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Studies of 2-(η^5-C_5H_5)CoB_4H_8, a Cobaltaborane Analogue of B_5H_9

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Received September 30, 1977

The chemistry of the title compound was examined in the light of known reactions of its structural counterpart, pentaborane(9). Like B_5H_9, 2-(η^5-C_5H_5)CoB_4H_8 undergoes deprotonation with NaH at a bridging position, forming the $(C_5H_5)CoB_4H_7^-$ ion; the proton removed is adjacent to cobalt. Reaction of the anion with HCl regenerates the neutral metalloborane. Treatment of the anion with $CoCl_2$ and NaC_5H_5 produces the known cobaltaborane cluster 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$ in moderate yield with lesser amounts of tri- and tetracobalt metalloboron species, all of which are identical with products of the $B_5H_8^-$–$CoCl_2$–$C_5H_5^-$ reaction previously reported. The reaction of 2-(η^5-C_5H_5)CoB_4H_8 with C_2H_2 produces the known metallocarborane 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$, a process formally analogous to the insertion of C_2H_2 into B_5H_9 to yield $C_2B_4H_8$. The reactions of 2-(η^5-C_5H_5)CoB_4H_8 with higher alkynes yield not only the corresponding metallocarboranes $(C_5H_5)CoRR'C_2B_3H_5$ but also in each case an "addition product" corresponding to $(C_5H_5)CoB_4H_8\cdot RR'C_2$ whose structures were not determined. The latter species were shown to be intermediates in the formation of the metallocarboranes. The reaction of the title compound with $Fe(CO)_5$ under ultraviolet light gave in low yield a novel mixed-metal metalloborane cluster, 1,2,3-(η^5-C_5H_5)$_2Co_2(CO)_4FeB_3H_3$, whose proposed structure consists of an octahedral Co_2FeB_3 cage with all metal atoms on the same triangular face.

The family of known metalloborane[1] cage compounds is rapidly expanding as discoveries of new and structurally novel compounds continue to be reported.[2] Understandably, most of the effort in this area has concentrated on the preparation and characterization of new compounds; detailed studies of the chemical behavior of individual metalloboranes have been relatively rare. In the work to be described here, we have examined the chemistry of a particular species,[3] 2-(η^5-C_5H_5)CoB_4H_8, a red crystalline solid structurally analogous to B_5H_9 from which it is formally derived by replacement of a basal BH unit with (η^5-C_5H_5)Co. In addition to its inherent structural interest, this compound is well suited for detailed investigation in that it is chemically stable, can be handled in air, and is readily prepared in workable quantity from commercially available reagents. The synthesis[3] involves treatment of $B_5H_8^-$ ion with $CoCl_2$ and NaC_5H_5 in tetrahydrofuran (THF), giving a complex reaction in which (η^5-C_5H_5)CoB_4H_8 is the major cobaltaborane product accompanied by a number of other species having one to four cage cobalt atoms.

The close relationship of 2-(η^5-C_5H_5)CoB_4H_8 to B_5H_9 was the point of most immediate interest to us, and accordingly our first chemical studies were designed to compare the behavior of the complex with known reactions of pentaborane(9). The essential question to be examined was, "what are the chemical consequences of substituting (η^5-C_5H_5)Co for a BH unit in the B_5H_9 framework?" At the outset two facts had been established. The structure of (η^5-C_5H_5)CoB_4H_8, proposed[3a] from ^{11}B and ^{1}H NMR evidence and later confirmed by x-ray crystallographic analysis,[4] is that of a distorted square pyramid with the metal in a basal location and four bridging hydrogen atoms (two B–H–B and two Co–H–B) on the open face (Figure 1); the bond angles and distances are close to those in B_5H_9 save for the distortions created by the introduction of a transition-metal atom in place of a boron. Second, the cobaltaborane contrasts dramatically with B_5H_9 in air stability, the former hydrolyzing only very slowly over several weeks while the borane exhibits well-known pyrophoricity and forms explosive mixtures with oxygen (kinetic effects arising from the large volatility difference may be a

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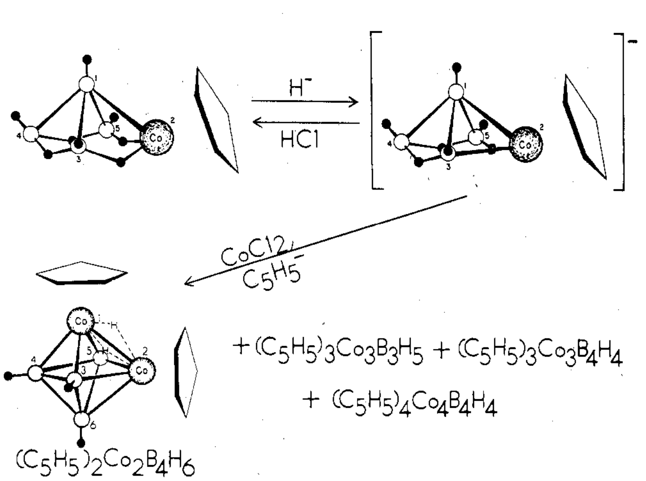


Figure 1. Reversible bridge deprotonation of 2-(η^5-C_5H_5)CoB_4H_8 and reaction of the anion with $CoCl_2$ and NaC_5H_5.

factor in this observation, but only to a limited extent).

As a basis for exploring the chemistry of (η^5-C_5H_5)CoB_4H_8, several well-established aspects of the chemistry of B_5H_9[5] were selected for the initial study: (1) bridge deprotonation to generate the $B_5H_8^-$ ion, and subsequent reactions of that ion; (2) reactions with alkynes to produce the *nido*-carborane 2,3-$C_2B_4H_8$ and its derivatives; (3) insertion of transition metals to generate metalloboranes.

Results and Discussion

Reversible Bridge Deprotonation. The reaction of B_5H_9 with hydride ion and other Lewis bases, forming the $B_5H_8^-$ ion by removal of a bridging proton, is well known.[6] The corresponding treatment of 2-(η^5-C_5H_5)CoB_4H_8 was expected to give similar results, generating the 2-(η^5-C_5H_5)$CoB_4H_7^-$ ion, and this was indeed the case. The addition of excess NaH in cold dry tetrahydrofuran (THF) with slow warming to room temperature over 1 h produced 1.16 equiv of H_2 based on the following equation. Reaction of the anion with excess dry HCl regenerated the original metalloborane in 84% yield.

$$\begin{tikzcd} (C_5H_5)CoB_4H_8 + NaH \arrow[r, "-H_2"'] & Na^+(C_5H_5)CoB_4H_7^- \arrow[l, bend left, "HCl", "-NaCl"'] \end{tikzcd}$$

The proton removed is abstracted from a Co–H–B rather than a B–H–B location, as shown by the ^1H NMR spectrum of the anion which contains a B–H–B signal of area 2 and a Co–H–B resonance of area 1 (Table II). Except for the decrease in the area of the Co–H–B signal, the spectrum of the anion closely resembles that of the neutral compound. Deuteration of the anion with dry DCl afforded μ(2,3)-D-2-(η^5-C_5H_5)CoB_4H_7, whose ^1H NMR spectrum contained B–H–B and Co–H–B peaks in a ~1.5:1 area ratio. (The latter figure is lower than the 2:1 expected for a pure monodeuterio species because of the presence of ~20% HCl in the DCl sample and also possibly as a consequence of some scrambling of deuterium among the bridging positions).

Reaction of the (η^5-C_5H_5)$CoB_4H_7^-$ Ion with $CoCl_2$ and NaC_5H_5. As mentioned above and described in detail elsewhere,[3,7] the $B_5H_8^-$ ion reacts with $CoCl_2$ in the presence of $C_5H_5^-$ ion to generate numerous cobaltaboranes of which (η^5-C_5H_5)CoB_4H_8 itself is the principal product. It was therefore of interest to examine the corresponding reaction of the (η^5-C_5H_5)$CoB_4H_7^-$ ion in the hope of inserting one or more additional cobalt atoms into the cage. As shown in Figure 1, four cobaltaboranes were isolated, all of which correspond to products of the $B_5H_8^-$–$CoCl_2$–$C_5H_5^-$ reaction; the major species formed is the dicobalt system 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$, obtained in 15% yield (compared to <1% in the $B_5H_8^-$ reaction). The compounds (η^5-C_5H_5)$_3Co_3B_4H_4$, (η^5-C_5H_5)$_3Co_3B_3H_5$, and (η^5-C_5H_5)$_4Co_4B_4H_4$ were isolated in a total yield of 4.5%, again larger than in the original preparation from $B_5H_8^-$. Thus, it appears highly likely that the cobalt-rich clusters which form in the treatment of $B_5H_8^-$ ion with excess $CoCl_2$ and $C_5H_5^-$ are generated primarily by the introduction of additional cobalt into the monocobalt species (η^5-C_5H_5)$CoB_4H_7^-$ which must certainly be present under the conditions of that reaction. It is interesting that (η^5-C_5H_5)CoB_9H_{13}, a compound isolated from the $B_5H_8^-$ reaction,[3] was *not* found in the treatment of (η^5-C_5H_5)$CoB_4H_7^-$ with $CoCl_2$; this material probably forms by attack of $B_5H_8^-$ on the cobaltaborane anion, a proposition we have not directly examined.

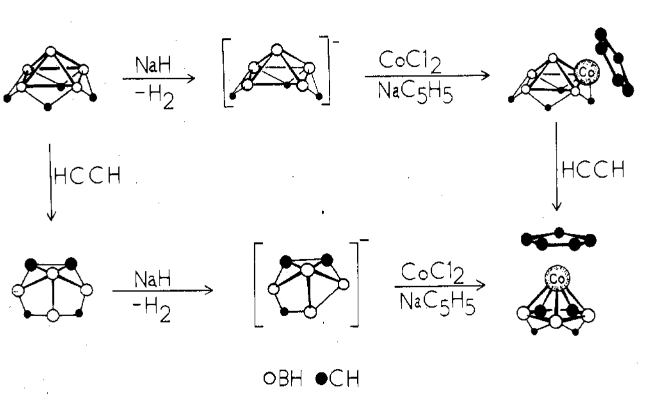


Figure 2. Two routes for the synthesis of 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$ from B_5H_9.

Several other cobaltaborane trace products which were isolated from the $B_5H_8^-$ reaction[3b] were not detected in the (η^5-C_5H_5)$CoB_4H_7^-$ treatment, but in view of the smaller scale of the present investigation their formation in extremely minute quantities cannot be excluded.

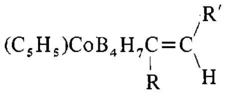
Addition and Insertion of Alkynes to (η^5-C_5H_5)CoB_4H_8. Formation of Metallocarboranes. It was demonstrated some time ago that B_5H_9 reacts readily with acetylene and other alkynes to give *nido*-carboranes, principally 2,3-$C_2B_4H_8$ and its derivatives.[8] This "alkyne insertion" occurs under a variety of conditions, including catalysis by hindered Lewis bases such as 2,6-dimethylpyridine at room temperature[8c] or pyrolysis of alkyne–B_5H_9 mixtures in the gas phase in sealed bulbs.[8a,8b] Although such reactions are complex and generate polymeric solids in addition to the carboranes, the formation of 2,3-$C_2B_4H_8$ from B_5H_9 and C_2H_2 can be schematically represented as a replacement of a BH_3 unit (in the base of the B_5H_9 molecule) with C_2H_2. The corresponding reaction of (η^5-C_5H_5)CoB_4H_8 with C_2H_2 would produce the metallocarborane 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$, which as it happens is a known compound[9] that can be prepared from $C_2B_4H_8$. Accordingly, the gas-phase reaction of 2-(η^5-C_5H_5)CoB_4H_8 with C_2H_2 was examined and found to give a small yield of 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$ as expected, representing the first known instance in which a metallocarborane has been synthesized by insertion of carbon into a metalloborane.[10] A coproduct of this reaction is the rearranged isomer 1-(η^5-C_5H_5)CoB_4H_8, previously characterized[3] as a square-pyramidal cage with the metal occupying the apex position. The acetylene-insertion process was further explored by investigating the reactions of (η^5-C_5H_5)CoB_4H_8 with several higher alkynes, which as anticipated produced C-substituted derivatives of 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$; except for (η^5-C_5H_5)$Co(CH_3)_2C_2B_3H_5$ (IC), these are known complexes which have previously been synthesized from $C_2B_4H_8$ derivatives.[9,11]

As a consequence of this work, two fundamentally different methods for the preparation of metallocarboranes from B_5H_9 now exist: one approach involves the insertion of carbon followed by incorporation of the metal, while the other utilizes initial metal insertion followed by carbon (Figure 2). To our knowledge, there are no previous examples of the synthesis of the same metalloboron cage system by two such radically different routes.

Unexpectedly, in each of the higher alkyne reactions the metallocarborane product was accompanied by another material whose composition corresponds to an adduct of the alkyne and metalloborane reagents; these species will be designated "addition products".

$RC{\equiv}CR' + (C_5H_5)CoB_4H_8 \rightarrow$
$(C_5H_5)CoRR'C_2B_3H_5 + (C_5H_5)CoB_4H_8{\cdot}RC_2R'$
metallocarboranes "addition products"
IA, $R = R' = H$
IB, $R = H, R' = CH_3$ IIB, $R = H, R' = CH_3$
IC, $R = R' = CH_3$ IIC, $R = R' = CH_3$
ID, $R = H, R' = C_6H_5$ IID, $R = H, R' = C_6H_5$

In the reaction with acetylene, only the metallocarborane $(C_5H_5)CoC_2B_3H_7$ is obtained, with no evidence for the "adduct". In the reactions with methylacetylene, dimethylacetylene, and phenylacetylene, mixtures of the two types of product were found, with the metallocarborane predominant. The pairs of products in all cases proved inseparable on TLC plates (also, the addition products tended to decompose during chromatography), and consequently each of the species IIB, IIC, and IID was examined as a mixture with its metallocarborane coproduct (IB, IC, ID). The formulas of the addition products were established from mass spectra, supported by high-resolution mass measurements in the cases of IIC and IID. The ratio of metallocarborane to addition product in each mixture was estimated from mass spectra and ^1H NMR spectra, using the area ratio of C_5H_5 signals. The ^{11}B NMR spectra, even with proton decoupling, did not offer much insight into the structures of the addition products due to heavy overlap of their resonances with those of the metallocarborane present; however, each of the ^{11}B spectra does exhibit a singlet at moderately low field which might reasonably be attributed to a boron atom attached to an external substituent in the addition product. The terminal hydrogen atom which is displaced by the substitution presumably is transferred to the alkynyl group, in which case the addition products could be alkenyl-substituted derivatives of $(C_5H_5)CoB_4H_8$, i.e.,



$$(C_5H_5)CoB_4H_7\underset{\substack{|\\R}}{C}{=}C\begin{smallmatrix}R'\\H\end{smallmatrix}$$

It appeared likely that the addition products are intermediates in the process of alkyne insertion into the metalloborane cage, particularly since the ratio of metallocarborane to addition product in each system tends to increase with increasing reaction temperature. Accordingly, mixtures of the addition and metallocarborane products from the dimethylacetylene reaction and from the phenylacetylene reaction were pyrolyzed at 190–195 °C. In each case, substantial enrichment of the metallocarborane and depletion of the addition product component were observed (see Experimental Section), indicating that the latter species are indeed precursors of the former.

It is notable that no addition product is seen in the reaction of acetylene with $(\eta^5\text{-}C_5H_5)CoB_4H_8$. It can be assumed that such a product is formed initially but is less stable than the corresponding species produced from higher alkynes. The acetylene–metalloborane addition product may be susceptible to polymer formation or other side reactions, which would also explain the lower yield of metallocarborane in this system compared to those of other alkynes. Also of interest here is the fact that no addition products were reported in the reactions of B_5H_9 with acetylene and several higher alkynes,[8] despite the fact that carboranes were obtained. On the basis of the present work, it is likely that the formation of carboranes from B_5H_9 and alkynes also proceeds via addition-product intermediates which are too reactive for detection among the final products. This point is discussed further in the concluding remarks.

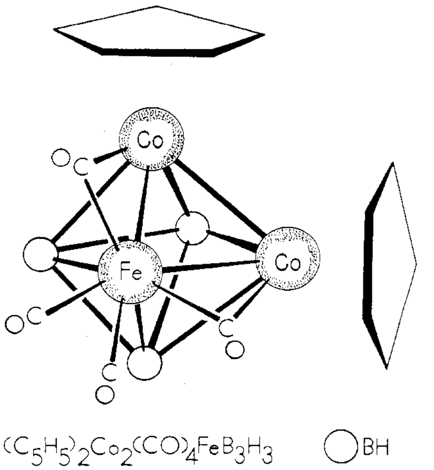


Figure 3. Proposed structure of $1,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CO)_4FeB_3H_3$ (III).

Reactions of $2\text{-}(\eta^5\text{-}C_5H_5)CoB_4H_8$ with Metal Carbonyls. The treatment of B_5H_9 with $Fe(CO)_5$, or of B_4H_{10} with $Fe_2(CO)_9$, yields the ferraborane $1\text{-}(CO)_3FeB_4H_8$, an analogue of B_5H_9 with the metal in the apex of the square pyramid.[12] It was of interest to determine whether the corresponding reaction of $2\text{-}(\eta^5\text{-}C_5H_5)CoB_4H_8$ with $Fe(CO)_5$ might incorporate iron to produce a mixed-metal metalloborane. Irradiation of a heptane solution of these reactants under UV light gave a multitude of products, of which four were separated on TLC plates. Three of these were identified as known compounds, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe_2(CO)_9Co(\eta^5\text{-}C_5H_5)$.[13] The fourth product was a brown solid characterized as $1,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2(CO)_4FeB_3H_3$ (III) from its unit- and high-resolution mass spectra and ^{11}B NMR and ^{11}B-decoupled ^1H NMR spectra. Assuming an octahedral Co_2FeB_3 cage (based on the framework electron count[14] and the electronic analogy with other octahedral metalloboranes and metallocarboranes), only three cage structures need be considered a priori, namely, those having (1) the three metals on the same triangular face, (2) the cobalt atoms trans to each other, and (3) the iron atom trans to one cobalt. Structure (3) is eliminated by the observation that the two $(\eta^5\text{-}C_5H_5)Co$ groups are equivalent, as shown by the single C_5H_5 ^1H NMR signal. Structure (2) is unlikely in that it would have two types of boron atoms, adjacent to two and three metals, respectively, which would be expected to generate widely separated ^{11}B NMR signals. The observation of two signals in a 1:2 ratio with similar chemical shifts points strongly to structure (1), which is depicted in Figure 3. The positions of the carbonyl groups cannot be determined at present, but at least one of them is probably in a bridging location; an arrangement which satisfies the twofold symmetry indicated by the NMR spectra is illustrated in the figure.

The new metalloborane is an electronic and structural analogue of the known octahedral systems $(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$,[3b,7] $(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$,[3] $(\eta^5\text{-}C_5H_5)CoC_2B_3H_5$,[15] $(CO)_3FeC_2B_3H_5$,[15] 1- and $2\text{-}C_2B_4H_6$,[16] CB_5H_7,[17] and the $B_6H_6^{2-}$ ion.[18] While we and others have pointed out such relationships many times in the past, it is perhaps worth reiterating again the value of the electron-count theory[14,19] in relating so varied a group of molecules not only to each other but also to nonboron organometallics and metal clusters. Assigning the $(CO)_4Fe$ group as a four-electron donor[14] to the central cage,[20] each (η^5-C_5H_5)Co and BH unit as a two-electron donor, and the CH and "extra" (nonterminal) hydrogen groups as three- and one-electron donors, respectively, one arrives at 14 skeletal valence electrons for each of the above systems, in agreement with the prediction of closed polyhedral geometry for an n-vertex cage having $n + 1$ skeletal electron pairs.

Compound III is particularly closely related to 1,2,3-(η^5-C_5H_5)$_3Co_3B_3H_5$,[3b,7] from which it is formally derived by replacing a (η^5-C_5H_5)Co group with an $Fe(CO)_3$ unit and two "extra" hydrogens with an additional CO ligand. The structures of the tricobalt species as well as the boron-capped cluster (η^5-C_5H_5)$_3Co_3B_4H_4$[3b,7] have been confirmed by x-ray crystallographic studies.[21] All of these compounds as well as 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$[3] and (η^5-C_5H_5)$_4Co_4B_4H_4$[3b,7] (both structurally established[22]), exhibit a clear tendency for the metal atoms to occupy adjacent polyhedral vertices; this presumably is a kinetic effect, since there is no good reason to believe that adjacent-metal isomers are thermodynamically favored.[23] The adjacent-metal phenomenon, previously noted in small metallocarborane chemistry,[15,25] is now quite evident in polyhedral metalloboranes[3,7,26] with III only the latest example.

Reactions of 2-(η^5-C_5H_5)CoB_4H_8 with $Fe_3(CO)_{12}$ and with $Mo(CO)_6$, both conducted in heptane under UV light, gave no isolable products.

Conclusions

The reversible deprotonation of 2-(η^5-C_5H_5)CoB_4H_8, formation of a stable anion, incorporation of alkynes into the cage, and insertion of iron on reaction with $Fe(CO)_5$ establish a clear correlation with the chemistry of B_5H_9. The formation of stable intermediates having the formula $(C_5H_5)CoB_4H_8 \cdot RC_2R'$ in the treatment of the metalloborane with alkynes implies that analogous species, $B_5H_9 \cdot RC_2R'$, may exist as intermediates in B_5H_9–alkyne reactions. Although these latter species evidently have too short a lifetime to be observed under reaction conditions, their existence as precursors to the carborane products can be inferred from the fact that the main carborane species isolated from the B_5H_9–alkyne reactions, *nido*-$RR'C_2B_4H_6$, are direct structural analogues of the $(C_5H_5)CoRR'C_2B_3H_5$ metallocarboranes which are formed in the $(C_5H_5)CoB_4H_8$–alkyne reactions. In this connection, it is perhaps worth recalling that a kinetic study[27] of the B_4H_{10}–C_2H_2 reaction at 25–50 °C produced evidence for a $B_4H_8 \cdot C_2H_2$ intermediate (formed following the initial rate-determining process $B_4H_{10} \rightarrow B_4H_8 + H_2$), which in turn generates the observed carborane products.

In the B_4H_{10} reaction a detailed examination of the mechanism was possible because the system is relatively clean and controllable; the B_5H_9–alkyne gas-phase reactions in contrast are exceedingly complex, producing large quantities of inhomogeneous polymers, and the task of unraveling the mechanism via a kinetic study would be horrendous to contemplate. Given this situation the alkyne–$(C_5H_5)CoB_4H_8$ reactions offer a useful means of gaining some insight into the insertion of carbon into small borane frameworks, made possible by the enhanced stabilization of the cage by the presence of the metal atom; the structural characterization of one or more of the intermediates described above (IIB, IIC, IID) would be a significant advance. Other candidates for alkyne-insertion studies include 1-(η^5-C_5H_5)CoB_4H_8 and 5-(η^5-C_5H_5)$CoB_{10}H_{13}$,[3] a decaborane(14) analogue whose interaction with alkynes should parallel the formation of carboranes from $B_{10}H_{14}$. It remains to be seen whether metalloboranes in general might function as "stabilized boranes" and allow the observation of processes and species which in the corresponding reaction of the parent borane could not be detected.

Experimental Section

Materials. 2-Cyclopentadienylcobaltapentaborane(9), (η^5-C_5H_5)CoB_4H_8, was prepared from B_5H_9, $CoCl_2$, NaH, and C_5H_6 as described elsewhere.[3b] All other reagents were commercially obtained (reagent grade) and used as received.

Spectra and Chromatography. Boron-11 and proton pulse Fourier transform NMR spectra at 32.1 and 100 MHz, respectively, were recorded on a Jeol PS-100P spectrometer interfaced to a Jeol-Texas Instruments EC-100 computer system. Unit-resolution mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer, while high-resolution mass measurements were conducted on an AEI MS-902 double-focusing instrument equipped with an SRI chemical ionization source. All high-resolution spectra were recorded under chemical ionizing conditions in methane or argon–water. Thin-layer and preparative-layer chromatography (TLC) were conducted in air on precoated plates of silica gel F-254 purchased from Brinkmann Instruments, Inc.

General Procedure. Except where otherwise indicated, all reactions were run in high-vacuum apparatus in an inert atmosphere.

Preparation of $Na^+(C_5H_5)CoB_4H_7^-$ and Reaction with HCl. Dry THF was condensed onto a mixture of 2-$(C_5H_5)CoB_4H_8$ (50.4 mg, 0.286 mmol) and excess NaH (0.76 mmol) at −196 °C. The reactor was slowly warmed to room temperature, during which evolution of gas was observed. After 0.5 h at room temperature gas evolution had effectively ceased. Following 1 h at room temperature, the reactor was refrozen in liquid nitrogen and the H_2 (0.33 mmol, 1.16 equiv) was Toepler pumped and measured. At this point 1.03 mmol of dry HCl was condensed onto the solid solution of the anion and the mixture was warmed to room temperature. After 30 min the reaction mixture was loaded onto a TLC plate and 2-$(C_5H_5)CoB_4H_8$ (42.3 mg, 83.9% yield based on starting cobaltaborane) was recovered, identified from its color, R_f value,[3b] and mass spectrum.

Preparation of μ(2,3)-D-$(C_5H_5)CoB_4H_7$. An excess of NaH (78.5 mg, 3.27 mmol) was allowed to react with $(C_5H_5)CoB_4H_8$ (21.3 mg, 0.12 mmol) in 10 mL of THF in vacuo. After the red solution was stirred for 75 min at 25 °C, the resulting solution was passed through a glass frit (to remove excess NaH) and then frozen at −196 °C while H_2 was removed. DCl (3.7 mmol, prepared from the addition of 98% D_2O to benzoyl chloride) was condensed into the flask and the resulting mixture was stirred at room temperature overnight (18 h). Solvent and unreacted DCl were distilled in vacuo, and the residue was sublimed at 25 °C to give a red solid. The mass spectrum of the solid showed a molecular ion cutoff at m/e 177, corresponding to $(C_5H_5)CoB_4H_7D$.

Reaction of $Na^+(C_5H_5)CoB_4H_7^-$ with $CoCl_2$ and NaC_5H_5. A THF solution of $Na^+(C_5H_5)CoB_4H_7^-$ (prepared from 0.240 mmol of 2-$(C_5H_5)CoB_4H_8$ and 0.665 mmol of NaH) and NaC_5H_5 (prepared from 0.963 mmol of C_5H_6 and 1.79 mmol of NaH) was filtered onto 1.29 mmol of $CoCl_2$ and allowed to react with stirring for 2 h. The products were separated and purified via TLC, and identified from their colors, R_f values, and spotting on TLC plates vs. bona fide samples of the known compounds. Yields based on 2-$(C_5H_5)CoB_4H_8$ consumed were the following: 1,2-(η^5-C_5H_5)$_2Co_2B_4H_6$, 14.9%; 1,2,3-(η^5-C_5H_5)$_3Co_3B_4H_4$, 2.0%; 1,2,3-(η^5-C_5H_5)$_3Co_3B_3H_5$, 1.75%; (η^5-C_5H_5)$_4Co_4B_4H_4$, 0.72%.

Reaction of 2-(η^5-C_5H_5)CoB_4H_8 with C_2H_2. A mixture of 2-$(C_5H_5)CoB_4H_8$ (39.4 mg, 0.22 mmol) and C_2H_2 (216 Torr, 5.7 mmol) was heated in a sealed 1000-mL bulb in vacuo at 175 °C for 17 h. After cooling to −196 °C, the bulb was opened into the vacuum line via a break-seal; essentially no noncondensable materials were observed. The solid contents of the flask were extracted first with hexane and then with CH_2Cl_2 to give yellow-brown solutions; these were combined, and two products were separated by TLC using 10% benzene/90% hexane as elutent. The more mobile band (R_f 0.76) was an air-sensitive yellow solid identified[3b] as 1-$(C_5H_5)CoB_4H_8$ (1.8 mg, 5%). The second band (R_f 0.60) was spectroscopically (IR and mass spectra) identified[9] as yellow 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$ (1.2 mg, 3%). The mass spectra of the products gave no evidence of an intermediate, in contrast to the alkyne reactions described below.

Reaction of 2-(η^5-C_5H_5)CoB_4H_8 with CH_3C_2H. A mixture of 45.9 mg (0.26 mmol) of the metalloborane and 5.1 mmol of propyne was heated in a 1000-mL bulb at 175 °C for 20 h, after which the solid products were extracted with 25 mL of hexane followed by 25 mL

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

Compound[a]	δ,[b] ppm (*J*, Hz)	Rel areas
1,2,3-(η^5-C_5H_5)Co$C_2B_3H_7$, IA[c]	2.7 (149),[d] 2.0 (147)[d]	~2, 1
1,2,3-(η^5-C_5H_5)Co(CH_3)$C_2B_3H_6$, IB[c]	−1.8 (121)[e]	
1,2,3-(η^5-C_5H_5)Co$(CH_3)_2C_2B_3H_5$, IC	0.9 (144)	
1,2,3-(η^5-C_5H_5)Co(C_6H_5)$C_2B_3H_6$, ID	4.4 (140),[d] 1.2 (140)[d]	1, 2[d]
(η^5-C_5H_5)CoB_4H_8·$CH_3C{\equiv}CH$, IIB[f]	18.9[g]	
(η^5-C_5H_5)CoB_4H_8·$CH_3C{\equiv}CCH_3$, IIC[f]	21.9[g]	
(η^5-C_5H_5)CoB_4H_8·$C_6H_5C{\equiv}CH$, IID[f]	18.1[g]	
1,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CO)_4FeB_3H_3$, III	87.5 (166), 73.0 (158)	1, 2

[a] All spectra were run in $CDCl_3$ solution. [b] Chemical shifts relative to $BF_3{\cdot}O(C_2H_5)_2$ with positive sign denoting downfield shift. [c] Reported in ref 9. [d] Estimated from overlapped resonances. [e] Asymmetric doublet, shoulder on downfield side. [f] Observed only in mixture with the corresponding metallocarborane (IB, IC, or ID); resonances other than the downfield singlet were obscured by the metallocarborane peaks. [g] Singlet resonance.

of CH_2Cl_2. TLC gave one yellow band which on mass spectroscopic analysis was shown to be a 9:1 mixture of two compounds, 1,2,3-(η^5-C_5H_5)Co(CH_3)$C_2B_3H_6$ (IB) and a minor component whose composition corresponded to (η^5-C_5H_5)CoB_4H_8·$CH_3C{\equiv}CH$ (IIB). The identity of IB was confirmed by spectroscopic comparison with the known compound.[9] Compound IIB could not be separated from IB but the ratio of IIB/IB was determined from the integrated areas of the C_5H_5 resonances in the 100-MHz proton NMR spectrum of the mixture. The combined yield was 12.2 mg (23%).

Reaction of 2-(η^5-C_5H_5)CoB_4H_8 with $(CH_3)_2C_2$. In a procedure identical with that employed in the preceding experiment, 48.4 mg (0.275 mmol) of the cobaltaborane and 5.6 mmol of 2-butyne were heated at 175 °C for 20 h. Extraction of the product mixture with hexane, followed by TLC, gave an inseparable mixture of 1,2,3-(η^5-C_5H_5)Co$(CH_3)_2C_2B_3H_5$ (IC) and (η^5-C_5H_5)CoB_5H_8·$CH_3C{\equiv}CH_3$ (IIC) in approximately a 5:1 ratio with a combined yield of 14.1 mg (22%). Compound IC was obtained in essentially pure form by pyrolysis of the mixture at 190 °C for 20 h and was characterized from its mass spectrum, ^{11}B and ^1H NMR spectra, and infrared spectrum IR of IC (KBr pellet, cm^{-1}): 3420 (m, br), 2945 (s), 2865 (m), 2540 (vs), 1865 (m), 1623 (w), 1558 (s), 1443 (m), 1421 (m), 1118 (w), 1013 (s), 954 (m), 892 (w), 831 (s), 786 (s), 743 (w), 695 (w).

The composition of IIC was confirmed by an exact mass measurement: calcd for $^{12}C_9{}^{11}B_4{}^{59}Co{}^1H_{19}$ 230.1191, found 230.1203. The IIC/IC ratio in the original product mixture was determined as described for IIB/IB.

In a separate experiment, thermolysis of 24.7 mg (0.14 mmol) of 2-(η^5-C_5H_5)CoB_4H_8 and 0.279 g (5.2 mmol) of 2-butyne at 165 °C for 9 h gave 12.9 mg of isolated product which consisted of 70% IC and 30% IIC.

Reaction of 2-(η^5-C_5H_5)CoB_4H_8 with $C_6H_5C_2H$. The procedure described for the preceding experiments was employed to conduct the thermolysis of a mixture of the cobaltaborane (32.9 mg, 0.19 mmol) and phenylacetylene (84.3 mg, 0.83 mmol) at 170 °C for 7 h. Following extraction of the product mixture with CH_2Cl_2, TLC gave one yellow band whose mass spectrum indicated a mixture of 1,-2,3-(η^5-C_5H_5)Co(C_6H_5)$C_2B_3H_6$ (ID) and (η^5-C_5H_5)CoB_4H_8·$C_6H_5C{\equiv}CH$ (ID), in a total yield of 19%. The composition of IID was confirmed by exact mass determination: calcd for $^{12}C_{13}$-$^{11}B_4{}^{59}Co{}^1H_{19}$ 278.1191, found 278.1178. The composition of the product mixture was 56% ID and 44% IID, found as described for the previous cases.

After pyrolysis of the mixture in a sealed bulb at 195 °C for 23 h followed by TLC purification and NMR analysis, the composition was 94% ID and 6% IID.

Although the phenyl-substituted metallocarborane ID has been prepared previously from 2-C_6H_5-2,3-$C_2B_4H_7$,[11,28] we report here for the first time its ^{11}B and ^1H NMR data (Tables I and II) and infrared absorptions. IR (KBr pellet, cm^{-1}): 2925 (s), 2850 (w), 2535 (vs), 2340 (w), 1978 (m), 1556 (m, br), 1494 (m), 1446 (w), 1418 (w), 1387 (s), 1314 (w), 1073 (m), 1010 (m), 918 (m), 830 (m), 785 (s), 765 (sh, w), 698 (s), 653 (w).

Table II. 100-MHz NMR Data

Compound[a]	δ,[b] ppm (rel area)	Assignment[h]
2-(η^5-C_5H_5)CoB_4H_8[c]	5.13 (5)	C_5H_5
	3.64 (1), 2.79 (1), 1.70 (2)	BH_t
	−3.59 (2)	B–H–B
	−15.28 (2)[d]	B–H–Co
$Na^+[(C_5H_5)CoB_4H_7]^-$ (toluene-d_8)	4.33 (5)	C_5H_5
	−3.51 (2)	B–H–B
	−15.40 (1)	B–H–Co
μ(2,3)-D-2-(η^5-C_5H_5)-CoB_4H_7	5.12 (5)	C_5H_5
	3.66 (1), 2.72 (1), 1.68 (2)	BH_t
	−3.58 (2)	B–H–B
	−15.26 (~1.5)[e]	B–H–Co
1A (CCl_4)[f]	5.44 (7)	C_5H_5, cage CH
	3.63 (3), −6.95 (2)	BH_t, B–H–B
1B[f]	4.80 (5), 4.63 (1)	C_5H_5, cage CH
	1.89 (3), −6.00	CH_3, B–H–B
1C	4.76 (5)	C_5H_5
	3.37 (2), 2.99 (1)	BH_t
	1.82 (6), −5.98 (2)	CH_3, B–H–B
1D	7.26 (5), 4.79 (5)	C_6H_5, C_5H_5
	4.63 (1)	CH
	3.58 (1), 2.28 (2)	BH_t
	−5.67 (2)	B–H–B
IIB[g]	4.78	C_5H_5
IIC[g]	4.74	C_5H_5
IID[g]	4.61	C_5H_5
III	4.98 (10)	C_5H_5
	9.46 (1), 8.01 (2)	BH

[a] All spectra obtained in $CDCl_3$ solution except where otherwise indicated. [b] Chemical shifts relative to $(CH_3)_4Si$ with positive sign indicating downfield shift. [c] Reported in ref 3. [d] Doublet, *J* = 72 Hz. [e] Doublet, *J* = 77 Hz. [f] Reported in ref 9. [g] Observed only in mixture with the corresponding metallocarborane (IB, IC, ID); resonances other than C_5H_5 could not be unambiguously assigned. [h] Key: t = terminal.

Reaction of 2-(η^5-C_5H_5)CoB_4H_8 with $Fe(CO)_5$. Iron pentacarbonyl (1.156 mmol) was condensed onto a frozen (−196 °C), degassed heptane solution of the cobaltaborane (101.4 mg, 0.576 mmol) in a quartz flask. The mixture was warmed to room temperature and stirred while irradiating under a sunlamp. After 35 min the solvent was removed on a rotary evaporator, and the products were separated on a TLC plate in 20% benzene in hexane. The products, each obtained in 1–2% yield, included $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Fe_2(CO)_9Co(\eta^5\text{-}C_5H_5)$[13] (all identified from color and mass spectrum), and brown 1,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2(CO)_4FeB_3H_3$ (III). The composition of III was indicated by its mass spectrum, which exhibited a strong parent grouping and peaks corresponding to successive loss of four CO units, and was confirmed by high-resolution mass measurement: calcd for $^{12}C_{14}{}^{11}B_3{}^{59}Co_2{}^{56}Fe{}^{16}O_4{}^1H_{14}{}^+$ 452.9184, found 452.9175.

Acknowledgment. This work was supported by the Office of Naval Research.

Registry No. IA, 50860-26-9; IB, 50860-27-0; IC, 65969-67-7; ID, 65969-66-6; IIB, 66119-53-7; IIC, 66102-11-2; IID, 66102-10-1; III, 66027-79-0; 2-(C_5H_5)CoB_4H_8, 43061-99-0; μ(2,3)-D-(C_5H_5)-CoB_4H_7, 66102-09-8; 1,2-$(\eta^5\text{-}C_5H_5)_2Co_2B_4H_6$, 50924-50-0; 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_4H_4$, 59458-52-5; 1,2,3-$(\eta^5\text{-}C_5H_5)_3Co_3B_3H_5$, 59217-07-1; $(\eta^5\text{-}C_5H_5)_4Co_4B_4H_4$, 59370-82-0; C_2H_2, 74-86-2; CH_3C_2H, 74-99-7; $(CH_3)_2C_2$, 107-00-6; $C_6H_5C_2H$, 536-74-3; $Fe(CO)_5$, 13463-40-6; $Na^+[(C_5H_5)CoB_4H_7]^-$, 66102-08-7.

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Studies of Phosphazenes. 5.[1] Synthesis and Nuclear Magnetic Resonance Spectra of Chloro(*N*-methylanilino)cyclotetraphosphazatetraenes

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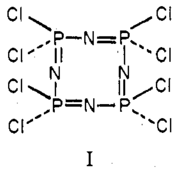
Received September 1, 1977

The reaction of $N_4P_4Cl_8$ (I) with *N*-methylaniline has been studied using a variety of experimental conditions, and the chloro(*N*-methylanilino) derivatives $N_4P_4Cl_{8-n}(NMePh)_n$ [n = 1, 2 (two isomers), 3, 4 (five isomers), and 6] have been isolated. Structures have been assigned to these compounds on the basis of ^1H NMR spectra (in some cases with the additional aid of ^{31}P NMR data) and chemical evidence. The methoxy derivatives $N_4P_4(OMe)_{8-n}(NMePh)_n$ [n = 2 (two isomers), 4 (two isomers), and 6] have also been prepared and in general their ^1H NMR spectra confirm the structures assigned to the chloro precursors. The chemical shifts of *N*-methyl and *O*-methyl protons and the "virtual-coupling" effects observed in the ^1H NMR spectra are discussed. *N*-Methylaniline replaces the chlorine atoms of $N_4P_4Cl_8$ by a predominantly nongeminal pathway. The results are compared with those observed in other aminolysis reactions of the octachloride I.

Aminolysis reactions of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, have received a great deal of attention, and several hypotheses have been suggested to rationalize the halogen replacement patterns.[4-6] Systematic studies of the analogous reactions of the tetrameric chloride $N_4P_4Cl_8$ (I) have been reported only recently. Ethylamine[7] and *tert*-butylamine[1] react with $N_4P_4Cl_8$ (I) to give chloro(alkylamino) derivatives which have nongeminal structures. In contrast, products formed in the reaction of *tert*-butylamine with $N_3P_3Cl_6$ and in the later stages of the analogous reaction of ethylamine have geminal structures.[5,6,8] Millington and Sowerby[9] have investigated the reaction of $N_4P_4Cl_8$ (I) with dimethylamine and isolated the derivatives $N_4P_4Cl_{8-n}(NMe_2)_n$ [n = 2, 3 (three isomers), 4 (four isomers), 5 (two isomers), 6, and 8]. The reaction proceeds predominantly via a nongeminal path. The reaction of *N*-methylaniline with $N_4P_4Cl_8$ (I) has been studied by Moeller and co-workers and two compounds, $N_4P_4Cl_6(NMePh)_2$, mp 146 °C, and $N_4P_4Cl_4(NMePh)_4$, mp 145 °C, have been isolated.[10] We have reinvestigated this reaction as part of a general program on the reactions of $N_4P_4Cl_8$ (I). The present study has revealed the great complexity of the system and the results are reported in this paper.



I

Results and Discussion

$N_4P_4Cl_8$ (I) reacts with *N*-methylaniline in organic solvents to give the chloro(*N*-methylanilino) derivatives $N_4P_4Cl_{8-n}(NMePh)_n$ [n = 1, 2 (two isomers), 3, 4 (five isomers), and 6] and *N*-methylaniline hydrochloride. Structural assignments for these compounds have been based mainly on ^1H NMR data which are summarized in Figure 1. Additional evidence for the structures of some of the compounds has been obtained from NMR data for the methoxy derivatives $N_4P_4(OMe)_{8-n}(NMePh)_n$ [n = 2 (two isomers), 4 (two isomers), and 6] (Figure 2).

The mono(*N*-methylanilino) compound (II) is conveniently prepared from a 1:2 $N_4P_4Cl_8$:*N*-methylaniline stoichiometric reaction carried out in benzene or methyl cyanide at ~25 °C. The two bis isomers $N_4P_4Cl_6(NMePh)_2$, mp 145 °C (III) and mp 105 °C (IV), have identical TLC R_f values. However, they can be separated by fractional crystallization from benzene; the high-melting isomer (III) crystallizes out preferentially. This observation may explain the previous isolation[10] of only one isomer (mp 145 °C). The ^1H NMR spectra of the mono

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