proton. The two aromatic bands possibly correspond to two geometrical arrangements of the substituents relative to the aromatic proton. Formally it bears two adjacent and one "lone" protonated groups. Benzenehexacarboxylic acid hexamethyl ester (**9**) is the substrate for a maximum degree of protonation. The proton spectrum of protonated **9** consists of one $^+$OH band and two methoxy bands (2:9:9, respectively). Here again the $^+$OH peak is attributed to the "lone" groups and it seems that this molecule consists of four "paired" and two such "lone" groups. This arrangement is represented by **9a**.[8] These two methoxy bands may represent three methyl groups in the plane and three methyl groups out of the plane of the molecule. The two methoxy groups coalesce at $-10°$ ($\Delta G^*_{-10} = 13.0$ kcal/mol) and appear as a single line at 0°. The hexaprotonated species derived from **9** represents a benzene ring surrounded by six positive charges, and it can be concluded that partial protonation does not reduce the basicities of the rest of the groups so that an exhaustive protonation is achieved.

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(4) No bands of protonated methanol could be detected, hence no cleavage of the esters occurred. Also the simplicity of the aromatic pattern showed that only exhaustive protonation occurred.
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Cobalt-Boron Clusters

Sir:

The close electronic and structural relationship between the metal clusters and the boron cage molecules implies the existence of intermediate systems composed about equally of metal and boron atoms. The isolation of such compounds would furnish important evidence that the boranes and the nonboron clusters are indeed members of a single broad family[1] governed by the same general rules of electronic structure and bonding. We report here the preparation and characterization of three such compounds which may be regarded as metal cluster–borane hybrids.

The reaction of $Na^+B_5H_8^-$ with excess $CoCl_2$ and NaC_5H_5 in tetrahydrofuran below 20° has previously been reported by us[2] to give a series of cobaltaboranes, including the B_5H_9 analogues 1- and 2-$(\eta^5\text{-}C_5H_5)CoB_4H_8$,[3] the $B_{10}H_{14}$ analogue 5-$(\eta^5\text{-}C_5H_5)CoB_9H_{13}$, and the octahedral species 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$, which was the first closed polyhedral metalloborane. This reaction is exceedingly complex, yielding a large number and variety of products, and a full report will be published on completion of our study. In the meantime we have isolated in low yields from the same reaction, as air-stable crystalline solids, brown $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$ (I), yellow $(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$ (II), and green $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$ (III). The products were purified by thick-layer chromatography on silica gel and characterized from their mass spectra and ^{11}B and ^{1}H pulse Fourier transform NMR spectra (Tables I and II), on the basis of which we propose the structures shown in Figures 1a–c.

Table I. 32.1-MHz ^{11}B NMR Data

Compound	δ, ppm (*J*, Hz)[a]	Rel. areas
I	−62.7 (~112)	
II	−141.4,[b] −86.6 (146)	1, 3
III	−121.4 (137)	

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$ in $CDCl_3$ solution. [b] Broad resonance, *J* not measurable; the existence of ^{11}B–H coupling was demonstrated by narrowing of peak width on proton decoupling.

Table II. 100-MHz ^{1}H NMR Data[a]

Compound	Resonance, τ[b] (rel. area)	Assignment
I	2.89 (3)	H_t-B
	5.10 (15)	C_5H_5
	24.48 (2)	H-Co
II	−4.45 (1)	H-B
	0.60 (3)	H-B
	5.35 (15)	C_5H_5
III	−1.83 (1)	H-B
	5.51 (5)	C_5H_5

[a] All spectra in $CDCl_3$ solution and ^{11}B-decoupled. [b] Chemical shifts relative to $Me_4Si = 10.00$.

Compounds I, II, and III exhibit intense mass spectroscopic cutoffs corresponding to the parent ions at *m/e* 410, 420, and 544, respectively, with smaller P + 1 peaks due to ^{13}C-containing ions. The pattern of intensities in each in-

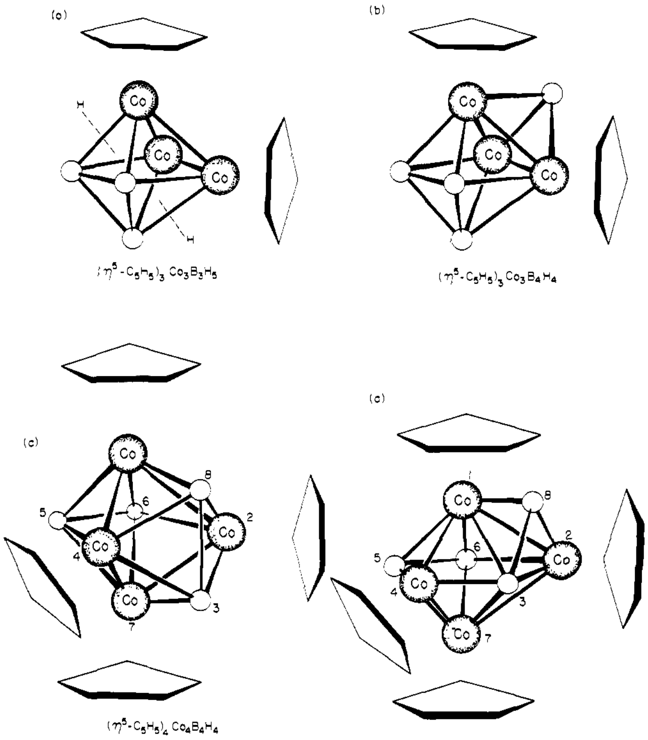

Figure 1. Proposed structures of I (a), II (b), and III (c), and a possible alternative structure of III (d). Open circles represent BH groups. One cyclopentadienyl group is omitted from structures a and b for clarity; the bridging hydrogens in a are shown schematically.

stance is consistent with the calculated isotopic composition.

Compound I is assigned an octahedral structure (Figure 1a) consistent with its 14 cage valence electrons (two from each $(\eta^5\text{-}C_5H_5)Co$ group, two from each BH group, and one from each "extra" H atom), corresponding to a $(2n + 2)$-electron system.[1,4] The equivalence of the three C_5H_5 and the three BH groups on the NMR time scale is shown in the ^1H and ^{11}B spectra; the lone B–H doublet in the ^{11}B spectrum collapses to a singlet on proton decoupling. The area 2 singlet at τ 24.48 in the proton spectrum is assigned to the "extra" hydrogens which are assumed to undergo rapid tautomeric movement through face-bonding locations on the polyhedral surface. In this respect the molecule resembles its cage-isoelectronic analogue CB_5H_7,[5] whose face-bridging proton has recently been defined in an electron-diffraction study.[6]

Compound II contains no "extra" hydrogens and thus is a $2n$-electron system (7 framework atoms and 14 electrons). A capped octahedron is the expected geometry based on the similar case of $Os_7(CO)_{21}$[7] and on the general observation[7-9] that $2n$-electron cages adopt capped polyhedral structures. The NMR indications of equivalent $(C_5H_5)Co$ groups, three equivalent BH units, and a unique BH suggest a threefold symmetry axis; such a situation would exist if the unique BH group capped either the B_3 or the Co_3 face on the octahedron. The extremely low field ^{11}B signal of the lone BH unit strongly supports the Co_3-capped geometry shown in Figure 1b.

Compound III is also a $2n$-electron system and might be expected to exhibit a capped pentagonal bipyramidal structure;[9] however, the NMR data show that all borons are equivalent, as are all of the $(C_5H_5)Co$ moieties. The dodecahedral D_{2d} geometry (Figure 1c) satisfies these observations. Although the $2n + 2$ rule would normally require two additional electrons to stabilize such a geometry, it is quite conceivable that stabilization could be achieved by partial bonding interactions between the formally nonbonded metal atoms 2 and 4, and similarly between 1 and 7. Alternatively, the static structure may be a capped pentagonal bipyramid (Figure 1d) which undergoes fluxional rearrangement in solution by breaking the Co(1)–B(3) bond and forming a Co(4)–B(8) link, thereby producing the dodecahedron (Figure 1c) as a time-averaged geometry. Although several eight-vertex boranes[10] and carboranes[11,12] have been postulated to undergo fluxional rearrangement in solution, such a process seems less likely for III with its relatively bulky $(C_5H_5)Co$ groups, and we favor the fixed D_{2d} structure.

Structures I–III are novel in several respects. Compounds I and III are the first metalloboron cage compounds having as many metal as boron atoms, and III is the first with four metal atoms. Furthermore, II is the only known polyhedral boron cage having an "isolated" boron (bound to no other boron atoms) and is related to the tricobalt–carbon clusters, $RCCo_3(CO)_9$.[13] Studies of these materials are continuing and we shall present a full report at a later date.

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Intercalate of Xenon Hexafluoride in Graphite. A Potential Mild Fluorinating Agent of Aromatic Compounds

Sir:

Recent discoveries that several halogen fluorides form intercalation compounds with graphite[1-3] prompted us to attempt the preparation of an analogous intercalate with xenon hexafluoride. Xenon hexafluoride does indeed form a spontaneous layer compound with graphite of nominal composition $C_{19.1\pm0.2}XeF_6$. The study of such a compound and its formation is of particular interest, because xenon hexafluoride is unique among the 16 known and readily isolable hexafluorides in that it does not possess a regular octahedral structure in the gas phase.[4-6] It also possesses many other unusual physical and chemical properties not common to other hexafluorides.[7] In some respects, though, it resembles the halogen fluorides in its ability to form salts containing either cationic or anionic derivatives of the parent molecule. In spite of the extremely aggressive fluorinating properties of XeF_6, the moderating influence of the graphite makes the intercalate a novel and useful fluorinating agent in aromatic systems.

Weighed quantities of graphite in preweighed Kel-F reaction vessels sealed with Kel-F valves were allowed to react with excess XeF_6.[8] The XeF_6 was prepared and purified as described previously.[9] After prolonged contact, the excess XeF_6 was pumped off at room temperature until the reactor contents attained constant weight. No noncondensible gases were released during the reaction other than occasional negligible quantities of xenon gas. Results of numerous experiments showed that the ratio of weight increase to amount of graphite starting material is constant. Assuming that the weight increase is due solely to XeF_6 we obtain a stoichiometry: $C_{19.1\pm0.2}XeF_6$, which was supported by chemical analysis. Identical results were obtained with native graphite powder from BDH or with GTA grade Grafoil from the Union Carbide Co. The reaction is accompanied by a change of the original glossy, black appearance of the Grafoil to a mottled dark gray color. Graphite powder assumes a slightly brownish hue upon reaction with XeF_6. X-Ray patterns of the intercalate obtained with copper radiation showed the complete absence of the original strong graphite line at d = 3.35 Å, and the appearance of a new pattern containing very broad, diffuse peaks centered at approximately 3.97 and 4.55 Å.

Preliminary wide line ^{19}F nuclear magnetic resonance spectra of the intercalate at room temperature performed at 15 and 35 MHz reveal the presence of a singlet–doublet