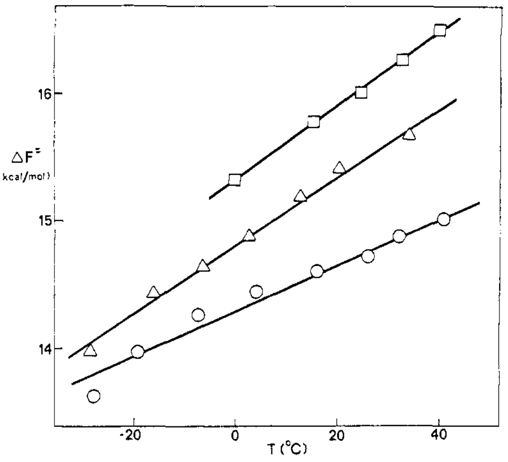


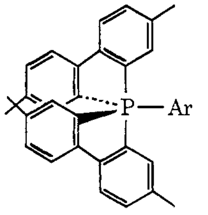
Figure 2. Temperature dependence of free energy of activation: □, **1a** in toluene-d_8: △, **1b** in toluene-d_8; ○, **1b** in tetrachloroethylene. The lines are least-squares fitting of the experimental points and correspond to $\Delta F^{\ddagger}$ (40°) = 16.5, 15.9, and 15.0 kcal/mol, and $\Delta S^{\ddagger} = -29, -27$, and -18 eu, respectively.

Figure 2 presents some results of variable temperature nmr rate studies of **1a** and **1b** by complete line shape fitting using computer generated spectra. To the extent that the large negative entropies of activation are real, these results make it doubtful that the degenerate isomerization is unimolecular.[8] The unreliability of dynamic nmr measurements for determination of activation entropies is well known,[9] and so we have attempted to extend the range of rate measurements to lower temperatures by the Forsen technique of saturation transfer.[10] These attempts were unsuccessful because of inability to cause complete saturation of one methyl peak while observing the other. This is apparently the result of very short spin lattice relaxation times (T_1 from 0.5 to 0.8 sec[11] for **1a**) which require the use of high decoupling power so that interference between observing and decoupling frequencies becomes too large.

Another feature inconsistent with a unimolecular mechanism is the observation that different samples of **1a** or **1b** in the same solvent showed definite variations in isomerization rate. For example, three nmr samples in tetrachloroethylene prepared from the same batch of **1b** showed rate constants of 56, 30, and 69 sec^{-1} at 15°.[12] Similar results were obtained for toluene-d_8 solutions. We have not, however, been able to trace these rate changes to any experimental variable. Dilution by as much as a factor of four resulted in no detectable change in isomerization rate. Addition of possible complexing agents or catalysts such as tetrahydrofuran, LiF, LiCl, LiBr, LiBr plus $\mathrm{Ph_3PO}$, or benzyltriethylammonium bromide resulted in no change in rate. Addition of tetra-*n*-butylammonium iodide caused a 1.3 rate increase, but this could have been because of introduction of traces of oxygen, which appears to affect the rate slightly.

The available evidence argues against a unimolecular isomerization mechanism, although the barrier for such an isomerization must then be higher than 15 kcal/mol. Bimolecular ligand exchange or bimolecular catalysis can also be ruled out, unless the compound is dimeric in solution or the catalyst concentration does not change upon dilution. The *p*-trifluoromethyl group causes a rate increase, but little significance can be attached to this until more specific mechanistic information is available. In this regard, it would be desirable to have more stable analogs of **1**, and work on this is in progress.

Compounds related to **1**, such as bis(biphenylyl)arylphosphorane (**2**)[13] and bisbiphenylyltellurium (**3**)[14]



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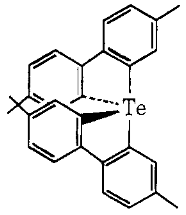

3

have been studied by nmr methods. Compound **2** (Ar = β-naphthyl) has $\Delta F^{\ddagger}$ = 11.9 kcal/mol for interchange of methyl environments (pseudorotation).[13a] The compound with Ar = phenyl presumably has an even lower activation energy.[13a] Variable temperature nmr studies of **3** have shown only broadening of the methyl singlet at −55°. No firm conclusions can be drawn from this experiment.[14] The triaryliodine compounds **1** thus appear to exhibit greater configurational stability than related phosphorus compounds (**2**), perhaps a consequence of different hybridization at the central element.[6]

Acknowledgment. We thank Leonard Waldenberger for technical assistance.

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(8) The clearly bimolecular exchange of nonequivalent fluorines in $\mathrm{SF_4}$[7b] has E_a = 4.5 kcal/mol and log A = 7–9. This corresponds to $\Delta S^{\ddagger} = -26$ to -30 eu.

(9) G. Binsch, *Top. Stereochem.*, 3, 97 (1968).

(10) (a) S. Forsen and R. A. Hoffman, *J. Chem. Phys.*, **40**, 1189 (1964); (b) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

(11) (a) Measurements of T_1 were carried out using the inversion–recovery method, as modified by Freeman and Hill (Varian Associates). R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968); R. Freeman and H. D. W. Hill, *ibid.*, **53**, 4103 (1970).

(12) To account for these rate changes in terms of temperature irreproducibility between samples, that error would have to be 10°, which is highly unlikely. The rate measurements are near coalescence, where the line shape is very sensitive to rate changes. Errors in relative rates are less than ±10%.

(13) (a) D. Hellwinkel, *Chimia*, 22, 488 (1968); (b) G. M. Whitesides and W. M. Bunting, *J. Amer. Chem. Soc.*, **89**, 6801 (1967).

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Preparation of Stable *closo*- and *nido*-Cobaltaboranes from $\mathrm{Na^+B_5H_8^-}$. Complexes of the Formal $\mathrm{B_4H_8^{2-}}$ and $\mathrm{B_4H_6^{4-}}$ Ligands

Sir:

We report the synthesis, isolation, and structural characterization of several crystalline, air- and water-stable metalloboranes which appear to represent novel metalloboron cage systems. The compounds have been identified as $\mathrm{B_4H_8Co}(\pi\text{-}\mathrm{C_5H_5})$ (Ia), 1,2-$\mathrm{B_4H_6Co_2}(\pi\text{-}\mathrm{C_5H_5})_2$ (II), 3-c-$\mathrm{C_5H_9}$-1,2-$\mathrm{B_4H_5Co_2}(\pi\text{-}\mathrm{C_5H_5})_2$ (III), 4-c-$\mathrm{C_5H_9}$-1,2-$\mathrm{B_4H_5Co_2}(\pi\text{-}\mathrm{C_5H_5})_2$ (IV), and 5-$\mathrm{B_9H_{13}Co}$-

(π-C_5H_5) (V), for which the structures in Figure 1 are proposed. The products are formed, together with a number of as yet unidentified materials, by the addition of excess $CoCl_2$ and NaC_5H_5 in tetrahydrofuran (THF) to a THF solution of $Na^+B_5H_8^-$ [1] at −196° and slow warming to room temperature, followed by evaporation to dryness, treatment with aqueous HCl, exposure to air, and extraction with methylene chloride. Separation by column and thin-layer chromatography on silica gel with benzene–hexane mixtures has given a total of 0.5 mmol (100 mg) of purified products, obtained from 10 mmol of $Na^+B_5H_8^-$. The predominant product (60 mg) is Ia.

The mass spectra of all five products contain cutoffs corresponding to the parent ions, as well as intensity profiles from which reasonable ^{11}B monoisotopic spectra can be calculated based upon four boron atoms (for Ia–IV) or nine borons (for V). Further confirmation of the elemental compositions is given by exact-mass measurements of the three parent compounds as follows: Ia, *m/e* 176.0721 (calcd 176.0721); II, 298.0285 (298.0287); V, 236.1585 (236.1577), corresponding respectively to the $^{12}C_5{}^{11}B_4{}^{59}Co^1H_{13}{}^+$, $^{12}C_{10}{}^{11}B_4{}^{59}Co_2{}^1H_{16}{}^+$, and $^{12}C_5{}^{11}B_9{}^{59}Co^1H_{18}{}^+$ parent ions.

The ^{11}B and ^1H nmr spectra of Ia–V are listed in Tables I and II, respectively. The structural assignments are consistent with these data and also rest upon empirical and theoretical arguments invoking the number of framework electrons.

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

Compound	δ, ppm (*J*, Hz)[a]	Rel areas
Ia[b]	−6.2(154), +15.9(136)	1, 3
Ib[c]	+4.4(162)	
II[b]	−60.2(147), −18.8(141)	2, 2
III[d]	−59.3(149), −39.2,[e] −18.7(122)	2, 1, 1
IV[d]	−76.2,[e] −55.9(142), −17.7(129)	1, 1, 2
V[b]	−30(170), −14(200), −12(160), −7(160), −2(160), +3(160), +16(160), +38(160)	1, 1, 1, 2, 1, 1, 1, 1

[a] Chemical shifts relative to $BF_3 \cdot O(C_2H_5)_2$. [b] $(CD_3)_2CO$ solution. [c] CH_2Cl_2 solution. [d] $CDCl_3$ solution. [e] Singlet assigned to B–C_5H_9 group.

Table II. 100-MHz ^1H Nmr Data

	δ,[a] ppm		
Compound	C_5H_5	H_{bridge}	Rel areas
Ia	−5.16	+3.6, +15.3[b]	5, 2, 2
Ib[c]	−5.01	+4.3	~5, 4
II	−5.27	+12.6	10, 2
III[d]	−5.16	+12.2	10, 2
IV[e]	−5.20, −5.11	+12.8	5, 5, 2
V	−5.3	+2.5, +19[f]	~5, 3, 1

[a] Chemical shifts relative to $(CH_3)_4Si$, $CDCl_3$ solution. Except for Ib, H_t–B quartets are weak and largely masked by other peaks. [b] Doublet, *J* = 72 Hz, attributed to H_t–H_b coupling; assigned to Co–H–B bridging protons. [c] Terminal H–B quartet centered at δ −2.82 (*J* = 160 Hz). [d] Multiplets with most intense peaks at δ −1.56 and −1.22 are assigned to the C_5H_9 group. [e] Multiplet with the most intense peak at δ −1.54 is assigned to C_5H_9 group. [f] Assigned to Co–H–B bridging proton.

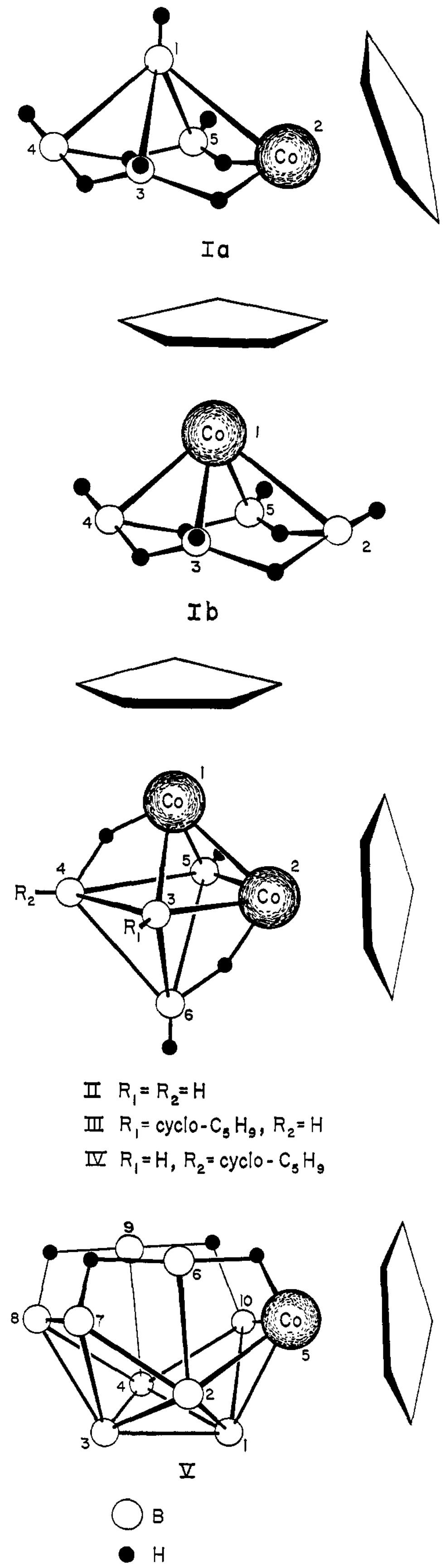

Figure 1. Proposed structures for complexes Ia–V. The terminal hydrogen atoms in V have been omitted for clarity.

Compound Ia, obtained as dark red needles, is an analog of B_5H_9 in which one BH group has been formally replaced by a $Co(C_5H_5)$ moiety, implying a

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(1) H. D. Johnson, II, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 9, 908 (1970).

square pyramidal open-cage structure. The same prediction is given by the "$2n + 2$" rule[2] (n = number of framework atoms), in that Ia contains 14 framework valence electrons,[3] two more than the optimum number for a closed (*e.g.*, trigonal bipyramidal) five-atom system such as $C_2B_3H_5$. Assuming B_5H_9-like geometry, the ^{11}B nmr spectrum places the cobalt atom in a basal position, with superposition of the resonances of three borons (probably those bonded to cobalt[4]). The ^1H nmr spectrum contains two well-separated bridge proton peaks, attributed to the B–H–B and B–H–Co groups, in addition to the C_5H_5 resonance and the weak BH_t quartets.

The gas-phase pyrolysis of Ia at 200° for 30 min in the presence of acetylene[4a] produces a second isomer, pale yellow crystalline Ib (10% yield) whose mass spectrum is similar to that of Ia. The lone doublet in the ^{11}B nmr spectrum of Ib is consistent with four equivalent BH groups and leads to the structure shown. The ^1H nmr spectrum also fully supports this structure, which appears to us to be the only reasonable possibility.

Compound II, a violet crystalline solid, is isoelectronic with the closed octahedral species $C_2B_4H_6$ and $B_6H_6^{2-}$, all of which contain 14 framework electrons and thus adhere to the $2n + 2$ rule for 6-atom closed polyhedra. Of the two possible isomers, that having adjacent cobalt atoms and two pairs of equivalent borons is indicated by the ^{11}B nmr spectrum. Some ambiguity exists with respect to the location of the bridging protons, but the presence of a broad ^1H nmr resonance at higher field than is normally associated with B–H–B bridges suggests B–H–Co bonding. These bridging hydrogens are not necessarily restricted to the "edge" locations indicated in Figure 1 and could well be present as face-bonded protons associated with the Co_2B or CoB_2 triangles on the octahedral surface. A related carborane, CB_5H_7, isoelectronic with II, is proposed to contain one bridging proton on a closed polyhedral cage system.[5]

The structural assignments of the cyclopentyl derivatives III and IV are straightforward based on the nmr data. The presence of two distinct π-cyclopentadienyl bands in the ^1H nmr spectrum of IV implies nonequivalent $Co(C_5H_5)$ groups consistent with ligand attachment at B(4); similarly, the spectrum of III contains only one π-C_5H_5 peak, indicating ligand substitution at B(3). The formation of cyclopentyl derivatives has not been observed by us during extensive studies on the synthesis of π-cyclopentadienyl metallocarboranes[6] and the isolation of III and IV in the present work suggests hydrogenation of C_5H_5 rings by $B_5H_8^-$ or other species during the course of the reaction.

Compound V, a trace product obtained as a red solid, is isoelectronic with $B_{10}H_{14}$ and accordingly has been assigned the structure in Figure 1 on the basis of its ^{11}B nmr spectrum, which indicates a molecule of very low symmetry. Assuming a decaborane-like framework, the metal atom is placed in the 5(7,8,10) position, since all other cage locations lie on a mirror plane and hence would be incompatible with the ^{11}B nmr spectrum. The ^1H nmr spectrum supports the proposed structure and contains two broad singlets at high field, assigned to B–H–B and B–H–Co groups as indicated in the table.

Studies of these materials and other products of this reaction are continuing.

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[2] (a) R. W. Rudolph and W. R. Pretzer, *Inorg. Chem.*, **11**, 1974 (1972); (b) K. Wade, *J. Chem. Soc. D*, 792 (1971).

[3] Excluding terminal B–H and Co–C_5H_5 bonding, the four borons, one cobalt, and four bridging hydrogens contribute respectively eight, two, and four electrons to the cage framework if all atoms are considered as neutral units. The molecule may alternatively be regarded as a $(\pi\text{-}C_5H_5)Co^{2+}$ complex of a formal $B_4H_8^{2-}$ ligand, yielding of course the same electron count.

[4] The observation of a single chemical shift for borons 1, 3, and 5 could be explained in terms of coincidental superposition. Alternatively, these boron atoms could be rendered equivalent on the nmr time scale by a rapid reversible rearrangement involving formation of a B(3)–B(5) bond and breaking of the B(1)–B(3) or B(1)–B(5) link, with accompanying rearrangement of the bridge protons.

[4a] NOTE ADDED IN PROOF. Recent work has shown that acetylene is not necessary in the thermal rearrangement of Ia to Ib.

[5] T. Onak, J. B. Leach, *Chem. Commun.*, 76 (1971), and references therein.

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Relative Signs of Spin–Spin Coupling Constants Involving Carbon-13 from Off-Resonance Proton Decoupling

Sir:

The off-resonance decoupling technique has been used almost exclusively for the assignment of ^{13}C resonances from various measurements[1–4] during off-resonance irradiation in the proton region. We have recently demonstrated[5] that coherent off-resonance proton irradiation experiments may also be conveniently used in ^{13}C nmr for determining the relative signs of $^nJ_{CX}$ and the corresponding $^{n+1}J_{HX}$ spin–spin coupling constants, X being a spin half-nucleus other than the proton, *i.e.* ^{13}C, ^{19}F, ^{31}P, etc. In this technique use is made of the difference observed for the reduced splittings, $J^r_{CH} = 2\pi\Delta\nu J_{CH}/\gamma H_2$, due to the *direct* ^{13}CH couplings in the ^{13}C spectrum of the $J_{^{13}C-X}$ doublet.[5] At first sight it appears that the determination of relative signs of J_{CX} coupling constants by off-resonance proton irradiation is restricted to systems where (a) carbon atoms are directly bonded to at least one proton and (b) X is a nucleus other than the proton. However, we here report on the determination of the signs of ^{13}C–X (X = ^{31}P and ^1H) coupling constants which involve a carbon atom that is not bonded to a proton and where use is made of the differences in residual splittings of the *long-range* ^{13}CH couplings which are observed during off-resonance proton irradiation.

In connection with a current ^{13}C nmr study on the effect of ortho substituents on the ^{13}C–^{31}P couplings in triarylphosphines,[6] the determination of the sign of

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[5] H. J. Jakobsen, T. Bundgaard, and R. S. Hansen, *Mol. Phys.*, **23**, 197 (1972).

[6] S. Sørensen, R. S. Hansen, and H. J. Jakobsen, *J. Amer. Chem. Soc.*, **94**, 5900 (1972).