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π-Dicarbollyl Derivatives of Chromium. Metallocene Analogs

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The (3)-1,2-$B_9C_2H_{11}^{2-}$ and (3)-1,7-$B_9C_3H_{11}^{2-}$ dicarbollide ions and their carbon-substituted derivatives react with chromium(III) chloride to produce the corresponding $(\pi\text{-}B_9C_2H_{11})_2Cr^-$ sandwich-bonded complexes which contain formal Cr(III). Similar reactions using dicarbollide ions and the cyclopentadienide ion produced formal Cr(III) complexes which contained π-$C_5H_5^-$ and π-$B_9C_2H_{11}^{2-}$ ligands simultaneously bonded to metal. The preparation, characterization, and structure of these complexes are discussed.

Introduction

The recent preparation of various metallocene analogs containing the (3)-1,2- and (3)-1,7-dicarbollide ion and its carbon-substituted derivatives[1] led to the study of similar chromium complexes reported here. Five dicarbollide ion systems were employed in this study and complexes containing chromium(III) were obtained with the (3)-1,2-dicarbollide and 1-methyl-, 1,2-dimethyl-, and 1-phenyl-(3)-1,2-dicarbollide, as well as (3)-1,7-dicarbollide ions. In addition, mixed π-cyclopentadienyl-π-(3)-1,2- and π-cyclopentadienyl-π-(3)-1,7-dicarbollylchromium derivatives were prepared.

Results and Discussion

Preparation and Characterization of Bis(π-(3)-1,2- and π(3)-1,7-dicarbollyl)chromium Derivatives.—When a slight excess of anhydrous chromium(III) chloride was treated with various dicarbollide ion salts in tetrahydrofuran under nitrogen, a dark violet solution resulted

$$2(3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + CrCl_3 \longrightarrow (\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Cr^- + 3Cl^-$$

The resulting chromium(III) derivatives were isolated from water by precipitation with cesium or tetramethylammonium ion. Yields ranged from 15 to 68%. When an excess of dicarbollide ion was employed in these preparations, the product was identical with that formed in the presence of an excess of Cr(III). Table I contains yield and analytical data pertaining to the bis-dicarbollide complexes obtained in this study.

Chromicinium salts are easily hydrolyzed, especially in acidic solution, with the attendant loss of both cyclopentadienyl groups.[2] In contrast to this behavior, the bis(π-dicarbollyl)chromium derivatives described in Table I are stable in the air and their cesium salts may be recrystallized from hot aqueous solutions. Although hot, concentrated sulfuric acid does not decompose these complexes, they are decomposed by hot aqueous base to form the parent dicarbadodecahydroundecaborate(−1) ion which may be quantitatively recovered as the tetramethylammonium salt.

All five bis(π-dicarbollyl)chromium derivatives reported in Table I are thermally stable up to 280°. Treatment with sodium amalgam did not produce chromium(II) complexes. Cyclic voltammetry data obtained in acetonitrile solution indicated that reduction is irreversible. The ^1H and ^{11}B nmr spectra were not obtainable owing to paramagnetism, as indicated by a magnetic moment of $\mu_{eff} = 3.85$ BM (theoretical value for spin-only μ_{eff} is 3.88 BM) for $Cs[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})_2Cr]$.

The infrared spectra of the five chromium(III) derivatives are presented in Table II. The large number of atoms and the lack of symmetry in these salts makes a detailed study of the infrared spectra very difficult. However, comparison of all available complexes containing the (3)-1,2-$B_9C_2H_{11}^{2-}$ ligand shows five absorptions at approximately 1145 m, 1090 m, 1020 m, 1006 m, and 975 s cm^{-1} to be characteristic of the presence of at least one π-(3)-1,2-dicarbollide group, regardless of the central metal or its oxidation state. Carbon-substitution derivatives generally follow this pattern although one or two characteristic absorptions may be weak or missing.

Electronic spectral data are given in Table III and have not yet been analyzed.

Preparation and Characterization of π-Cyclopentadienyl-π-(3)-1,2- and π-Cyclopentadienyl-π-(3)-1,7-dicarbollylchromium Derivatives.—The successful preparation of the bis(π-dicarbollyl)chromium derivatives described above suggested that mixed complexes which contained both π-cyclopentadienyl and π-dicarbollyl groups as ligands might be prepared. Accordingly, a mixture of sodium cyclopentadienide and the desired disodium dicarbollide derivative was allowed to react with anhydrous chromium(III) chloride in tetrahydrofuran. The desired π-cyclopentadienyl-π-(3)-dicarbollylchromium(III) was obtained in yields ranging from 18 to 32%.

$$C_5H_5^- + (3)\text{-}1,2\text{-}B_9C_2H_{11}^{2-} + CrCl_3 \longrightarrow \pi\text{-}C_5H_5Cr(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11})^0 + 3Cl^-$$

Elemental analyses, melting points, and yields of the mixed ligand complexes are given in Table IV. The mass spectrum of the sublimable $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ and $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3\ \text{-}1,7\text{-}B_9C_2H_{11}]$ exhibited parent peaks at *m/e* 253 (calcd for $^{12}C_5H_5{}^{54}Cr$-

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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, Jr., and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 879 (1968).

[2] E. O. Fischer and K. Ulm, *Ber.*, **95**, 692 (1962).

TABLE I

ELEMENTAL ANALYSES AND YIELDS OF BIS(π-(3)-DICARBOLLYL)CHROMIUM DERIVATIVES

	Analyses, %										
	B		C		H		N		Cr		
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Yield, %
$Cs[(1,2\text{-}B_9C_2H_{11})_2Cr]$	43.27	43.54	10.68	10.70	4.93	5.37	...	...	11.56	11.68	68
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}\text{-}CH_3)_2Cr]$	46.44	46.54	28.67	28.11	9.14	9.03	3.34	3.47	12.41	11.89	21
$(CH_3)_4N[(1,2\text{-}B_9C_2H_9\text{-}(CH_3)_2)_2Cr]$	43.53	43.62	32.24	30.59	9.47	9.52	3.13	3.46	11.63	11.13	15
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}\text{-}C_6H_5)_2Cr]$	35.83	36.72	44.23	43.36	7.79	7.78	2.58	2.66	9.57	9.73	19
$Cs[(1,7\text{-}B_9C_2H_{11})_2Cr]$	43.27	43.06	10.68	10.45	4.93	5.10	...	...	11.56	11.35	32

TABLE II

INFRARED SPECTRAL DATA (CM^{-1}) FOR THE BIS(π-(3)-DICARBOLLYL)CHROMIUM DERIVATIVES IN NUJOL–FLUOROLUBE MULLS

$(CH_3)_4N[(1,2\text{-}B_9C_2H_{11})_2Cr]$

3049 w, 3030 w, 2572 s, 2543 s, 2510 s, 1487 s, 1418 w, 1287 w, 1219 w, 1167 w, 1148 m, 1089 m, 1046 w, 1024 m, 1006 m, 972 s, 947 s, 880 w, 849 w, 771 w, 738 m, 708 w, 646 s

$(CH_3)_4N[(B_9C_2H_{10}CH_3)_2Cr]$

3050 w, 3018 m, 2930 m, 2555 s, 2525 s, 1480 s, 1450 w, 1382 w, 1206 w, 1160 w, 1113 m, 1075 m, 1056 m, 1022 m, 1007 m, 980 s, 942 s, 915 w, 878 w, 853 w, 761 m, 752 w, 683 w, 660 w, 629 w, 615 m

$(CH_3)_4N[(B_9C_2H_9(CH_3)_2)_2Cr]$

3054 w, 3025 w, 2936 m, 2860 w, 2584 m, 2530 s, 2478 m, 1478 s, 1414 w, 1388 w, 1373 w, 1283 w, 1123 m, 1086 m, 1009 s, 948 s, 919 w, 899 w, 858 w, 793 w, 765 m, 750 m, 688 m

$(CH_3)_4N[(B_9C_2H_{10}C_6H_5)_2Cr]$

3087 w, 3030 w, 3010 w, 2952 w, 2920 w, 2525 s, 1595 w, 1581 w, 1495 m, 1484 s, 1448 m, 1417 w, 1236 w, 1182 w, 1176 w, 1163 w, 1156 w, 1085 w, 1067 m, 1045 m, 1010 m, 1003 m, 985 s, 974 w, 947 s, 920 w, 907 w, 875 w, 842 w, 779 s, 738 w, 697 s, 684 w, 664 w, 630 m

$(CH_3)_4[(1,7\text{-}B_9C_2H_{11})_2Cr]$

3021 w, 2975 w, 2922 w, 2890 w, 2541 s, 1478 s, 1414 w, 1299 w, 1214 m, 1148 w, 1098 m, 1054 s, 1004 m, 974 s, 943 s, 917 w, 892 w, 837 w, 796 w, 764 w, 735 m, 701 m, 640 m

TABLE III

ELECTRONIC SPECTRAL DATA FOR THE BIS(π-(3)-DICARBOLLYL)CHROMIUM DERIVATIVES IN ACETONITRILE SOLUTION

Compound	λ_{max}, mμ (ϵ, M^{-1} cm^{-1})
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{11})_2Cr]$	236 (20,500), 298 (21,470), 463 sh (220), 530 (230)
$(CH_3)_4N[(B_9C_2H_{10}CH_3)_2Cr]$	242 (18,900), 308 (19,100), 534 (250)
$(CH_3)_4N[(B_9C_2H_9(CH_3)_2)_2Cr]$	251 (16,000), 328 (17,000), 505 sh (200), 555 (250)
$(CH_3)_4N[(B_9C_2H_{10}C_6H_5)_2Cr]$	226 (27,900), 245 sh (17,200), 321 (15,800), 548 (350)
$Cs[(1,7\text{-}B_9C_2H_{11})_2Cr]$	242 (20,500), 303 (19,000), 379 (1500), 470 (250), 520 (230)

${}^{11}B_9{}^{12}C_2{}^1H_{11}$: *m/e* 253) and confirmed the assigned molecular composition.

Air oxidation in solution results in complete destruction of the complexes, and, in benzene solution, a dark blue intermediate can be observed, similar to the oxidation of chromocene with insufficient amounts of oxygen, that leads to $[C_5H_5CrO_4]$.[3] Hydrochloric acid stabilizes acetone solutions against air oxidation, which normally is very fast. Treatment with bases results in complete decomposition. All derivatives are thermally stable up to their melting points. They are sublimable under high vacuum above 170°. Cyclic voltammetry data indicated that reversible reduction does not occur.

The infrared spectra of the mixed ligand complexes are presented in Table V. In addition to the frequencies characteristic for the $B_9C_2H_{11}{}^{2-}$ system outlined above, absorptions of the symmetric C_5H_5 ring appear at about 3105 w, 1422 m, 1008 m, and 824 s cm^{-1}. Electronic spectral data are given in Table VI.

Structure.—A single-crystal X-ray diffraction study[4] of the $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_3)_2]Cr^-$ cesium salt resulted in the confirmation of the symmetrical sandwich structure presented in Figure 1. The great similarity of the infrared spectra of all bis(π-(3)-1,2-dicarbollyl)metal derivatives, including those of iron(III) and cobalt(III) derivatives which have been well characterized as true sandwich complexes,[1] strongly suggests that identical bonding is involved in all chromium complexes. The mixed-ligand π-C_5H_5 derivatives of π-(3)-dicarbollylchromium as well as iron and cobalt show the absorptions characteristic of π-bonded cyclopentadienyl groups.[5]

Experimental Section

Physical Measurements.—Ultraviolet–visible spectra were measured with a Cary Model 14 spectrophotometer. Infrared spectra was determined using a Perkin-Elmer Model 621 grating infrared spectrophotometer. The absorptions listed in Tables II and V were compounded from spectra obtained by using both Nujol and Fluorolube mulls. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials.—The preparation of the dicarbadodecahydroundecaborate(-1) ions and their carbon-substituted derivatives was carried out as recently described.[6] Anhydrous $CrCl_3$ was obtained from Alfa Inorganics, a 15.2% (*ca.* 1.6 *M*) *n*-butyllithium solution in hexane from Foote Mineral Co., Exton, Pa., and chromatographic polyamide (Polyamide-CC6) from Brinkmann Instruments, Westbury, N. Y. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride under nitrogen. Ultraviolet and visible spectra were measured in Spectrograde solvents.

Preparation of the Dicarbollide Dianions. (a) Disodium (3)-1,2-Dicarbollide Derivatives.—The preparation from trimethylammonium salts was conducted as recently described.[1]

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(3) E. O. Fischer, K. Ulm, and H. P. Fritz, *Ber.*, **93**, 2167 (1960).

(4) We are indebted to Professor David Templeton and Dr. Allan Zalkin for this structural information received prior to publication.

(5) H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

(6) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Am. Chem. Soc.*, **90**, 862 (1968).

TABLE IV

ELEMENTAL ANALYSES, MELTING POINTS, AND YIELDS OF π-CYCLOPENTADIENYL-π-(3)-DICARBOLLYLCHROMIUM DERIVATIVES

	Analyses, %									
	B		C		H		Cr			
Compound	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Yield, %	Mp,[a] °C
C_5H_5Cr-1,2-$B_9C_2H_{11}$	39.00	38.89	33.70	33.38	6.46	6.38	20.84	20.65	23	248–249
C_5H_5Cr-1,2-$B_9C_2H_{10}CH_3$	36.92	36.28	36.46	36.19	6.89	6.87	19.73	19.59	32	219–220
C_5H_5Cr-1,2-$B_9C_2H_9(CH_3)_2$	35.06	35.52	38.95	39.39	7.26	7.38	18.73	18.99	20	261–262
C_5H_5Cr-1,2-$B_9C_2H_{10}C_6H_5$	29.88	29.67	47.96	47.40	6.19	6.26	15.97	15.83	18	208–209
C_5H_5Cr-1,7-$B_9C_2H_{11}$	39.00	39.21	33.70	33.87	6.46	6.37	20.84	21.35	22	217–218

[a] Uncorrected melting point.

TABLE V

INFRARED SPECTRAL DATA (CM^{-1}) FOR THE π-CYCLOPENTADIENYL-π-(3)-DICARBOLLYLCHROMIUM DERIVATIVES IN NUJOL–FLUOROLUBE MULLS

C_5H_5Cr-1,2-$B_9C_2H_{11}$

3110 w, 3098 w, 3020 w, 2614 m, 2605 s, 2578 s, 2568 s, 2542 s, 2535 s, 2522 s, 2495 s, 1841 w, 1756 w, 1657 w, 1418 w, 1215 m, 1142 w, 1114 w, 1092 s, 1048 m, 1008 s, 971 s, 947 w, 936 w, 924 w, 893 w, 878 m, 846 m, 818 s, 783 w, 775 m, 743 w, 687 w, 668 w, 628 m

$C_5H_5CrB_9C_2H_{10}CH_3$

3101 w, 3016 w, 2601 w, 2594 m, 2576 m, 2541 s, 2521 s, 2493 m, 2484 s, 1836 w, 1758 w, 1658 w, 1422 m, 1382 w, 1206 w, 1154 w, 1114 w, 1076 w, 1059 w, 1010 s, 982 m, 842 w, 824 s, 774 w, 762 w, 694 w, 677 m, 660 m, 614 m

$C_5H_5CrB_9C_2H_9(CH_3)_2$

3111 m, 2966 w, 2928 w, 2856 w, 2610 m, 2580 s, 2536 s, 2508 s, 2493 s, 1842 w, 1766 w, 1666 w, 1426 m, 1390 m, 1306 w, 1266 w, 1208 w, 1171 w, 1156 w, 1136 w, 1081 w, 1014 s, 976 w, 943 w, 922 w, 898 w, 854 w, 840 w, 831 s, 766 w, 731 w, 686 w, 652 w

$C_5H_5CrBr_9C_2H_{10}C_6H_5$

3101 w, 3062 w, 3033 m, 2595 m, 2585 m, 2675 s, 2532 s, 2520 m, 2510 m, 2495 m, 2484 m, 1840 w, 1756 w, 1661 w, 1596 w, 1580 w, 1495 m, 1446 m, 1427 w, 1280 w, 1244 w, 1194 w, 1176 w, 1158 w, 1109 w, 1082 w, 1067 m, 1042 m, 1007 m, 1002 m, 985 m, 918 w, 875 w, 840 w, 824 s, 782 s, 758 w, 751 w, 736 w, 694 s, 672 w, 630 w

C_5H_5Cr-1,7-$B_9C_2H_{11}$

3100 m, 8009 w, 2561 s, 2519 m, 2502 m, 1839 w, 1756 w, 1656 w, 1424 m, 1356 w, 1266 w, 1227 w, 1205 w, 1159 w, 1103 w, 1055 m, 1013 m, 976 m, 921 w, 824 s, 763 w, 737 m, 696 m, 637 m

TABLE VI

ELECTRONIC SPECTRAL DATA FOR THE π-CYCLOPENTADIENYL-π-(3)-DICARBOLLYLCHROMIUM DERIVATIVES IN BENZENE SOLUTION

Compound	λ_{max}, mμ (ϵ, M^{-1} cm^{-1})
C_5H_5Cr-1,2-$B_9C_2H_{11}$[a]	283 (6240), 483 (260)
C_5H_5Cr-1,2-$B_9C_2H_{10}CH_3$	288 (6829), 497 (321)
C_5H_5Cr-1,2-$B_9C_2H_9(CH_3)_2$	293 (17,400), 373 (2100), 497 (380)
C_5H_5Cr-1,2-$B_9C_2H_{10}C_6H_5$	295 (7560), 382 (1647), 502 (388)
C_5H_5Cr-1,7-$B_9C_2H_{11}$	285 (12,500), 381 (1100), 426 (850)

[a] In acetonitrile solution.

(b) **Lithium Potassium (3)-1,7-Dicarbollide, LiK[(3)-1,7-$B_9C_2H_{11}$]**.—A 1.6 *M* solution of *n*-butyllithium in hexane (19.0 ml, 32.0 mmol) was slowly added to a stirring solution of 5.0 g (30.8 mmol) of K[(3)-1,7-$B_9C_2H_{12}$] in 100 ml of tetrahydrofuran. The reaction mixture was stirred at room temperature under nitrogen for 1 hr. The solution was used for subsequent reactions.

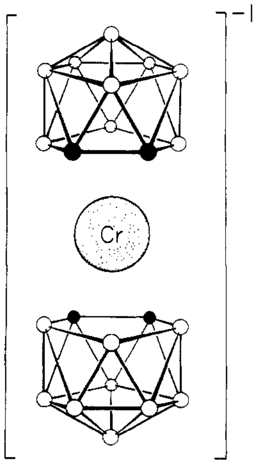

Figure 1.—Schematic drawing of the structure of the [(3)-1,2-$B_9C_2H_9(CH_3)_2]_2Cr^-$ ion: ○, BH; ●, C–CH_3.

Preparation of the Bis(π-(3)-dicarbollyl)chromium Derivatives. General Procedure.—Chromium trichloride was added as a solid under nitrogen to a stirring solution of the desired dicarbollide ion salt in tetrahydrofuran at room temperature. The resulting mixture was subsequently brought to reflux temperature and stirred for 3 hr. The solvent was removed *in vacuo*, the dark residue was dissolved in 200 ml of water, and the solution was filtered. The pink solids that precipitated upon addition of excess concentrated aqueous cesium chloride or tetramethylammonium chloride were purified following individual procedures described below. The general procedure described above was used in preparation of all the bis-π-(3)-$B_9C_2H_{11}$ derivatives.

(a) **Cs[(π-(3)-1,2-$B_9C_2H_{11})_2$Cr]**.—Chromium trichloride (2.06 g, 13.0 mmol) was added to a solution of Na_2[(3)-1,2-$B_9C_2H_{11}$] (25.9 mmol from 5.0 g of $(CH_3)_5NH$[(3)-1,2-$B_9C_2H_{11}$]) in 150 ml of THF. The cesium salt was precipitated, filtered, and washed with a small amount of ice water. Crystallization from water gave dark violet crysals of Cs[(π-(3)-1,2-$B_9C_2H_{11})_2$Cr] (3.98 g, 8.85 mmol, 68%); mol wt: calcd, 449.75; found, 440.

The molar magnetic susceptibility, measured on the solid using the Faraday technique,[7] with copper sulfate pentahydrate as the standard, gave a spin-only magnetic moment of 3.85 BM (corrected for diamagnetism using Pascal's constant) corresponding to three unpaired electrons.

(b) **$(CH_3)_4$N[(π-(3)-1,2-$B_9C_2H_{10}CH_3)_2$Cr]**.—To 17.8 mmol of Na_2[(3)-1,2-$B_9C_2H_{10}CH_3$] (from 3.7 g of $(CH_3)_3NH$[(3)-1,2-$B_9C_2H_{11}CH_3$] in 150 ml of THF was added 1.58 g (10.0 mmol) of $CrCl_3$. The tetramethylammonium salt was precipitated from aqueous solution. Crystallization from absolute ethanol gave dark violet crystals of $(CH_3)_4$N[(π-(3)-1,2-$B_9C_2H_{10}CH_3)_2$Cr] (0.785 g, 1.86 mmol, 21%).

(c) **$(CH_3)_4$N[(π-(3)-1,2-$B_9C_2H_9(CH_3)_2)_2$Cr]**.—To 41.6 mmol of Na_2[(3)-1,2-$B_9C_2H_9(CH_3)_2$] (from 9.2 g of $(CH_3)_3NH$[(3)-1,2-$B_9C_2H_{10}(CH_3)_2$) in 150 ml of THF was added 4.75 g (30.0 mmol) of $CrCl_3$. Precipitation with tetramethylammonium chloride and crystallization from acetonitrile–dichloromethane–hexane gave dark blue-violet crystals of $(CH_3)_4$N[(π-(3)-1,2-$B_9C_2H_9$-$(CH_3)_2)_2$Cr] (1.40 g, 3.14 mmol, 15%).

(d) **$(CH_3)_4$N[(π-(3)-1,2-$B_9C_2H_{10}C_6H_5)_2$Cr]**.—To 30.0 mmol of

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(7) B. N. Figgis and T. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 6.

$Na_2[(3)\text{-}1,2\text{-}B_9C_2H_{10}C_6H_5]$ (from 8.07 g of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{11}C_6H_5]$) in 150 ml of THF was added 3.17 g (20.0 mmol) of $CrCl_3$. Precipitation with tetramethylammonium chloride and crystallization from ethanol–acetone gave dark violet microcrystalline $(CH_3)_4N[(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}C_6H_5)_2Cr]$ (1.55 g, 2.85 mmol, 19%).

(e) $Cs[(\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11})_2Cr]$.—To 29.0 mmol of $KLi[(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ (from 5.0 g of $K[(3)\text{-}1,7\text{-}B_9C_2H_{12}]$) in 150 ml of THF was added 2.85 g (18.0 mmol) of $CrCl_3$. Precipitation with CsCl and crystallization from water gave brown plates of $Cs[(\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11})_2Cr]$ (2.08 g, 4.63 mmol, 32%). The analytical data and infrared and electronic spectra for the bis(π-(3)-dicarbollyl)chromium derivatives are given in Tables I–III.

Preparation of the π-Cyclopentadienyl-π-dicarbollylchromium Derivatives. General Procedure.—A tetrahydrofuran solution of freshly prepared cyclopentadiene and the desired dicarbadodecahydroundecaborate(-1) ion salt was treated with a slight excess of sodium hydride at reflux temperature for 3 hr as recently described.[1] Solid chromium trichloride was then added under nitrogen at room temperature to the resultng filtered $C_5H_5^-$ and dicarbollide ion solution.

After heating for 3 hr, the green solution was cooled and the solvent was removed *in vacuo*. The residue was dissolved in benzene and repeatedly filtered through a 10-cm column of chromatographic polyamide to retain $(\pi\text{-}C_5H_5)_2Cr^+$ and other charged products. Crystals were obtained by adding hexane to the resulting dark red solution and letting it stand overnight. This procedure was used in the preparation of all $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ derivatives.

(a) $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$.—Chromium trichloride (8.71 g, 55.0 mmol) was treated with the solution obtained by allowing 4.0 g (60.5 mmol) of C_5H_6 and 5.25 g (27.0 mmol) of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{12}]$ to react with 3.9 g (162.5 mmol) of NaH (7.0 g of a 56% suspension in mineral oil) in 200 ml of THF. Dark red crystals of $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ (1.55 g, 6.21 mmol, 23%) were obtained.

(b) $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}CH_3]$.—Chromium trichloride (5.55 g, 35.0 mmol) was treated with the solution obtained by allowing 2.64 g (40.0 mmol) of C_5H_6 and 5.19 g (25.0 mmol) of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{11}CH_3]$ to react with 3.36 g (140.0 mmol) of NaH (6.0 g of a 56% suspension) in 200 ml of THF. Dark red crystals of $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}CH_3]$ (2.11 g, 8.0 mmol, 32%) were obtained.

(c) $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_3)_2]$.—Chromium trichloride (7.15 g, 45.0 mmol) was treated with the solution obtained by allowing 3.31 g (50.0 mmol) of C_5H_6 and 6.63 g (30. 0 mmol) of $(CH_3)_3NH[(3)\text{-}1,2\text{-}B_9C_2H_{10}(CH_3)_2]$ to react with 3.9 g (162.5 mmol) of NaH (7.0 g of 56% suspension) in 200 ml of THF. Dark red crystals of $[\pi\text{-}C_5H_5]Cr[(3)\text{-}1,2\text{-}B_9C_2H_9(CH_3)_2]$ (1.67 g, 6.0 mmol, 20%) were obtained.

(d) $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}C_6H_5]$.—Chromium trichloride (6.35 g, 40.0 mmol) was added to the solution obtained by allowing 1.99 g (30.0 mmol) of C_5H_6 and 8.07 g (29.9 mmol) of $(CH_3)_3NH[(3\text{-})1,2\text{-}B_9C_2H_{11}C_6H_5]$ to react with 3.36 g (140.0 mmol) of NaH (6.0 g of a 56% suspension) in 200 ml of THF. Dark red crystals of $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{10}C_6H_5]$ (1.67 g, 5.13 mmol, 18%) were obtained.

(e) $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$.—To a solution of 5.0 g (29.0 mmol) of $K[(3)\text{-}1,7\text{-}B_9C_2H_{12}]$ and 3.4 g (51.4 mmol) of C_5H_6 in 150 ml of THF was added 50.0 ml (80 mmol) of a 15.2% hexane solution of *n*-butyllithium. After stirring for 30 min at reflux temperature, 6.35 g (40.0 mmol) of $CrCl_3$ was added and the solution was stirred for 3 hr. The reaction product was isolated as described above. Dark red crystals of $[\pi\text{-}C_5H_5]Cr[\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11}]$ (1.59 g, 6.37 mmol, 22%) were obtained. The analytical data and infrared and electronic spectra of the π-cyclopentadienyl-π-(3)-dicarbollylchromium derivatives are given in Tables IV–VI.

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Crystal Chemistry of the Rare Earth Sesquisulfides

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Rare earth sesquisulfides of La through Lu as well as Y have been prepared and characterized. The structures occurring for these compounds are now all known, and the cell dimensions are given, many for the first time. Three structure types are found. The A type exists from La through Dy, the D type from Dy through Tm, including Y, and the E type, for Yb and Lu. It is apparent that Pu_2S_3 may also have the A-type structure, and its cell dimensions have been refined by least squares. Although the Th_3P_4 structure (C type) may represent a fourth structure type, it is possible that sesquisulfides with this structure must be deficient in sulfur or impure. In order to help clarify the Th_3P_4 structure, a refinement of C-type Ce_2S_3 was undertaken using previously published data. Single crystals of most of the rare earth sesquisulfides have been prepared in a rare earth iodide melt. Electrical measurements on the single crystals generally showed semiconductor behavior as expected.

Introduction

The rare earth sesquisulfides have been investigated by Klemm, *et al.*,[1] and more recently by Flahaut and coworkers.[2,3] The characterization and structure determination of Sc_2S_3 have been reported by Dismukes and White.[4] Although some rare earth sesquiselenides and sesquitellurides have the Sc_2S_3 structure, no other sesquisulfides are known to have this structure. For the remaining rare earth sesquisulfides it has been proposed[2,3] that there are five commonly occurring structure types; however, until recently the structures

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