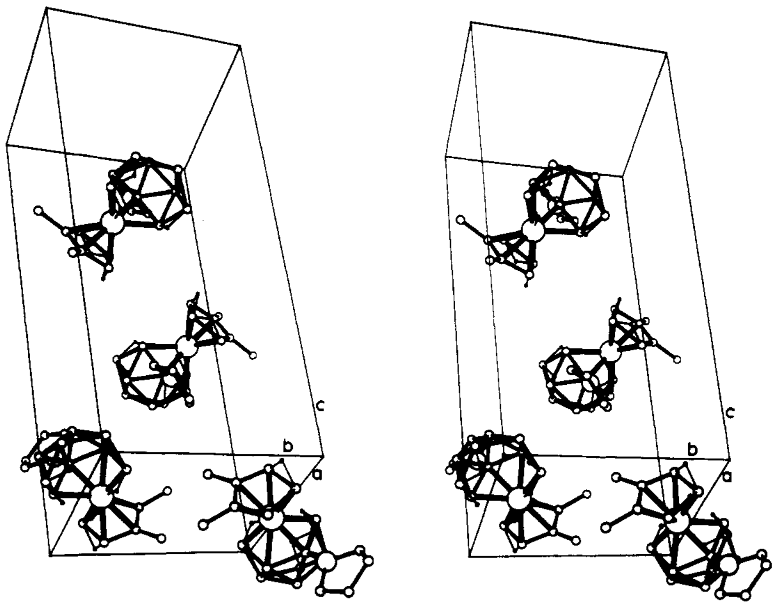

Figure 5. Unit cell packing in III.

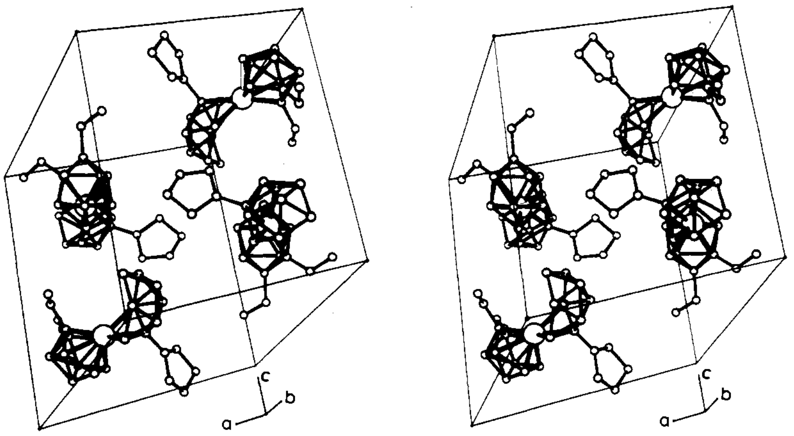

Figure 6. Unit cell packing in V.

Table IV. Positional Parameters and Their Estimated Standard Deviations for $[1,2\text{-}(C_2H_5)_2C_2B_7H_7]\text{-}6\text{-}Co[B_9H_{12}\text{-}2\text{-}O(CH_2)_4]$

atom	*x*	*y*	*z*
Co	0.22971 (9)	0.73631 (8)	0.29502 (6)
O	0.4530 (4)	0.7807 (4)	0.4278 (3)
C(3)	0.4547 (7)	0.7730 (7)	0.5292 (4)
C(4)	0.5434 (8)	0.6980 (8)	0.5691 (5)
C(5)	0.6125 (8)	0.6965 (9)	0.5054 (6)
C(6)	0.5376 (7)	0.7146 (7)	0.4087 (5)
C(1′)	0.1668 (7)	0.5267 (6)	0.1975 (5)
C(2′)	0.1163 (6)	0.6370 (6)	0.2040 (5)
C(1M)	0.1534 (9)	0.4647 (8)	0.1047 (6)
C(1E)	0.2062 (12)	0.3603 (10)	0.1114 (8)
C(2M)	0.0531 (9)	0.6826 (8)	0.1125 (6)
C(2E)	0.0089 (11)	0.7926 (9)	0.1113 (8)
B(1)	0.4176 (7)	0.9227 (8)	0.2817 (6)
B(2)	0.3646 (8)	0.8312 (7)	0.3521 (5)
B(3)	0.3526 (9)	0.9737 (7)	0.3659 (6)
B(4)	0.3442 (10)	1.0499 (8)	0.2608 (7)
B(5)	0.3473 (7)	0.8018 (7)	0.2310 (5)
B(7)	0.2489 (8)	0.8873 (7)	0.3715 (6)
B(8)	0.2368 (10)	1.0357 (8)	0.3064 (7)
B(9)	0.2244 (11)	1.0341 (8)	0.1851 (7)
B(10)	0.3263 (9)	0.9496 (8)	0.1695 (6)
B(3′)	0.2804 (9)	0.5821 (8)	0.2588 (6)
B(4′)	0.2059 (11)	0.4765 (8)	0.3016 (7)
B(5′)	0.0760 (9)	0.5216 (9)	0.2544 (7)
B(7′)	0.2784 (8)	0.5860 (8)	0.3730 (6)
B(8′)	0.1473 (10)	0.5457 (10)	0.3744 (7)
B(9′)	0.0851 (10)	0.6601 (8)	0.3008 (6)
B(10′)	0.1915 (10)	0.6741 (9)	0.4037 (6)
H(31)	0.388 (5)	0.749 (5)	0.527 (4)
H(32)	0.474 (5)	0.849 (5)	0.549 (4)
H(41)	0.516 (5)	0.635 (5)	0.564 (4)
H(42)	0.582 (6)	0.717 (6)	0.633 (5)
H(51)	0.629 (6)	0.623 (7)	0.501 (5)
H(52)	0.656 (8)	0.764 (9)	0.519 (7)
H(61)	0.483 (6)	0.645 (6)	0.372 (5)
H(62)	0.568 (5)	0.768 (6)	0.389 (4)
H(1)	0.477 (6)	0.416 (6)	0.201 (5)
H(3)	0.390 (6)	1.011 (6)	0.439 (5)
H(4)	0.392 (6)	1.123 (6)	0.263 (5)
H(5)	0.412 (6)	0.744 (6)	0.205 (5)
H(56)	0.252 (6)	0.791 (6)	0.197 (5)
H(67)	0.162 (5)	0.839 (5)	0.299 (4)
H(7)	0.246 (6)	0.892 (6)	0.436 (5)
H(8)	0.198 (6)	1.096 (6)	0.338 (5)
H(89)	0.179 (6)	0.978 (6)	0.241 (5)
H(9)	0.179 (6)	1.074 (6)	0.139 (5)
H(910)	0.211 (6)	0.938 (6)	0.143 (5)
H(10)	0.363 (6)	0.962 (6)	0.103 (5)
H(3′)	0.320 (6)	0.572 (6)	0.219 (5)
H(4′)	0.228 (6)	0.390 (6)	0.318 (5)
H(5′)	−0.013 (5)	0.479 (5)	0.223 (4)
H(7′)	0.366 (5)	0.566 (5)	0.428 (4)
H(8′)	0.123 (6)	0.506 (6)	0.419 (5)
H(9′)	0.981 (5)	0.191 (5)	0.186 (4)
H(10′)	0.184 (6)	0.718 (6)	0.477 (5)
H(11M)	0.079 (6)	0.452 (6)	0.076 (5)
H(12M)	0.181 (6)	0.512 (6)	0.064 (5)
H(21M)	0.095 (5)	0.691 (5)	0.086 (4)
H(22M)	−0.005 (6)	0.621 (6)	0.078 (5)
H(11E)	0.154 (7)	0.318 (7)	0.140 (5)
H(12E)	0.280 (6)	0.365 (6)	0.155 (5)
H(13E)	0.216 (6)	0.333 (6)	0.053 (5)
H(21E)	−0.035 (5)	0.782 (5)	0.129 (4)
H(22E)	0.094 (7)	0.860 (7)	0.141 (6)
H(23E)	−0.027 (6)	0.834 (6)	0.057 (5)

Figures 1–3 show the molecular structures and atom numbering while Figures 4–6 depict the unit cell packing.

$[2,3\text{-}(C_2H_5)_2C_2B_4H_4]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (II) and $[2,3\text{-}(CH_3)_2C_2B_3H_5]\text{-}5\text{-}Co[B_9H_{12}\text{-}1\text{-}O(CH_2)_4]$ (III). Compounds II and III are structurally related, both species containing a *nido*-CoB_9 cage framework analogous to $B_{10}H_{14}$ with cobalt occupying the 5-position. In II, the cobalt atom also completes a 7-vertex *closo*-CoC_2B_4 polyhedron, while in III the cobaltacarborane moiety is a *nido*-CoC_2B_3 system; II can be converted to III by removal of the apex BH unit on the carborane ligand and addition of two protons in B–H–B bridging locations (such a conversion has been experimentally observed).[2]

An obvious, and at first perhaps surprising, feature of the structures of II and III is the relative orientation of the borane and carborane ligands, in which the midpoint of the C(2′)–C(3′) bond in the carborane cage is approximately aligned above B(6) of the borane framework. This arrangement is not easily explained on grounds of steric repulsion between the ligands; examination of models of II and III suggests that such interactions would be small and that, from steric considerations alone, almost any ligand conformation could be readily accommodated. Hence we postulate that the observed ligand orientation in II and III is dictated by orbital directive effects on cobalt. In both species, the borane and carborane ligands are highly asymmetric, and thus it is reasonable to expect a strong dependence of energy on ligand conformation. The fact that II and III, with different carborane ligands and different alkyl substituents on carbon, adopt essentially the same ligand orientation tends to support an electronic rather than a steric explanation for the observed arrangement. At this point we are not prepared to offer a detailed picture of metal–ligand orbital overlap in these complexes, although with imagination this could undoubtedly be done.

The Cobaltaborane Cages. One would expect the CoB_9 frameworks in II and III to be closely similar, and this is indeed the case, as shown by comparison of the corresponding bond distances and angles (Tables V and VII). The previously reported cobaltaborane $5\text{-}(\eta^5\text{-}C_5H_5)CoB_9H_{13}$,[8] the only other structurally characterized MB_9 cage in which the metal occupies a 5(7,8,10)-vertex, also resembles II and III except for a slightly shorter average boron–boron distance in the C_5H_5 compound. Another obvious comparison is with $B_{10}H_{14}$ itself,[9] whose individual B–B bond lengths differ from their counterparts in II and III by an average of 0.016 Å, less than 3 standard deviations. In all four compounds—II, III, $B_{10}H_{14}$, and $5\text{-}(\eta^5\text{-}C_5H_5)CoB_9H_{13}$—the longest B–B bonding interaction is B(7)–B(8) and the shortest is B(4)–B(9). The latter trend also holds true for the dicobaltaborane $5,7\text{-}[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$ (another $B_{10}H_{14}$ analogue) and its 6-chloro derivative.[10]

As expected from previous structural studies of MB_9 nido complexes,[8,10,11] the Co–H–B bridges are unsymmetrical, with the Co–H distances substantially longer than the corresponding B–H legs. Trends involving the B–H–B bridges are less clear; some of these appear symmetrical (i.e., with nearly equal B–H lengths) while others do not (Table V), but as is usually the case with X-ray investigations of such species, the hydrogen locations can be viewed only in approximate terms.

A number of previous crystallographic studies of MB_9 and M_2B_8 analogues of $B_{10}H_{14}$ have been reported, including the cobaltaboranes $5\text{-}(C_5H_5)CoB_9H_{13}$,[8] $6\text{-}[C_5(CH_3)_5]CoB_9H_{13}$,[10] $5,7\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}$,[10] $6\text{-}Cl\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{11}$,[10] and $6,9\text{-}[C_5(CH_3)_5]_2Co_2B_8H_{12}$,[10] and several mangana- and

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Table V. Bond Distances (Å) in II and III

	II	III
Cobaltaborane Framework		
Co-B(1)	2.066 (4)	2.067 (3)
Co-B(2)	2.128 (4)	2.158 (3)
Co-B(6)	2.091 (4)	2.085 (3)
Co-B(10)	2.197 (4)	2.190 (3)
B(1)-B(2)	1.768 (5)	1.756 (4)
B(1)-B(3)	1.779 (6)	1.787 (4)
B(1)-B(4)	1.811 (6)	1.813 (4)
B(1)-B(10)	1.774 (6)	1.757 (4)
B(2)-B(3)	1.803 (6)	1.790 (4)
B(2)-B(6)	1.751 (6)	1.735 (4)
B(2)-B(7)	1.787 (6)	1.789 (4)
B(3)-B(4)	1.770 (6)	1.781 (4)
B(3)-B(7)	1.742 (6)	1.724 (4)
B(3)-B(8)	1.764 (7)	1.739 (4)
B(4)-B(8)	1.778 (6)	1.762 (4)
B(4)-B(9)	1.715 (7)	1.707 (4)
B(4)-B(10)	1.807 (6)	1.795 (4)
B(6)-B(7)	1.796 (7)	1.805 (5)
B(7)-B(8)	1.994 (6)	1.981 (5)
B(8)-B(9)	1.773 (8)	1.789 (5)
B(9)-B(10)	1.805 (7)	1.798 (4)
Co-H(56)	1.51 (3)	1.688 (3)
B(6)-H(56)	1.25 (3)	1.060 (3)
B(6)-H(67)	1.34 (3)	1.291 (3)
B(7)-H(67)	1.20 (4)	1.292 (3)
B(8)-H(89)	1.34 (3)	1.281 (3)
B(9)-H(89)	1.29 (3)	1.210 (4)
B(9)-H(910)	1.29 (4)	1.250 (3)
B(10)-H(910)	1.22 (4)	1.257 (3)
Cobaltacarborane Framework		
Co-C(2′)	2.072 (4)	2.145 (2)
Co-C(3′)	2.076 (4)	2.131 (3)
Co-B(4′)	2.104 (5)	2.056 (3)
Co-B(5′)	2.122 (5)	2.036 (3)
Co-B(6′)	2.128 (5)	2.076 (3)
C(2′)-C(3′)	1.466 (5)	1.398 (4)
C(2′)-B(6′)	1.542 (6)	1.509 (4)
C(2′)-B(7′)	1.760 (6)	
C(3′)-B(4′)	1.539 (6)	1.522 (4)
C(3′)-B(7′)	1.773 (6)	
B(4′)-B(5′)	1.665 (6)	1.763 (5)
B(4′)-B(7′)	1.759 (6)	
B(5′)-B(6′)	1.678 (6)	1.795 (5)
B(5′)-B(7′)	1.715 (6)	
B(6′)-B(7′)	1.769 (6)	
C(2′)-C(2M)	1.514 (6)	1.502 (4)
C(2M)-C(2E)	1.412 (8)	
C(3′)-C(3M)	1.512 (5)	1.522 (4)
C(3M)-C(3E)	1.449 (8)	
B(4′)-H(45′)		1.281 (4)
B(5′)-H(45′)		1.055 (3)
B(5′)-H(56′)		1.309 (4)
B(6′)-H(56′)		1.157 (3)
Terminal Hydrogen Atoms (Mean Distances)		
⟨B-H⟩	1.092	1.086
⟨C(CH_3)-H⟩	1.030	0.890
⟨C(CH_2)-H⟩	0.954	
⟨C(THF)-H⟩	0.938	0.915
Tetrahydrofuran Ring		
O-B(1)	1.524 (4)	1.526 (3)
O-C(4)	1.469 (5)	1.471 (3)
O-C(7)	1.480 (4)	1.469 (3)
C(4)-C(5)	1.506 (6)	1.484 (4)
C(5)-C(6)	1.512 (6)	1.473 (5)
C(6)-C(7)	1.490 (6)	1.445 (4)

Table VI. Bond Distances (Å) in V

Cobaltaborane Framework			
Co-B(2)	2.091 (6)	B(4)-B(9)	1.675 (10)
Co-B(5)	2.176 (6)	B(4)-B(10)	1.786 (8)
Co-B(7)	2.135 (5)	B(5)-B(10)	2.000 (8)
B(1)-B(2)	1.791 (7)	B(7)-B(8)	2.033 (8)
B(1)-B(3)	1.804 (8)	B(8)-B(9)	1.756 (9)
B(1)-B(4)	1.806 (9)	B(9)-B(10)	1.755 (11)
B(1)-B(5)	1.788 (8)	B(5)-H(56)	1.224 (6)
B(1)-B(10)	1.790 (8)	Co-H(56)	1.685 (6)
B(2)-B(3)	1.758 (7)	Co-H(67)	1.546 (6)
B(2)-B(5)	1.777 (7)	B(7)-H(67)	1.457 (7)
B(2)-B(7)	1.764 (9)	B(8)-H(89)	1.268 (7)
B(3)-B(4)	1.787 (8)	B(9)-H(89)	1.327 (7)
B(3)-B(7)	1.744 (9)	B(9)-H(910)	1.309 (7)
B(3)-B(8)	1.712 (10)	B(10)-H(910)	1.470 (7)
B(4)-B(8)	1.735 (11)		
Cobaltacarborane Framework			
Co-C(2′)	2.096 (5)	B(4′)-B(5′)	1.748 (11)
Co-B(3′)	2.108 (6)	B(4′)-B(7′)	1.802 (8)
Co-B(7′)	2.162 (6)	B(4′)-B(8′)	1.709 (10)
Co-B(9′)	2.141 (8)	B(5′)-B(8′)	1.789 (9)
Co-B(10′)	1.963 (6)	B(5′)-B(9′)	1.811 (9)
C(1′)-C(2′)	1.513 (7)	B(7′)-B(8′)	1.801 (10)
C(1′)-B(3′)	1.663 (9)	B(7′)-B(10′)	1.718 (10)
C(1′)-B(4′)	1.603 (7)	B(8′)-B(9′)	1.817 (10)
C(1′)-B(5′)	1.641 (9)	B(8′)-B(10′)	1.682 (9)
C(2′)-B(3′)	2.192 (9)	B(9′)-B(10′)	1.770 (11)
C(2′)-B(5′)	1.739 (8)	C(1′)-C(1M)	1.533 (7)
C(2′)-B(9′)	1.619 (7)	C(2′)-C(2M)	1.487 (7)
B(3′)-B(4′)	1.831 (9)	C(1M)-C(1E)	1.439 (9)
B(3′)-B(7′)	1.696 (8)	C(2M)-C(2E)	1.457 (8)
Terminal Hydrogen Atoms (Mean Distances)			
⟨B-H⟩	1.113	⟨C(CH_2)-H⟩	0.949
⟨C(CH_3)-H⟩	1.006	⟨C(THF)-H⟩	0.953
Tetrahydrofuran Ring			
O-B(2)	1.506 (6)	C(3)-C(4)	1.471 (8)
O-C(3)	1.496 (4)	C(4)-C(5)	1.480 (8)
O-C(6)	1.463 (6)	C(5)-C(6)	1.513 (7)

rhenaboranes of general formula 6-$(CO)_3MB_9H_{12}R$, where R = H, THF, $(C_2H_5)_2O$, or $(C_2H_5)_3N(CH_2)_4O$.[11] In all cases, the metal atoms are located on the open face of a decaborane-like 10-vertex framework, and the four bridge hydrogens are disposed on the open face in a manner analogous to that of $B_{10}H_{14}$. One example of an MB_9 system in which the metal is *not* on the open face, i.e., 2-$(C_5H_5)CoB_9H_{13}$, has been prepared[12a] and its structure established.[12b] Insofar as the CoB_9 cages in II and III are concerned, the gross geometries retain the remarkable similarity to $B_{10}H_{14}$ that has previously been noted in the other metallaboranes cited.

The Cobaltacarborane Cages. The 7-vertex CoC_2B_4 cage in II is isostructural and isoelectronic with a large family of *closo*-MC_2B_4 species, of which several have been crystallographically characterized; of these, the three most directly related to II are 1,2,3-$(C_5H_5)Co(CH_3)_2C_2B_4H_4$,[13] the 5-cobaltocenium derivative of the [2,3-$(CH_3)_2C_2B_3H_5$]Co[2,3-$(CH_3)_2C_2B_4H_4$]$^-$ ion,[14] and the bis(carboranyl) complex [2,3-$(CH_3)_2C_2B_4H_4$]$_2FeH_2$.[15] (The parent carborane system 2,3-$C_2B_5H_7$ and its borane anion analogue $B_7H_7^{2-}$ are both known[16,17] but have not been structurally studied by rigorous methods.) In addition, the formal $R_2C_2B_4H_4^{2-}$ ligand in II can be compared with the corresponding *nido*-carborane $R_2C_2B_4H_6$ (R = H or CH_3) for which X-ray data are available.[18] In all of these the gross pentagonal-pyramidal or -bipyramidal geometry is preserved, with a framework C–C distance between ~1.40 and 1.49 Å, suggesting a degree of localized double-bond character between the carbons;[19] the value in II [1.466 (5) Å] is within this range.

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Table VII. Selected Bond Angles (Deg) in II and III

	II	III
B(1)–Co–B(2)	49.8 (2)	49.1 (1)
B(1)–Co–B(10)	49.1 (2)	48.6 (1)
B(1)–Co–C(2′)	163.3 (2)	170.3 (1)
B(1)–Co–C(3′)	142.9 (2)	133.4 (1)
B(1)–Co–B(4′)	102.9 (2)	98.7 (1)
B(1)–Co–B(5′)	90.7 (2)	96.7 (1)
B(1)–Co–B(6′)	120.5 (2)	138.8 (1)
B(2)–Co–B(6)	49.0 (2)	48.2 (1)
B(2)–Co–C(2′)	145.6 (2)	130.8 (1)
B(2)–Co–C(3′)	109.2 (2)	103.2 (1)
B(2)–Co–B(4′)	95.8 (2)	99.0 (1)
B(2)–Co–B(5′)	121.2 (2)	134.3 (1)
B(2)–Co–B(6′)	167.1 (2)	172.0 (1)
B(6)–Co–B(10)	104.7 (2)	103.2 (1)
B(6)–Co–C(2′)	106.0 (2)	96.2 (1)
B(6)–Co–C(3′)	93.5 (2)	94.9 (1)
B(6)–Co–B(4′)	116.0 (2)	123.9 (1)
B(6)–Co–B(5′)	162.0 (2)	172.8 (1)
B(6)–Co–B(6′)	143.8 (2)	125.0 (1)
B(10)–Co–C(2′)	121.2 (2)	136.9 (1)
B(10)–Co–C(3′)	159.0 (2)	161.9 (1)
B(10)–Co–B(4′)	131.1 (2)	123.3 (1)
B(10)–Co–B(5′)	89.5 (2)	83.9 (1)
B(10)–Co–B(6′)	85.5 (2)	96.9 (1)
C(2′)–Co–C(3′)	41.4 (2)	38.2 (1)
C(2′)–Co–B(6′)	43.1 (2)	41.8 (1)
C(3′)–Co–B(4′)	43.2 (2)	42.6 (1)
B(4′)–Co–B(5′)	46.4 (2)	51.0 (1)
B(5′)–Co–B(6′)	46.5 (2)	51.8 (1)
Co–B(1)–O	121.6 (2)	119.1 (2)
B(2)–B(1)–O	116.7 (3)	118.0 (2)
B(3)–B(1)–O	113.7 (3)	116.0 (2)
B(4)–B(1)–O	110.5 (3)	110.4 (2)
B(10)–B(1)–O	119.3 (3)	117.5 (2)
B(1)–O–C(4)	123.8 (3)	122.7 (2)
B(1)–O–C(7)	125.2 (3)	125.6 (2)
C(4)–O–C(7)	111.0 (3)	108.7 (2)
O–C(4)–C(5)	104.5 (3)	104.4 (3)
C(4)–C(5)–C(6)	103.4 (3)	107.3 (3)
C(5)–C(6)–C(7)	104.9 (4)	106.5 (3)
C(6)–C(7)–O	102.5 (3)	103.7 (3)
Co–C(2′)–C(2M)	133.8 (3)	127.4 (2)
C(3′)–C(2′)–C(2M)	120.0 (4)	121.8 (3)
B(6′)–C(2′)–C(2M)	126.1 (4)	121.5 (3)
B(7′)–C(2′)–C(2M)	134.9 (4)	
Co–C(3′)–C(3M)	137.0 (3)	129.7 (2)
C(2′)–C(3′)–C(3M)	120.1 (4)	123.5 (3)
B(4′)–C(3′)–C(3M)	127.6 (4)	121.8 (3)
B(7′)–C(3′)–C(3M)	132.2 (4)	
C(2′)–C(2M)–C(2E)	116.7 (5)	
C(3′)–C(3M)–C(3E)	115.8 (4)	
Co–B(6)–B(7)	113.1 (3)	114.1 (2)
B(6)–B(7)–B(8)	114.0 (3)	115.7 (2)
B(7)–B(8)–B(9)	119.8 (3)	118.5 (2)
B(8)–B(9)–B(10)	107.2 (3)	106.1 (2)
Co–B(10)–B(9)	116.8 (3)	119.2 (2)
H(56)–B(6)–H(67)	96 (2)	88 (2)
H(89)–B(9)–H(910)	92 (2)	92 (2)
Co–H(56)–B(6)	98 (2)	96 (2)
B(6)–H(67)–B(7)	90 (2)	89 (2)
B(8)–H(89)–B(9)	85 (2)	92 (2)
B(9)–H(910)–B(10)	92 (3)	92 (2)
B(4′)–H(45′)–B(5′)		98 (2)
B(5′)–H(56′)–B(6′)		93 (2)

Table VIII. Selected Bond Angles (Deg) in V

B(2)–Co–B(5)	49.2 (2)	Co–C(2′)–B(3′)	58.9 (2)
B(2)–Co–B(7)	49.3 (2)	C(1′)–C(2′)–B(5′)	60.1 (4)
B(5)–Co–B(7)	87.5 (2)	Co–C(2′)–B(9′)	69.0 (3)
C(2′)–Co–B(3′)	62.8 (2)	B(5′)–C(2′)–B(9′)	65.2 (4)
B(3′)–Co–B(7′)	46.8 (2)	Co–C(2′)–C(2M)	119.4 (4)
B(7′)–Co–B(10′)	48.9 (3)	C(1′)–C(2′)–C(2M)	114.8 (4)
B(9′)–Co–B(10′)	50.9 (3)	B(3′)–C(2′)–C(2M)	134.3 (6)
C(2′)–Co–B(9′)	44.9 (2)	B(5′)–C(2′)–C(2M)	122.0 (5)
B(2)–Co–C(2′)	162.3 (2)	B(9′)–C(2′)–C(2M)	121.7 (5)
B(2)–Co–B(3′)	107.5 (3)	C(2′)–C(2M)–C(2E)	118.4 (6)
B(2)–Co–B(7′)	99.1 (2)	Co–B(7)–B(8)	122.1 (3)
B(2)–Co–B(9′)	152.7 (2)	B(7)–B(8)–B(9)	116.5 (4)
B(2)–Co–B(10′)	105.3 (2)	B(8)–B(9)–B(10)	106.4 (5)
B(5)–Co–C(2′)	113.5 (2)	B(5)–B(10)–B(9)	118.8 (5)
B(5)–Co–B(3′)	84.4 (2)	Co–B(5)–B(10)	120.1 (3)
B(5)–Co–B(7′)	113.6 (2)	Co–H(56)–B(5)	97.9 (6)
B(5)–Co–B(9′)	157.4 (2)	Co–H(67)–B(7)	90.6 (6)
B(5)–Co–B(10′)	151.6 (3)	B(8)–H(89)–B(9)	84.7 (7)
B(7)–Co–C(2′)	142.7 (2)	B(9)–H(910)–B(10)	78.0 (8)
B(7)–Co–B(3′)	154.2 (3)	H(56)–Co–H(67)	87.4 (4)
B(7)–Co–B(7′)	118.1 (2)	H(89)–B(9)–H(910)	78.7 (6)
B(7)–Co–B(9′)	109.1 (2)	Co–B(2)–O	118.1 (3)
B(7)–Co–B(10′)	85.3 (3)	B(1)–B(2)–O	109.9 (4)
C(2′)–C(1′)–B(3′)	87.2 (4)	B(3)–B(2)–O	113.1 (4)
C(2)–C(1′)–B(5′)	66.8 (4)	B(5)–B(2)–O	121.7 (4)
B(3′)–C(1′)–B(4′)	68.2 (4)	B(7)–B(2)–O	124.2 (4)
B(4′)–C(1′)–B(5′)	65.2 (4)	B(2)–O–C(3)	124.4 (4)
C(2′)–C(1′)–C(1M)	123.3 (4)	B(2)–O–C(6)	123.7 (3)
B(3′)–C(1′)–C(1M)	123.5 (5)	C(3)–O–C(6)	110.9 (3)
B(4′)–C(1′)–C(1M)	126.9 (5)	O–C(3)–C(4)	103.4 (4)
B(5′)–C(1′)–C(1M)	121.3 (5)	C(3)–C(4)–C(5)	108.1 (5)
C(1′)–C(1M)–C(1E)	116.0 (5)	C(4)–C(5)–C(6)	104.2 (5)
C(1′)–C(2′)–B(3′)	49.3 (3)	O–C(6)–C(5)	103.3 (4)

The C_2B_3 ring in II, which is the face presented to cobalt, is planar and located 1.616 Å from the metal. The methyl group carbons are significantly deflected out of the C_2B_3 plane in a direction away from cobalt, which interestingly is opposite to the situation in III (vide infra).

In compound III the carborane moiety is a 6-vertex *nido*-CoC_2B_3 framework having two B–H–B bridges on the open face. Although this is a common structural type, the only other species of this class for which X-ray structures have been reported are 1,2,3-$(CO)_3FeC_2B_3H_7$[20] and the previously mentioned cobaltocenium derivative of $[2,3\text{-}(CH_3)_2C_2B_3H_5]$-$Co[2,3\text{-}(CH_3)_2C_2B_4H_4]^-$.[14] In both the latter species and III, the methyl carbons on the open C_2B_3 ring are bent out of plane *toward* cobalt; in contrast, the substituents on pyramidal $R_2C_2B_4H_4^{2-}$ ligands are invariably bent away from the metal (as in II, noted above). This effect is undoubtedly associated with differences in orbital hybridization of the framework carbon atoms in open (C_2B_3) vs. closed (C_2B_4) ligands. A related observation is the shorter carbon–carbon distance in the C_2B_3 rings as compared to that in the C_2B_4 group; compounds II and III, for example, exhibit C–C bond lengths of 1.466 (5) and 1.398 (4) Å. This trend is quite general and has been attributed[14,19,21] to the lower coordination of the C_2B_3 carbons as opposed to that of their C_2B_4 counterparts, which produces higher C–C bond order (probably multiple-bond character) in the C_2B_3 ligands. Another consequence of the difference in coordition is that the cobalt atom is closer to the C_2B_3 ligand in III than to the C_2B_4 ligand in II, the respective vector distances being 1.575 vs. 1.616 Å. Again, the same effect is seen elsewhere, notably in $(C_5H_5)Co(C_5H_4)^+[2,3\text{-}(CH_3)_2C_2B_3H_5]Co[2,3\text{-}(CH_3)_2C_2B_4H_4]^-$, which contains both types of ligands.[14] It has been suggested that in metal complexes of C_2B_4 ligands, the presence of the apex atom [B(7)] diverts electron density out of the C–C and C–Co bonds and weakens them in comparison to those of the C_2B_3 complexes.[14]

In both II and III, the cobalt atom is much closer to the borane than to the carborane ligand; the vector distances are respectively 1.297 and 1.616 Å in II, while in III they are 1.318 and 1.575 Å. This effect arises from the relatively large "spread" of the B_4 bonding face on the borane ligand, which requires that the cobalt move closer to that group in order to achieve normal Co–B bonding (a similar observation[8] was noted for 5-(η^5-C_5H_5)CoB_9H_{13}). When the metal is in the 6-position of the MB_9 cage, as in V, the situation is very

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different because the bonding face on the borane ligand is now only η^3 (if bridging hydrogens are ignored); consequently, the metal–cage vector is relatively long (e.g., 1.521 Å in V). This contrast between 5- and 6-cobalt substitution is also dramatically evident in the structures of several $[\eta^5\text{-}C_5(CH_3)_5]CoB_9H_{13}$ and $[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$ species reported elsewhere,[10] in which the metal–borane vectors are about 1.33 Å in the 5-CoB_9 and 5,7-Co_2B_8 complexes and 1.45–1.47 Å in the 6-CoB_9 and 6,9-Co_2B_8 systems.

Comparison of $R_2C_2B_4H_6^{2-}$ and $R_2C_2B_3H_5^{2-}$ Ligands with $C_5R'_5$. In view of the larger covalent radius of boron compared to that of carbon (~0.82 vs. 0.77 Å), one might have expected to find metal–carborane ligand vectors slightly longer than metal–C_5R_5 vectors in comparable species. Yet comparison of II and III with their C_5R_5 counterparts[10]—5-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$, 5,7-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$, and the 6-Cl derivative of the latter complex—reveals that the metal–carborane ring distances are in fact much *shorter*; typical Co–C_5R_5 vectors exceed 1.7 Å, about 0.1–0.2 Å greater than the corresponding metal–C_2B_3 or metal–C_2B_4 values. We interpret this large effect as evidence of much greater covalence in the metal–carborane interaction and, accordingly, of a large degree of ionic character in the metal–C_5R_5 bonds. This qualitative view is consistent with theoretical and UV photoelectron spectroscopic studies of related metallaboranes and metal–hydrocarbon complexes.[22]

Tetrahydrofuran Ligands. A curious feature of the structures of II and III is the presence of $O(CH_2)_4$ substituents in two different conformations. In II, the THF ring adopts the "twist" mode of approximate C_2 symmetry, while in III the "envelope" (C_s) conformation is found. In V, discussed below, the THF group is of the twist type, while X-ray studies of the 2- and 6-THF derivatives of 6-$(CO)_3MnB_9H_{13}$ revealed both envelope and twist forms, respectively.[11a] Clearly, no distinct preference exists for either conformation; indeed, one reported structure[23] contains different THF molecules in both the twist and the envelope modes!

The location of THF at B(1) in II and III marks that boron as the most electrophilic site on the cage and, together with V, extends the previously noted[11] tendency of THF to attack at a boron adjacent to the metal in MB_9 nido systems.

$[1,2\text{-}(C_2H_5)_2C_2B_7H_7]$-6-Co$[B_9H_{12}$-2-$O(CH_2)_4]$ (V). Compound V, another boranocobaltacarborane similar to II and III, differs from them in two major respects: cobalt occupies the 6- rather then the 5-vertex in the CoB_9 nido framework, and the cobaltacarborane cage is a CoC_2B_7 system (Figure 3). The molecule is at present the only known example of a system incorporating fused 10-vertex nido and closo cages. As is the case with II and III, the borane and carborane units are oriented with a peculiar "twist" such that the RCCR portion of the carborane ligand is well out of alignment with the open face on the CoB_9 cage. Again, a probable explanation of this arrangement is that it is controlled by requirements of orbital geometry on the cobalt atom, and not primarily by steric interaction between the ligands. A notable and somewhat unusual aspect of the structure is the presence of only one carbon atom on the carborane–metal bonding face despite the open C_2B_3 face on the original $R_2C_2B_3H_5^{2-}$ reagent.

The CoB_9 Cage System. As with II, III, and all other *nido*-MB_9 frameworks thus far characterized structurally, the molecular parameters closely resemble those of $B_{10}H_{14}$ when one allows for the distortion introduced by introduction of a cobalt atom at the 6-position. Of previously reported cobaltaborane structures, those most closely related to V are 6-$[\eta^5\text{-}C_5(CH_3)_5]CoB_9H_{13}$ and 6,9-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$,[10] and as expected there is considerable similarity between these species and V. The Co–H–B bridges in V are typically asymmetric with the longer legs attached to cobalt. The vector distance from cobalt to the B(2)–B(5)–B(7) bonding face is 1.521 Å, slightly longer than the corresponding vectors in 6-$[\eta^5\text{-}C_5(CH_3)_5]CoB_9H_{13}$ and 6,9-$[\eta^5\text{-}C_5(CH_3)_5]_2Co_2B_8H_{12}$ (~1.47 Å). This is what one would expect if the cobalt atom in V participates in largely covalent bonding interactions with *both* ligands; in the $C_5(CH_3)_5$–Co complexes, the Co–C_5 bonding is viewed as primarily ionic (see above), allowing the Co–B_9 covalent cage interaction in those species to be measurably stronger than it is in V.

The CoC_2B_7 Cage System. The cobaltacarborane unit in V has the gross geometry of a 10-vertex closo polyhedron, i.e. a bicapped square antiprism with the cobalt in one of the equatorial belts. The two framework carbon atoms are located respectively in an apex position and in an equatorial vertex adjacent to cobalt; there is only one Co–C bonding interaction. The ethyl substituent groups are directed away from each other and form a nearly coplanar array with the cage carbon atoms.

With one notable exception, the bond distances in the cobaltacarborane cage are within normal ranges. However, the C(2′)–B(3′) interaction is extremely long [2.192 (9) Å], indicating a weak bond but a bond nevertheless (C–B distances of 2.12–2.25 Å have been observed in earlier studies of carboranes.[24] As a consequence of the elongation of the C(2′)–B(3′) edge, the C(2′)–C(1′)–B(3′)–Co array could be regarded as a pseudoopen face. There being no indication whatever of any steric interaction to account for the long C–B bond, we must look for an electronic cause. In the accompanying paper,[2] the CoC_2B_7 polyhedron in V is described as a 22-electron, 10-vertex closo system that obeys the Wade electron-count formalism.[25] For the determination of the 22-electron total, a contribution of 2 electrons from cobalt to the CoC_2B_7 cage was assumed; this, together with a contribution of 1 electron to the CoB_9 framework plus 6 electrons assigned, as usual, to "nonbonding" orbitals on the metal, would account for the 9 valence electrons of the cobalt atom. If, however, some of the assumed "nonbonding" electron density finds its way into the carborane cage, the anticipated result would be a distortion in the form of bond-stretching or bond-breaking, depending on the magnitude of the effect. Moreover, it is quite reasonable that the stretched bond would involve C(2′) as this atom thereby approaches a favored lower coordinate state; the apex carbon C(1′) is already low coordinate, so the "incentive" for bond stretching or cleavage would lie with the nominal high-coordinate carbon, C(2′).

Why might there be some leakage of electron density from "nonbonding" orbitals on cobalt into the skeletal bonding molecular orbitals in the cobaltacarborane polyhedron? The answer may lie in the peculiarly crowded and asymmetric arrangement of the borane and carborane ligands around cobalt, which may well drastically alter the hybrid orbital energies relative to more symmetric arrangements as are found in cobaltocene or in bis(carboranyl)metal complexes such as $(R_2C_2B_4H_4)_2FeH_2$ and $(R_2C_2B_4H_4)_2CoH$.

A related report involving anomalous bond stretching in an MC_2B_7 polyhedron occurs in the platinacarborane 7,1,6-$[(C_2H_5)_3P]_2Pt(CH_3)_2C_2B_7H_7$, which has a $PtCB_2$ open face.[26] In this case the "stretched" edge is a B–B interaction of 2.57 Å, clearly nonbonding. Polyhedral distortions of this type are common in heavy-metal metallacarboranes, especially those of platinum and palladium; the effect has been attributed to

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unequal contributions of the metal $5d_{xz}$ and $5d_{yz}$ orbitals to skeletal bonding, which lead to "violations" of Wade's rules.[27] However, such arguments seem inapplicable to cobaltacarboranes, which rarely exhibit distortion in $(2n + 2)$-electron polyhedra.

Aside from the long C(2′)–B(3′) bond, the CoC_2B_7 framework in V is comparable to those of other 10-vertex closo borane systems that have been characterized by X-ray diffraction, including the $[(1,6\text{-}C_2B_7H_9)_2\text{-}2\text{-}Co]^-$ ion,[28] $2,6,1,10\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_6H_8$[29] (in which the skeletal carbon atoms occupy the 1,6- and 1,10-vertices, respectively), $2,3,10\text{-}(\eta^5\text{-}C_5H_5)_2NiCoCB_7H_8$,[30] $1,6\text{-}(CH_3)_2C_2B_8H_8$,[31] and the $B_{10}H_{10}^{2-}$ ion.[32] All of these are 22-electron $(2n + 2)$ systems that adopt regular bicapped-square-antiprism geometry as expected.

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Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, and selected least-squares planes (46 pages). Ordering information is given on any current masthead page.

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Platinum(II) Complexes with Terminal Hydroxo and Aquo Groups: Crystal Structures of Hydroxo-*cis*-diammine(1-methylcytosine-N^3)platinum(II) Nitrate Dihydrate, $[Pt(OH)(NH_3)_2(C_5H_7N_3O)]NO_3\cdot 2H_2O$, and *cis*-Diammineaquo(1-methylcytosine-N^3)platinum(II) Dinitrate Hydrate, $[Pt(NH_3)_2(H_2O)(C_5H_7N_3O)](NO_3)_2\cdot H_2O$

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The preparation of *cis*-diammine(1-methylcytosine-N^3)platinum(II) complexes containing terminal H_2O, OH, and NO_3 groups, respectively, as fourth ligands, is reported: *cis*-$[Pt(NH_3)_2C(H_2O)](NO_3)_2\cdot H_2O$ (I), *cis*-$[Pt(NH_3)_2C(NO_3)]NO_3$ (Ib), *cis*-$[Pt(NH_3)_2C(OH)]NO_3\cdot 2H_2O$ (II), and *cis*-$[Pt(NH_3)_2C(OH)]NO_3$ (IIa) (C = 1-methylcytosine). The X-ray structures of I and II have been determined. I crystallizes in the triclinic form: $P\bar{1}$, $a = 12.380$ (6) Å, $b = 6.580$ (3) Å, $c = 10.895$ (3) Å, $\alpha = 90.39$ (3)°, $\beta = 110.26$ (3)°, $\gamma = 114.68$ (3)°, and $Z = 2$. II was obtained as monoclinic crystals, $P2_1/c$, $a = 12.207$ (4) Å, $b = 6.203$ (1) Å, $c = 18.853$ (5) Å, and $\beta = 109.64$ (2)°. Data for both crystals were collected with Mo Kα radiation and a Syntex $P2_1$ (II) or $P3$ (I) diffractometer. The crystal structures were determined by standard methods; that of I was refined to $R_1 = 0.0575$ and $R_2 = 0.0610$ on the basis of 3442 independent reflections and that of II to $R_1 = 0.0657$ and $R_2 = 0.0688$ on the basis of 3100 independent reflections. The structures of the two cations are very similar with the pyrimidine plane at roughly right angles to the ligand square plane. Bond lengths (Pt–N = 2.02 (1)–2.036 (8) Å; Pt–O = 2.027 (9), 2.052 (8) Å) are normal. To our knowledge, I and II represent the first examples of Pt(II) complexes containing terminal H_2O and OH ligands, respectively, that have been characterized with X-ray techniques. Their formation has been made possible by the specific hydrogen-bonding properties of H_2O and OH ligands in these complexes and by the poor donor strength of O(2) of the 1-methylcytosine toward platinum in aqueous solution. When warmed, II is readily transferred into compounds containing the N(4)-deprotonated C ligand as a bridge. Brief IR and Raman spectroscopic data are presented which enabled us to make predictions on the structures of I and II before verification by X-ray analysis.

Introduction

Platinum(II) complexes with terminal aquo and/or hydroxo groups are generally assumed to occur in aqueous solution.[2] Though the existence of hydroxo complexes in the solid state in some cases has been deduced by spectroscopic means, there have also been doubts as to whether other complexes claimed to contain OH ligands indeed were formulated correctly.[3] In recent years, we and others have reported the crystal structures of a series of di- and trimeric complexes of Pt(II) with hydroxo bridges,[4-7] thus proving that Pt(II) in this respect behaves very much like other transition metals, for which hydroxo-bridged complexes are quite common.[8] The large majority of the published structures on (μ-OH)Pt^{II} complexes contained the *cis*-$Pt(NH_3)_2^{2+}$ moiety, which was of particular interest because of the remarkable antitumor activity of many of its derivatives.[9] As has been demonstrated by ^{195}Pt NMR, hy-

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