well-documented "inverse electronegativity dependence of metal shielding" in low-valent (d^0) complexes.[12b,17a,25] Further, the ionicity of the V–X bond increases with increasing χ(X), and concomitantly, C(3d) should decrease. While this is observed on going from $VOCl_3$ to VOF_3 (cf. Figure 3) and may well contribute to the high shielding for the latter, the V 3d character of the HOMOs is virtually the same for $VOCl_3$ and $VOBr_3$, a fact that may reflect the similar π-donating capacities of the chloro and bromo ligands.

Interpolation between $VOCl_3$ and VOF_3 places the trigonal-pyramidal $VO(O)_3$ (ca. −570 ppm) in a similar position as VOF_3, i.e. with the π(V=O) level as the main HOMO taking part in relevant transitions. The situation does not change to a great extent, if we consider CN = 5 (e.g. $[VO(OH)_2glycolate]^-$, −522 ppm[15b]) and 6 (e.g. $[VO(OH)_3oxalate]^{2-}$, −536 ppm[15a,18c]). This has been exemplified for $[VO(H_2O)_5]^{2+}$, where the π(V=O) MO is again energetically closer to the nonbonding V(3d) level than any of the MOs arising from the interaction of V^{4+} with the aqua ligands.[26]

The "inverse chelate effect" of metal shielding in low-valent complexes is less straightforwardly rationalized. We may assume, however, that strains in 4-ring structures (η^2-carboxylato and -carbonato complexes) and 3-ring structures (e.g. peroxo complexes) give rise to overlap perturbations and thus to diminished oxygen π donation into V(3d) and V(4p) orbitals and hence a net depletion of electron population resulting in decreased C^2 in (1). Alternatively, delocalization of bonding electron density over the three- or four-membered ring can give rise to an increase of r, which in turn diminishes σ'(para).

In conclusion, we have shown that *high* ^{51}V shielding is generally induced by ligands Z with large electronegativity values χ (Z = O, F), the gap between π(V=O) orbitals of sizable V(3d) character and chiefly nonbonding V(3d) orbitals being the major factor responsible for the shielding variations at the ^{51}V nucleus. While variations of the coordination number between 4 and 6 (and 7) do not influence shielding significantly, additional shielding can be expected if bidentate ligands forming chelate-3 and -4 rings are constituents of the coordination sphere. A similar but less pronounced effect is also observed with very bulky Z. *Low* shielding values go along with highly polarizable ligands (Z = Br, S), for which electronic excitations from bonding orbitals associated with the V–Z bond become increasingly important as χ decreases. Ligands coordinating via nitrogen (Z = N) generally induce shielding values close to those of oxygen ligands.

The main bonding site of vanadate with dipeptides at pH 7.5 seems to involve the N function of the peptide linkage. The $\delta(^{51}V)$ value for the vanadate–peptide species is −501 ± 8 ppm relative to $VOCl_3$.

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Metal Atom Synthesis of Metallaborane Clusters. 9.[1] Synthesis and Structural Characterization of *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$

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We have previously demonstrated that metal vapor reactions can be used to generate a wide variety of metallaborane and -carborane clusters.[1-8] Although most of our studies have involved reactions with the smaller, more reactive boranes and carboranes, we have also achieved the synthesis of, for example, (η^6-arene)-metallaboranes derived from higher cage systems, such as $B_{10}H_{14}$,[6] SB_9H_{11}, and $SB_{10}H_{12}$.[9] We have recently begun to explore the synthesis of metal complexes based on larger fused and linked-cage boranes and carboranes, and we report here the isolation and structural characterization of a unique cobaltaborane complex, *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$, obtained from the reaction of cobalt vapor with cyclopentadiene and *n*-$B_{18}H_{22}$.

Experimental Section

Materials and Procedure. Cobalt metal (99.9% 50 mesh) was obtained from Alfa Ventron Corp. Cyclopentadiene was freshly distilled from dicyclopentadiene (Aldrich). The *n*-$B_{18}H_{22}$ was synthesized by using a modified version of Gaines' method,[10] in which the oxidation of *nido*-$B_9H_{12}^-$ was accomplished by ferrocenium ion.[11] Flash column chromatography was performed with silica gel (230–400 mesh, EM Science). The Chromatotron (7924T) was purchased from Harrison Research, Palo Alto, CA. The preparative 2-mm rotor for the Chromatotron was prepared by using silica gel PF-254 with $CaSO_4\cdot{}^1/_2H_2O$ from EM Science and was oven dried for a day prior to use.

The ^{11}B NMR spectra at 160.5 MHz were obtained on a Bruker AM-500 Fourier transform spectrometer. All boron-11 shifts are referenced to $BF_3\cdot O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual C_6H_6 from the lock solvent (99.5% C_6D_6) and are referenced to Me_4Si (0.00 ppm). High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. The infrared spectrum was obtained on a Perkin-Elmer 1310 spectrophotometer.

The metal vapor reactor used for this work was based on a design by Klabunde[12] and is described elsewhere.[2] Cobalt vapor was generated by electrical heating (~7.2 V, 60 A).

Reaction of Cobalt Vapor with Cyclopentadiene and *n*-$B_{18}H_{22}$. In a typical reaction, approximately 0.6 g of cobalt powder was placed in the evaporation crucible and 0.8 g of *n*-$B_{18}H_{22}$ (3.6 mmol) in the bottom of the metal atom reactor. The reactor was then evacuated and cobalt vapor and 20 mL of cyclopentadiene were condensed on the walls of the reactor that was maintained at −196 °C. After metal vaporization was complete, the reactor was allowed to warm to −78 °C and stirred for 30 min. The resulting dark slurry was then warmed to room temperature and stirred for an additional 90 min. Excess ligands were removed in vacuo, and the reactor was flushed with nitrogen gas. The dark residue was extracted with methylene chloride and filtered through a coarse frit. The filtrate was placed on a flash column and eluted with benzene. The first band was identified as *n*-$B_{18}H_{22}$ (0.2 g, 0.9 mmol). A second red band was collected, concentrated, and further separated by using the Chromatron with a 80:20 hexane/benzene mixture. This separation gave 20.1 mg of *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$ (0.06 mmol, 2.2%): R_f 0.23 in hexane/benzene (80:20); red; mp 163–164 °C; mass measurement calcd for $^{12}C_5{}^{59}Co^{11}B_{17}{}^1H_{26}$ 332.2949, found 332.2921; ^{11}B NMR (ppm, C_6D_6, 160.5 MHz) 27.0 (d, J_{BH} ~ 125 Hz), 18.7 (d, J_{BH} = 130), 17.2 (d, J_{BH} = 130), 14.9 (d, J_{BH} = 145), 12.3 (d, J_{BH} = 145), 8.9 (d, J_{BH} ~ 160), 7.8 (s), 2.9 (d, J_{BH} = 160), 1.8 (d, J_{BH} = 130), −0.5 (d, J_{BH} ~ 160), −1.0 (s), −4.9 (d, J_{BH} = 130), −19.8 (d, J_{BH} = 145), −20.1 (d, J_{BH} = 145), −27.3 (d, J_{BH} = 160), −28.7 (d, J_{BH} = 160), −37.1 (d, J_{BH} = 145); ^1H NMR(δ, C_6D_6, 250 MHz) 4.5 (s, 5, C_5H_5); ^1H NMR (δ, C_6D_6, 200 MHz, ^{11}B spin decoupled) −0.1 (s, br), −0.5 (s, br), −0.7 (s, br), −2.9 (s, br), −3.7 (s, br), −17.2 (s, br); IR (KBr pellet, cm^{-1}), 2960 (w), 2550 (s), 1425 (s, br), 1260 (m), 1190 (w), 1090 (m, br), 1020 (m), 840 (w), 800 (s), 650 (w).

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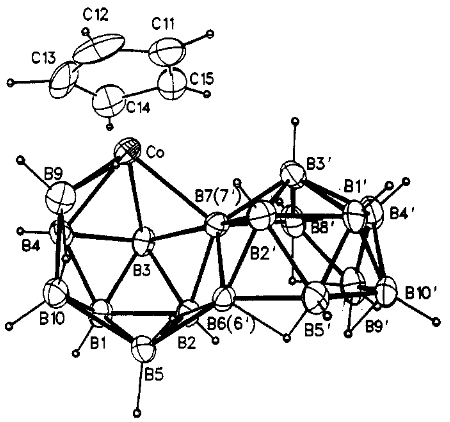

Figure 1. ORTEP drawing of the molecular structure of *iso*-8-(η-C_5H_5)-$CoB_{17}H_{21}$.

Crystallographic Data for *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$. Single crystals were grown over several days by slow evaporation in air of dichloroethane/heptane solutions. A suitably sized crystal was mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing Mo Kα radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at intervals of 100 reflections showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects by using the Enraf-Nonius program START.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer by using the Enraf-Nonius structure package.[13] The full-matrix least-square refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections were taken from ref 14 and 15. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

A three-dimensional Patterson synthesis gave the coordinates of the metal atom. Subsequent Fourier maps led to the location of the remaining heavy atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all the cage hydrogens along with hydrogens of the cyclopentadienyl ring. All hydrogens were refined and included in the structure factor calculations. The final refinement included a numerical absorption correction along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms (6 Å^2).

Results and Discussion

The reaction of cobalt vapor with cyclopentadiene and n-$B_{18}H_{22}$ resulted in the low-yield production of a single metallaborane product that was isolated as a red crystalline material.

Several metal complexes[16,17] have previously been prepared from n-$B_{18}H_{22}$ by the insertion of a metal fragment(s) into the open face(s) of the borane, with the complexes retaining the B_{18} framework. More recently, Greenwood et al.[18] have prepared several new clusters from n-$B_{18}H_{22}$ that contain either one or two Cp*Rh units bound to a B_{17} cage. Exact mass measurements on the new cobaltaborane complex support its composition as (C_5H_5)$CoB_{17}H_{21}$, indicating the compound has similarly lost one of the BH units from the cage.

Table I. Data Collection and Structure Refinement Information

space group	*Pbca*
a, Å	13.099 (2)
b, Å	9.783 (2)
c, Å	28.069 (6)
V, Å	3596.91
Z	8
ρ(calcd), g cm^{-3}	1.215
cryst dimens mm	0.05 × 0.53 × 0.28
mol formula	$C_5H_{26}B_{17}Co$
mol wt	328.98
λ	Mo Kα, 0.71703 Å
scanning range, deg	$4 \leq 2\theta \leq 55$
scan mode	ω–2θ
$\pm h,\pm k,\pm l$ collcd	17, −12, 36
no. of measured I's	4636
no. of $F_o^2 > 3\sigma(F_o^2)$	1720
no. of variables	286
abs coeff (μ), cm^{-1}	9.317
transmissn coeff, %	90.49
max, %; min, %	97.70; 75.60
R	0.060
R_w	0.065

Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å^2
Co8	0.06230 (7)	0.04823 (9)	0.14873 (3)	3.86 (2)
B1	−0.1621 (6)	0.0096 (7)	0.1939 (3)	3.8 (2)
B2	−0.1705 (5)	−0.1072 (7)	0.1474 (3)	3.3 (1)
B3	−0.0947 (6)	0.0459 (7)	0.1404 (2)	3.5 (2)
B4	−0.0488 (6)	0.1055 (7)	0.1977 (3)	3.6 (2)
B5	−0.1563 (6)	−0.1655 (8)	0.2073 (3)	3.8 (2)
B6	−0.0955 (5)	−0.2469 (7)	0.1581 (2)	2.9 (1)
B7	−0.0432 (5)	−0.1135 (7)	0.1193 (3)	3.2 (2)
B9	0.0513 (6)	0.0069 (8)	0.2200 (3)	4.5 (2)
B10	−0.0756 (6)	−0.0273 (8)	0.2396 (3)	4.2 (2)
B1′	0.0075 (7)	−0.3823 (8)	0.0816 (3)	4.9 (2)
B2′	0.0216 (6)	−0.2757 (7)	0.1312 (3)	3.9 (2)
B3′	0.0244 (6)	−0.2030 (8)	0.0733 (3)	4.3 (2)
B4′	−0.0466 (7)	−0.3021 (8)	0.0315 (3)	5.1 (2)
B5′	−0.0710 (6)	−0.4108 (7)	0.1311 (3)	3.9 (2)
B8′	−0.0879 (7)	−0.1372 (9)	0.0498 (3)	4.7 (2)
B9′	−0.1740 (7)	−0.273 (1)	0.0385 (3)	5.6 (2)
B10′	−0.1182 (7)	−0.4222 (8)	0.0650 (3)	4.6 (2)
C11	0.1923 (6)	0.0470 (9)	0.1077 (3)	7.0 (2)
C12	0.2116 (6)	0.1148 (9)	0.1495 (3)	9.1 (3)
C13	0.1449 (6)	0.2251 (8)	0.1528 (3)	7.2 (2)
C14	0.0831 (6)	0.2265 (7)	0.1127 (3)	6.1 (2)
C15	0.1162 (6)	0.1128 (8)	0.0843 (2)	6.1 (2)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

The 160.5-MHz ^{11}B NMR spectrum of the compound shows 17 different resonances indicating the absence of molecular symmetry. Two of the resonances appear as singlets consistent with the compound retaining a edge-fused structure as in $B_{18}H_{22}$. The $^1H\{^{11}B\}$ NMR also indicates a lack of symmetry, showing six separate bridging hydrogen resonances, with the resonance at −17.2 ppm suggesting the presence of a cobalt–boron bridging hydrogen. A single-crystal X-ray structural determination of the compound is consistent with these conclusions as is shown in the ORTEP drawing given in Figure 1.

As can be seen in Figure 1, the compound has an asymmetric fused-cage framework; however, it should be noted that the structure is not based on a n-$B_{18}H_{22}$ geometry but is instead derived from an *iso*-$B_{18}H_{22}$ framework. Thus, n-$B_{18}H_{22}$ is composed[19] of two edge-fused decaborane cages sharing the 5,6′- and 6,7′-borons,

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Table III. Selected Bond Distances (Å)

Co8–B3	2.070 (7)	B9–B10	1.78 (1)
Co8–B4	2.079 (7)	B1′–B2′	1.75 (1)
Co8–B7	2.257 (7)	B1′–B3′	1.78 (1)
Co8–B9	2.045 (8)	B1′–B4′	1.76 (1)
B1–B2	1.74 (1)	B1′–B5′	1.75 (1)
B1–B3	1.78 (1)	B1′–B10′	1.76 (1)
B1–B4	1.76 (1)	B2′–B3′	1.77 (1)
B1–B5	1.76 (1)	B2′–B5′	1.79 (1)
B1–B10	1.75 (1)	B3′–B4′	1.78 (1)
B2–B3	1.81 (1)	B3′–B8′	1.74 (1)
B2–B5	1.79 (1)	B4′–B8′	1.78 (1)
B2–B6	1.71 (1)	B4′–B9′	1.70 (1)
B2–B7	1.84 (1)	B4′–B10′	1.77 (1)
B3–B4	1.81 (1)	B5′–B10′	1.96 (1)
B3–B7	1.80 (1)	B8′–B9′	1.77 (1)
B4–B9	1.74 (1)	B9′–B10′	1.80 (1)
B4–B10	1.79 (1)	Co8–C11	2.056 (8)
B5–B6	1.78 (1)	Co8–C12	2.062 (8)
B5–B10	1.94 (1)	Co8–C13	2.044 (8)
B6–B7	1.83 (1)	Co8–C14	2.034 (7)
B6–B2′	1.73 (1)	Co8–C15	2.043 (7)
B6–B5′	1.80 (1)	C11–C12	1.37 (1)
B7–B2′	1.83 (1)	C11–C15	1.36 (1)
B7–B3′	1.79 (1)	C12–C13	1.39 (1)
B7–B8′	2.05 (1)	C13–C14	1.39 (1)
		C14–C15	1.44 (1)

resulting in a structure that has a center of symmetry, while *iso*-$B_{18}H_{22}$ has a structure[20] based on the sharing of the 6,6′- and 7,7′-borons,[21] which has 2-fold symmetry but lacks an inversion center. The compound *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$ clearly has a structure derived from the latter geometry in which the (η-C_5H_5)Co unit has replaced the 8-BH unit in the *iso*-$B_{18}H_{22}$ framework.

Thus, the reaction leading to the formation of the compound involves both the degradative insertion of a cobalt atom and the isomerization of the cage framework from a *n*- to *iso*-B_{18} structure. Fontaine et al.[18a] first noted such a rearrangement of a *n*-$B_{18}H_{22}$ cage during the synthesis of the complex (η-C_5Me_5)$_2Rh_2B_{17}H_{19}$. They proposed that the conversion between structures may occur by a process involving the insertion of a metal vertex at one edge (B7–B8) of a *n*-B_{18} framework followed by elimination of a BH unit (B10) on the opposite side of the same cage. Such a process generates the *iso*-B_{18} framework in a straightforward manner, and our results are consistent with this type of mechanism.

The cobalt atom is coordinated to the four borons B7, B3, B4, and B9 and is 1.343 (1) Å from the plane of these atoms and 1.672 (1) Å from the plane of the cyclopentadienyl ring. The dihedral angle between the B7,B3,B4,B9 plane and that of the cyclopentadienyl ring is only 3.8°. These values as well as the remaining bond distances and angles in the cobaltaborane half of the molecule are similar to those observed in the analogous cage system, 5-(η-C_5H_5)CoB_9H_{13}.[22] The bond parameters in the non-metal half are similar to those found in *iso*-$B_{18}H_{22}$. The substitution of the cobalt atom thus seems to have had little influence on the bonding in the opposite cage.

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Registry No. *iso*-8-(η-C_5H_5)$CoB_{17}H_{21}$, 112139-07-8; *n*-$B_{18}H_{22}$, 21107-45-9; Co, 7440-48-4; cyclopentadiene, 542-92-7.

Supplementary Material Available: Tables of general temperature factors, intermolecular angles, bond distances, molecular planes, and hydrogen positions (10 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Emission Wavelength Independence of the Excitation Polarization of $[Ru(bpy)_3]^{2+}$

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A recent publication by Krausz and Ferguson[1] states that frozen-solution photoselection data[2,3] for $[Ru(bpy)_3]^{2+}$ were the result of solvent heterogeneity, a "red edge" effect.[4,5] The physical basis for this statement was the observation that excitation photoselection (ExP) spectra exhibit a strong dependence upon detection wavelength. This experimental result was in direct conflict with the findings of our own laboratory[2] that variation of the ExP spectra with detection wavelength is negligible, for this complex.

The importance of obtaining the proper ExP spectra must be stressed. Such data[2] are key to the present controversy surrounding the identification and origin of *localization* in the excited states of $[Ru(bpy)_3]^{2+}$ and its analogues. Tazuke and co-workers,[6] as well as Krausz and Ferguson,[1] have argued that the localization is *only* a fluid-solution phenomenon. If the anomalous rigid-solution (77 K) photoselection of these complexes may be discarded as a red edge effect, their case is greatly strengthened, and the converse is also true. Hence, it is necessary to be certain of the ExP dependence observed by Krausz and Ferguson.[1]

Photoselection spectroscopy is an established emission polarization technique used with much success in many areas of research.[7-9] It does, however, require precise experimental methodology to prevent acquisition of erroneous data, and we therefore felt sufficient reason to question the data of ref 1.

The choice, in ref 1, of 110 K as the experimental temperature seems a needless, and in many respects, counterproductive complication for comparison with the original Carlin–DeArmond 77 K experiments.[2] In addition, the 110 K temperature is one at which viscous flow occurs for the EtOH/MeOH system, causing rotational depolarization to be a factor. However, to provide data to compare with ref 1 and 2, we have performed experiments at 110 and 77 K.

Figure 1 illustrates the 110 K result obtained in pure EtOH solution. As shown, we have detected only minor variations of ExP upon detection at the wavelengths used by Krausz and Ferguson.[1] While our experiments were performed in pure EtOH instead of 4:1 EtOH/MeOH, the difference between these solvents is negligible for our purposes. Therefore, this figure may be contrasted with Figure 3 of ref 1, which purports to show the same data. The data obtained at 77 K are identical with those at 110 K, given slight rotational depolarization at the latter temperature, and are also shown in Figure 1.

The reason for the inaccurate results of Krausz and Ferguson is unknown, but several possibilities exist. During the acquisition of the data in Figure 1, we noted that there is significant instability of ethanol glasses at 110 K. At 77 K, ethanol will glass, and the characteristics of that glass are not seen to alter over a period of hours. Major glassy defects, such as cracks or stress-related birefringence, are easily visible to the eye of the observer, and glasses may be obtained that do not contain these defects. Data obtained in these clear glasses are reproducible and give photoselection polarization values (*P*) with accuracies better than

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