Friedel–Crafts Acetylation Products of (η-Cyclopentadienyl)[η-(3)-1,2-dicarbaundecaborane(11)]cobalt and their Molecular Structures

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Friedel–Crafts acetylation of [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}] with aluminium chloride in carbon disulphide results in the formation of [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}Cl$}], (I), [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-OCOMe)}], (II), [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-OH)}], (III), and [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-COMe)}], (IV) (cp = η-cyclopentadienyl). The complexes have been characterized by i.r., n.m.r., and mass-spectral measurements. *X*-Ray structure analyses of (II) and (IV) have been made and the substituents are bonded to B(8). Possible mechanisms for the production of these complexes are described.

FRIEDEL–CRAFTS reaction of ferrocene with acetyl chloride and aluminium trichloride in carbon disulphide solvent affords 1,1′-diacetylferrocene in high yield. This typical aromatic electrophilic-substitution reaction of ferrocene, discovered by Woodward *et al*,[1] made a remarkable contribution to ferrocene chemistry.

Metallacarbaboranes have been known since 1965, when Hawthorne and his co-workers [2] obtained transition-metal π-complexes of the $[C_2B_9H_{11}]^{2-}$ ion similar to the well known metallocenes. Compared with ferrocene, the derivative chemistry of transition-metal carbaborane complexes has not been thoroughly investigated. Hawthorne and his co-workers prepared some interesting derivatives of [(cp)Co(η-1,6-$B_7C_2H_9$)],[3a] [M{η-(3)-1,2-$B_9C_2H_{11}$}$_2$]$^-$ (M = Fe^{III} or Co^{III}),[3b] and [(cp)M{η-(3)-1,2-$B_9C_2H_{11}$}] (cp = η-cyclopentadienyl).[3b] The aromaticity of the complex [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}] is of interest. We have therefore attempted the Friedel–Crafts acetylation of this complex. The present paper describes the characterization of some of the products, with additional findings including evidence for the reaction mechanism.

RESULTS AND DISCUSSION

More than 2 mol of acetyl chloride–aluminium trichloride was consumed per mol of [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}] in carbon disulphide under a nitrogen atmosphere at room or reflux temperature. After hydrolysis of $AlCl_3$, the solvent was removed to give a yellow mixture of products. The solid mixture was chromatographed on a silica-gel column and separated into four bands. The order of elution from the column with chloroform was (I), (II), (III), and (IV). These compounds were crystallized as in the Experimental section. Their structure was determined from the following significant spectral features.

The ^1H n.m.r. spectrum of (I) in $(CD_3)_2CO$ contained a sharp cp signal at τ 4.04 and a broad singlet due to the carbaborane-carbon proton at τ 5.47. This suggests that the five protons of the cp ring and the two attached to the two carbaborane carbon atoms are not substituted by other atoms or substituents. The i.r. spectrum of (I), excepting an additional intense peak at 829 cm^{-1}, resembled that of the starting material in the fingerprint region. The mass spectrum of (I) provided structural information, the spectral cut-off at *m/e* 294 being indicative of the ion $[^{11}B_9{}^{12}C_7{}^1H_{15}{}^{37}Cl^{59}Co]^+$. Elemental analyses calculated for $B_9C_7H_{15}ClCo$ support the structure [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}Cl$}]. The observation of a single carbaborane C–H resonance for the substituted ligand indicates that the chlorine is bound to one of the unique boron atoms in the ligand, for which the magnetic

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[1] R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Amer. Chem. Soc.*, 1952, **74**, 3458; M. Rosenblum and R. B. Woodward, *ibid.*, 1958, **80**, 5443.

[2] M. F. Hawthorne and R. L. Pilling, *J. Amer. Chem. Soc.*, 1965, **87**, 3987; M. F. Hawthorne and T. D. Andrews, *Chem. Comm.*, 1965, 443; M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, jun., and P. A. Wegner, *J. Amer. Chem. Soc.*, 1968, **90**, 879.

[3] (*a*) B. M. Graybill and M. F. Hawthorne, *Inorg. Chem.*, 1969, **8**, 1799; (*b*) M. R. Churchill, K. Gold, J. N. Francis, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1969, **91**, 1222; M. F. Hawthorne, L. F. Warren, jun., K. P. Kallahan, and N. F. Travers, *ibid.*, 1971, **93**, 2407; J. N. Francis, C. J. Jones, and M. F. Hawthorne, *ibid.*, 1972, **94**, 4878; J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, 1971, **10**, 594; J. Plešek, S. Heřmánek, and Z. Janoušek, *Chem. and Ind.*, 1974, 108.

equivalence of the C–H groups is maintained after substitution. Complex (I) was also obtained directly on heating the starting material under reflux in benzene with excess of $AlCl_3$.

$$[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}] \longrightarrow \underset{(I)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}Cl\}]} \quad (1)$$

The ^1H n.m.r. spectrum of (II) in $(CD_3)_2CO$ showed a sharp resonance due to cp protons at τ 4.05 (5 H) and a broad singlet due to carbaborane-carbon protons at τ 5.52 (2 H). Another sharp peak at τ 7.89 (3 H) observed in a solution of C_5D_5N is presumed to be due to a methyl bonded to a carbonyl group. The strong absorption bands at 1 706 and 1 262 cm^{-1} in the i.r. spectrum of (II) suggest the existence of an ester group in the molecule. On the basis of these data, the structure $[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(OCOMe)\}]$ is in accord with the mass-spectral cut-off at *m/e* 316, $[^{11}B_9{}^{12}C_9{}^{1}H_{18}{}^{16}O_2{}^{59}Co]^+$. This complex was also derived from (III) as described later. In addition, (II) was hydrolysed to (III) under acidic conditions according to equation (2).

$$\underset{(II)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(OCOMe)\}]} \xrightarrow{H^+,\ \text{excess of } H_2O} \underset{(III)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(OH)\}]} \quad (2)$$

The ^1H n.m.r. spectrum of (III) in $(CD_3)_2CO$ contained a sharp singlet at τ 4.22 (5 H) and a broad singlet at τ 5.60 (2 H), assigned to the cp-ring and carbaborane-carbon protons respectively. A broad band at 3 130m cm^{-1} in the i.r. spectrum of (III) can be assigned to a hydroxy-group together with the absorption at 1 112vs cm^{-1}. The mass-spectral cut-off at *m/e* 274 is unequivocally caused by $[^{11}B_9{}^{12}C_7{}^{1}H_{16}{}^{16}O{}^{59}Co]^+$. From the above spectroscopic data, the structure $[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(OH)\}]$ is proposed. This was supported by elemental analyses and the esterification reaction (3), found by Zakharkin *et al.*[4] for $1,2\text{-}B_{10}C_2H_{11}(OH)$ and acetic anhydride.

$$\underset{(III)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(OH)\}]} \xrightarrow{(MeCO)_2O \text{ or } MeCOCl} \underset{(II)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(OCOMe)\}]} \quad (3)$$

The ^1H n.m.r. spectrum of (IV) in $CDCl_3$ exhibited a sharp singlet at τ 4.36 (5 H), a broad singlet at τ 5.93 (2 H), and a sharp singlet at τ 7.81 (3 H), corresponding to the cp, carbaborane C–H, and methyl protons, respectively. An i.r. band at 1 628s cm^{-1} indicates that complex (IV) does not contain any ester group but does contain a carbonyl group. Electrophilic-substitution reactions should occur in a similar way to the Friedel–Crafts acetylations of benzene and ferrocene. We obtained (IV), as expected, from reaction (4). The fact that no splitting was observed in the cp resonance and that a carbaborane C–H proton signal had an integral ratio of 2 in the ^1H n.m.r. spectrum of (IV), confirm that an acetyl group is attached to a boron atom of the carbaborane cage rather than to a carbon of the cp ring. The observation of mass-spectral cut-off at *m/e* 300 is reasonably ascribed to $[^{11}B_9{}^{12}C_9{}^{1}H_{18}{}^{16}O{}^{59}Co]^+$. The acetyl group was easily removed as evidenced by the appearance of intense peaks centred at *m/e* 255 and displaying the largest *m/e* at 257. A 2,4-dinitrophenylhydrazone derivative of (IV) was made in order to confirm the existence of an acetyl group.

$$[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}] \xrightarrow[AlCl_3]{MeCOCl} \underset{(IV)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(COMe)\}]} + HCl \quad (4)$$

The ethyl derivative of (IV) was obtained by Clemmensen reduction [equation (5)]. The ^1H n.m.r. spectrum of the Et derivative in $CDCl_3$ gave a complicated signal having relative intensity 5 at τ 8.83—9.17 and signals due to the cp ring (τ 4.45, s, 5 H) and carbaborane C–H (τ 5.90, br.s, 2 H). The complicated signals at the highest field were assigned to an Et group attached to boron. Complication of the Et signal is consistent with the intermediate coupling (*J ca.* 8) seen in the case of triethylboron and diethyl(diethylamino)borane, reported previously.[5] The Et derivative exhibited strong parent peaks in its mass spectrum with a clear cut-off of the molecular-ion peak, $[^{11}B_9{}^{12}C_9{}^{1}H_{20}{}^{59}Co]^+$, at *m/e* 286. A peak at *m/e* 257 accompanied by peaks having a similar pattern to those of the parent ion was indicative of removal of the Et group (—29).

$$\underset{(IV)}{[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(COMe)\}]} \xrightarrow{Zn\text{-}HCl} [(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}(Et)\}] \quad (5)$$

These results are illustrated in Scheme 1.

Relative Amounts of Products.—In Friedel–Crafts acetylation of $[(cp)Co\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}]$ the cp ring is not attacked by the reagents employed, while a carbaborane B–H proton is easily substituted by chlorine, oxygen, or carbon to generate the four complexes described. Further interest in this reaction lies in the constancy of relative amounts of the complexes produced. Whenever the reaction was carried out at room or reflux temperature in CS_2 or CH_2Cl_2 under a nitrogen atmosphere, the relative amounts of the four products were almost invariable regardless of varying the molar ratio of acetyl chloride–aluminium trichloride to the starting material from 1 to 8:1.*

The ^1H n.m.r. spectra of the reaction mixture were recorded in $(CD_3)_2CO$ and C_5D_5N solutions (Figure 1).

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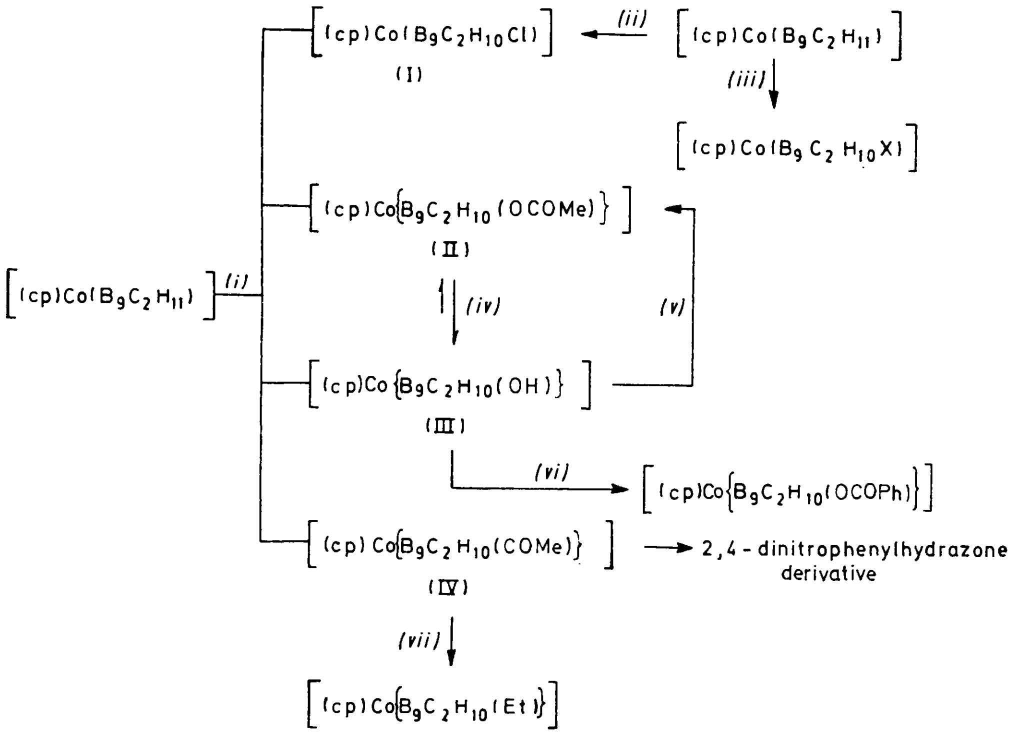
* When the amount of $AlCl_3$ used was greater than twice that of MeCOCl, the yields were variable and produced more of the derivative (III).

[4] L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskya, *Zhur. obshchei Khim.*, 1966, **36**, 1786.

[5] O. Ohashi, Y. Kurita, T. Totani, H. Watanabe, T. Nakagawa, and M. Kubo, *Bull. Chem. Soc. Japan*, 1962, **35**, 1317; T. Totani, H. Watanabe, T. Nakagawa, O. Ohashi, and M. Kubo, *Adv. Chem. Ser.*, 1964, **42**, 108.

Four partially overlapping sharp signals at τ 4.0—4.3 were observed in the spectra of both solutions. Since it is known that the cp ring protons of each complex show a sharp singlet in this range, the four signals of the reaction mixture are probably attributable to the four complexes (I)—(IV). The relative amounts of these complexes were then determined as shown below by taking into account the assignment of the cp protons and their integral ratio (I):(II):(III):(IV) = 2.8:1.4:3.6:1. Although this ratio, found by integration of the ^{1}H n.m.r. intensity, is very approximate, the order of yield (III) > (I) > (II) > (IV) agrees with that of the isolation yield.



SCHEME 1 (*i*), $AlCl_3$ and MeCOCl in CS_2; (*ii*), $AlCl_3$ in C_6H_6; (*iii*), AlX_3 (X = Br or I); (*iv*), H^+ and H_2O; (*v*), $(MeCO)_2O$ or MeCOCl; (*vi*), PhCOCl; (*vii*), Zn and HCl.

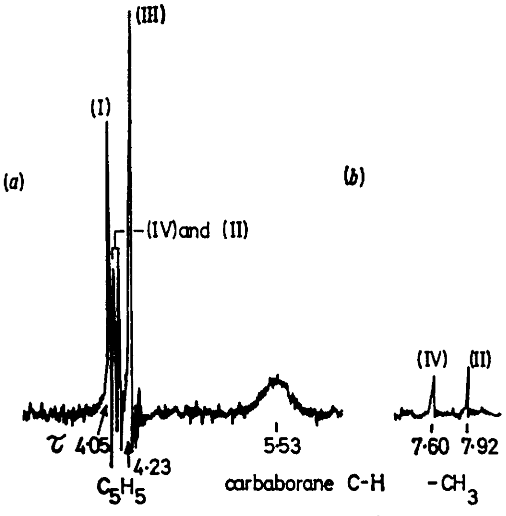


FIGURE 1 ^{1}H N.m.r. spectra (60 MHz) of a mixture of the products in (*a*) $(CD_3)_2CO$ and (*b*) C_5D_5N

Crystal Structures of the Products.—In order to confirm the positions of the substituents in the product molecules, *X*-ray crystal-structure analyses of (II) and (IV) were carried out.

Preliminary Weissenberg and precession photographs taken with Cu-K_α radiation indicated that (II) had crystallized in the monoclinic space group $P2_1/c$ and (IV) in Pc or $P2/c$. Three-dimensional intensity data were collected with a Hilger and Watts automatic four-circle Y290 diffractometer. Integrated intensities were measured up to 27.5° by the θ—2θ scan technique by use of Mo-K_α radiation; a scintillation counter, pulse-height analyzer, and zirconium filter were used. No absorption correction was applied. The structures were solved by the usual Patterson and Fourier method and refined by a block-diagonal least-squares technique. Anisotropic thermal parameters were used for non-hydrogen atoms and an overall isotropic one for hydrogen atoms. The conventional R factors were 4.8% for (II) and 4.7% for (IV). The correct structure of (IV) was deduced in the space group Pc.

Crystal data and details of the structure determination are summarized in Table 1, and final positional and thermal parameters of the non-hydrogen atoms are listed in Tables 2 and 3. There are two crystallographically independent molecules in the asymmetric unit of (IV), one of which is indicated by the corresponding primed atom number in Table 3. Figure 2 shows perspective views of

TABLE 1

Summary of single-crystal X-ray data

	(II)	(IV)
$a/\text{Å}$	7.895(1)	12.030(1)
$b/\text{Å}$	12.592(1)	8.297(1)
$c/\text{Å}$	14.950(2)	15.509(1)
$\beta/°$	99.30(1)	112.19(1)
Z	4	4
M	314.5	298.5
$U/\text{Å}^3$	1 466.7	1 433.2
$D_m/\text{g cm}^{-3}$	1.42	1.38
$D_c/\text{g cm}^{-3}$	1.42	1.38
μ/cm^{-1}	50.27	51.12
Space group	$P2_1/c$	Pc
No. of reflections measured:	3 237	3 071
Number used in refinement:*	3 107	2 981
Weighting scheme †	$c^2 = 0.001\ 79$	0.000 80
$R/\%$	4.8	4.7
$R'/\%$	1.28	1.14

* *i.e.* $|F_c| > \sigma(F_o)$. † The weighting function (derived on the basis of counting statistics and random-setting errors) was $w^{\frac{1}{2}} = 1/\sigma(F_o) = 1/[\sigma_1{}^2(F_o) + c^2|F_o|^2]^{\frac{1}{2}}$ where $\sigma_1(F_o)$ is the estimated standard deviation depending on the counting errors (D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Cryst.*, 1969, **B25**, 374.) $R' = [\Sigma\{w(|F_o| - |F_c|)^2\}/(m - n)]^{\frac{1}{2}}$.

the two complexes, and also the atom-numbering schemes employed in the analyses. Carbon and boron atoms in the carbaborane were distinguished by examination of their isotropic temperature factors, which converged after least-squares refinement when they were correctly assigned in the structures. In the carbaborane portion, two carbon and nine boron atoms are approximately at the corners of an icosahedron, which has one vacant position. The two carbon atoms occupy the successive positions in its open side. The substituents, OCOMe in (II) and COMe in (IV), bond to B(8) (Figure 2). Two C–H and eight B–H bonds extend out from the centre of the icosahedron. In the cp portion, five carbon and five hydrogen atoms form a plane. The root-mean-square vibrational displacements along each principal axis and the bond lengths are shown in Table 4. The major axes of all the atoms, except C(15) in (IV), lie close to the tangents of the ring. The anisotropic thermal vibration in the molecular plane is more significant in (II) than in (IV).

The plane through the five atoms in the open side of the substituted carbaborane and that of the cp ring are almost parallel. The configuration of the two pentagons is almost eclipsed in (II) and almost staggered in (IV), though found to be eclipsed in $[(cp)Fe\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}]$.[6] The cobalt atom is sandwiched between the two pentagons and lies approximately on the line through their centres.

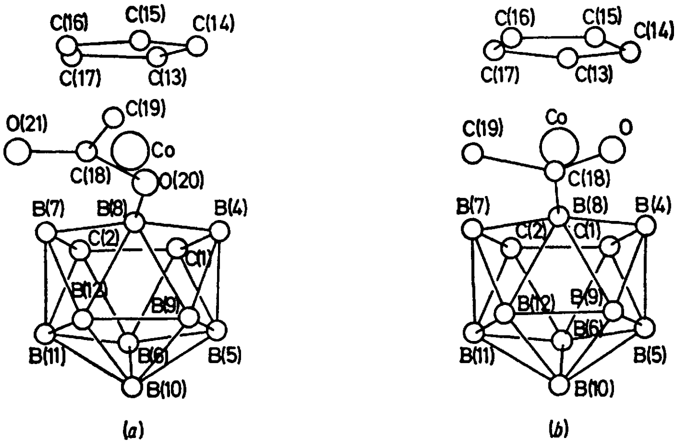


FIGURE 2 Perspective views of (*a*) (II) and (*b*) (IV)

Mean bond lengths are listed in Table 5, uncorrected for the effects of thermal motion. The mean standard deviations are 0.005 Å for Co–C and Co–B bonds, and 0.007 Å for other bonds. The present bond lengths are somewhat longer than the corresponding ones in $[(cp)Fe\{\eta\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}\}]$. The mean bond angles are 60° around boron and 63° around carbon in the carbaborane

TABLE 2

Positional and thermal (× 10^4)* parameters, with estimated standard deviations in parentheses, for (II)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.74419(4)	0.59971(3)	0.33344(2)	108(1)	37(1)	32(1)	17(1)	6(1)	−7(1)
C(1)	0.9193(3)	0.6466(2)	0.2585(2)	133(4)	29(1)	48(1)	−2(4)	21(4)	10(2)
C(2)	0.7339(4)	0.6160(2)	0.1989(2)	142(4)	45(2)	37(1)	25(4)	8(4)	16(2)
B(4)	0.9927(4)	0.5493(2)	0.3340(2)	105(4)	35(2)	42(1)	−2(4)	−10(4)	5(2)
B(5)	1.0763(4)	0.5684(3)	0.2314(2)	116(5)	44(2)	56(2)	−5(5)	43(5)	14(3)
B(6)	0.9111(5)	0.6163(3)	0.1463(2)	171(6)	50(2)	47(2)	20(5)	46(5)	30(3)
B(7)	0.6622(4)	0.4954(2)	0.2285(2)	121(4)	44(2)	33(1)	−1(4)	−3(4)	−1(2)
B(8)	0.8307(4)	0.4456(2)	0.3153(2)	116(4)	35(2)	33(1)	−9(4)	8(4)	5(2)
B(9)	1.0234(4)	0.4393(2)	0.2638(2)	121(5)	37(2)	42(1)	13(4)	21(4)	3(3)
B(10)	0.9716(4)	0.4787(3)	0.1485(2)	179(6)	51(2)	42(2)	28(5)	55(5)	0(3)
B(11)	0.7518(4)	0.5147(3)	0.1275(2)	168(6)	57(2)	31(1)	15(5)	9(4)	2(3)
B(12)	0.8201(4)	0.4060(2)	0.1994(2)	146(5)	37(2)	37(1)	−1(4)	9(4)	−11(2)
C(13)	0.6988(9)	0.7349(3)	0.4012(4)	663(18)	48(2)	136(4)	−78(11)	434(15)	−83(5)
C(14)	0.7751(5)	0.6531(4)	0.4639(3)	205(7)	163(5)	53(2)	53(10)	0(6)	−94(5)
C(15)	0.6667(5)	0.5712(3)	0.4542(2)	281(9)	96(3)	47(2)	65(8)	92(6)	2(4)
C(16)	0.5295(6)	0.5906(4)	0.3929(3)	226(8)	124(4)	56(2)	−11(8)	106(6)	−34(4)
C(17)	0.5379(5)	0.6882(4)	0.3579(3)	267(8)	121(4)	59(2)	210(9)	75(7)	3(4)
C(18)	0.6871(4)	0.3068(2)	0.3903(2)	179(6)	44(2)	42(1)	−26(5)	52(4)	0(2)
C(19)	0.7181(5)	0.2273(3)	0.4656(2)	260(7)	64(2)	55(2)	−13(6)	85(6)	34(3)
O(20)	0.8247(3)	0.3655(2)	0.3847(1)	156(3)	47(1)	40(1)	−26(3)	12(3)	18(2)
O(21)	0.5525(3)	0.3160(2)	0.3411(2)	201(5)	89(2)	69(1)	−110(5)	−12(4)	48(3)

* In the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)]$.

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[6] A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Amer. Chem. Soc.*, 1965, **87**, 3988.

TABLE 3

Positional and thermal ($\times 10^4$)* parameters, with estimated standard deviations in parentheses, for (IV)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.28844(0)	0.25860(6)	0.37643(0)	60(1)	106(1)	24(1)	−10(1)	32(1)	−10(1)
C(1)	0.2008(5)	0.1199(6)	0.4365(4)	117(6)	97(7)	59(3)	−44(10)	104(7)	2(3)
C(2)	0.3463(5)	0.1280(6)	0.4929(3)	126(6)	143(8)	39(3)	99(12)	83(7)	52(8)
B(4)	0.1373(6)	0.3052(7)	0.4093(5)	94(6)	108(8)	57(4)	−21(12)	72(8)	−5(9)
B(5)	0.1244(7)	0.1838(9)	0.5035(5)	139(9)	159(11)	70(5)	−18(16)	125(11)	2(12)
B(6)	0.2599(8)	0.0713(9)	0.5537(5)	194(10)	146(11)	62(4)	86(17)	155(11)	54(11)
B(7)	0.3966(5)	0.3230(8)	0.5095(4)	68(5)	152(9)	33(3)	36(11)	33(6)	−1(8)
B(8)	0.2625(4)	0.4450(6)	0.4586(4)	39(4)	119(8)	40(3)	18(9)	26(5)	−11(8)
B(9)	0.1641(5)	0.3954(8)	0.5188(5)	62(5)	149(10)	65(4)	23(11)	63(7)	−26(10)
B(10)	0.2369(10)	0.2503(8)	0.6093(6)	197(12)	180(13)	59(4)	114(19)	127(13)	60(12)
B(11)	0.3790(7)	0.2051(10)	0.5998(5)	133(8)	221(13)	35(3)	191(17)	41(8)	57(11)
B(12)	0.3242(6)	0.4045(8)	0.5806(4)	87(6)	178(11)	37(3)	47(13)	49(7)	−34(9)
C(13)	0.3283(6)	0.1170(7)	0.2816(4)	179(8)	172(10)	51(3)	−33(15)	135(9)	−66(10)
C(14)	0.2155(6)	0.1946(10)	0.2362(4)	111(7)	381(17)	35(3)	−114(18)	37(7)	−88(12)
C(15)	0.2353(6)	0.3611(9)	0.2461(4)	125(7)	281(15)	40(3)	8(16)	44(7)	78(11)
C(16)	0.3586(5)	0.3840(7)	0.2965(4)	120(6)	172(10)	36(3)	−51(12)	81(6)	16(8)
C(17)	0.4164(5)	0.2368(7)	0.3204(4)	78(5)	238(12)	37(3)	17(11)	68(6)	−12(8)
C(18)	0.2554(4)	0.6228(6)	0.4232(4)	80(5)	116(7)	63(3)	−15(10)	85(6)	−27(8)
C(19)	0.1338(7)	0.6889(7)	0.3632(5)	122(7)	104(8)	97(5)	36(13)	7(9)	34(11)
O	0.3424(4)	0.7097(5)	0.4428(4)	107(4)	131(6)	122(4)	−35(8)	114(7)	−10(8)
Co′	0.71197(6)	0.75103(7)	0.62335(4)	57(1)	107(1)	26(1)	−2(1)	35(1)	1(1)
C(1′)	0.6180(4)	0.7192(6)	0.4864(3)	47(3)	183(9)	34(2)	4(9)	30(5)	−23(7)
C(2′)	0.7276(4)	0.5907(5)	0.5318(3)	71(4)	110(7)	36(2)	−22(9)	59(5)	−19(6)
B(4′)	0.6633(5)	0.9112(7)	0.5123(4)	69(5)	137(9)	36(3)	66(11)	20(6)	28(8)
B(5′)	0.6362(6)	0.8296(9)	0.4009(4)	84(6)	260(14)	26(3)	62(15)	36(6)	16(10)
B(6′)	0.6735(5)	0.6210(9)	0.4127(4)	67(5)	216(12)	39(3)	−29(12)	35(6)	−63(10)
B(7′)	0.8588(4)	0.6891(6)	0.5942(4)	32(3)	118(7)	34(2)	−1(8)	19(5)	−2(7)
B(8′)	0.8220(5)	0.8988(6)	0.5798(4)	69(5)	96(7)	32(2)	−3(9)	36(5)	1(7)
B(9′)	0.7684(6)	0.9392(8)	0.4584(4)	105(6)	174(11)	35(3)	−10(14)	50(7)	52(10)
B(10′)	0.7717(6)	0.7630(8)	0.3985(4)	101(6)	234(14)	30(3)	−8(14)	73(7)	−29(9)
B(11′)	0.8272(5)	0.6068(7)	0.4792(4)	75(5)	148(9)	39(3)	−8(11)	67(6)	−34(8)
B(12′)	0.8890(5)	0.8004(7)	0.5100(4)	67(5)	134(8)	38(3)	−27(10)	61(6)	−7(8)
C(13′)	0.6279(6)	0.6230(9)	0.6927(4)	135(7)	268(14)	52(3)	−166(16)	109(8)	−15(11)
C(14′)	0.5786(6)	0.7781(8)	0.6758(4)	108(7)	286(15)	55(4)	36(15)	107(8)	26(11)
C(15′)	0.6727(6)	0.8867(8)	0.7149(4)	135(7)	220(12)	50(3)	59(15)	100(8)	−12(10)
C(16′)	0.7783(5)	0.8016(8)	0.7598(4)	90(5)	254(11)	29(2)	−68(13)	51(6)	−18(9)
C(17′)	0.7532(5)	0.6391(7)	0.7477(4)	119(6)	215(11)	34(3)	81(13)	72(7)	78(9)
C(18′)	0.8987(5)	1.0336(6)	0.6535(4)	85(5)	106(7)	63(3)	−28(10)	67(6)	−4(8)
C(19′)	0.8540(7)	1.2075(8)	0.6370(6)	165(9)	123(9)	98(6)	36(15)	55(12)	4(12)
O′	0.9861(4)	1.0046(5)	0.7194(3)	99(4)	171(7)	72(3)	−17(8)	−17(5)	−49(6)

* See footnote to Table 2.

TABLE 4

Root-mean-square vibrational displacements (Å) and bond lengths (Å) in each cyclopentadienyl ring

		(II)	(IV)	
(*a*) Displacements				
	C(13)	0.520, 0.261, 0.148 *	0.342, 0.265, 0.150	0.358, 0.249, 0.161
	C(14)	0.397, 0.246, 0.194	0.380, 0.266, 0.173	0.322, 0.272, 0.173
	C(15)	0.316, 0.262, 0.205	0.329, 0.286, 0.180	0.309, 0.268, 0.184
	C(16)	0.327, 0.280, 0.198	0.287, 0.240, 0.154	0.308, 0.224, 0.161
	C(17)	0.377, 0.257, 0.180	0.289, 0.230, 0.158	0.311, 0.245, 0.147
(*b*) Bond lengths †				
	C(13)–C(14)	1.456	1.426	1.400
	C(14)–C(15)	1.333	1.401	1.393
	C(15)–C(16)	1.325	1.404	1.389
	C(16)–C(17)	1.342	1.385	1.379
	C(17)–C(13)	1.453	1.411	1.431

* These values, three for each atom, correspond to values along the major, intermediate, and minor axes. † No librational corrections applied; mean σ 0.007 Å.

portion. The angles in the cp ring range from 104 to 112°.*

Possible Mechanisms.—One of the ligands, [η-(3)-1,2-$B_9C_2H_{11}]^{2-}$, bonded to cobalt can be derived from the degradation reaction of the carbaborane 1,2-$B_{10}C_2H_{12}$. Friedel–Crafts alkylation of this carbaborane was studied by Grafstein *et al.*[7] Friedel–Crafts acetylation was also found in the reaction between $[B_{10}H_{10}]^{2-}$ and benzoyl chloride with acid catalysis.[8] Recently, Graybill and Hawthorne [3b] studied the Friedel–Crafts acetylation of [(cp)Co{η-1,6-$B_7C_2H_9$}] in which only an acetyl derivative was obtained in fairly high yield; it was also reported that the acetyl group was bound to the boron atom, B(8), away from the open pentagonal face. In the present

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* Detailed molecular dimensions and structure-factor tables are listed in Supplementary Publication No. SUP 21330 (18 pp., 1 microfiche). For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue.

[7] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, 1963, **2**, 1120.

[8] W. H. Knoth, J. C. Sauer, D. C. England, W. H. Hertler, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1964, **86**, 3973.

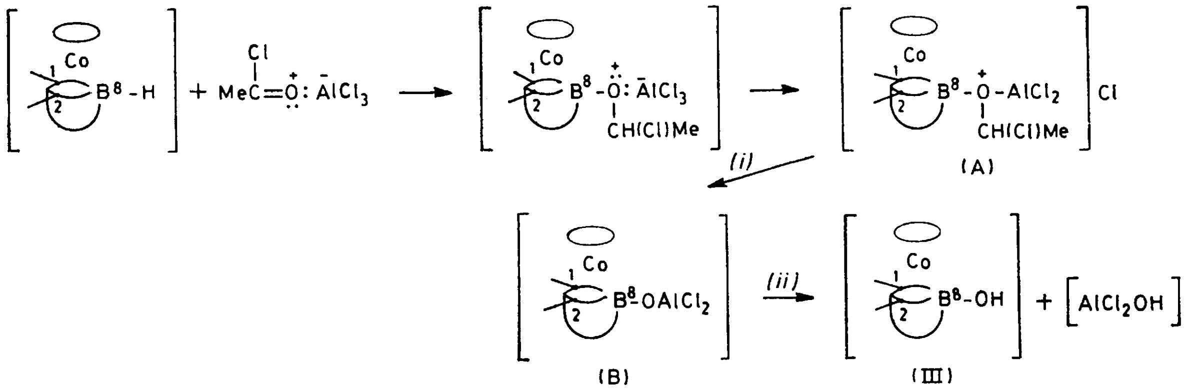
TABLE 5

Mean bond lengths (Å)

		(II)	(IV) *
(*a*) Carbaborane portion			
Co–B	3 †	2.072	2.078
Co–C	2	2.007	2.005
B–B	18	1.782	1.781
B(o)–B(o) ‡	2	1.816	1.807
B(o)–B	6	1.790	1.784
B–B	10	1.771	1.774
C(o)–C(o)	1	1.631	1.635
C–B	6	1.701	1.707
C(1)–B(6), C(2)–B(6)	2	1.716	1.726
C(1)–B(5), C(2)–B(11)	2	1.684	1.694
C(o)–B(o)	2	1.704	1.702
(*b*) cp portion			
Co–C	5	2.041	2.039
C–C	5	1.382	1.402
(*c*) Substituents			
C=O		1.197	1.196
$C-CH_3$		1.496	1.518
B–O		1.453	
B–C			1.591
C–O		1.327	

* Mean values of the two independent molecules. † No. of bonds in molecule. ‡ B(o) and C(o) refer to atoms in the open side.

investigation it is interesting to note that although no acetylation of cp took place with $[(\mathrm{cp})\mathrm{Co}\{\eta\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}\}]$ under the same conditions,[3a] (I), (II), and (III) were the major products rather than the anticipated acetyl derivative (IV). No satisfactory interpretation for the relative amounts of these products, however, can be supplied at present. Attempts to obtain complex (IV) from the reaction between $[(\mathrm{cp})\mathrm{Co}\{\eta\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}\}]$ and acetic anhydride in the presence of boron trifluoride were unsuccessful.



SCHEME 2 (*i*), 46 °C, $-\mathrm{MeCHCl_2}$; (ii), H_2O

In complexes (II) and (III) an oxygen atom is bonded directly to a boron atom. There is no oxygen source except that of MeCOCl under the conditions employed. Reaction of a *closo*-borane, $[B_{12}H_{12}]^{2-}$, with ketones resulted in boron–oxygen bond formation.[8] Since the presence of acidic protons seems to be indispensable to this reaction, the proton yielded from reaction (4) may participate in the production of (II) and/or (III). Heating $[(\mathrm{cp})\mathrm{Co}\{\eta\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}\}]$ under reflux in carbon disulphide with excess of MeCOCl under dry hydrogen chloride, however, resulted in 100% recovery of the starting material. Aluminium trichloride therefore plays an important role in the production of (II) and/or (III). We propose the intermediate (A) in the course of formation of complex (III).

Aluminium trichloride is known as a dealkylation reagent in the reaction with anisole, where the intermediate $[\mathrm{Ph(Me)O{\cdot}AlCl_2}]\mathrm{Cl}$ is readily converted by heating to $[\mathrm{(PhO)AlCl_2}]$ which affords PhOH after hydrolysis.[9] This model in the formation of phenol appears to be applicable to the present work though the intermediate has not been isolated.

Equation (3) suggests a reaction path for the formation of acetate (II). Indeed, hydroxy-derivative (III) affords exclusively the acetate when treated with an excess of aluminium trichloride–acetyl chloride in carbon disulphide solvent. Since, in the Friedel–Crafts reaction of $[(\mathrm{cp})\mathrm{Co}\{\eta\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}\}]$, the acetate and hydroxy-derivative are simultaneously obtained on treating the reaction mixture with water, the acetate is probably formed before the species (A) or (B) are hydrolysed. The hydroxy-complex is presumably produced by some other route and is esterified to the acetate. No interconversion reaction was observed among the products except that of (III) into (II).

Direct reaction of $[(\mathrm{cp})\mathrm{Co}\{\eta\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}\}]$ with $AlCl_3$ yielded monochlorinated species as in equation (1). When the bromide or iodide was employed instead of $AlCl_3$ the corresponding halogeno-derivative was obtained. The reaction mechanism and position of insertion of the halogen atom, however, have not been established. All complexes obtained in this study, excepting the monohalogeno-derivatives, were shown to be substituted at B(8) on the open pentagonal face. This can be associated with the results of an electron-delocalization study in paramagnetic metallacarbaboranes[10] which suggest a preferential electrophilic reaction on the metal bonding face. Our experimental results imply that the reactivity of the diamagnetic $[(\mathrm{cp})\mathrm{Co}\{\eta\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}\}]$ system is similar to that of paramagnetic systems.

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[9] R. B. Wagner and H. D. Zook, 'Synthetic Organic Chemistry,' Wiley, New York, 1953, p. 171; C. R. Dawson, D. Wasserman, and H. Keil, *J. Amer. Chem. Soc.*, 1946, **68**, 534.

[10] R. J. Wiersema and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1974, **96**, 761.

Conclusion.—Friedel–Crafts acetylation, including some other side reactions, occurs only at a boron atom in the carbaborane ligand [complex (IV)], no reaction with cp taking place. This leads us to the conclusion that the π electrons of the cp ring in [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}] transfer to the cobalt to some extent and, as a result, electrophilic substitution of the cp ring may be hindered. Direct attack of the oxygen atom of MeCOCl on the starting material produces the hydroxy-complex (III) and/or the ester derivative (II), whereas direct reaction of the starting material with $AlCl_3$ without MeCOCl produces the chlorinated complex (I).

The substituents in complexes (II) and (IV) have been shown to bond to B(8) by *X*-ray analyses. The hydroxy-complex (III) is similarly substituted.

EXPERIMENTAL

Physical Measurements.—I.r. spectra were recorded on a Japan Spectroscopic Co. DS-402G spectrometer in the range 4 000—600 cm^{-1} in Nujol mulls or hexachlorobuta-1,3-diene. ^1H N.m.r. spectra (60 MHz) were obtained with a Varian A-60 spectrometer, mass spectra with a Hitachi RMU-6 spectrometer. Elemental analyses for carbon, hydrogen, and nitrogen were made in this laboratory; boron and cobalt analyses were by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

Materials.—The carbaborane transition-metal complex, [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}], was synthesized by the procedure reported.[2]

Friedel–Crafts Acetylation of [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}].—In a typical run, to a stirred mixture of anhydrous $AlCl_3$ (6.4 g, 0.048 mol), acetyl chloride (3.6 g, 0.046 mol), and dry carbon disulphide (300 cm^3) were added under a nitrogen atmosphere at 0 °C a solution of [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}] (4.0 g, 0.0156 mol) in CS_2 (100 cm^3). The mixture was stirred for 40 min at room temperature.* The reaction solution was then poured into ice-water and chloroform was added to dissolve the suspended yellow solid. After separation of the aqueous layer, the organic layer was washed with water and dried over sodium sulphate, filtered, and evaporated to dryness. This residue was redissolved in chloroform and the solution concentrated to half volume at *ca.* 50 °C using a rotatory evaporator. The resulting orange crystals [complex (III)] were collected on a glass filter and the filtrate was chromatographed as shown below.

Chromatographic Separations.—Mixtures from the Friedel–Crafts reaction. The mixture resulting from the Friedel–Crafts acetylation was chromatographed using a silica-gel column (4 × 40 cm, Kieselgel 60, 70—230 mesh, Merck). Separation of the complexes (I)—(IV) was accomplished with chloroform. Each chloroform solution was then evaporated at ambient temperatures under reduced pressure and the residue was weighed. Approximate yields of the isolated complexes were: (I), 830 (18.2); (II), 740 (15.1); (III), 2 120 (50); and (IV), 310 mg (6.6%).

Complex (I), [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}Cl$}]. This was crystallized from methylene chloride as yellow *prisms*, m.p. 300—302 °C; $\nu_{max.}$ at 3 107w, 3 050w, 2 598(sh), 2 573s, 1 421m, 1 193w, 1 127w, 1 106m, 1 011m, 985m, 943m, 914w, 897w, 875w, 850s, 829s, 748(sh), 734w, 694w, 657w, 646w, and 611w cm^{-1} (Found: C, 28.95; H, 5.25; B, 33.3; Cl, 13.0; Co, 20.15. $C_7H_{15}B_9ClCo$ requires C, 28.9; H, 5.20; B, 33.45; Cl, 12.2; Co, 20.25%). The i.r. spectrum of the complex obtained from reaction of [(cp)Co{η-(3)-1,2-$B_9C_2H_{11}$}] with excess of $AlCl_3$ was consistent with that of (I). The derivatives [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}Br$}] and [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}I$}] were also identified from their mass spectra and elemental analyses.

Complex (II), [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-OCOMe)}]. Recrystallization of (II) from methylene chloride gave yellow-brown *prisms* decomposed at 281—282° C; $\nu_{max.}$ at 3 110w, 3 060m, 3 024m, 2 635w, 2 571(sh), 2 545s, 1 706s, 1 422m, 1 368m, 1 262s, 1 211w, 1 124m, 1 103w, 1 083m, 1 015m, 974m, 935(sh), 926w, 910w, 900w, 870w, 853m, 796w, 749w, 736w, 695w, and 654w cm^{-1} (Found: C, 35.05; H, 6.00; B, 30.5; Co, 18.55. $C_9H_{18}B_9CoO_2$ requires C, 34.35; H, 5.75; B, 30.95; Co, 18.75).

Complex (III), [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-OH)}].—Complex (III) was crystallized from chloroform as brown *prisms*, m.p. 288—291 °C; $\nu_{max.}$ at 3 130s,br, 3 123w, 3 098w, 3 040w, 3 023w, 2 600(sh), 2 542s, 1 421m, 1 192w, 1 132m, 1 112s, 1 091s, 1 055w, 1 010m, 987w, 969m, 923w, 901w, 889w, 878w, 845s, 785w, and 747m cm^{-1} (Found: C, 30.15; H, 5.65; B, 36.7; Co, 23.15. $C_7H_{16}B_9CoO$ requires C, 30.85; H, 5.90; B, 35.7; Co, 21.65%). Complex (III) was dissolved in acetic anhydride and heated under reflux for 2 h. When the reaction was complete, excess of acetic anhydride was removed under reduced pressure. The i.r. spectrum of the resulting complex coincided completely with that of (II). According to reaction (3), complex (II) was obtained quantitatively. Treatment of (III) with benzoyl chloride also yielded the benzoate [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-OCOPh)}], m.p. 242.5—244 °C.

Complex (IV), [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$(8-COMe)}], *and its hydrazone.* Complex (IV) was recrystallized from chloroform–hexane as yellow *plates*, m.p. 233.5—236° C; $\nu_{max.}$ at 3 105w, 3 043w, 3 015w, 2 602(sh), 2 548s, 1 640(sh), 1 628s, 1 420m, 1 339m, 1 195m, 1 124m, 1 113m, 1 084w, 1 010m, 985w, 969w, 922w, 902w, 876w, 849s, 755w, 733w, 697w, 677w, 662w, 649w, and 613w cm^{-1} (Found: C, 35.55; H, 6.20; B, 32.75; Co, 19.5. $C_9H_{18}B_9CoO$ requires C, 36.2; H, 6.10; B, 32.6; Co, 19.75%). An equimolar mixture of (IV) and 2,4-dinitrophenylhydrazine was heated under reflux in ethanol in the presence of a trace amount of dilute hydrochloric acid. The orange hydrazone was precipitated, filtered off, and dried *in vacuo*. It became black at 298 °C with decomposition (Found: C, 37.4; H, 4.85; N, 11.7. $C_{15}H_{22}B_9CoN_4O_4$ requires C, 37.6; H, 4.65; N, 11.7%).

Reduction of Complex (IV) *to* [(cp)Co{η-(3)-1,2-$B_9C_2H_{10}$-(8-Et)}].—Zinc pellets (5.2 g), mercury(II) chloride (0.6 g), conc. HCl (3 cm^3), and water (9 cm^3) were shaken in a flask for 10 min and then decanted. To the zinc amalgam, acetic acid (5 cm^3), toluene (8 cm^3), conc. HCl (14 cm^3), and complex (IV) (10 mg) were added. The mixture was heated under reflux for 24 h during which conc. HCl (2 × 4 cm^3) was supplied. The organic phase was treated with dilute potassium carbonate solution, washed with water, and dried over $Na_2[SO_4]$. The solvent was removed and the residue crystallized from chloroform–hexane. The resulting yellow crystals melted at 189—192 °C; $\nu_{max.}$ at 3 095w, 3 040w, 2 920m, 2 875(sh), 2 585(sh), 2 545s, 1 452w, 1 421m, 1 376w, 1 190w, 1 113m, 1 062w, 1 013m, 978m, 903w, 874w, and 847s cm^{-1}.

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* Even when the reaction time was prolonged to 2 h at room temperature or the reaction solution was heated under reflux for 2 h the results were the same. Evolution of an acidic gas was observed during the reaction.