1-[(η^5-C_5R_5)Co]B_4H_8 (R = H or Me)† Sandwich Complexes containing a Square Cyclic $B_4H_8{}^{2-}$ Ligand Analogous to $C_4H_4{}^{2-}$: Structural and Spectroscopic Studies

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The title complexes, prepared in moderate yields *via* an improved procedure, have been investigated by *X*-ray crystallography, n.m.r., u.v., and i.r. spectroscopy, and compared with their structural relatives B_5H_9, 1-[(CO)$_3$Fe]B_4H_8, and [Co(η^5-C_5H_5)(η^4-C_4H_4)] as well as their 2-[(η^5-C_5R_5)Co]B_4H_8 (R = H or Me) isomers. Disorder of the C_5Me_5 ring prevented satisfactory refinement of the crystallographic data for 1-[(η^5-C_5R_5)Co]B_4H_8 (R = Me); however, for the parent (R = H) molecule, a model having four-fold disorder in the C_5H_5 ring was found to refine satisfactorily. The complex has a sandwich structure in agreement with the geometry previously assigned from n.m.r. data. The molecular bond lengths and angles are close to those of their counterparts in B_5H_9, and the unusually short Co–B distance [1.977(2) Å] suggests a strong covalent metal–$B_4H_8{}^{2-}$ linkage; this value is similar to the mean Co–C(C_4H_4) distance in [Co(η^5-C_5H_5)(η^4-C_4H_4)] [1.965(1) Å] despite the smaller covalent radius of carbon *versus* boron. The terminal H atoms on the $B_4H_8{}^{2-}$ ligand, like those in [Co(η^5-C_5H_5)(η^4-C_4H_4)], are only slightly out of the B_4 (or C_4) plane, in contrast to B_5H_9 where these hydrogens are substantially bent toward the apex.

The cobaltaborane isomers 1- and 2-[(η^5-C_5H_5)Co]B_4H_8 [(1a) and (1b), Figure 1] are structural and electronic analogues of pentaborane(9), B_5H_9, in which a Co(C_5H_5) unit replaces an isolobal BH group in an apical or basal position. These compounds were first prepared in 1973 by Miller and Grimes,[1a] who isolated the red, crystalline, air-stable 2-isomer from the reaction of $Na^+B_5H_8{}^-$, $CoCl_2$, and $Na^+C_5H_5{}^-$ in cold tetrahydrofuran and discovered its thermal rearrangement (200 °C) to the slightly less robust 1-isomer, obtained as pale yellow crystals. Subsequent reports have dealt with the chemistry [1b,2] and crystal structure [3] of the 2-isomer.

The 1-isomer can also be described as a sandwich complex of Co^{3+} with $C_5H_5{}^-$ and $B_4H_8{}^{2-}$ ligands. The square cyclic $B_4H_8{}^{2-}$ ion, which has never been observed as a free species, is isoelectronic with $C_4H_4{}^{2-}$ (cyclobutadienediide) and hence is of unusual theoretical interest. However, aside from 1-[(η^5-C_5H_5)Co]B_4H_8 and 1-[(η^5-C_5Me_5)Co]B_4H_8 (2a),[4] the only other characterized complex of square $B_4H_8{}^{2-}$ is the orange liquid 1-[(CO)$_3$Fe]B_4H_8, which was prepared independently by several groups [5] soon after the discovery of the [(η^5-C_5H_5)Co]B_4H_8 isomers but still lacks *X*-ray structural confirmation.

In the present study, *X*-ray crystallographic and spectroscopic investigations were conducted on 1-[(η^5-C_5H_5)Co]B_4H_8 and 1-[(η^5-C_5Me_5)Co]B_4H_8. Unfortunately, the C_5 ring proved to be highly disordered in both structures, and only the data on the C_5H_5 complex refined successfully. In the course of this research we developed an improved synthesis of (1a).

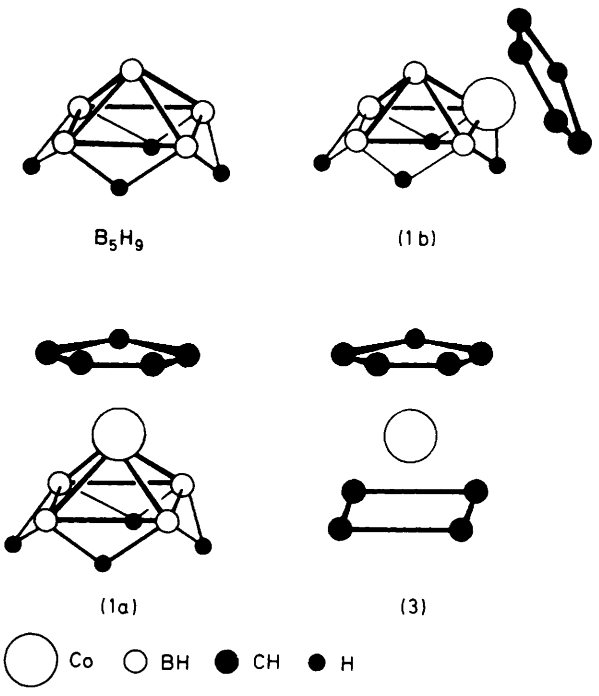

Figure 1. Structures of B_5H_9, 2-[(η^5-C_5H_5)Co]B_4H_8 (1b), 1-[(η^5-C_5H_5)Co]B_4H_8 (1a), and [Co(η^5-C_5H_5)(η^4-C_4H_4)] (3)

Results and Discussion

Isomerization of (1b) *to* (1a).—In the original work,[1] small samples of the yellow 1-isomer were obtained by heating the 2-isomer in sealed tubes at 180—200 °C; the conversion occurred in about 10% yield with substantial decomposition to non-volatile residues. We have found that with careful temperature programming between 100 and 175 °C, and fractional sublimation of the product, yields as high as 60% (routinely 40%) can be obtained.

The thermal rearrangement of 2- to 1-[(η^5-C_5Me_5)Co]B_4H_8 is conducted similarly, as described elsewhere.[4] The conversion is not, however, observed under u.v. light at ambient temperatures; instead, quantitative 'reverse isomerization' of the 1- to the 2-isomer takes place.[6] This unexpected observation and

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† 1-(η^5-Cyclopentadienyl)cobalta- and 1-(η^5-pentamethylcyclopentadienyl)cobalta-*nido*-pentaborane.

Supplementary data available (No. SUP 56012, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

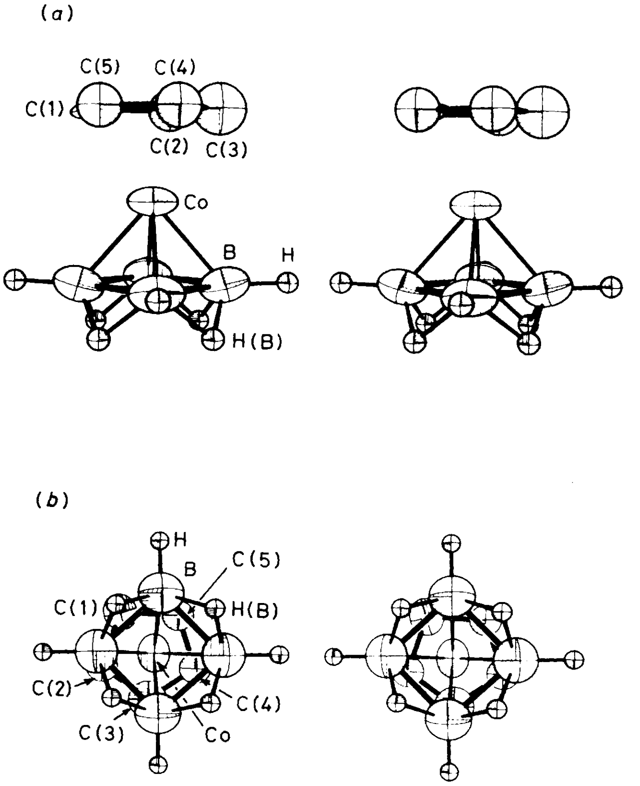

Figure 2. Stereoviews of 1-[(η^5-C_5H_5)Co]B_4H_8 (1a): (*a*) view parallel to the C_5H_5 ring; (*b*) view normal to the B_4 face. One position of the four-fold disordered C_5H_5 ring is depicted in each case

Table 1. *X*-Ray diffraction parameters and crystal data [a]

M	175	Transmission factors (max, min)	0.25, 0.14
Space group	*P*4/*n*	2θ range/°	1.4—60
a/Å	7.909(1)	Observed reflections	720
c/Å	6.985(3)	Refined reflections	552
U/Å^3	436.9	*R*	0.052
μ/cm^{-1}	19.5	*R'*	0.070
D_c/g cm^{-3}	1.33 g cm^{-3}	E.s.d. unit weight	3.2
A, *B* [b]	0.60, 0.30	*Z*	2

[a] Crystal dimensions (mm from centroid): (110), 0.23; ($\bar{1}\bar{1}0$), 0.23; ($\bar{1}10$), 0.33; ($1\bar{1}0$), 0.33; (001), 0.30; ($00\bar{1}$), 0.30. [b] For definition of these parameters see ref. 20.

Table 2. Atomic co-ordinates with estimated standard deviations

Atom	*x*	*y*	*z*
Co	0.00	0.50	0.116 5(2)
C(1)	−0.122(2)	0.411(2)	−0.126(2)
C(2)	0.047(2)	0.357(2)	−0.126(2)
C(3)	0.151(2)	0.501(2)	−0.126(2)
C(4)	0.046(2)	0.644(2)	−0.126(2)
C(5)	−0.122(2)	0.588(2)	−0.126(2)
B	−0.000(1)	0.664(1)	0.330 2(9)
H	0.006(8)	0.194(8)	0.325(9)
H(B)	0.879(8)	0.385(8)	0.446(9)
H(1)	−0.219	0.340	−0.126(2)
H(2)	0.085	0.243	−0.126(2)
H(3)	0.027	0.500	−0.126(2)
H(4)	0.083	0.758	−0.126(2)
H(5)	−0.220	0.658	−0.126(2)

other aspects of the chemistry of 1-[(η^5-C_5H_5)Co]B_4H_8 and its $C_5Me_5^-$ counterpart will be presented later.

X-Ray Structure Determination of 1-[(η^5-C_5H_5)Co]B_4H_8 (1a).—As a consequence of disorder in the $C_5H_5^-$ ring (described in the Experimental section) the molecule crystallizes in the *P*4/*n* space group with a crystallographically imposed four-fold axis, so that the point group symmetry is C_4; the B_4 ring is therefore constrained to square-planar geometry, parallel to the $C_5H_5^-$ ligand. However, the molecular symmetry is lower than in B_5H_9 (C_{4v} point group) [7] as reflected in the apparent asymmetry of the B–H–B bridges in the cobaltaborane. Stereoviews of the molecule are shown in Figure 2, which is drawn with an arbitrarily selected position for the disordered cyclopentadienyl ligand. Tables 1—3 list the relevant crystallographic and structural data. The observed solid-state geometry is completely compatible with the ^{11}B, ^{1}H, and ^{13}C Fourier-transform n.m.r. data obtained in solution (Table 4), which reveal single boron, terminal hydrogen, and bridging hydrogen environments as well as equivalence (on the n.m.r. time-scale) of the five cyclopentadienyl CH units.

In Table 3 are listed bond lengths and angles for (1a) together with comparable parameters for [Co(η^5-C_5H_5)(η^4-C_4H_4)] (3) and B_5H_9. [In complex (3), the C_4 ring contains two crystallographically independent C–C distances which, however, are statistically identical so that square geometry is indicated; in B_5H_9, as noted, the geometry is rigorously square pyramidal.]

Comparison of (1a) *with* B_5H_9.—The geometry of (1a) is closely similar to that of pentaborane, as will be clear from Table 3. For completeness, B–B and B–H distances obtained from both *X*-ray and microwave studies are listed, but the reader is cautioned that these methods measure different properties and are not directly comparable. The difference in apex-to-basal distances in the two species (*ca.* 0.3 Å) simply reflects the larger covalent radius of cobalt relative to boron (1.16 *vs.* 0.82 Å); even the B–H–B regions, where some dissimilarities might be expected, are nearly identical. Of those small differences that are apparent (*e.g.*, in the basal B–B distance), most are probably not significant. In the cobaltaborane the B–H–B bridges appear to be asymmetric (allowable within the crystallographic constraints of C_4 symmetry), but the location of this hydrogen (H_{br}) is sufficiently imprecise as to leave some doubt on this point [in the *X*-ray [7a] and microwave studies [7c,7d] (the data of ref. 7*d* are the most precise) of B_5H_9, symmetric B–H–B bridges were *imposed* by the choice of space group and assumption of C_{4v} symmetry, respectively]. In both molecules, the bridging hydrogen atoms are nearly coplanar with their respective pyramidal faces (apex–base–base), which in 1-[(η^5-C_5H_5)Co]B_4H_8 are defined by the planes Co–B–B'. However, there is a significant difference in the orientation of the *terminal* B–H hydrogens: in B_5H_9 they are well above the plane of the four basal boron atoms [24° (0.5 Å) from *X*-ray data, [7a] 10° (0.2 Å) from microwave data [7d]] while in (1a) these hydrogens are only 3° (0.06 Å) above the corresponding plane (Figure 3). This effect probably arises from the optimization of orbital overlap between the basal boron atoms and the apex boron or cobalt; our observations are qualitatively consistent with a theoretical investigation on metal complexes of cyclic polyenes, in which the bending of C–H hydrogens out of the ring plane was shown to be a function of the relative size of the ring and the metal.[8] The corresponding cyclobutadiene sandwich complex [Co(η^5-C_5H_5)(η^4-C_4H_4)] exhibits a similar effect (see below).

Comparison of (1a) *with* [Co(η^5-C_5H_5)(η^4-C_4H_4)] (3).—The complex (η^4-cyclobutadienediyl)(η^5-cyclopentadienyl)cobalt

Table 3. Bond distances (Å) and angles (°) in 1-[η^5-C_5H_5)Co]B_4H_8 (1a) and related molecules[a]

	(1a)[b]	B_5H_9[c]	B_5H_9[d]	(3)[e]
B_{ba}–B_{ba}	1.834(3)	1.77(2)	1.803(2)	—
B_{ba}–B_{ap}	—	1.66(2)	1.690(2)	—
B_{ba}–Co	1.977(2)	—	—	—
B_{ba}–H_t	1.121(17)	1.20(7)	1.186(2)	—
B–H_{br}	1.315(17) 1.259(17)	1.35(4)	1.352(4)	—
C–C(C_5H_5)[f]	1.401(3)	—	—	1.390(2)
C–C(C_4H_4)[f]	—	—	—	1.437(1)
Co–C(C_5H_5)[f]	2.069(17)	—	—	2.038(1)
Co–C(C_4H_4)[f]	—	—	—	1.965(1)
C–H(C_5H_5)[f]	0.95(1)	—	—	0.91(2)
Co–B_4 plane[g]	1.493	—	—	—
Co–C_4 plane[g]	—	—	—	1.681
Co–C_5 plane[g]	1.686	—	—	1.660
B_{ba}–B_{ba}–B_{ba}	90.0	90.0	90.0	—
B–H_{br}–B	90.0(6)	82(5)	83.9	—
H_t–B_{ba}–B_{ba}	137.0(6)	130(5)	134.1	—
H_t–B_{ba}–H_{br}	108.7(6), 107.8(6)	117(5)	110.9	—
H_{br}–B_{ba}–H_{br}	93.0(6)	93(5)	89.4	—
H_{br}–B_{ba}–B_{ba}	43.3(6), 45.8(6)	49(5)	48.1	—
B–Co–B[h]	52.9(1)	—	—	—

[a] B_{ba} = basal boron, B_{ap} = apical boron, H_t = terminal hydrogen, H_{br} = bridging hydrogen. [b] This work. [c] Ref. 7*a* (*X*-ray). [d] Ref. 7*d* (microwave). [e] Ref. 11. [f] Mean value. [g] Distance from cobalt to calculated least-squares plane of ring. [h] Adjacent boron atoms in base.

was prepared in 1968[9] (a tetraphenylcyclobutadiene derivative was reported in 1961[10]), and its subsequent *X*-ray structure determination[11] confirmed the sandwich structure with square C_4H_4 and pentagonal C_5H_5 ligands that are virtually parallel and centred over the metal atom (Figure 1). The molecule is precisely isoelectronic with (1a) and, like the latter complex, can be described as a five-vertex, 14-electron ($2n + 4$) *nido* cage wherein the four CH units each contribute three skeletal bonding electrons and the Co(C_5H_5) group provides two electrons; equivalently, as noted above, it can be seen that the formal $C_4H_4{}^{2-}$ and $B_4H_8{}^{2-}$ square ligands are isoelectronic counterparts. It is, therefore, of interest to compare the molecular structures.

Table 3 reveals that, while the gross features of 1-[(η^5-C_5H_5)Co]B_4H_8 and [Co(η^5-C_5H_5)(η^4-C_4H_4)] are similar, there are some notable differences that are clearly of electronic origin. First, the basal B–B distance [1.834(3) Å] is considerably (28%) longer in (1a) than the comparable C–C(cyclobutadienediyl) bond length in (3) [1.437(1) Å]; the covalent radius of boron is only 6—7% larger than that of carbon (0.82 *vs.* 0.77 Å), therefore the difference is clearly greater than could be explained on that basis alone. In part, the larger B–B separation can be ascribed to the bridging hydrogens, which *in general* have been shown theoretically[12] and experimentally[13] to divert electron density out of the B–B vector. Consequently there is little *direct* interaction between the borons, in contrast to the situation in (3) where the short C–C distance[11] suggests strong carbon–carbon bonding in the C_4H_4 ligand.

A second point of difference lies in the position of cobalt relative to the $C_5H_5{}^-$ and $C_4H_4{}^{2-}$ or $B_4H_8{}^{2-}$ ligands in the two species (Table 3). In (3) the metal atom is nearly equidistant from the two ligands (the slightly closer approach to the larger C_5 ring is as expected for optimum Co–C bonding). In (1a), however, cobalt is nearly 0.2 Å closer to the B_4 plane than to the C_5 plane; moreover, the Co–B distance of 1.977(2) Å is among the shortest cobalt–boron interactions known,[*] and is equivalent to the sum of covalent radii. This suggests that the cobalt–$B_4H_8{}^{2-}$ bonding is substantially stronger, and more covalent, than the corresponding cobalt–$C_4H_4{}^{2-}$ interaction in (3). A similar conclusion was reached in the case of the complexes 1-[(CO)$_3$Fe]B_4H_8 and 1-[(CO)$_3$Fe]C_4H_4 [which are cage-isoelectronic with (1a) and (3)] on the basis of u.v. photoelectron spectroscopy.[14] These studies cast doubt on the conclusions of a theoretical investigation on 1-[(η^5-C_5H_5)Co]-B_4H_8 using self-consistent field (SCF) methods,[15] in which the Co(C_5H_5) unit was described as weakly bound to the borane cluster *via* a one-electron, two-orbital interaction.[†] The Co–C(C_4H_4) bond distances in (3) are also unusually short (mean value 1.965 Å), and INDO-SCF calculations[16] indicate that the cobalt interacts more strongly with the $C_4H_4{}^{2-}$ ligand (*via* d_{xz},d_{yz} orbitals) than with the $C_5H_5{}^-$ orbitals.

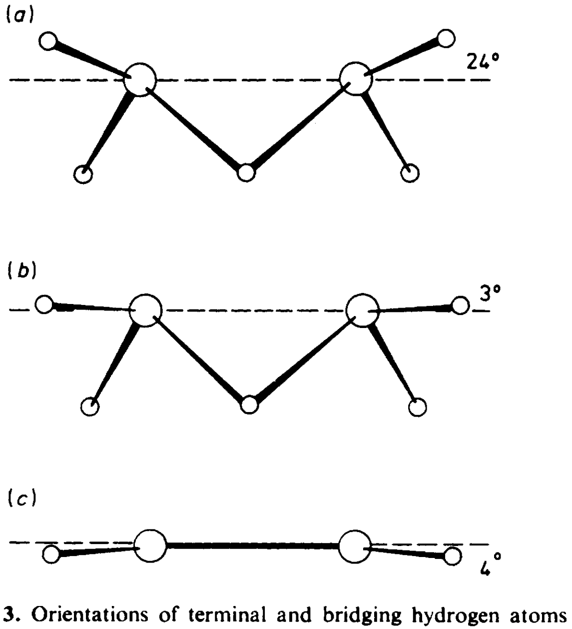

Figure 3. Orientations of terminal and bridging hydrogen atoms relative to the basal (B_4) plane in (*a*) B_5H_9 and (*b*) 1-[(η^5-C_5H_5)Co]-B_4H_8; (*c*) orientation of C_4H_4 hydrogens relative to the C_4 plane in [Co(η^5-C_5H_5)(η^4-C_4H_4)]

The four cyclobutadienediyl hydrogen atoms in (3) are located slightly *below* the C_4 plane on the opposite side from cobalt [Figure 3(*c*)], unlike 1-[(η^5-C_5H_5)Co]B_4H_8, discussed above. From the orbital-overlap arguments[8] referred to earlier, this difference is explained by the smaller size of the $C_4H_4{}^{2-}$ ligand which results in a larger Co–C–H angle, as compared to the $B_4H_8{}^{2-}$ group in (1a).

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[*] The only examples of shorter Co–B bond lengths, to our knowledge, occur in the capped-octahedral clusters [(η^5-C_5H_5)$_3$Co$_3$]-B_4H_4 (J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, 1977, **16**, 3255) and [(η^5-C_5Me_5)$_3$Co$_3$]B_4H_4 (T. L. Venable, E. Sinn, and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 904) where the mean B_{cap}–Co distances are 1.95 Å in each case.

[†] *Ab initio* calculations by C. O. Trindle and D. D. Shillady reinforce our view that the bonding between B_4H_8 and Co(C_5H_5) is strong and primarily covalent. If one views the compound as a complex of the aromatic fragments $C_5H_5{}^-$ and $B_4H_8{}^{2-}$ with Co^{3+}, the resulting Mulliken charge on cobalt (+0.73 electrons) is a clear indication of the extent of co-ordinate covalent bond formation between the Co-(C_5H_5) and borane groups. Details of the calculations and a thorough analysis of the bonding and charge distribution in this compound will be presented elsewhere. We thank Professors Trindle and Shillady for permission to quote their results prior to publication.

Table 4. N.m.r. data (δ/p.p.m.) [a] for B_5H_9 and its analogues

Nucleus observed	B_5H_9 [b]	(1a) [c]	(2a) [d]	1-[$(CO)_3FeB_4H_8$] [e]	(3) [f]
^1H (basal, terminal)	2.49	2.82	2.64	2.44	3.66
^1H (bridge)	− 2.28	−4.30	−4.04	−3.65	—
^1H (C_5H_5)	—	5.01	(1.79) [g]	—	4.90
^{11}B (basal)	−13.4	−4.40	−2.90	−4.69	—
^{13}C (C_5H_5)	—	83.2	*h*	—	*h*, *i*

[a] Chemical shifts relative to $SiMe_4 = 0$ for ^1H and ^{13}C spectra; relative to $BF_3{\cdot}OEt_2 = 0$ for ^{11}B spectra. [b] Neat sample (see P. M. Tucker, T. Onak, and J. B. Leach, *Inorg. Chem.*, 1970, **9**, 1430). [c] $CDCl_3$ solution (see ref. 1*b*). [d] $CDCl_3$ solution (see ref. 4). [e] CD_2Cl_2 solution (see ref. 5). [f] CCl_4 solution (see ref. 9*b*). [g] CH_3 resonance. [h] Not available. [i] Carbon-13 shift for [$Fe(CO)_3(\eta^4\text{-}C_4H_4)$] (cyclobutadienediyl carbons) is 61.0 p.p.m. (see H. G. Preston and J. C. Davis, *J. Am. Chem. Soc.*, 1966, **88**, 1585).

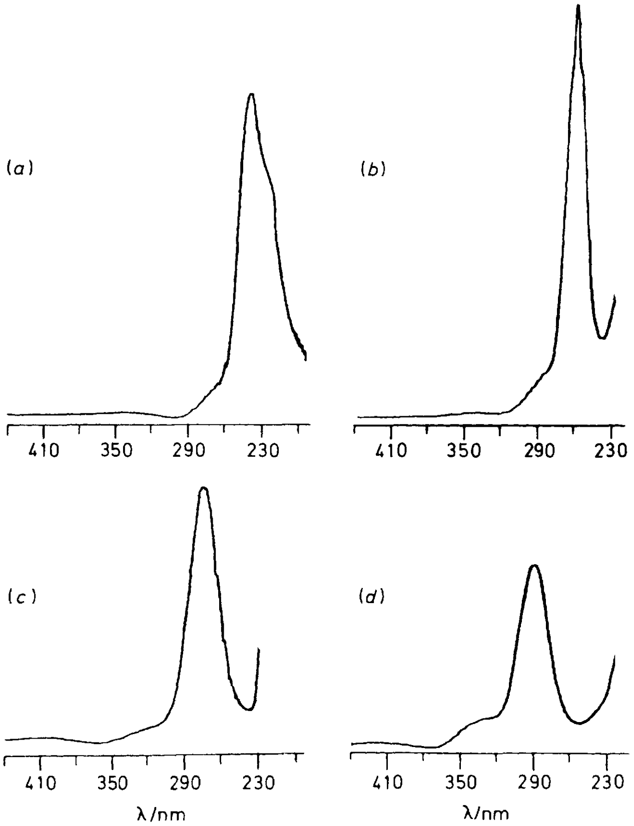

Figure 4. U.v. spectra (230—440 nm) of (*a*) (1a), $\lambda_{max.}$ = 240 nm (ε = 18 000 dm^3 mol^{-1} cm^{-1}), 275 (1 200), 335 (300); (*b*) (2a), 260 (25 000), 295 (2 000), 340 (400); (*c*) (1b), 275 (11 000), 330 (600); (*d*) (2b), 290 (11 000), 335 (1 600). All spectra were recorded in n-hexane solution on a Varian 634 u.v.-visible spectrophotometer

Spectroscopic Properties of 1-[(η^5-C_5H_5)Co]B_4H_8 *and* 1-[(η^5-C_5Me_5)Co]B_4H_8 *in Solution.*—Table 4 lists ^1H, ^{11}B, and ^{13}C n.m.r. data for the cobaltaboranes and their borane, ferraborane, and metallocene analogues. Comparison of B_5H_9 with 1-[(η^5-C_5H_5)Co]B_4H_8, 1-[(η^5-C_5Me_5)Co]B_4H_8, and 1-[$(CO)_3$Fe]B_4H_8 reveals modest downfield shifts in the basal $^{11}B_{ba}$ and ^1H_t (terminal) resonances of the metal complexes relative to the parent borane, although the effect is far smaller than is normally observed for low-co-ordinate BH units adjacent to transition metals.[17] The bridging protons in the metal species, on the other hand, are shifted to *higher* field for reasons that are presently unclear.

The B−H_t and B−H−B i.r. stretching frequencies in the four molecules are very similar (Table 5), indicating that boron-hydrogen bond strengths in B_5H_9 are little affected by replacement of the apex BH by Co(C_5H_5); again, this is consistent with the conclusions based on u.v. photoelectron studies of 1-[$(CO)_3$Fe]B_4H_8 that 'the electronic structure of the cage is qualitatively unaffected by the substitution' of $Fe(CO)_3$ for BH.[14]

Table 5. I.r. stretching frequencies (cm^{-1}) for B_5H_9 and analogous cobaltaboranes

	B_5H_9 [a]	(1a) [b]	(2a) [c]	1-[$(CO)_3$Fe]B_4H_8 [d]
B−H_t	2 600	2 555	2 530	2 568
B−H−B	1 800	1 815	1 805	1 856

[a] H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, 1954, **76**, 998. [b] V. R. Miller and R. N. Grimes, unpublished work (frequencies given in ref. 1*b* are erroneous). [c] Ref. 4. [d] Ref. 5.

Figure 4 depicts the u.v. absorption spectra of (1a) and (1b) and their pentamethylcyclopentadienyl counterparts, (2a) and (2b). The spectra of the yellow 1-isomers [(*a*) and (*b*)] are closely similar to that of (3) [$\lambda_{max.}$ (ε): 258 (20 000), 290 (1 200), 385 nm (320 dm^3 mol^{-1} cm^{-1})],[18] further supporting the electronic analogy between these species. It should be noted that the value of $\lambda_{max.}$ is lower for (1a) than for (2a), and that the same trend holds for the respective 2-isomers [Figure 4(*c*) and (*d*)]. This shift to higher wavelength for the high-intensity transition in the C_5Me_5 complexes may reflect the decrease in valence ionization energy that accompanies methylation of the C_5 ring.[19]

Experimental

Isomerization of 2-[(C_5R_5)Co]B_4H_8 *to* 1-[(C_5R_5)Co]B_4H_8 (R = H *or* Me).—Alteration of the previously published method[4] for conversion of the 2- to the 1-isomers led to substantially improved yields. Typically, a sample (27.8 mg, 0.158 mmol) of red (1b)[1b] was dissolved in pentane and placed in a Pyrex bulb (1 l) fitted with a Teflon stopcock and Viton O-rings. The flask was attached to the vacuum line, the solvent removed, and sealed under vacuum and placed in an oven heated to 50 °C for several hours (higher temperatures, at which the material melted prior to subliming, led to extensive decomposition). The temperature was then increased in stages [100 °C (1—2 h), 150 °C (1—2 h), and finally to 175 °C (*ca.* 12 h)] after which the bulb was removed from the oven, attached to a vacuum line, and the contents sublimed into a Pyrex tube (15 × 0.5 cm) which was sealed under vacuum. Slight heating (37 °C) of one end of the tube caused yellow tetragonal crystals of the 1-isomer (1a) to sublime to the cold end of the tube, thus affording a simple means of separation when unconverted 2-isomer (1b) remained. This procedure permits isolation of both compounds in pure, crystalline form. The yield of the 1-isomer (1a) in this preparation was 17.1 mg

(62%); in repeated syntheses, yields were routinely >40%. It should be noted that solutions of (1a) are more susceptible than (1b) to degradation in air, although both isomers are evidently air-stable in the solid state.

Conversion of (2b) (21.9 mg) to the 1-isomer (2a) was conducted *via* the same procedure, except that the temperature was increased to 180 °C for 5.5 h and then to 200 °C overnight as described elsewhere[4] giving sublimed crystals in 25% yield.

X-Ray Structure Determination of 1-[(η^5-C_5H_5)Co]B_4H_8 (1a).—A pale yellow tetragonal crystal, obtained by sublimation *in vacuo*, was mounted on a glass fibre enclosed in a Pyrex capillary, examined by precession photography, and judged acceptable. Parameters for the data collection and structure determination are given in Table 1; the procedures followed in data collection and processing have been described elsewhere.[20] Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer using Mo-K_α radiation from a highly oriented graphite-crystal monochromator.

The intensities of four 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. Only those reflections for which $F_o^2 > 3\sigma(F_o^2)$, where F_o^2 was estimated from counting statistics ($p = 0.03$)[21] were used in the final refinement of the structural parameters, after averaging for equivalent reflections.

Solution and refinement of the structure. The choice of space group was based on the observation of systematic absences for $h + k = 2n + 1$ on $hk0$, which are consistent with the tetragonal space groups $P4/n$ and $P4/nmm$. However, refinement in these two space groups gave only marginally (not statistically significant) better agreement for $P4/n$; there were, moreover, no meaningful differences in the structure determined. Given this situation, the space group of lower symmetry ($P4/n$) was chosen for final refinement of the data, but we have no real preference for one space group over the other.

Full-matrix least-squares refinement was based on F, and the function minimized was $w(|F_o| - |F_c|)^2$. 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. The atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[22] and those for hydrogen from Stewart *et al.*[23] The effects of anomalous dispersion for all non-hydrogen atoms were included in F using the values of Cromer and Ibers[24] for $\Delta f'$ and $\Delta f''$.

The position of the cobalt atom on a four-fold axis at 0, $\frac{1}{2}$, and z was determined from a three-dimensional Patterson function calculated from all intensity data. These data were phased sufficiently well by these positional co-ordinates to permit location of the remaining non-hydrogen atoms from Fourier-difference functions. Following the introduction of anisotropic thermal parameters for the non-hydrogen atoms, additional difference maps revealed the terminal and bridging hydrogen atoms on the cobaltaborane cage.

The presence of C_4 axial symmetry required the C_5H_5 ring to be four-fold disordered. Consequently, in order to facilitate data refinement, one quarter-weight carbon atom that was located from a Fourier-difference map was used to calculate co-ordinates of the remaining four carbon atoms in the ring. In the early refinement, the co-ordinates of the first (located) carbon atom were permitted to shift, after which new co-ordinates were calculated for the four remaining carbons. For the final cycles of refinement, the x and y co-ordinates for all carbon atoms were held fixed, but z was permitted to vary (though constrained to the same value for all ring carbons, as required by symmetry). The maximum shift/error for all parameters was 0.25 for the last cycle.

The C_5H_5 hydrogen atoms were placed in calculated positions, and all hydrogen locations were held fixed in the final least-squares cycles. The model converged to the final values of R and R' given in Table 1, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o|) - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. The computing system and programs are described elsewhere.[25]

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