Chemistry of Bis(π-7,8-dicarbollyl)metalates. Reaction between $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ and Aryl Diazonium Salts

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Received December 2, 1971

Abstract: The thermal decomposition of $[ArN_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ (Ar = C_6H_5 or $C_6H_4CH_3$) in aromatic solvents has been investigated and the new complexes $[(CH_3)_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2C_6H_4Co]$ and $[(CH_3)_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2C_6H_3CH_3Co]$ isolated. The aryl group is thought to occupy a bridging position between two $B_9C_2H_{10}$ moieties in each complex and is shown to be derived from the solvent which constitutes the reaction medium. A possible mechanism for the formation of these compounds is discussed and evidence for the presence of radical intermediates during the reaction is presented.

Previous work in this laboratory has established that the complex $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ will undergo a variety of reactions. These include substitution with bromine[1] or $S(C_2H_5)_2$[2] and degradation followed by metal insertion to afford bimetallic species.[3,4] An unusual type of substitution reaction was observed with CS_2 or CH_3COOH which afforded species containing HC^+S_2 or $CH_3C^+O_2$ groups bridging two $B_9C_2H_{10}$ moieties.[5,6] In all cases substitution was found to occur at position 10 on the B_9C_2 polyhedron and, with bromine, positions 5 and 6 were also substituted. In view of the previously reported coupling reaction between $B_{10}H_{10}^{2-}$ and aryl diazonium cations,[7,8] it was felt that the known chemistry of $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ might be extended by an investigation of the reaction between this complex and aryl diazonium compounds.

Results and Discussion

Attempts to isolate a coupling product, analogous to that formed with $B_{10}H_{10}^{2-}$, from the reaction between $[C_6H_5N_2][BF_4]$ and $[(CH_3)_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ were unsuccessful. Thus only $[(CH_3)_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ was recovered from refluxing mixtures of these two compounds in benzene or acetonitrile. The ^{11}B nmr spectrum of a mixture of these compounds in acetonitrile at room temperature showed no evidence of a singlet which would arise from a substitution reaction on boron.

Mixing aqueous solutions of $[C_6H_5N_2][BF_4]$ and $K[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ at 0° precipitated a heat sensitive yellow solid, I, which decomposed slowly at room temperature. In the solid state the decomposition resulted in the formation of intractable materials; when the decomposition was allowed to occur in the presence of water $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ could be recovered.

The compound I could be dried under continuous vacuum without substantial decomposition and could be stored at 0° for short periods. The infrared spectrum of I exhibited a band at 2280 cm^{-1} attributed to the $-^+N{\equiv}N$ moiety in addition to bands at *ca.* 2550 cm^{-1} assigned to B–H stretching vibrations. Thus I is thought to be the salt $[C_6H_5N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$.

Although almost insoluble in benzene at room temperature, I dissolved on heating to form an orange solution; on further heating above 60° the solution became red and gas was evolved. An examination of the infrared spectrum of the benzene solution during the heating process showed the gradual appearance of a band at 2550 cm^{-1} due to B–H stretching vibrations. However, no band could be detected in the region 2000–2400 cm^{-1} which could be attributed to the presence of an $-N^+{\equiv}N$ group in solution. These data indicate to us that the ions $C_6H_5N_2^+$ and $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ undergo a reaction to produce a benzene soluble species, II, which does not contain the $-N^+{\equiv}N$ group. Since gas evolution occurs at a later stage in the reaction, it would seem that a coupling product may be at first formed which then decomposes with liberation of nitrogen at higher temperatures. Heating acetonitrile solutions of I resulted in the formation of yellow solutions from which $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ could be recovered.

The red solution resulting from the decomposition of I in benzene was extracted with water to afford a red aqueous layer and an orange benzene layer. The benzene layer gave an orange tar after evaporation at reduced pressure. Sublimation of this material afforded a white crystalline solid which was identified as biphenyl by ^1H nmr and mass spectroscopy. No other pure compounds could be isolated from the sublimation residue.

The aqueous layer was treated with tetramethylammonium chloride to precipitate a mixture of anions. Chromatography of this mixture on silica gel with methylene chloride eluent resulted in the development of a red band, III, which was collected. A mixture of red and yellow materials, IV, remained on the column, but attempts to isolate the components of this mixture using thick layer chromatography were unsuccessful.

The infrared spectrum of III exhibited bands at *ca.* 2550 cm^{-1} assigned to B–H stretching vibrations. A band at 746 cm^{-1} was assigned to aromatic C–H bending vibrations. The presence of an aryl group in III

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[1] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

[2] M. F. Hawthorne, L. F. Warren, K. P. Callahan, and N. F. Travers, *ibid.*, **93**, 2407 (1971).

[3] J. N. Francis and M. F. Hawthorne, *ibid.*, **90**, 1663 (1968).

[4] D. St. Clair, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **8**, 2080 (1969).

[5] M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1222 (1969).

[6] J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, **10**, 594 (1971).

[7] M. F. Hawthorne and F. P. Olsen, *J. Amer. Chem. Soc.*, **86**, 4219 (1964).

[8] M. F. Hawthorne and F. P. Olsen, *ibid.*, **87**, 2366 (1965).

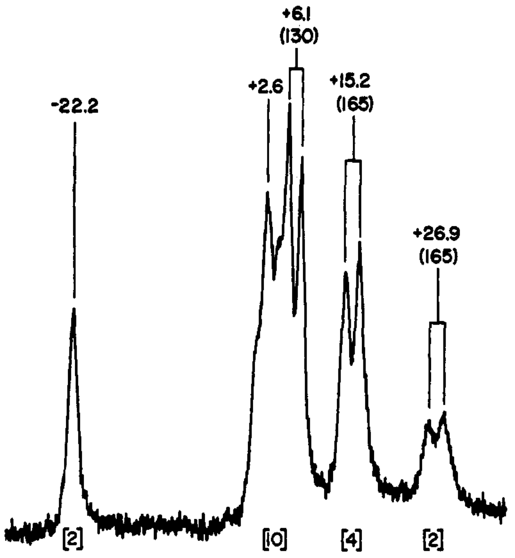

Figure 1. The 80.5-MHz ^{11}B nmr spectrum of III, $[(CH_3)_4N][(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2C_6H_4Co]$, in CH_3CN solution. The spectrum of V is of similar appearance consisting of the following signals: -23.9 ppm (singlet, area 2); *ca.* $+5.1$ ppm (multiplet, area 10); $+14.0$ ppm (doublet, $J_{BH} = 130$ MHz, area 4); $+25.3$ ppm (doublet, $J_{BH} = 160$ MHz, area 2).

was confirmed by the observation of a multiplet of relative area 4 at -6.79 ppm in the 100-MHz ^1H nmr spectrum (D_3CCN solution). Signals due to carborane C–H at -3.40 ppm (area 4) and $(CH_3)_4N^+$ at -2.94 ppm (area 12) were also observed in this spectrum. The 80.5-MHz ^{11}B nmr spectrum of III (Figure 1) consisted of a singlet of relative area 2 at -22.2 ppm, a multiplet of area 10 centered at $+5.8$ ppm, a doublet of area 4 at $+15.2$ ppm ($J_{BH} = 165$ Hz), and a doublet of area 2 at $+26.9$ ppm ($J_{BH} = 165$ Hz). From this spectrum it can be seen that both $B_9C_2H_{10}$ units are substituted in the same position and that this position lies in the plane of symmetry of the $7,8\text{-}B_9C_2H_{10}$ unit. If this were not the case a more complex spectrum would result. The marked similarity between the ^{11}B nmr spectrum of III and those of the known complexes $[(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2S_2CH_2Co]^-$ and $[(\pi\text{-}7,8\text{-}B_9C_2H_{10}S)_2Co]^-$ [5,6] suggests that all these compounds have very similar structures. On the basis of these data we assign the structure illustrated to III (Figure 2). Further confirmation of this proposed structure is provided by solution molecular weight and ^{13}C nmr measurements. The average particle weight of the tetramethylammonium salt of III in *N,N*-dimethylformamide was found to be 250 compared to an expected value of 236. Thus the complex does not contain two $[(B_9C_2H_{10})_2Co]$ units bridged by phenyl groups.

The ^{13}C nmr spectrum of the complex contains two doublets of equal intensity at $+72.3$ and $+68.7$ ppm ($J_{CH} = 185$ and 185 Hz, respectively) assigned to phenyl C–H groups. In addition a doublet assigned to carborane C–H was observed at $+154.2$ ppm ($J_{CH} = 140$ Hz) and a quartet at $+143.6$ ppm ($J_{CH} = 140$ Hz) assigned to the $(CH_3)_4N^+$ methyl groups. Such a spectrum could only arise from a complex containing an ortho-substituted phenyl ring. No signals were observed which could be asigned to the aryl carbon atoms bonded to boron. However, it has been found that carbon atoms in environments of this type have long relaxation times.[9] Thus the signal due to the aryl C–B carbon atoms would be saturated under the conditions used to observe the aryl C–H carbon atoms.

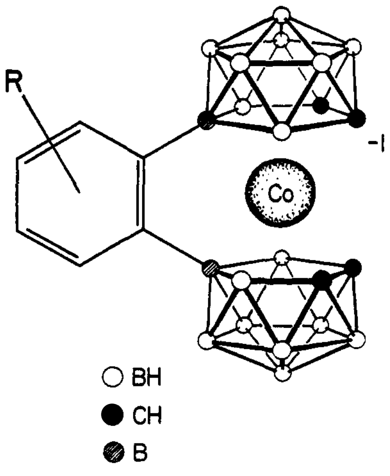

Figure 2. The proposed structure of III and V $[(\pi\text{-}7,8\text{-}B_9C_2H_{10})_2C_6H_3RCo]^-$ (R = H or CH_3).

The decomposition of $[p\text{-}CH_3C_6H_4N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$, which was prepared in a similar manner to the phenyldiazonium salt, in toluene also resulted in the formation of a red solution. The products of the reaction were separated as described above; dimethylbiphenyl could be isolated from the toluene layer and was identified by mass spectrometry (a molecular ion was observed at *m/e* 182). A red material V could be isolated from the aqueous layer in the manner described for III above. The infrared spectrum of V contained bands at *ca.* 2550 cm^{-1} assigned to B–H groups; however, only weak bands were observed in the region 700–750 cm^{-1}. The ^{11}B nmr spectrum of this complex was almost identical with that of III, the only differences being small chemical shift changes (Figure 1).

Thus it appears that V has a structure analogous to that proposed for III with a methyl substituent on the bridging phenyl ring. Further support for this structure is provided by the ^1H nmr spectrum of V which, in addition to resonances at -3.40 (area 4) and -2.97 ppm (area 12) assigned to carborane CH and $(CH_3)_4N^+$, respectively, exhibits a multiplet of area 3 at -6.60 ppm assigned to phenyl CH and a singlet of area 3 at -2.14 ppm assigned to the methyl substituent on the phenyl ring. The position of this methyl substituent on the phenyl ring was not determined.

Attempts to effect a similar reaction by decomposition of *o*-, *m*-, and $[p\text{-}FC_6H_4N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ in fluorobenzene did not yield ionic products which could be extracted into water. No pure products were isolated from the red organic phase.

In order to obtain a greater insight into the nature of the decomposition reaction, $[C_6H_5N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ was decomposed in toluene and $[p\text{-}CH_3C_6H_4N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ was decomposed in benzene. The products of these reactions were isolated in the manner described for III and V above. Both reactions afforded only methylbiphenyl from the organic phase. Mass and ^1H nmr spectral data showed no evidence for the formation of significant amounts of

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[9] P. S. Pregosin and E. W. Randall, *Chem. Commun.*, 399 1971, and references cited therein.

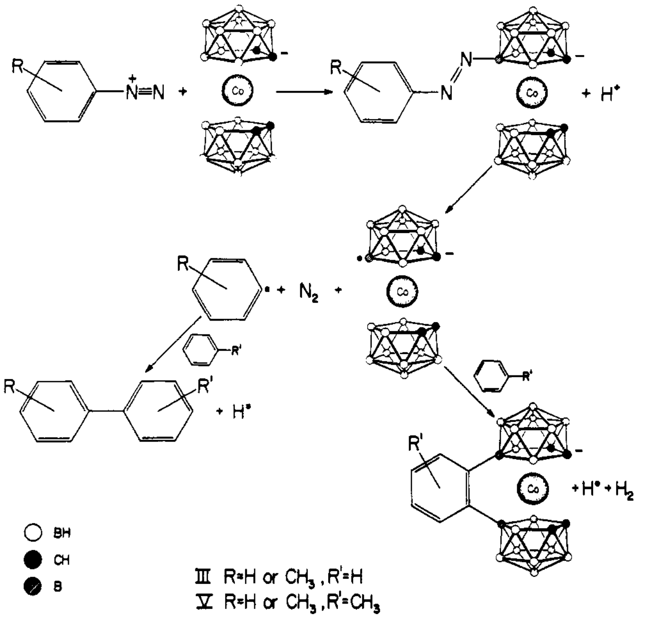

Figure 3. Reaction scheme for the formation of III or V by a radical mechanism.

biphenyl or dimethylbiphenyl in either reaction. The decomposition of the benzenediazonium salt in toluene formed only V as identified by ^{11}B and ^{1}H nmr spectroscopy. (The signals assigned to phenyl CH and the CH_3 substituent on the phenyl ring of V integrated to a 3:3 ratio in the ^{1}H nmr spectrum.)

Similarly, only III was isolated from the decomposition of the toluenediazonium salt in benzene. (The ^{1}H nmr spectrum showed no evidence of a signal at −2.14 ppm attributable to the methyl substituent of the phenyl ring in V.) Thus the bridging aryl group in III and V must be derived solely from the solvent which constitutes the reaction medium.

This result demonstrates that the aryl group from the diazonium cation is not the reacting species in the formation of III or V. Also, since only methylbiphenyl was detected in the decomposition of the toluene- and benzenediazonium salts in benzene and toluene, respectively, it would seem unlikely that an activated form of the solvent is involved in the formation of III or V. If, for example, aryl radicals were formed from the solvent one would expect to detect symmetric biphenyls in the mixed reactions, due to the reaction of such species with solvent. Thus it seems most probable that an activated form of $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ is produced during the decomposition and that this reacts with solvent to give III or V.

Using the information described above it is possible to make some tentative remarks about the mechanism of formation of III and V. Assuming, as the infrared study suggested, that a coupling product, II, is formed initially, two mechanisms can be postulated which could lead to the formation of III or V. The first of these involves the decomposition of II by a radical pathway to give $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})Co(\pi\text{-}7,8\text{-}B_9C_2H_{10}\cdot)]^-$, N_2, and an aryl radical (Figure 3). These radicals could then be quenched by solvent to give III or V and a biaryl, respectively (in the case of the mixed reactions this would account for the formation of methylbiphenyl only). The mechanism of formation of the second C–B bond remains obscure. However, it appears likely that the reaction between $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})Co(\pi\text{-}7,8\text{-}B_9C_2H_{10}\cdot)]^-$ and solvent might initially form a boron-substituted hexadienyl radical. The proximity of this reactive substituent to the second $B_9C_2H_{11}{}^{2-}$ cage would then facilitate reaction of the radical with this second cage. As a qualitative test, diphenylpicrylhydrazyl (DPPH) was added to a mixture of $[C_6H_5N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ in benzene prior to heating. The initial violet color of the solution was discharged to green on heating, thus indicating the presence of radicals during the reaction.[10,11] The violet color of DPPH was also discharged during the decomposition of $[p\text{-}CH_3C_6H_4N_2][(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ in toluene. However, heating $K[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ or $[C_6H_5N_2][BF_4]$ with DPPH in benzene failed to effect a color change. Carrying out the decomposition under a nitrogen atmosphere or in the presence of an ultraviolet source did not produce significant differences in the outcome of the reaction. The failure of air to suppress the formation of III or V is not surprising since one of the reactants is the solvent which would be a very effective competitor for the proposed radical intermediate. The effect of ultraviolet light on the reaction remains in doubt since the solvents employed are quite opaque in ultraviolet region.

The second mechanism involves the decomposition of II to give cationic intermediates which would react with solvent. For example, a protonated form of II, $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})Co(\pi\text{-}7,8\text{-}B_9C_2H_{10}NNHC_6H_5)]^0$, might eliminate benzene to form the diazo compound, $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})Co(\pi\text{-}7,8\text{-}B_9C_2H_{10}N_2)]^0$, which could decompose with loss of nitrogen to give a complex formally containing the $>B^+$ moiety, $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})Co(\pi\text{-}7,8\text{-}B_9C_2H_{10})]^0$. Such a compound could then react with solvent to give III or V, H_2 and H^+.

Although we do not have definitive evidence regarding the mechanism of formation of III and V the results described suggest that, while a cationic mechanism cannot be ruled out, a radical mechanism would seem to be the most reasonable.

Experimental Section

Physical Measurements. ^{11}B nmr spectra at 80.5 MHz and ^{13}C nmr spectra at 63.1 MHz were measured using an instrument designed and built by Professor F. A. L. Anet and Dr. C. H. Bradley of this department. ^{1}H nmr spectra at 100 MHz were recorded on a Varian Associates HA-100 instrument. Chemical shifts are quoted in parts per million relative to the following standards: ^{1}H relative to tetramethylsilane, ^{11}B relative to $BF_3\cdot O(C_2H_5)_2$, and ^{13}C relative to carbon disulfide. Coupling constants are quoted in hertz. Infrared spectra were recorded on a Perkin-Elmer 137 instrument and elemental analyses were determined by Galbraith Analytical Laboratories.

Materials. Spectrograde solvents were used for spectral measurements and reactions were carried out using reagent grade solvents. Aryl diazonium tetrafluoroborates were prepared according to the literature method[12] and $K[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$ was prepared by a modification of the previously reported method[1] as described below.

Preparation of $K[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$. The procedure described for the aqueous preparation of $[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]^-$ was followed using 20.0 g of $[(CH_3)_3NH][7,8\text{-}B_9C_2H_{12}]$.[1] The residue after evaporation of the ether extract was dissolved in water (*ca.* 100 ml) and the solution added to a hot saturated solution of potassium chloride (*ca.* 250 ml). On cooling yellow needles of $K[(\pi\text{-}7,8\text{-}B_9C_2H_{11})_2Co]$

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(10) A. Henglein, *Makromol. Chem.*, **15**, 188 (1955).

(11) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Amer. Chem. Soc.*, 77, 3244 (1955).

(12) A. Roe, *Org. React.*, **5**, 193 (1949).

precipitated along with some potassuim chloride. This mixture was isolated by filtration, washed with a little saturated aqueous potassium chloride, and dried *in vacuo* over P_2O_5. The product was then placed in the thimble of a Soxhlet extractor and extracted with ether to give an ether solution of K[(π-7,8-$B_9C_2H_{11}$)$_2$Co]. Toluene was added to the solution and evaporation of the ether caused the complex to crystallize as yellow needles (14 g, 74%).

Preparation of Aryl Diazonium Salts of [(π-7,8-$B_9C_2H_{11}$)$_2$Co]$^-$. A solution of the appropriate aryl diazonium tetrafluoroborate (1.2 g, *ca.* 6 mmol) in ice water (75 ml) was added, dropwise with vigorous stirring, to an ice-cooled solution of K[(π-7,8-$B_9C_2H_{11}$)$_2$Co] (1.0 g, 2.8 mmol) in water (50 ml). The yellow diazonium salt which precipitated was collected by filtration, washed with a little ice water, and immediately transferred to a vacuum desiccator containing P_2O_5. The salt was dried under continuous high vacuum, which maintained the temperature of the salt below 0° until all the water had been removed. This process usually took 12–18 hr. The yield of salt, which could be stored at 0° for 2–3 days without gross decomposition, was almost quantitative. The wet *p*-$CH_3C_6H_4N_2^+$ salt decomposed rapidly at room temperature and it was necessary to transfer the material to a desiccator immediately after its isolation to avoid substantial decomposition.

Decomposition of [$C_6H_5N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] in Benzene. Preparation of [$(CH_3)_4N$][(π-7,8-$B_9C_2H_{10}$)$_2C_6H_4$Co] (III). A suspension of [$C_6H_5N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] (2.0 g, 4.7 mmol) in benzene (350 ml) was heated to boiling using a steam bath with rapid magnetic stirring. The solid dissolved on heating to give an orange solution which turned red and evolved gas above *ca.* 60°. The mixture was maintained at reflux for 15 min, then allowed to cool, and was extracted with water (3 × 100 ml). The benzene layer was separated and retained. The aqueous layer was treated with an aqueous solution of tetramethylammonium chloride to precipitate a pink solid which was isolated by filtration and dried *in vacuo* over P_2O_5. The dry solid was dissolved in acetone and stripped onto silica gel (*ca.* 50 ml of 60–200 mesh). This was then mounted on a silica gel column (500 ml of 60–200 mesh silica gel in a 2 in. diameter column) and eluted with methylene chloride. The first band which separated contained the red complex III which was evaporated to dryness to give the crude product (600 mg, 27%). This was recrystallized from acetone–ethanol containing tetramethylammonium chloride. Treatment with tetramethylammonium chloride was necessary to allow for some ion exchange which took place on the column. *Anal.* Calcd for $C_{14}H_{36}NB_{18}Co$: C, 35.64; H, 7.64; N, 2.97; B, 41.24. Found: C, 35.35; H, 7.87; N, 3.17; B, 41.39. Average particle weight in *N*,*N*-dimethylformamide found was 250 (calcd 236).

Isolation of Biphenyl. The benzene layer from the decomposition reaction was dried over magnesium sulfate, filtered, and evaporated to dryness using a rotary evaporator and a 40° water bath. The remaining orange tar was sublimed at elevated temperature onto a Dry Ice-cooled probe to give biphenyl (200 mg, 28%) which was identified by mass and ^{1}H nmr spectroscopy.

Decomposition of [*p*-$CH_3C_6H_4N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] in Toluene. Preparation of [$(CH_3)_4N$][(π-7,8-$B_9C_2H_{10}$)$_2CH_3C_6H_3$Co] (V). A suspension of [*p*-$CH_3C_6H_4N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] (1.3 g, 3 mmol) in toluene (200 ml) was heated on a steam bath with rapid magnetic stirring for 30 min. During this time the solid dissolved with gas evolution to give a red solution. The mixture was allowed to cool and then extracted with water (2 × 100 ml). The toluene layer contained dimethylbiphenyl which was isolated in the manner described for biphenyl and identified by mass spectrometry, exhibiting a molecular ion at *m*/*e* 182. The aqueous layer was treated with an aqueous solution of tetramethylammonium chloride to precipitate a red semisolid tar. This material was extracted into methylene chloride to give a red solution which was dried over magnesium sulfate and stripped on to silica gel (*ca.* 25 ml of 60–200 mesh). This material was then mounted onto a silica gel column (300 ml of 60–200 mesh in a 2-in. diameter column) and eluted with methylene chloride. The first band contained the red complex V (150 mg, 10%) which was isolated by evaporation of the methylene chloride solution and purified by recrystallization from acetone–ethanol containing tetramethylammonium chloride. *Anal.* Calcd for $C_{15}H_{38}NB_{18}Co$: C, 37.08; H, 7.83; N, 2.88; B, 40.05; Co, 12.15. Found: C, 37.07; H, 7.71; N, 2.78; B, 40.35; Co, 11.87.

Decomposition of [*p*-$CH_3C_6H_4N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] in Benzene. A suspension of [*p*-$CH_3C_6H_4N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] (1.5 g, 3.4 mmol) in benzene (250 ml) was decomposed as described above. The benzene layer contained methylbiphenyl which was isolated by sublimation. The mass spectrum of this compound exhibited a molecular ion at *m*/*e* 168 in addition to an ion at *m*/*e* 182 of *ca.* 0.5% the intensity of the ion at *m*/*e* 168. The ^{1}H nmr spectrum of this compound consisted of a multiplet of area 9 at −7.44 ppm and a singlet of area 3 at −2.37 ppm.

A red complex was isolated by chromatography as described for III above and was identified as III by its ^{1}H and ^{11}B nmr spectra. No signal was observed at −2.14 ppm in the ^{1}H nmr spectrum showing that significant amounts of V were not present.

Decomposition of [$C_6H_5N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] in Toluene. A suspension of [$C_6H_5N_2$][(π-7,8-$B_9C_2H_{11}$)$_2$Co] (1.0 g, 2.3 mmol) in toluene (200 ml) was decomposed as described for V above. The toluene layer contained methylbiphenyl which was isolated by sublimation and identified by its mass spectrum which exhibited a molecular ion at *m*/*e* 168 in addition to an ion at *m*/*e* 182 of *ca.* 0.5% the intensity of the ion at *m*/*e* 168.

A red complex was isolated by chromatography as described for V above and was identified as V by ^{1}H and ^{11}B nmr spectroscopy. The ^{1}H nmr spectrum of this material contained signals at −6.60 and −2.14 ppm which integrated for a 3:3 ratio showing that significant amounts of III were not present.

Acknowledgment. The authors are indebted to Dr. R. J. Wiersema for running the ^{13}C and ^{11}B nmr spectra. The award of a NATO Fellowship to C. J. J. is gratefully acknowledged. This work was supported, in part, by the Office of Naval Research and National Science Foundation under Grant No. GP14372.