unsaturated species $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$ containing a metal–metal double bond as a consequence of steric interactions between the *t*-butyl and the PF_3 groups is paralleled by the stabilization of *di*carbonyl complexes $[M[\eta\text{-}C_5(CH_3)_5](CO)_2]_2$ (M = Cr or Mo) containing metal–metal triple bonds when cyclopentadienyl is replaced by pentamethylcyclopentadienyl.[18-20]

Registry No. $Rh_2(PF_3)_5(t\text{-}Bu_2C_2)$, 56783-55-2; $Rh_2(PF_3)_6\text{-}t\text{-}Bu_2C_2)$, 56783-56-3; $Rh_2(PF_3)_8$, 14876-96-1.

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Group 5 Boranes. II. Phosphaundecaboranes and Their η-Cyclopentadienylcobalt(III) Complexes[1,2]

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In the presence of excess sodium hydride, decaborane reacts with $RPCl_2$ (R = CH_3, C_2H_5, *n*-C_3H_7, C_6H_5) to give $7\text{-}B_{10}H_{11}PR^-$, which on protonation gives $7\text{-}B_{10}H_{12}PR$. Pure $(CH_3)_4N^+$ salts of $7\text{-}B_{10}H_{11}PR^-$ are prepared by dissolving $7\text{-}B_{10}H_{12}PR$ in aqueous dilute ammonia solution and precipitating with $(CH_3)_4NCl$ solution. Reacting $7\text{-}B_{10}H_{12}PR$, $CoCl_2$, C_5H_6, and excess KOH in anhydrous ethanol produces the complexes $(\eta\text{-}C_5H_5)Co(\eta\text{-}7\text{-}B_{10}H_{10}PR)$ and the unsubstituted complex $(\eta\text{-}C_5H_5)Co(\eta\text{-}7\text{-}B_{10}H_{10}P)^-$. The P-methyl, -ethyl, and -propyl complexes are obtained in high yield by alkylation of $(\eta\text{-}C_5H_5)Co(\eta\text{-}7\text{-}B_{10}H_{10}P)^-$ in THF.

Methods for the high-yield preparation of icosahedral η-cyclopentadienylcobalt(III) carborane complexes containing one[3] or two[4] carbons have recently appeared. The two-carbon complexes are very useful reagents for the preparation of lower closo complexes,[5] bimetallo[6] complexes, and nido complexes.[7]

We now report the synthesis of 7-phosphaundecaboranes and their η-cyclopentadienylcobalt(III) complexes. A preliminary report has appeared on the 7-phosphaundecaboranes.[8]

Results and Discussion

Decaborane in diethyl ether in the presence of 4 equiv of sodium hydride reacts with alkyl- or arylphosphorus dichlorides to produce 15–35% yields of the *nido*-phosphaundecaboranes $7\text{-}B_{10}H_{11}PR^-$ (eq 1). The cage numbering system is illustrated in Figure 1. These compounds may also be produced, although in lower yield, using triethylamine as base and THF as solvent (eq 2). Precipitation with aqueous tetramethylammonium chloride solution gives the impure salts $(CH_3)_4N(7\text{-}B_{10}H_{11}PR)$. The impure salts are protonated by dissolving them in acetonitrile and adding concentrated HCl. The protonated form, $7\text{-}B_{10}H_{12}PR$ (R = CH_3 (I), C_2H_5 (II), *n*-C_3H_7 (III), C_6H_5 (IV)) is extracted from this two-layer system with many portions of 75% hexane–25% ether. The solvent is removed in vacuo, the residue sublimed, and the sublimate crystallized from hexane–ether. Low-resolution mass spectra of crystallized I–IV show cutoffs at *m/e* 168, 182, 196, and 230, corresponding to the parent ions $^{11}B_{10}{}^1H_{15}{}^{12}C^{31}P^+$, $^{11}B_{10}{}^1H_{17}{}^{12}C_2{}^{31}P^+$, $^{11}B_{10}{}^1H_{19}{}^{12}C_3{}^{31}P^+$, and $^{11}B_{10}{}^1H_{17}{}^{12}C_6{}^{31}P^+$, respectively.

$$B_{10}H_{14} + RPCl_2 \xrightarrow[(C_2H_5)_2O]{\text{xs NaH}} \xrightarrow{H_2O} NaB_{10}H_{11}PR^- \qquad (1)$$

$$B_{10}H_{14} + RPCl_2 + 3(C_2H_5)_3N \xrightarrow{THF} 2(C_2H_5)_3NH^+Cl^- + (C_2H_5)_3NHB_{10}H_{11}PR \qquad (2)$$

Boron (^{11}B) NMR spectra (Table I) of I, II, III, and IV are generally in a 1:2:2:2:1:2 pattern, indicative of C_s cage symmetry. I and II show a 1:2:2:2:3 pattern of doublets, but the doublet of area 3 is unsymmetrical, and thus consists of a doublet of area 1 and a doublet of area 2 which are not quite degenerate. Boron NMR spectra of the analogous $7\text{-}B_{10}H_{12}AsR$[2] (R = CH_3, C_6H_5) show the same pattern of doublets, but a slight downfield shift of the resonances for $7\text{-}B_{10}H_{12}AsR$ compared to $7\text{-}B_{10}H_{12}PR$ is observed.

Proton NMR spectra of I, II, and III (Table II) are readily interpreted in terms of a phosphorus alkyl group. I shows a doublet (J_{PCH} = 11 Hz) at τ 7.92, which compares very well with the results for the known compounds[9] $7,8\text{-}B_9H_{10}CHPCH_3$ and $7,9\text{-}B_9H_{10}CHPCH_3$. In the case of II the resonance at lowest field corresponding to the methylene group is a pentet of relative intensity 1:4:6:4:1. Thus $J_{CH} = J_{PCH}$ = 8 Hz, where J_{CH} is the splitting from the methyl protons. The complexity of the spin system in IV has not allowed separation of the multiplet centered at τ 2.2 in the proton NMR spectrum.

Unlike $7\text{-}B_{10}H_{12}AsCH_3$,[2] I is not demethylated by Na in liquid NH_3. The starting material is recovered as a large

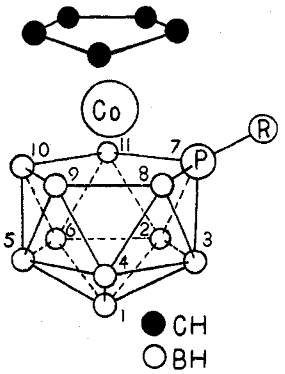

Figure 1. Proposed structure for (η-C_5H_5)Co(η-$B_{10}H_{10}$PR).

Table I. Boron (^{11}B) NMR Spectra at 70.6 MHz

No.	Rel int	Chem shifts, δ^a (J_{BH}, Hz)
I[b]	1:2:2:2:3	−2.9 (133), 8.2 (169), 12.0 (163), 17.0 (147), 25.0[f] (130)
II[b]	1:2:2:2:3	−2.9 (139), 9.3 (169), 12.6 (~165), 17.2 (146), 25.6[f] (129)
III[b]	1:2:2:2:1:2	−2.9 (147), 9.2 (167), 12.7 (166), 17.3 (148), ~24.6 (~140), 25.6 (151)
IV[c]	1:2:2:2:1:2	−3.0 (146), 8.3 (162), 12.5 (163), 17.2 (149), ~24.3 (~145), 25.8 (143)
V[d]	2:6:1:1	11.2 (146), 21.1[f] (135), 28.2 (136), 36.7 (142)
VI[e]	2:4:2:1:1	11.6 (135), ~21.5 (~130), ~22.5 (~150), 28.3 (137), 37.2 (139)
VII[d]	2:4:2:1:1	11.4 (136), 21.2 (~140), 22.2 (~140), 28.1 (146), 37.0 (140)
VIII[d]	2:4:2:1:1	11.5 (137), 20.8 (~130), 22.6 (~130), 27.5 (137), 36.4 (138)
IX[d]	2:1:1:4:2	−10.2 (149), −8.0 (168), 1.8 (141), 7.7[f] (142), 17.3 (157)
X[d]	2:1:1:4:2	−10.1 (146), −7.9 (164), 1.4 (138), 8.0[f] (143), 18.5 (152)
XI[d]	2:1:1:4:2	−10.0 (150), −7.8 (161), 1.4 (140), 8.0[f] (143), 18.3 (154)
XII[d]	2:1:1:4:2	−10.5 (147), −8.4 (155), 0.6 (144), 8.1[f] (143), 16.8 (154)
XIII[d]	3:1:2:2:2	−8.9 (133), ~−2.1 (~150), ~−1.1 (~120), 5.4 (134), 14.4 (140)

[a] Relative to $(C_2H_5)_2O{\cdot}BF_3 = 0$. [b] Chloroform solution. [c] Methylene chloride solution. [d] Acetone solution. [e] Acetonitrile solution. [f] Unsymmetrical doublet.

cation salt of 7-$B_{10}H_{11}PCH_3^-$. Sodium hydride in refluxing THF also fails to demethylate I.

Deprotonation of 7-$B_{10}H_{12}$PR using dilute ammonia (eq 3)

$$B_{10}H_{12}PR + NH_3 \rightarrow NH_4^+B_{10}H_{11}PR^- \quad (3)$$

and subsequent precipitation with aqueous tetramethylammonium chloride solution gives $(CH_3)_4N$(7-$B_{10}H_{11}$PR) (R = CH_3 (V), C_2H_5 (VI), C_3H_7 (VII), C_6H_5 (VIII)). $B_{10}H_{12}S$ was shown[10] to be similarly acidic, and salts of $B_{10}H_{11}S^-$ can easily be prepared.

Boron-11 NMR spectra (Table I) for VI, VII, and VIII show a 2:4:2:1:1 distribution of doublets, indicating C_s ion symmetry and that the "extra" proton must be either bridging the 9,10 cage positions (i.e., on the mirror plane) or rapidly tautomerizing in solution. V shows a 2:6:1:1 distribution of doublets but the resonance of intensity 6 is unsymmetrical with the lowest amplitude for the upfield side of the doublet allowing breakdown into an almost degenerate 4:2 pattern.

Proton NMR (Table II) for V–VIII are quite similar to those of I–IV, except for addition of a $(CH_3)_4N^+$ resonance at about τ 6.60, an upfield shift of the alkyl resonances and a slight lowering of the coupling constants.

Table II. Proton NMR Data[a]

No.	Resonance (J, Hz)	Rel int	Assignment
I[g]	7.92[b] (11)		P–CH_3
II[g]	7.49[c] (8)	2.0	P–CH_2
	8.48[d] (7, 26)	3.0	CH_3
III[g]	7.47[d] (7)	2.0	P–CH_2
	8.26[e]	2.0	CH_2
	8.85[f] (6)	3.1	CH_3
IV[g]	2.2[e]		P–C_6H_5
V[h]	6.51	12.0	$(CH_3)_4N^+$
	8.40[b] (9)	3.0	P–CH_3
VI[h]	6.60	11.9	$(CH_3)_4N^+$
	8.0[c]	2.1	P–CH_2
	8.86[d] (7, 20)	2.9	CH_3
VII[i]	6.67	12.1	$(CH_3)_4N^+$
	8.4[e]	3.9	P–CH_2CH_2
	9.03[f] (6)	2.9	CH_3
VIII[h]	6.52	12.0	$(CH_3)_4N^+$
	2.35[e]	4.9	C_6H_5
IX[h]	4.25	5.0	C_5H_5
	7.25[b] (14)	3.0	CH_3
X[h]	4.30	5.0	C_5H_5
	6.94[e]	2.1	P–CH_2
	8.50[d] (7, 29)	2.9	CH_3
XI[i]	4.25	5.1	C_5H_5
	6.94[e]	1.9	PCH_2
	8.25[e]	2.0	CH_2
	8.91[d] (1.5, 7)	3.0	CH_3
XII[i]	2.07[e]	5.1	P–C_6H_5
	4.29	4.9	C_5H_5
XIII[h]	4.99[d] (1.5)	5.0	C_5H_5
	6.62	12.0	$(CH_3)_4N^+$

[a] Relative to TMS = 10.0. [b] Doublet. [c] Pentet, 1:4:6:4:1. [d] Doublet of a triplet. [e] Multiplet. [f] Unsymmetrical triplet. [g] $CDCl_3$ solution. [h] Acetone-d_6 solution. [i] Dimethyl sulfoxide-d_6 solution.

Using the method of Hawthorne and coworkers,[3,4] η-cyclopentadienylcobalt(III) complexes of substituted and unsubstituted phosphaboranes were synthesized. Thus reacting anhydrous cobalt chloride, cyclopentadiene, and 7-$B_{10}H_{12}$PR (eq 4) gives low to moderate yields of (η-C_5H_5)Co(η-7-$B_{10}H_{10}$PR) (R = CH_3 (IX), C_2H_5 (X), n-C_3H_7 (XI), and C_6H_5 (XII)). IX is obtained in the lowest yield (9.1%) and XII in the highest yield (60.3%). A general structure for the complexes is illustrated in Figure 1.

$$3CoCl_2 + 2C_5H_6 + 2B_{10}H_{12}PR + 4C_2H_5O^- \xrightarrow[C_2H_5OH]{KOH}$$
$$2[(\eta\text{-}C_5H_5)Co(\eta\text{-}B_{10}H_{10}PR)] + 4C_2H_5OH + Co^0 + 6Cl^- \quad (4)$$

Absorptions are observed in the infrared spectra (Table III) attributable to C_5H_5 at about 3100 cm^{-1}. This absorption in the case of IX is split into a doublet (3118 and 3100 cm^{-1}). Low-resolution mass spectra of IX–XII show cutoffs at m/e 290, 304, 318, and 352, corresponding to the parent ions $^{11}B_{10}{}^{1}H_{18}{}^{12}C_6{}^{31}P^{59}Co^+$, $^{11}B_{10}{}^{1}H_{20}{}^{12}C_7{}^{31}P^{59}Co^+$, $^{11}B_{10}{}^{1}H_{22}{}^{12}C_8{}^{31}P^{59}Co^+$, and $^{11}B_{10}{}^{1}H_{20}{}^{12}C_{11}{}^{31}P^{59}Co^+$, respectively.

A by-product of these reactions is (η-C_5H_5)Co(η-$B_{10}H_{10}P)^-$, a complex of the "phosphollide" ion, $B_{10}H_{10}P^{3-}$. The precursor compound $B_{10}H_{12}P^-$ is as yet unknown. Reaction of $B_{10}H_{14}$ and PCl_3 in diethyl ether in the presence of excess sodium hydride gives on hydrolysis and precipitation with tetramethylammonium chloride solution a compound for which the analysis is close to that calculated for $(CH_3)_4NB_{10}H_{12}P$.[11] However, boron-11 NMR indicates that it is a mixture, and we have not been able to effect complete separation. The mixture undoubtedly contains $B_{10}H_{12}P^-$, since the σ complexes (η-C_5H_5)Fe$(CO)_2$(σ-$B_{10}H_{12}$P) and (η-C_7H_7)Mo$(CO)_2$-σ-$B_{10}H_{12}$P) were prepared from it by Todd and coworkers.[12] $(CH_3)_4N$[(η-C_5H_5)Co(η-$B_{10}H_{10}$P)] (XIII) shows a 3:1:2:2:2 pattern of doublets, a C_s pattern with a doublet of area 2, and a doublet of area 1 accidently degenerate.

Table III. Infrared Data (KBr Pellet) (cm^{-1})

I	3003 (w), 2921 (w), 2560 (vs), 1399 (m), 1287 (m), 1074 (m), 1017 (s), 985 (s), 923 (w), 906 (w), 892 (w), 856 (w), 758 (m), 695 (m), 615 (m)
II	2981 (w), 2962 (w), 2940 (w), 2882 (w), 2560 (vs), 1453 (w), 1406 (w), 1386 (w), 1240 (m), 1084 (w), 1034 (w), 1018 (s), 1003 (w), 984 (s), 923 (w), 884 (w), 787 (w), 767 (m), 756 (w), 699 (s)
III	2970 (w), 2930 (w), 2874 (w), 2555 (vs), 1460 (m), 1401 (w), 1382 (w), 1216 (m), 1080 (m), 1039 (w), 1016 (s), 1005 (w), 981 (s), 936 (w), 905 (w), 879 (w), 856 (w), 786 (w), 757 (m), 730 (w), 720 (w), 699 (s), 616 (w)
IV	3055 (w), 2560 (vs), 1480 (m), 1437 (m), 1334 (w), 1311 (w), 1225 (w), 1184 (w), 1160 (w), 1100 (m), 1079 (w), 1066 (w), 1027 (w), 1014 (s), 997 (w), 980 (s), 925 (w), 882 (w), 856 (w), 786 (w), 763 (m), 744 (s), 726 (m), 702 (m), 685 (s), 536 (w), 479 (m)
V	3025 (w), 2955 (w), 2920 (w), 2510 (vs), 1483 (s), 1414 (w), 1286 (w), 1064 (m), 1014 (s), 997 (w), 949 (s), 782 (w), 755 (w), 733 (w), 692 (w)
VI	3025 (w), 2960 (w), 2930 (w), 2875 (w), 2510 (vs), 1483 (s), 1454 (w), 1413 (w), 1263 (w), 1064 (s), 1019 (s), 994 (m), 946 (s), 803 (m), 745 (w), 717 (m), 692 (w)
VII	3030 (w), 2963 (m), 2030 (w), 2870 (w), 2505 (vs), 1484 (s), 1415 (w), 1286 (w), 1085 (w), 1065 (m), 1016 (s), 984 (s). 947 (s), 804 (w), 775 (w), 736 (m), 690 (w)
VIII	3025 (w), 2510 (vs), 1484 (s), 1446 (w), 1436 (m), 1416 (w), 1105 (w), 1058 (m), 1026 (w), 1015 (s), 988 (m), 945 (s), 804 (w), 746 (s), 742 (s), 713 (m), 693 (m), 635 (w), 573 (w), 545 (w), 513 (w), 466 (m), 457 (m)
IX	3118 (w), 3100 (w), 2998 (w), 2918 (w), 2525 (vs), 1424 (w), 1416 (w), 1397 (w), 1010 (s), 924 (w), 896 (w), 885 (w), 868 (w), 849 (s), 776 (m), 755 (w), 722 (m), 508 (w), 455 (m), 430 (w), 420 (m), 407 (m)
X	3108 (w), 2992 (w), 2978 (w), 2939 (w), 2918 (w), 1450 (w), 1425 (w), 1416 (w), 1400 (w), 1380 (w), 1042 (m), 1014 (s), 924 (w), 884 (w), 869 (w), 851 (s), 803 (w), 733 (m), 722 (m), 614 (w), 577 (w), 514 (w), 452 (w), 417 (w), 407 (m)
XI	3118 (w), 2998 (w), 2530 (vs), 1461 (w), 1425 (w), 1417 (w), 1223 (w), 1084 (w), 1044 (w), 1014 (s), 886 (w), 847 (s), 805 (w), 755 (w), 719 (m), 448 (m), 439 (w), 418 (w), 407 (m),
XII	3108 (w), 2992 (w), 2958 (w), 2939 (w), 2908 (w), 2525 (vs), 1450 (w), 1433 (w), 1415 (w), 1397 (w), 1378 (w), 1042 (m), 1014 (s), 923 (w), 884 (w), 818 (w), 851 (s), 804 (w), 732 (m), 721 (m), 613 (w), 577 (w), 513 (w), 451 (w), 405 (m)
XIII	3100 (w), 3022 (w), 2500 (vs), 1484 (m), 1418 (w), 1022 (s), 946 (s), 895 (w), 862 (m), 824 (s), 757 (w), 726 (w), 692 (w)

The proton NMR spectra of IX–XIII (Table II) are very similar to those of I–IV except for the addition of a C_5H_5 peak at about τ 4.30. The C_5H_5 resonance in the proton NMR spectrum of XIII is split (J_{PH} = 1.5 Hz). Similar long-range ^{31}P–^{1}H coupling was also observed[13] in the spectrum of the η-cyclopentadienylferraphosphacarborane (η-C_5H_5)Fe(η-7,9-$B_9H_9CHPCH_3$) (J = 1 Hz).

Electronic spectra of IX–XIII are compared in Table IV with electronic spectra of analogous η-cyclopentadienylcobalt(III) complexes of 7,8-$B_9C_2H_{11}^{2-}$, 7-$B_{10}H_{10}S^{2-}$, and 7-$B_{10}H_{10}CH^{3-}$. All spectra contain an intense band at about 275 mμ. All the spectra except that for (η-C_5H_5)Co(η-7-$B_{10}H_{10}S$) contain a band at about 415 mμ and a shoulder at about 315 mμ. A band was reported[10] at 324 mμ for (η-C_5H_5)Co(η-7-$B_{10}H_{10}S$), but was not reported as a shoulder. Thus the electronic spectra of these analogous compounds are quite similar.

Table IV. Electronic Spectra of η-Cyclopentadienylcobalt(III) Boranes

Compd	λ_{max}, mμ	(ϵ)	Ref
IX[b]	407	(339)	
	314[a]	(1960)	
	276	(25200)	
X[b]	407	(294)	
	312[a]	(1800)	
	276	(24400)	
XI[b]	408	(325)	
	312[a]	(1790)	
	275	(24100)	
XII[b]	412	(357)	
	317[a]	(1840)	
	281	(20300)	
	269	(16600)	
	218	(12600)	
(C_5H_5)Co(7,8-$B_9C_2H_{11}$)[c]	422	(364)	14
	320[a]	(545)	
	273	(33600)	
	208	(54000)	
(C_5H_5)Co(7-$B_{10}H_{10}S$)[b]	324	(431)	10
	287	(24000)	
	232	(6370)	
XIII[b]	427	(336)	
	326[a]	(1550)	
	272	(14900)	
(C_5H_5)Co(7-$B_{10}H_{10}CH$)$^-$ [b]	416	(296)	3
	303[a]	(1900)	
	267	(39700)	
	232[a]	(6320)	

[a] Shoulder. [b] Acetronitrile solution. [c] Methanol solution.

Reacting (η-C_5H_5)Co(η-7-$B_{10}H_{10}P$)$^-$ in THF with CH_3I, C_2H_5I, or n-C_3H_7I produces IX, X, or XI in high yield. The anion is probably produced by reaction of the strong base $C_2H_5O^-$ with the neutral complexes during the synthesis. Similarly, reaction of Fe(η-7,9-$B_9H_9CHPCH_3$) with NaH in monoglyme demethylated one of the phosphorus atoms[13] to give (η-7,9-B_9H_9CHP)Fe(η-7,9-$B_9H_9CHPCH_3$)$^-$.

Experimental Section

All preparations were carried out in a nitrogen atmosphere. The alkyl phosphonous chlorides were used as received from Ethyl Corporation, and $C_6H_5PCl_2$ was obtained from Aldrich Chemical Co. Anhydrous cobalt chloride was prepared by heating $CoCl_2\cdot6H_2O$ at 110° and 0.1 Torr for 2 days. Tetrahydrofuran and diethyl ether were distilled from lithium hydroaluminate just prior to use. Decaborane was vacuum sublimed. All other reagents were used as received. Melting points were taken in sealed evacuated capillaries and are uncorrected.

Boron (^{11}B) NMR spectra at 70.6 MHz (Table I) were obtained with a Varian HR-220 spectrometer and are externally referenced to $(C_2H_5)_2O\cdot BF_3$. Proton NMR spectra (Table II) were obtained with a Varian A-60A spectrometer. Carbon, hydrogen, boron, phosphorus, and cobalt analyses and osmometric molecular weight determinations were performed at Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Analytical data are summarized in Table V. Low-resolution mass spectra were obtained with a CEC-492 double-focusing high-resolution spectrometer.

Infrared spectra were obtained with a Perkin-Elmer 621 instrument and uv–visible spectra with a Cary 17 instrument. Infrared spectra are reported in Table III for KBr disks as very strong (vs), strong (s), medium (m), or weak (w). Electronic spectra are reported in Table IV.

Preparation of 7-$B_{10}H_{12}PR$ (R = CH_3 (I), C_2H_5 (II), C_3H_7 (III), C_6H_5 (IV)). The general method is illustrated below in the preparation of $B_{10}H_{12}PC_6H_5$ (IV). II, III, and IV were obtained in 30–35% yield, while I was obtained in 15–20% yield.

7-$B_{10}H_{12}PC_6H_5$ (IV). Fifty percent NaH dispersion (9.6 g) was added to a 500-ml three-necked flask fitted with a nitrogen inlet, reflux condenser, mechanical stirrer, and pressure equalized dropping funnel. The NaH dispersion was washed twice with hexane and twice with ether and 100 ml of ether was added to the flask. A solution of 6.1 g of decaborane in ether was added dropwise from the funnel and the resulting solution was stirred for 10 min. A solution of 6.8 ml (50 mmol) of $C_6H_5PCl_2$ in 100 ml of ether was then prepared in the dropping funnel. This solution was added dropwise with stirring over

Table V. Analytical Data

			Calcd					Found				
No.	Compd	Mp, °C	% C	% H	% P	% Co	Mol wt	% C	% H	% P	% Co	Mol wt[a]
I	$B_{10}H_{12}PCH_3$	88-89	7.23	9.10	18.63		166	7.23	9.28	17.93		166
II	$B_{10}H_{12}PC_2H_5$	82-83	13.32	9.50			180	14.03	9.56			180
III	$B_{10}H_{12}PC_3H_7$	50-51	18.54	9.85			194	18.48	9.89			200
IV	$B_{10}H_{12}PC_6H_5$	82-84	31.58	7.51	13.57		228	31.62	7.51	13.54		235
V	$(CH_3)_4NB_{10}H_{11}PCH_3$		25.09	10.95	12.94			25.19	10.76	13.28		
VI	$(CH_3)_4NB_{10}H_{11}PC_2H_5$		28.42	11.13				28.68	11.46			
VII	$(CH_3)_4NB_{10}H_{11}PC_3H_7$		31.55	10.97				31.25	11.23			
VIII	$(CH_3)_4NB_{10}H_{11}PC_6H_5$		39.85	9.36	10.36			39.67	9.42	10.17		
IX	$(C_5H_5)Co(B_{10}H_{10}PCH_3)$	295-297	25.00	6.29		20.45		25.14	6.31		20.60	
X	$(C_5H_5)Co(B_{10}H_{10}PC_2H_5)$	223-225	27.81	6.67		19.49	302	28.15	6.94		19.24	306
XI	$(C_5H_5)Co(B_{10}H_{10}PC_3H_7)$	199-201	30.37	7.01		18.63	316	31.00	7.11		17.77	322
XII	$(C_5H_5)Co(B_{10}H_{10}PC_6H_5)$	221-223	37.71	5.75		16.82	350	37.42	5.66		16.50	368
XIII	$(CH_3)_4N[(C_5H_5)Co(B_{10}H_{10}P)]$		31.11	7.83		16.96		31.18	7.75		16.80	

[a] Osmometric in benzene.

several hours, and stirring was continued overnight to give a gummy precipitate (alkyl phosphonous chlorides do not precipitate the gum). Distilled water was added very slowly until gas evolution became slow. Then 50 ml of water was added and the ether was removed in vacuo. The dark aqueous solution was diluted with 100 ml of distilled water and precipitated with tetramethylammonium chloride solution. The malodorous yellow precipitate was isolated by filtration and air dried in a hood. The salt (crude $(CH_3)_4NB_{10}H_{11}PC_6H_5$) was dissolved in 100 ml of acetonitrile and the solution transferred to a dropping funnel, and to this was added 20 ml of concentrated HCl. Extraction was carried out with 100-ml portions of 75% hexane–25% diethyl ether, while occasionally adding 10-ml portions of concentrated HCl, until the middle acetonitrile layer almost disappeared. The ether–hexane was removed in vacuo and the solid was transferred to a sublimer. Sublimation was carried out at 0.1 mm and 90° to obtain an oily solid. The oily solid was crystallized by slow rotary evaporation of an ether–hexane solution to give 3.4–4.0 g (30–35% yield).

Preparation of $(CH_3)_4NB_{10}H_{11}PR$ (R = CH_3 (V), C_2H_5 (VI), C_3H_7 (VII), C_6H_5 (VIII)). Crystallized $B_{10}H_{12}PR$ was dissolved in 3 *M* ammonia solution and the resulting solution was precipitated with aqueous tetramethylammonium chloride. The white solid was isolated by filtration, briefly air dried, and dissolved in acetone. Any solids were removed by filtration and the acetone was removed in vacuo. Recrystallization was carried out with 95% ethyl alcohol under a nitrogen blanket to give a 75–85% yield of $(CH_3)_4NB_{10}H_{12}PR$.

Preparation of $(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}PR)$ (R = CH_3 (IX), C_2H_5 (X), *n*-C_3H_7 (XI), C_6H_5 (XII)) and $(CH_3)_4N[(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}P)]$ (XIII). The procedure will be illustrated by the preparation of $(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}PC_3H_7)$. The same ratios of millimoles of reagents are used in preparation of all the complexes.

$(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}PC_3H_7)$ (XI). A 500-ml three-necked flask was fitted with mechanical stirrer, reflux condenser, and pressure equalized dropping funnel. Anhydrous ethyl alcohol (200 ml) and solid KOH (8.0 g) were added and the solution was stirred until all the solid dissolved, and then the flask and contents were chilled in an ice bath. Freshly cracked cyclopentadiene (4.5 ml, 55 mmol) was added and the solution was stirred for 10 min. A solution of 3.5 g of $CoCl_2$ (27 mmol) in 100 ml of anhydrous ethanol was added and the resulting slurry was stirred for 1 hr. Then a solution of 2.00 g of $B_{10}H_{12}PC_3H_7$ (10.3 mmol) in ethanol was added and stirring was continued for 15 hr. After the addition of 4.0 g of solid KOH and stirring at room temperature for 3 hr, refluxing was carried out for 1 hr. The solution was cooled to room temperature and poured into 600 ml of distilled water with stirring. The solid thus formed was isolated by filtration, washed with water, and air dried. The filtrate and washings were precipitated with aqueous tetramethylammonium chloride and isolated by filtration. Isolation of $(CH_3)_4N[(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}P)]$ from this crude salt is discussed below. The air-dried precipitate from above was dissolved in 400 ml of acetone and any solids were removed by filtration. Methylene chloride (400 ml) was added and the red-orange solution was clarified by filtration. It was dried over magnesium sulfate, and the solvent was removed in vacuo. The solid was dissolved in methylene chloride, silica gel was added, and the solvent was stripped off. Chromatography on silica gel with 75% methylene chloride–25% hexane gave a yellow band. After discarding the tail end of this band, the solvent was removed and the yellow solid was recrystallized from ethylene dichloride or ethylene dichloride–heptane. Yields from 2.00 g of starting material were as follows: IX, 0.31 g (9.1%); X, 0.45 g (13.5%); XI, 0.92 g (28.2%); XII, 1.85 g (60.3%).

$(CH_3)_4N[(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}P)]$ (XIII). The crude tetramethylammonium salt from the above procedure was air dried and extracted with two 10-ml protions of hot ethylene dichloride. The remaining solid was then extracted with several portions of boiling methanol and the solution was filtered while hot. The solid which forms on cooling was redissolved by reheating the methanol. After boiling off part of the methanol, the solution was allowed to cool slowly giving large orange-brown crystals. Yields of the complex anion with 2.00 g of a given starting material were as follows: I, 0.86 g (20.6%); II, 1.30 g (33.7%); III, 1.30 g (36.4%), IV, 0.097 g (3.2%).

Alkylation of $(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}P)^-$. $(CH_3)_4N[(\eta$-$C_5H_5)Co(\eta$-$B_{10}H_{10}P)]$ was dissolved in THF and a large excess of CH_3I, C_2H_5I, or *n*-C_3H_7I was added. In the case of methyl iodide, the reaction mixture was stirred at room temperature until no more starting material was detected by TLC (about 4 hr). The ethyl iodide reaction was reflexed for 12 hr and the *n*-butyl iodide reaction was refluxed for 24 hr. The reaction was cooled and the $(CH_3)_4NI$ was removed by filtration, and the solid was washed with THF. The solvent was removed in vacuo and the residue was crystallized from ethylene dichloride or ethylene dichloride–heptane. Percent yields: $(C_5H_5)CoB_{10}H_{10}PCH_3$, 94%, $(C_5H_5)CoB_{10}H_{10}PC_2H_5$, 78%; $(C_5H_5)CoB_{10}H_{10}PC_3H_7$, 78%.

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