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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(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.

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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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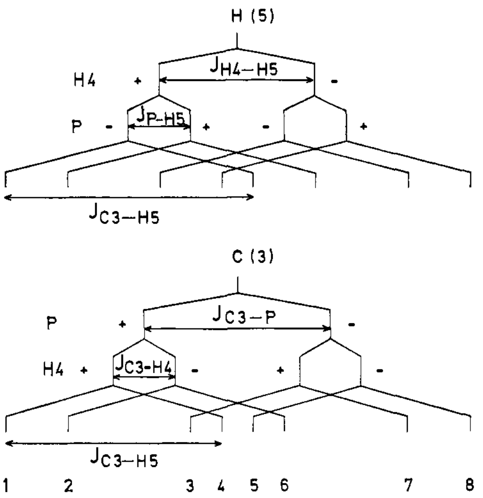

Figure 1. First-order stick diagrams of the H-5 proton (upper part) and C-3 carbon spectrum (lower part) in tri(3-bromo-2-thienyl)-phosphine-*3*-^{13}C (see text). The relative magnitudes of the coupling constants are not drawn to scale.

$^2J_{CP}$ involving the non-proton-bonded C-3 atom in tri(3-bromo-2-thienyl)phosphine was attempted using $^{13}C-\{^1H\}$ double resonance techniques. It was found that the sign may be most conveniently obtained from the C-3 spectrum as observed under conditions of slight off-resonance irradiation of the H-5 inner satellites. However, this required a weaker decoupling field ($\gamma H_2/2\pi \approx$ 100–150 Hz) than that generally applied in off-resonance proton decoupling experiments. First-order stick diagrams showing the H-5 proton inner satellite spectrum and the undecoupled C-3 spectrum are presented in Figure 1. The spin states of the nuclei coupled to H-5 and C-3 are given for all transitions, with the convention that a positive sign for a low-field peak denotes a positive coupling to the nucleus in question. Magnitudes of the coupling constants were obtained from ^1H and undecoupled ^{13}C spectra (experimental parameters are given in the legend of Figure 2). The negative sign for $J_{P-H\text{-}5}$ was determined from $^1H-\{^1H\}$ spin tickling experiments; otherwise the signs are indicated in accordance with literature data for related compounds and with the experiments described here.

The effect on the C-3 spectrum of irradiating in the proton region at a frequency slightly higher than any of the H-5 effective chemical shifts, $\nu_{H\text{-}5}^{\text{eff}} = \nu_{H\text{-}5} \pm {}^1/_2J_{H\text{-}5-H\text{-}4} \pm {}^1/_2J_{H\text{-}5-P}$, is shown in Figure 2 (actual values are given in the legend of Figure 2). Using the stick diagrams and signs indicated in Figure 1 it is estimated that under these experimental conditions the four reduced $J_{C\text{-}3-H\text{-}5}$ doublet splittings in the C-3 spectrum should show a wider spacing for the doublets in the order: [3–7] < [1–4] < [5–8] < [2–6]. As seen in Figure 2 the same order is followed for the reduced $J_{C\text{-}3-H\text{-}5}$ couplings in the experimental spectrum (the smallest reduced splitting observed in Figure 2 arises from $J_{C\text{-}3-H\text{-}5}$). Furthermore, the simulated double resonance spectrum obtained by diagonalization of the double resonance Hamiltonian matrix using the experimental parameters given in Figure 2 is shown below the experimental spectrum. The actual values for the observed (±0.03 Hz) and calculated (in parentheses) residual splittings are: [3–7] 0.45 Hz (0.44 Hz), [1–4] 0.60 Hz (0.59 Hz), [5–8] 0.62 Hz (0.60 Hz), and [2–6] 0.74 Hz (0.74 Hz). From the off-resonance decoupled spectrum the following sets of relative signs of coupling constants may be obtained: $J_{C\text{-}3-P}$ and $J_{H\text{-}5-P}$ are of opposite sign, *i.e.* $J_{C\text{-}3-P} > 0$; $J_{C\text{-}3-H\text{-}4}$ and $J_{H\text{-}4-H\text{-}5}$ have the same sign, *i.e.* $J_{C\text{-}3-H\text{-}4} > 0$.

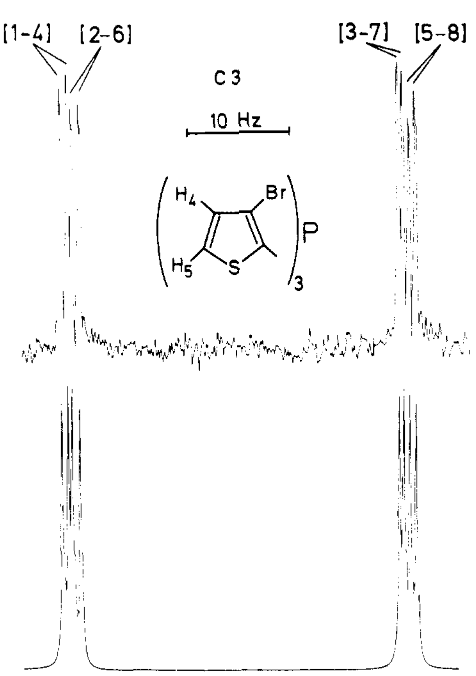

Figure 2. Experimental (upper part) and calculated (lower part) ^{13}C spectrum (55 scans) of C-3 in tri(3-bromo-2-thienyl)phosphine obtained during slight off-resonance (high-frequency) irradiation of H-5. The experimental parameters used for the simulation of the double resonance spectrum are: ν_2 = 756.30 Hz and $\gamma_{^1H}H_2/2\pi$ = 132.5 Hz for the irradiation frequency and amplitude, respectively; $\nu_{H\text{-}4}$ = 698.37 Hz, $\nu_{H\text{-}5}$ = 750.38 Hz, $J_{H\text{-}4-H\text{-}5}$ = +5.12 Hz, $J_{P-H\text{-}4}$ = +2.45 Hz; $J_{P-H\text{-}5}$ = −1.52 Hz, $J_{C\text{-}3-H\text{-}4}$ = +2.71 Hz, $J_{C\text{-}3-H\text{-}5}$ = +13.23 Hz, $J_{C\text{-}3-P}$ = +32.90 Hz. The irradiation frequency and proton chemical shifts are relative to Me_4Si (100.1 MHz). ^{13}C nmr spectra were recorded on a Varian XL-100-15 spectrometer (25.2 MHz, ^2H lock, continuous wave mode, C-1024 CAT). The sample solution was *ca.* 38% w/w in CS_2–acetone-d_6 (50:12, w/w).

The off-resonance proton decoupling technique appears therefore to be generally applicable for determination of signs of ^{13}C–X coupling constants, *i.e.* it is not restricted only to carbon atoms which are directly bonded to protons.[5] Furthermore, under certain conditions it may also be useful for relative sign determination in cases where X = ^1H.

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CO_2 Fixation Leading to Stable Molecular Bicarbonato Complexes of d^8 Metals

Sir:

Although literally hundreds of carbonato–transition metal complexes are known,[1] isolable and well-defined analogous compounds containing *bicarbonate*

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(1) For a review, see K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 70, 171 (1970).