were made at 62° (134 mm) and 72–74° (32 mm), respectively The C,C′-dimethyl derivative of $B_7C_2H_9$ was isolated in two cuts, 80–94° (134 mm) and 70–72° (32 mm). The seventh cut (126–148°, 32 mm) was essentially pure diphenyl ether. The total weight of the fractions, excluding the diphenyl ether fraction, was 16.5 g including the material collected in the pump trap. Vapor phase chromatographic analysis gave the yield data shown in Table V. In addition, trace amounts of the C,C′-dimethyl derivative of $B_5C_2H_7$ were collected. The carboranes in those cuts which were mixtures were isolated by preparative vpc employing a preparative Apiezon L column at 130° and collecting the cuts at $-80°$ in U tubes fitted with stopcocks. Analytically pure samples were obtained by preparative vpc employing a preparative Apiezon L column and then a preparative Carbowax 20M column; the pure carboranes were transferred under high vacuum from the vpc collection U tube into another U tube containing a few grams of Fisher Scientific Co. molecular sieve type 4A to remove any moisture present.

Pyrolysis of 1,3-Dimethyl-1,3-dicarbanonaborane(13) in Diphenyl Ether in the Presence of Diborane. Diborane was prepared by standard literature methods.[25] The reaction vessel for the pyrolysis was a 500-ml, three-necked, round-bottom flask fitted with a mechanical stirrer, Dry Ice reflux condenser, diborane inlet extending into the flask, and a nitrogen inlet which also served as a diborane and hydrogen outlet. Into the flask were placed 26.5 g (0.182 mole) of 1,3-dimethyl-1,3-dicarbanonaborane(13) and 300 ml of diphenyl ether. The system was thoroughly flushed with nitrogen. The contents of the reaction vessel were then rapidly heated to 215 ± 10° for a period of 50 min. During this 50-min heating period, 1.5 moles of diborane, which was generated at the time, was added as evenly as possible. The excess diborane was passed through an acetone trap. As the reaction vessel cooled to room temperature, a slow stream of nitrogen was passed through the solution to remove the residual diborane. The solution was then transferred to a spinning-band distillation column, and the products were distilled under nitrogen. The first fraction was collected at 70–73.5° (32 mm) and was identified by vpc analysis as 99% pure C,C′-dimethyl derivative of 1,6-$B_8C_2H_{10}$. The yield was 11.2 g (41%). The second fraction collected was 2.4 g (8%) of 1,7-dimethyl-1,7-dicarbaclovododecaborane(12).[7]

Preparation of the C,C′-Dimethyl Derivative of 1,10-$B_8C_2H_{10}$. In a thick-walled tube was placed 2.2 g of the pure C,C′-dimethyl derivative of 1,6-$B_8C_2H_{10}$. The tube was sealed off under vacuum and placed in a bomb to which diphenyl ether had been added for pressure equalization. The bomb was heated at 350 ± 5° for 12 hr. After cooling, the tube was opened and its contents distilled into a weighing tube attached to a high-vacuum line. No hydrogen pressure was observed when the tube was opened. The yield of 1,10-$B_8C_2H_{10}$ derivative was 2.1 g (95%). An analytically pure sample (mp 26.5–27.5°) was obtained by preparative vpc. The sample was first passed through a preparative Apiezon L column at 172° and then through a preparative Carbowax 20M column at 170°. The product was collected at $-80°$ in a U tube fitted with a stopcock and was transferred under high vacuum into another U tube containing a few grams of molecular sieve to remove moisture.

Reaction of the C,C′-Dimethyl Derivative of 1,6-$B_8C_2H_{10}$ with Diborane. The apparatus employed here was the same as that described above in the reaction of 1,3-dimethyl-1,3-dicarbanonaborane(13) with diborane. Into the reaction vessel was placed 5.0 g (0.0338 mole) of the C,C′-dimethyl derivative of 1,6-$B_8C_2H_{10}$ and 150 ml of diphenyl ether. The solution was heated to 225 ± 5° under a nitrogen atmosphere. With stirring, 1.5 moles of diborane was then added over 1.5 hr, maintaining the temperature at 225°. After cooling, the solution was transferred to a spinning-band distillation column and distilled under reduced pressure. The products are described in Table V.

Acknowledgment. This research was generously supported by the National Cancer Institute, U. S. Public Health Service, under Grant No. CA 06773, and the Army Research Office (Durham). The authors express their thanks for this support. We also wish to acknowledge the assistance of Messrs. James C. Smart and David A. Owen for certain experimental assistance.

---

(25) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

π-Dicarbollyl Derivatives of the Transition Metals. Metallocene Analogs

M. Frederick Hawthorne, Donald C. Young, Timothy D. Andrews, David V. Howe,[1a] Richard L. Pilling, A. Denise Pitts, Marten Reintjes, Leslie F. Warren, Jr.,[1b] and Patrick A. Wegner

Contribution from the Department of Chemistry, The University of California, Riverside, California. *Received August 18, 1967*

Abstract: The (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$ ions are converted to the "dicarbollide" ions, (3)-1,2-$B_9C_2H_{11}^{-2}$ and (3)-1,7-$B_9C_2H_{11}^{-2}$, when treated with bases. The dicarbollide ions serve as ligands in the formation of transition metal complexes which often resemble the well-known metallocenes. The preparation, characterization, reactions, and structures of these complexes are discussed.

The relatively young areas of boron hydride and carborane chemistry and the much older area of transition metal coordination chemistry have become established, in their own right, as nearly sacrosanct subdisciplines of inorganic chemistry. However, a point of separate development was reached which allowed the fusion of these two quite different fields of endeavor and the appearance of the chemistry described in this paper and, in part, in preliminary communications.[2–6] The striking similarity of this new chemistry to that of the

---

(1) (a) National Science Foundation Trainee, 1965–1968; (b) National Institutes of Health Predoctoral Fellow, 1967–1968.

(2) (a) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965). (b) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

(3) M. F. Hawthorne and R. L. Pilling, *J. Am. Chem. Soc.*, **87**, 3987 (1965).

(4) M. F. Hawthorne and T. D. Andrews, *ibid.*, **87**, 2496 (1965).

(5) P. A. Wegner and M. F. Hawthorne, *Chem. Commun.*, 861 (1966).

(6) L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, **89**, 470 (1967).

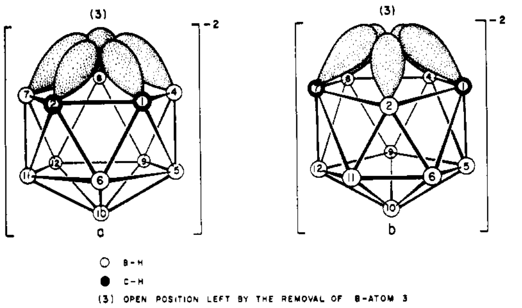

Figure 1. Schematic drawings of (a) the (3)-1,2- and (b) the (3)-1,7-$B_9C_2H_{11}^{-2}$ ions showing approximately sp^3 orbitals directed at vacant 3-vertex.

well-known metallocenes suggests many new problems in synthesis and chemical bonding, and we here present a compilation of the more significant results thus far obtained.

The (3)-1,2- and (3)-1,7-Dicarbollide Ions

Preparation. The isomeric (3)-1,2- and (3)-1,7-$B_9C_2H_{12}^-$ ions[7-9] contain one hydrogen atom in excess over those required to form terminal B–H and C–H bonds. It was therefore reasonable to expect that they might be deprotonated to form two isomeric $B_9C_2H_{11}^{-2}$ ions. The resulting (3)-1,2- and (3)-1,7-

$$B_9C_2H_{12}^- + \text{base} \rightleftharpoons B_9C_2H_{11}^{2-} + \text{H base}^+$$

$B_9C_2H_{11}^{-2}$ ions would be isoelectronic with the unknown $B_{11}H_{11}^{-4}$ ion.

Treatment of the (3)-1,2-$B_9C_2H_{12}^-$ ion with sodium hydride in tetrahydrofuran leads to the production of hydrogen and the desired (3)-1,2-$B_9C_2H_{11}^{-2}$ ion.[2a] In one instance, the disodium salt of (3)-1,2-$B_9C_2H_{11}^{-2}$

$$\text{(3)-1,2-}B_9C_2H_{12}^- + NaH \longrightarrow Na^+ + \text{(3)-1,2-}B_9C_2H_{11}^{-2} + H_2$$

was isolated and treated with water to produce authentic (3)-1,2-$B_9C_2H_{12}^-$ and hydroxide ion. Titration of the

$$\text{(3)-1,2-}B_9C_2H_{11}^{-2} + H_2O \rightleftharpoons \text{(3)-1,2-}B_9C_2H_{12}^- + OH^-$$

hydroxide ion produced by hydrolysis gave an equivalent weight value of 178 for the disodium salt (theory 178.5). More recent work[6] has shown that a very concentrated solution of alkali metal hydroxide apparently produces a low concentration of the (3)-1,2-$B_9C_2H_{11}^{-2}$ ion in aqueous solution, and this method has been employed in certain instances for the preparation of transition metal complexes in aqueous media. The reactions described above are observed with all carbon-substituted (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$ ions. The cesium, tetramethylammonium, potassium, and trimethylammonium salts of the monoanions gave equivalent results. The easily purified trimethylammonium salts[9] were the most convenient for routine laboratory preparations when employed in tetrahydrofuran with 2 moles of sodium hydride. The volatile trimethylamine was removed from the dianion solution by distillation.

$$(CH_3)_3NHB_9C_2H_{12} + 2NaH \longrightarrow Na_2B_9C_2H_{11} + (CH_3)_3N + 2H_2$$

Structure and Bonding. As will be shown by several crystallographic studies described within this paper, the structures of the coordinated (3)-1,2- and (3)-1,7-$B_9C_2H_{11}^{-2}$ ion may be represented by the schematic drawing in Figure 1 and consist of 11-particle icosahedral fragments composed of 9 BH and 2 CH units. In the (3)-1,2-$B_9C_2H_{11}^{-2}$ ion, the carbon atoms are nearest neighbors in the open pentagonal face while in the case of the (3)-1,7-$B_9C_2H_{11}^{-2}$ ion, the carbon atoms are assumed[8,9] to be separated by a single boron atom.

Moore, Lohr, and Lipscomb[10] have discussed the bonding present in a hypothetical $B_{11}H_{11}^{-2}$ ion having C_{5v} symmetry. The addition of two electrons to that ion leads to the formation of the hypothetical $B_{11}H_{11}^{-4}$ ion which is isoelectronic with both isomeric $B_9C_2H_{11}^{-2}$ ions. The molecular orbital scheme used to describe the hypothetical $B_{11}H_{11}^{-2}$ ion[10] is equally applicable to the $B_{11}H_{11}^{-4}$ ion. This description places 6 electrons in the pentagonal pyramid in the apical region of the $B_{11}H_{11}^{-4}$ ion, 14 electrons between the two five-membered rings of boron atoms, and 6 electrons in five sp^3 orbitals directed toward the vacant apex position associated with the open pentagonal face. In the $B_{11}H_{11}^{-4}$ ion, the five atomic orbitals present in the open pentagonal face may be used to generate three bonding and two antibonding molecular orbitals. These would include a strongly bonding a_1 orbital, two degenerate and bonding e_1 orbitals, and two strongly antibonding e_2 orbitals. The six electrons would occupy the a_1 and the two e_1 orbitals. In the case of the two isomeric $B_9C_2H_{11}^{-2}$ ions, the exact orbital degeneracy of the two e_1 and two e_2 orbitals would be removed. However, the removal of orbital degeneracy would not change the gross orbital energy or symmetry scheme, and one would expect the $B_9C_2H_{11}^{-2}$ ions to resemble the well-known $C_5H_5^-$ ion in its reactions with transition metal ions.[11] These reactions have been observed[2-6] and are described in the following sections of this paper.

Nomenclature. The nomenclature associated with the transition metal complexes of the isomeric $B_9C_2H_{11}^{-2}$ ions and their carbon-substituted derivatives poses a formidable problem for two reasons. (1) No formally accepted nomenclature system exists for polyhedral borane species, and (2) the *ad hoc* system in use is much too cumbersome for convenient verbal or written communication. We have therefore devised a specific nomenclature system for the hypothetical $B_{11}H_{11}^{-4}$ ion, the recently discovered $B_{10}CH_{11}^{-3}$ ion,[12,13] and the isomeric $B_9C_2H_{11}^{-2}$ ions under discussion. The Spanish noun "olla" describes a water jar which resembles the 11-particle icosahedral fragment. We therefore have named the $B_{11}H_{11}^{-4}$ ion the "ollide ion."[3] The $B_{10}CH_{11}^{-3}$ ion and the $B_9C_2H_{11}^{-2}$ ions therefore become the "carbollide" and "dicarbollide"[3] ions, respectively. The positions of the carbon atoms and substituents may be denoted by removing a boron atom from the icosaheron and numbering all other positions in accordance with the rules set forth by Adams.[14] The position of the vacant icosahedral vertex is denoted by a prefix numeral in parentheses. Thus, the two known $B_9C_2H_{11}^{-2}$ ions become (3)-1,2- and (3)-1,7-dicarbollide ions.[15]

---

[7] R. A. Wiesboeck and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 1642 (1964).

[8] P. M. Garrett, F. N. Tebbe, and M. F. Hawthorne, *ibid.*, **86**, 5016 (1964).

[9] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *ibid.*, **90**, 862 (1968).

[10] E. B. Moore, L. L. Lohr, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

[11] J. M. Birmingham, *Advan. Organometal. Chem.*, **2**, 365 (1964).

[12] D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *J. Am. Chem. Soc.*, **89**, 3342 (1967).

[13] W. H. Knoth, *ibid.*, **89**, 3343 (1967).

[14] R. M. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

Table I. Elemental Analyses, Molecular Weights, Equivalent Weights, and Yields of π-(3)-1,2-Dicarbollyliron(III) Derivatives

Compound		% B	% C	% H	% N	% Fe	Mol wt[a]	Equiv wt[b]	Yield, %
$(CH_3)_4N[(B_9C_2H_{11})_2Fe]$	Calcd	49.32	24.31	8.68	3.55	14.14	394.9	394.9	61,[c] 56[d]
	Found	49.00	24.56	8.73	3.65	14.39	402.0	406.0	
$(CH_3)_4N[(B_9C_2H_9(CH_3)_2)_2Fe]$	Calcd	43.19	31.93	9.39	3.11	12.38	450.9	450.9	78[c]
	Found	43.49	32.23	9.64	3.47	12.70	468.0	444.0	
$(CH_3)_4N[(B_9C_2H_{10}(C_6H_5))_2Fe]$	Calcd	35.61	43.88	7.74	2.56	10.21	546.9	605.7[e]	68[c]
	Found	35.42	44.21	7.89	2.69	10.50	572.0	624.0[e]	
$(C_5H_5)Fe(B_9C_2H_{11})$	Calcd	38.42	33.18	6.50		22.04			25[c]
	Found	37.64	30.59	6.36		21.63			

[a] Determined by osmometry with acetone as solvent. [b] Determined by titrating the hydronium salts with standard base. [c] Using non-aqueous preparation. [d] Using aqueous preparation. [e] Determined on cesium salt.

Their transition metal complexes would then be named as the appropriately numbered "dicarbollyl" complexes by analogy with the cyclopentadienyl complexes.

π-(3)-1,2-Dicarbollyliron Derivatives. The expected similarity of the cyclopentadienide and the (3)-1,2-dicarbollide ions led to the initial study of iron complexes of the (3)-1,2-dicarbollide ion and its carbon-substituted derivatives.[2a,3] Three dianion systems were employed in this study, and bis-(3)-1,2-dicarbollyl, bis-1-phenyl-(3)-1,2-dicarbollyl, and bis-1,2-dimethyl-(3)-1,2-dicarbollyl complexes of iron(II) and iron(III) were obtained. In addition, mixed π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron complexes were prepared which contained iron(II) and iron(III). X-Ray crystallographic studies (*vide infra*) coupled with ^{11}B nmr spectra confirmed sandwich bonding in all of these derivatives, and they are designated as π-bonded derivatives in accordance with these observations.

Preparation and Characterization of Bis-π-(3)-1,2-dicarbollyliron Derivatives Containing Formal Iron(III). When the unsubstituted (3)-1,2-dicarbollide ion was allowed to react with anhydrous ferrous chloride in tetrahydrofuran[2a] under nitrogen and with the rigid exclusion of oxygen, a brownish purple color resulted. In analogous reactions, the 1,2-dimethyl- and the 1-phenyl-(3)-1,2-dicarbollide ions gave blue solutions. These reactions proceed according to the equation

$$2[(3)\text{-}1,2\text{-}B_9C_2H_{11}]^{-2} + FeCl_2 \longrightarrow [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Fe^{-2} + 2Cl^-$$

Upon exposure to oxygen, the color of the solutions changed from brownish purple to brownish red in the case of the bis-unsubstituted derivative, and from blue to burgundy red in the case of the bis-1,2-dimethyl and the bis-1-phenyl derivatives. This color change, which indicated the oxidation of the iron(II) complex to the corresponding iron(III) complex, was rapid under the reaction conditions. If oxygen was not rigidly excluded, the initially formed color of the reduced species was observed fleetingly, if at all. After oxidation, the iron(III) derivatives were isolated from water as their tetramethylammonium salts. The yields for the iron(III) complexes ranged from 60 to 80%. These ferric complexes could not be prepared directly from ferric chloride but were only obtained by oxidation of the ferrous complexes. The preparation of the bis-unsubstituted iron complex was also accomplished in aqueous media[6] in 56% yield. The attempted preparation of the carbon-substituted derivatives by this means was unsuccessful.

The elemental analyses of the bis-unsubstituted, bis-1,2-dimethyl, and bis-1-phenyl derivatives as tetramethylammonium salts are given in Table I. The equivalent and formula weights for all three derivatives are also given in Table I. The molecular weights were determined by conventional osmometry using acetonitrile as the solvent. The equivalent weight data were obtained using hydronium ion salts of the complexes which were obtained by ion exchange of analytical samples of the tetramethylammonium salts. The hydronium ion salts, in all cases, behaved as strong acids, and the molecular weight results precluded the possibility of dimerized products, and the equivalent weight results confirmed the charge of −1 for these complexes.

All three derivatives of the iron(III) complex, analogs of the ferricenium ion,[16] were stable toward strong acid and thermally stable up to 300°. The bis-1,2-dimethyl complex as its tetramethylammonium salt melted at 247–249°, while the same salts of the bis-1-phenyl and bis-unsubstituted derivatives do not melt below 300°. The iron(III) complexes produced their respective iron(II) complexes upon treatment with sodium amalgam in acetone or acetonitrile. The corresponding iron(III) complexes were regenerated when oxygen was admitted to the reaction mixture.

The infrared spectra of the tetramethylammonium salts of the three iron(III) derivatives are presented in Table II. The large number of atoms and the lack of symmetry of these salts precluded a detailed analysis of the infrared spectra. The bis-1-phenyl and the bis-unsubstituted derivatives exhibited a carborane C–H stretching absorption near 3000 cm^{-1}, and the former derivative exhibited phenyl absorption bands at 1610 cm^{-1}.

Although the three derivatives of the iron(III) complex were stable toward strong mineral acid, the bis-1,2-dimethyl and the bis-1-phenyl complexes were completely degraded by base. The potassium salts of the three complexes were each subjected to aqueous potassium hydroxide at the reflux temperature. Within 1–2 hr, the color due to the bis-1,2-dimethyl and the bis-1-phenyl complexes was discharged. The color of the bis-unsubstituted complex was not discharged over a 4-day period and, based upon visible spectrophotometric data, 100% of the initial complex remained unchanged. The degradation of the bis-1,2-dimethyl and

---

(15) In a previous communication[3] we have denoted these ions as the (1)-2,3- and (1)-2,4-dicarbollide ions. We have arbitrarily altered this procedure in order to accommodate the smallest numerals as carbon atom positions.

(16) See M. Rosenblum, "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene," Part I, Interscience Publishers, Inc., New York, N. Y., 1965, for a collection of pertinent references and discussion.

Table II. Infrared Spectral Data (cm^{-1}) for the π-(3)-1,2-Dicarbollyliron(III) Derivatives (Nujol Mulls)

$(CH_3)_4N[(B_9C_2H_{11})_2Fe]$	2552 (s), 1205 (w), 1142 (w), 1100 (w), 1095 (m), 1068 (w), 1018 (m), 995 (w), 977 (s), 946 (s), 918 (w), 748 (w), 645 (w)
$(CH_3)_4N[(B_9C_2H_9(CH_3)_2)_2Fe]$	2500 (s), 1275 (w), 1080 (m), 1010 (s), 948 (s), 917 (w), 870 (w), 767 (m), 745 (m)
$(CH_3)_4N[(B_9C_2H_{10}(C_6H_5))_2Fe]$	2490 (s), 1580 (w), 1280 (w), 1230 (w), 1170 (m), 1075 (m), 1040 (m), 995 (s), 945 (s), 880 (w), 780 (m), 698 (s)
$(C_5H_5)Fe(B_9C_2H_{11})$	2503 (s), 2348 (w), 1512 (w), 1508 (w), 1503 (w), 1206 (m), 1142 (w), 1096 (s), 1013 (s), 975 (m), 842 (s), 740 (w)

the bis-1-phenyl complexes most likely proceeded according to the following equation since the (3)-1,2-$B_9C_2H_{10}(CH_3)_2^-$ and the (3)-1,2-$B_9C_2H_{11}(C_6H_5)^-$ ions

$$2[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_3)_2]_2Fe^- + 2OH^- + 4H_2O \longrightarrow 4[(3)\text{-}1,2\text{-}B_9C_2H_{10}(CH_3)_2]^- + 2Fe(OH)_3$$

were isolated in nearly quantitative yields as their tetramethylammonium salts and identified by comparison of their infrared spectra and melting points with authentic samples. Iron hydroxide released by hydrolysis was also obtained in quantitative yield. The preparation of the bis-unsubstituted iron complex in 40% aqueous base and the failure of the 1,2-dimethyl and 1-phenyl derivatives to form under similar conditions qualitatively support these degradation experiments.

The ultraviolet and visible spectral data of the iron(III) derivatives (as the tetramethylammonium salts in acetonitrile) are given in Table III and have not yet been rigorously analyzed.

Table III. Electronic Spectral Data for the π-(3)-1,2-Dicarbollyliron(III) Derivatives in Acetonitrile Solution

λ_{max}, mμ (ϵ)			
$(CH_3)_4N$-$[(B_9C_2H_{11})_2$-Fe]	$(CH_3)_4N$-$[(B_9C_2H_9$-$(CH_3)_2)_2$-Fe]	$(CH_3)_4N$-$[(B_9C_2H_{10}$-$(C_6H_5))_2$-Fe]	$(C_5H_5)Fe$-$(B_9C_2H_{11})$
272 (21,200)	220 (7900)	225 (24,900)	205 (9640)
296 (18,000)	296 (16,380)	282 (17,710)	258 (17,400)
444 (585)	327 (15,900)	314 (13,800)	285 (6420)^a
520 (400)^a	460 (621)	488 (827)	504 (270)^a
	525 (558)	564 (596)^a	570 (296)

[a] Shoulder.

Preparation and Characterization of Bis-π-(3)-1,2-dicarbollyliron Derivatives Containing Formal Iron(II). Direct isolation of the iron(II) complexes from the original reaction solution was difficult because oxidation to the iron(III) complex, due to trace amounts of oxygen, was rapid under the reaction conditions since trace amounts of ferric ion catalyzed the oxidation. The preferred method for isolation of the reduced complexes entailed the reaction of the iron(III) complex with sodium amalgam in acetonitrile or acetone solution in an inert atmosphere followed by the addition of aqueous tetramethylammonium chloride solution. The bis-tetramethylammonium salts of the three iron(II) derivatives were recrystallized in the absence of oxygen. The bis-1,2-dimethyl- and bis-1-phenyliron(II) complexes were lavender blue while the bis-unsubstituted derivative was pink. Oxidation of these complexes to their respective iron(III) complexes by air was slow in the solid state. In solution, the oxidation was moderately fast, and the addition of a small amount of ferric ion greatly accelerated the oxidation. The reduced complexes have the same high thermal stability as the oxidized complexes. As tetramethylammonium salts, the iron(II) complexes are moderately soluble in acetonitrile and acetone and are insoluble in water.

Polarographic measurements in 50:50 acetone–water were carried out with the tetramethylammonium salts of the three iron(III) complexes. A single-wave reduction polarogram was obtained in each case. The polarographic data (Table IV) indicate that a reversible one-electron reduction has occurred. The values of $E_{1/2}$ reported in Table IV indicate the following series of relative $E°$ values: bis-1,2-dimethyl > bis-1-phenyl > bis-unsubstituted. The formulation of the reduced species as formal iron(II) derivatives is indicated.

Table IV. Reduction Potentials for the π-(3)-1,2-Dicarbollyliron(III) Derivatives

Compound	Method	$E_{1/2}$ *vs.* sce^c
$(CH_3)_4N[(B_9C_2H_{11})_2Fe]$	Polarography^a	−0.424
$(CH_3)_4N[(B_9C_2H_9(CH_3)_2)_2Fe]$	Polarography^a	−0.538
$(CH_3)_4N[(B_9C_2H_{10}(C_6H_5))_2Fe]$	Polarography^a	−0.464
$(C_5H_5)Fe(B_9C_2H_{11})$	Cyclic voltammetry^b	−0.08

[a] In 50% aqueous acetone, 0.1 *N* $LiClO_4$ supporting electrolyte, with a dropping mercury electrode. [b] In acetonitrile solution, 0.1 *N* $(C_2H_5)_4NClO_4$ supporting electrolyte; reversible half-peak reduction potential reported. [c] For $M^{III} + e^- \rightarrow M^{II}$.

If the reduced species are formal iron(II) complexes, the iron atom would, in each case, have a d^6 electronic configuration and, like ferrocene, the complex would be diamagnetic. The observation of normal proton nuclear magnetic resonance spectra for all three derivatives of the reduced complex supports the d^6 diamagnetic formulation for these complexes. The ^1H nmr spectra of the three iron(II) complexes are presented in Table V. Because of the low solubility of the tetramethylammonium salt of the bis-1-phenyliron(II) complex in deuterioacetonitrile, the carborane C–H resonance was not observed. All other expected resonances in the bis-1-phenyl, bis-unsubstituted, and bis-1,2-dimethyl complexes were observed. The integral ratios observed in the ^1H nmr spectra were in agreement with the formulation of the reduced complex as a dinegative anion containing two (3)-1,2-dicarbollide ions per iron atom in the formal +2 oxidation state.

The 19.3-Mc/sec ^{11}B nmr spectra for the three iron(II) complexes were obtained and found to have a breadth of approximately 30 ppm and to consist of a series of unresolved doublets which arise from boron–hydrogen spin–spin coupling. Because of the poor resolution seen in these spectra, they presented no definitive structural data. In qualitative terms, the envelopes of these spectra resembled those observed with the correspond-

Table V. ^{1}H Nmr Data for the π-(3)-1,2-Dicarbollyliron(II) Derivatives[a]

Compound	Resonance,[b] ppm (rel area)	Assignment
$[(CH_3)_4N]_2(B_9C_2H_{11})_2Fe$	Broad singlet, −3.48 (1.0)	Carborane C–H
	Sharp singlet, −3.17 (6.1)	Methyl protons of cation
$[(CH_3)_4N]_2[B_9C_2H_9(CH_3)_2]_2Fe$	Singlet, −3.18 (2.0)	Methyl protons of cation
	Singlet, −2.66 (1.0)	Carborane methyl protons
$[(CH_3)_4N]_2[B_9C_2H_{10}(C_6H_5)]_2Fe$[c]	Multiplet, −6.85 (1.0)	Carborane phenyl protons
	Sharp singlet, −3.18 (2.5)	Methyl protons of cation
$(CH_3)_4N[(C_5H_5)Fe(B_9C_2H_{11})]$	Sharp singlet, −4.37 (5.0)	Cyclopentadienyl protons
	Broad singlet, −3.58 (2.0)	Carborane C–H
	Sharp singlet, −3.09 (12.0)	Methyl protons of cation

[a] Determined in deuterioacetonitrile. [b] Relative to tetramethylsilane. [c] Carborane C–H resonance not observed.

ingly carbon-substituted $B_9C_2H_{12}^-$ ions. The ^{11}B nmr spectra of the paramagnetic iron(III) derivatives will be presented below.

The electronic spectra of the three iron(II) derivatives are presented in Table VI without interpretation.

Table VI. Electronic Spectral Data for the π-(3)-1,2-Dicarbollyliron(II) Derivatives in Acetonitrile Solution

λ_{max}, mμ (ϵ)			
$[(CH_3)_4N]_2$-$(B_9C_2H_{11})_2$-Fe	$[(CH_3)_4N]_2$-$[B_9C_2H_9$-$(CH_3)_2]_2$-Fe	$[(CH_3)_4N]_2$-$[B_9C_2H_{10}$-$(C_6H_5)]_2$-Fe	$(CH_3)_4N$-$[(C_5H_5)Fe$-$(B_9C_2H_{11})]$
229 (28,100)	207 (16,800)	290 (7860)	213 (30,600)
273 (12,600)	234 (11,600)	325 (3390)	358 (268)
304 (5210)	258 (19,500)	360 (2420)	475 (219)
380 (91)	294 (6500)	557 (150)	
504 (192)	327 (3610)		
	408 (73)		
	561 (128)		

π-Cyclopentadienyl-π-(3)-1,2-dicarbollyliron Complexes. The successful preparation of bis-π-(3)-1,2-dicarbollyliron(II) and -iron(III) derivatives described above suggested that a mixed iron system might be prepared in which a π-cyclopentadienyl group replaced one of the π-(3)-1,2-dicarbollyl ligands. Accordingly, the reaction of an equimolar mixture of sodium cyclopentadienide and disodium (3)-1,2-dicarbollide with ferrous chloride was carried out.[3] The products of

$$C_5H_5^- + (3)\text{-}1,2\text{-}B_9C_2H_{11}^{-2} + FeCl_2 \longrightarrow (\pi\text{-}C_5H_5)Fe[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]^- + 2Cl^-$$

this reaction were identified as ferrocene (42%), bis-π-(3)-1,2-dicarbollyliron(III) (12%), and the desired π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) (25%). Reduction of the latter material with sodium amalgam produced the $(\pi\text{-}C_5H_5)Fe[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]^-$ ion which contained iron in the formal +2 oxidation state. Table I presents the relevant characterization data.

The ^{1}H nmr spectrum of the iron(III) complex could not be obtained due to its paramagnetic character. The iron(II) complex, as its tetramethylammonium salt, exhibited three resonances in its ^{1}H nmr spectrum: a broad carborane C–H of intensity 2 at −3.58 ppm, a sharp singlet of intensity 12 at −3.09 ppm which was assigned to the methyl protons of the tetramethylammonium cation, and sharp singlet of intensity 5 at −4.37 ppm which was assigned to the five equivalent protons of the rapidly rotating π-C_5H_5 group. In comparison, ferrocene exhibits a sharp singlet at −4.17 ppm. These results are summarized in Table V.

The ^{11}B nmr spectrum of the iron(II) anion was uninformative and resembled the ^{11}B nmr spectrum of the bis-π-(3)-1,2-dicarbollyliron(II) dianion. The ^{11}B nmr spectrum of the paramagnetic iron(III) complex is presented below.

Table II presents the infrared spectrum of the π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) complex. Table III contains the electronic spectrum of the iron(III) complex, and Table VI contains the corresponding data for the iron(II) complex. Polarographic data associated with the interconversion of the mixed iron(II) and iron(III) complexes are presented in Table IV.

Paramagnetic Phenomena, Structure, and Bonding. Zalkin, Templeton, and Hopkins[17] have carried out a single-crystal X-ray diffraction study of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) which confirmed sandwich bonding in this complex. The determined structure is reproduced in Figure 2. The distances between iron and the atoms of the pentagonal face of the dicarbollide ion are approximately 2.07 Å, and the cyclopentadienyl ring carbon atoms are also 2.07 Å from iron.

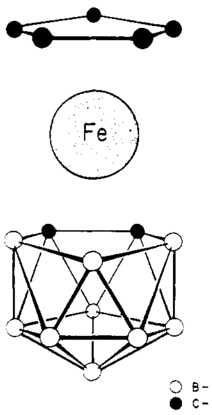

Figure 2. Schematic drawing of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III).

Maki and Berry[18] have carried out an electron spin resonance study of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) as well as the unsubstituted and two carbon-substituted bis-π-(3)-1,2-dicarbollyliron(III) derivatives described above. In each case a single unpaired electron was observed, and the data were best

---

[17] A. Zalkin, D. H. Templeton, and T. E. Hopkins, *J. Am. Chem. Soc.*, **87**, 3988 (1965).

[18] A. H. Maki and T. E. Berry, *ibid.*, **87**, 4437 (1965).

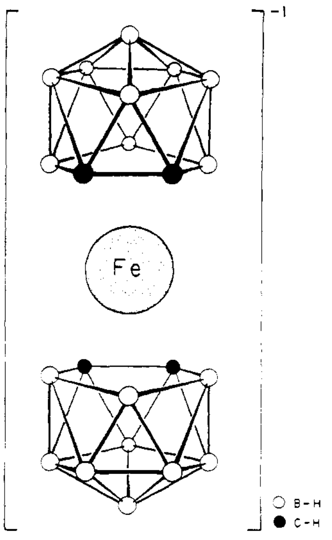

Figure 3. Proposed structure of the bis-π-(3)-1,2-dicarbollyliron(III) ion in schematic form.

described by Moffit's ferrocene model with the unpaired electron in an $e_{2g}^{\pm}$ molecular orbital.[19] The great similarity of the bis-π-(3)-1,2-dicarbollyliron(III) ion and the structurally characterized π-cyclopentadienyl-(3)-1,2-dicarbollyliron(III) species[17] strongly suggested that the former derivative is sandwich bonded (Figure 3) as in the case of the mixed ligand species of known structure. An as yet unreported X-ray diffraction study of the bis-π-(3)-1,7-dicarbollyl cobalt(III) complex and a hexabromobis-π-(3)-1,2-dicarbollylcobalt(III) complex (*vide infra*) further supports this conclusion as do the ^{11}B nmr data presented below.

Figure 4 presents the ^{11}B nmr spectra of the paramagnetic iron(III)species discussed above. These spectra represent the first observation[3] of paramagnetic contact and psuedo-contact shifts using ^{11}B as the excited nucleus. In addition, these spectra contained no evidence of spin-spin coupling of the ^{11}B nuclei with the proton to which they are bonded.[20] The individual resonances in the ^{11}B nmr spectra of the paramagnetic complexes (Figure 4) are much broader than normally observed ^{11}B resonances; however, since they exhibit very large chemical shifts and are singlets, these spectra provide much valuable structural information. If the bis-π-(3)-1,2-dicarbollyliron(III) complexes indeed have the "sandwich" structure shown in Figure 3, the two dicarbollide ion ligands would have identical resonances and would yield ^{11}B nmr spectra containing the integral ratios 1:1:1:2:2:2:2. An identical situation exists in the case of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III).

The lowest field resonance of the four derivatives, a, is separated from the multiplet resonances, b and c, and has an integral ratio of 1. The second highest field resonance, d, has an integral raio of 1.1–1.4 when compared with the lowest peak, a. The unresolved resonances, b and c, have an integral ratio of about 4.4–4.7 as compared with a. For the symmetrically substituted derivatives (unsubstituted and 1,2-dimethyl), a broad, highest field resonance of weight 2, e, is observed. The 1-phenyl derivative has a similar high-field resonance of weight 2 but it is split into two resonances by unsymmetrical substitution at carbon.

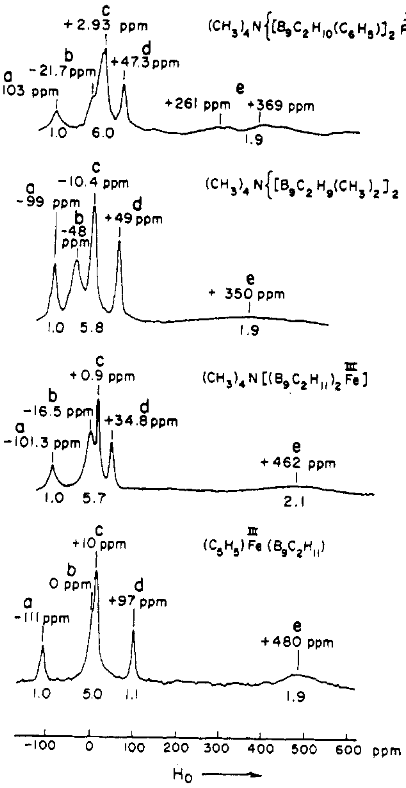

Figure 4. Boron-11 nmr spectra (19.3 Mc/sec) of iron(III) dicarbollyl derivatives. Chemical shifts were measured relative to $BF_3 \cdot O(C_2H_5)_2 = 0$.

Since the high-field resonances, e, of weight 2 are greatly affected by the unpaired electron on the iron, they may be assigned to the two borons bonded to carbon in the open face of the (3)-1,2-dicarbollide ion. The resonances a, b, c, and d have not been assigned.

The other two expected resonances of weight 2 are probably peaks b and c, although their combined integral ratio is greater than 4.0. Of the three expected resonances of weight 1, one is clearly at low field, a; another is most likely peak d which has an integral ratio only slightly greater than 1. Five of the six expected resonances are thus easily observed. The remaining resonance of weight 1 is not obvious. This resonance, based upon the integration ratios, must lie under the multiple resonances in the center of the spectrum and be quite broad. Because this resonance is greatly affected by the unpaired electron, it was assigned to the unique boron in the pentagonal face of the (3)-1,2-dicarbollide ion which is not bonded to carbon.

The unique nature of the reported ^{11}B nmr spectra virtually proves the existence of sandwich bonding in the bis-(3)-1,2-dicarbollyliron(III) derivatives since the spectra of these ions are quantitatively identical with that of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron(III) of known[17] sandwich structure. In addition, the simplicity of the observed spectra strongly suggests that the (3)-1,2-dicarbollide ion ligands of the bis-π-(3)-1,2-dicarbollyliron(III) complexes are equivalent and in rapid

---

[19] In this treatment, the reduced symmetry of the dicarbollide ion ligand brought about by the presence of two carbon atoms and three boron atoms in the face of the ligand was treated by introducing an effective crystal-field Hamiltonian of lower than fivefold symmetry.

[20] W. N. Lipscomb and A. Kaczmarczyk, *Proc. Natl. Acad. Sci. U. S.*, **47**, 1796 (1961), have observed the loss of ^{11}B–H spin coupling in certain instances in which Fe(III) was added to the solution of the boron hydride derivative under examination.

Table VII. Elemental Analyses, Equivalent Weight Data, and Yields of π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt(III) Derivatives

Compound		% B	% C	% H	% Co	%, other	Equiv wt[a]	Yield, %
$\mathrm{Cs[(1,2\text{-}B_9C_2H_{11})_2Co]}$	Calcd	42.63	10.52	4.85	12.90	Cs, 29.10	456.82	72,[c] 79[d]
	Found	42.40	10.58	5.09	13.00	Cs, 29.28	459	
$\mathrm{(CH_3)_4N[(1,2\text{-}B_9C_2H_8Br_3)_2Co]}$	Calcd	22.35	11.02	3.24		Br, 55.02	871.3	77[c]
	Found	22.37	11.19	3.13		Br, 55.00	805[b]	
$\mathrm{(CH_3)_4N[(1,2\text{-}B_9C_2H_9(CH_3)_2)_2Co]}$	Calcd	42.80	31.75	9.27	13.00	N, 3.09	453.32	63[c]
	Found	42.75	31.77	9.23	12.68	N, 2.88	455	
$\mathrm{(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}(C_6H_5))_2Co]}$	Calcd	35.41	43.63	7.70	10.70	N, 2.55	550.23	70[c]
	Found	35.71	43.61	7.86	10.49	N, 2.66	554	
$\mathrm{(C_5H_5)Co(1,2\text{-}B_9C_2H_{11})}$	Calcd	37.94	32.79	6.29	22.98		...	15[c]
	Found	37.89	33.01	6.14	22.88		...	
$\mathrm{Cs[(1,7\text{-}B_9C_2H_{11})_2Co]}$	Calcd	42.63	10.52	4.85	12.90	Cs, 29.10	456.82	80,[c] 90[d]
	Found	42.54	11.06	4.82	13.27	Cs, 28.66	454.6[b]	

[a] Determined by titrating the hydronium salts with standard base. [b] Determined by osmometry with acetone as solvent. [c] Using non-aqueous preparation. [d] Using aqueous preparation.

rotation which respect to one another on the nmr time scale. Although two isomers of the bis-π-1-phenyl-(3)-1,2-dicarbollyliron systems would be expected (*meso* and *dl*), data presently available suggest that only one isomer was isolated. The identity of this isomer, or mixture of isomers, is presently unknown.

Based upon the above discussion, the two iron complexes $[\pi\text{-(3)-1,2-B_9C_2H_{11}}]_2\mathrm{Fe}^-$ and $[\pi\text{-(3)-1,2-B_9C_2H_{11}}]_2\mathrm{Fe}^{-2}$ are analogs of the ferricinium ion[16] and ferrocene,[16] respectively. The (3)-1,2-dicarbollide derivatives possess greater thermal stability, greater stability toward acid, and, in the case of the unsubstituted derivative, greater stability toward base than their cyclopentadienyl analogs. The redox interconversion of the iron(II) and iron(III) complexes is much more facile in the case of the dicarbollide derivatives. The iron(III) complexes show greater stability toward a wide range of conditions than their analog, $(\pi\text{-C_5H_5})_2\mathrm{Fe}^+$, which is most difficult to isolate and work with because of its intrinsic instability.[16] One reason the (3)-1,2-dicarbollide complexes of iron show greater stability when compared to ferrocene and the ferricinium ion may be their more favorable charge situation. Also, in these dicarbollide complexes the π orbitals in the $\mathrm{B_9C_2H_{11}}^{-2}$ ligand are directed toward the iron atom which increases overlap with the bonding orbitals of the iron atom and thus increases the strength of the metal–ligand bond compared to that present in ferrocene and the ferricinium ion.

π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt Derivatives. Preparation and Characterization of Bis-π-(3)-1,2-dicarbollylcobalt(III) Ions. The successful preparation of ferrocene and ferricinium ion analogs suggested that the analogs of the very stable cobalticinium ion and the less stable cobaltocene could be obtained. Accordingly, the reaction of anhydrous cobalt(II) chloride with the unsubstituted, 1,2-dimethyl- and 1-phenyl-(3)-1,2-dicarbollide ions was investigated[2b] as in the case of the corresponding iron system. In each case a high yield of the corresponding diamagnetic bisdicarbollylcobalt(III) derivative was isolated as its cesium or tetramethylammonium salt. The direct isolation of the complexes having cobalt in the formal +3 oxidation state was accompanied by the formation of cobalt metal. This observation suggests that the initially

$$1.5\mathrm{CoCl_2} + 2(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}^{-2} \longrightarrow [\pi\text{-}(3)\text{-}1,2\text{-}\mathrm{B_9C_2H_{11}}]_2\mathrm{Co}^- + 3\mathrm{Cl}^- + 0.5\mathrm{Co}^0$$

formed cobalt(II) complex is rapidly oxidized by cobaltous ion to form the more stable d^6 dicarbollyl complex. The preparation of the bis-(3)-1,2-dicarbollide ion complex of cobalt(III) was also accomplished using the dicarbollide ion generated in strong, aqueous base[6] and cobaltous chloride. Table VII presents the yield and characterization data associated with this complex and its carbon-substituted derivatives, and Table VIII contains infrared data useful for the identification of these compounds.

Table VIII. Infrared Spectral Data (cm^{-1}) for the π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt(III) Derivatives (Nujol Mulls)

$\mathrm{Cs[(1,2\text{-}B_9C_2H_{11})_2Co]}$	2595 (s), 2517 (s), 1223 (m), 1203 (w), 1190 (w), 1130 (w), 1100 (s), 1088 (m), 1010 (m), 978 (s), 933 (w)
$\mathrm{(CH_3)_4N[(1,2\text{-}B_9C_2H_8Br_3)_2Co]}$	2560 (s), 1176 (m), 1101 (s), 1084 (m), 1008 (m), 980 (m), 947 (s), 929 (w), 906 (w), 890 (w), 859 (s), 837 (m), 789 (m), 752 (m), 722 (w), 690 (w)
$\mathrm{(CH_3)_4N[(1,2\text{-}B_9C_2H_9(CH_3)_2)_2Co]}$	2542 (s), 1282 (w), 1213 (w), 1076 (m), 1003 (m), 942 (m), 915 (w), 888 (w)
$\mathrm{(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}(C_6H_5))_2Co]}$	2508 (s), 1590 (w), 1288 (w), 1190 (w), 1167 (m), 1078 (s), 1040 (m), 1000 (s), 948 (m), 888 (m), 845 (w), 748 (m), 766 (s), 702 (s)
$\mathrm{(C_5H_5)Co(1,2\text{-}B_9C_2H_{11})}$	3110 (w), 3050 (w), 2540 (s), 1418 (m), 1193 (w), 1102 (s), 985 (m), 917 (w), 843 (s), 725 (m), 673 (w)
$\mathrm{Cs[(1,7\text{-}B_9C_2H_{11})_2Co]}$	2560 (s), 2528 (s), 1106 (m), 1042 (w), 1010 (m), 981 (w), 740 (w), 710 (w)

As in the case of the corresponding iron derivatives described above, the electronic spectra of the bis-π-(3)-1,2-dicarbollylcobalt(III) derivatives were found to be complex, and no satisfactory interpretation can be supplied at this time. These data appear in Table IX.

The polarographic data presented in Table X for the reversible one-electron reduction of bis-π-(3)-1,2-dicarbollylcobalt(III) and its carbon-substituted derivatives ($\mathrm{d}^6 \rightarrow \mathrm{d}^7$) indicate that the effect of substituent upon the half-wave potential (*vs.* sce) is opposite to that observed in the bis-π-(3)-1,2-dicarbollyl iron(III) series ($\mathrm{d}^5 \rightarrow \mathrm{d}^6$) shown in Table IV. At the present time, we are unable to present a definitive explanation for these

Table IX. Electronic Spectral Data for the π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt(III) Derivatives

λ_{max}, mμ (ε)					
$Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$[b]	$(CH_3)_4N[(1,2\text{-}B_9C_2H_8Br_3)_2Co]$[c]	$(CH_3)_4N[(1,2\text{-}B_9C_2H_9(CH_3)_2)_2Co]$[b]	$(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}(C_6H_5))_2Co]$[b]	$(C_5H_5)Co(B_9C_2H_{11})$[b]	$Cs[(1,7\text{-}B_9C_2H_{11})_2Co]$[b]
216 (36,300)	233 (5640)	221 (18,000)	215 (10,800)	208 (54,000)	285 (30,600)
293 (45,000)	290 (10,000)[a]	304 (14,300)	318 (22,300)	273 (33,600)	433 (272)
345 (2200)[a]	329 (34,000)	480 (475)	390 (760)[a]	320 (545)[a]	
445 (440)	385 (5730)		495 (478)	422 (364)	
	470 (600)[a]				

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

Table X. Reduction Potentials for the π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt(III) Derivatives

Compound	Method	$E_{1/2}$ *vs.* sce		
		$M^{IV} + e^- \rightarrow M^{III}$	$M^{III} + e^- \rightarrow M^{II}$	$M^{II} + e^- \rightarrow M^{I}$
$Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$	Polarography[a]	...	−1.42	...
	Cyclic voltammetry[b]	+1.57	−1.46	...
$(CH_3)_4N[(1,2\text{-}B_9C_2H_8Br_3)_2Co]$	Cyclic voltammetry	Irrev	−0.48	−1.58
$(CH_3)_4N[(1,2\text{-}B_9C_2H_9(CH_3)_2)_2Co]$	Polarography	...	−1.16	...
	Cyclic voltammetry	Irrev	−1.13	...
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}(C_6H_5))_2Co]$	Polarography	...	−1.28	...
$(C_5H_5)Co(1,2\text{-}B_9C_2H_{11})$	Cyclic voltammetry	Irrev	−1.25	...
$Cs[(1,7\text{-}B_9C_2H_{11})_2Co]$	Cyclic voltammetry	Irrev	−1.17	...

[a] Polarography done in 50% aqueous acetone, 0.1 *N* $LiClO_4$ supporting electrolyte, using a dropping mercury electrode; all reductions were reversible one-electron waves. [b] Cyclic voltammetry done in acetonitrile solution, 0.1 *N* $(C_2H_5)_4NClO_4$ supporting electrolyte; reversible half-peak reduction potentials reported.

Table XI. ^1H Nmr Data of the π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt(III) Derivatives

Compound	Solvent	Resonance,[a] ppm (rel area)	Assignment
$Cs[(1,2\text{-}B_9C_2H_{11})_2Co]$	Pyridine	Broad singlet, −4.40	Carborane C–H
$(CH_3)_4N[(1,2\text{-}B_9C_2H_8Br_3)_2Co]$	Acetone	Broad singlet, −4.62 (3.86)	Carborane C–H
		Sharp singlet, −3.42 (12.0)	Methyl protons of cation
$(CH_3)_4N[(1,2\text{-}B_9C_2H_9(CH_3)_2)_2Co]$	Pyridine	Sharp singlet, −3.16 (1.0)	Methyl protons of cation
		singlet, −2.60 (1.0)	Carborane methyl protons
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{10}(C_6H_5))_2Co]$	Acetonitrile	Multiplet, −7.29 (10.2)	Carborane phenyl protons
		Broad singlet, −4.26 (2.0)	Carborane C–H
		Sharp singlet, −3.09 (12.9)	Methyl protons of cation
$(C_5H_5)Co(1,2\text{-}B_9C_2H_{11})$	Acetonitrile	Sharp singlet, −5.70 (5.0)	Cyclopentadienyl protons
		Broad singlet, −4.26 (2.0)	Carborane C–H
$Cs[(1,7\text{-}B_9C_2H_{11})_2Co]$	Pyridine	Broad singlet, −3.33	Carborane C–H

[a] Relative to tetramethylsilane.

observations. In the case of the bis-unsubstituted cobalt(III) complex, a reversible one-electron oxidation was observed (+1.57 *vs* sce) in acetonitrile solution which suggests the existence of a species which contains cobalt in the formal +4 oxidation state. The ease of oxidation of species which contained formal cobalt(II) precluded their isolation and characterization.

The ^{11}B nmr spectra of the bis-π-(3)-1,2-dicarbollylcobalt(III) ion and its derivatives were uninformative because of a lack of resolution at 19.3 Mc/sec. Each spectrum extended over approximately 35 ppm. The 60-Mc/sec ^1H nmr spectra of these same species are presented in Table XI, and the observed resonances are typical of the carbon substituents present in each system.

Bromination of the Bis-π-(3)-1,2-dicarbollylcobalt(III) Ion. Treatment of the rubidium salt of the bis-π-(3)-1,2-dicarbollylcobalt(III) ion with excess bromine in glacial acetic acid solution at the reflux temperature produced a crystalline hexabromo derivative in 77% yield. Tables VII–XI present the analytical, spectroscopic, electrochemical, and ^1H nmr data associated with this compound. The occurrence of a second reversible one-electron reduction wave suggests that the reduction of the cobalt(III) derivative proceeds in two steps to the corresponding d^8 cobalt(I) species. The high (−3) charge associated with such an ion is probably stabilized by the electron-withdrawing effect associated with the bromine substituents.

Subsequent single-crystal X-ray diffraction studies[21] proved the existence of sandwich bonding in the hexabromo derivative and placed the six bromine atoms at the 8, 8′, 9, 9′, 12, and 12′ positions. These six positions are as far removed from the carbon atoms as is possible, and it appears likely that these six positions establish the region of highest electron density if one assumes that the bromine substitution reaction is electrophilic in character. Figure 5 presents the gross features of the established[21] structure.

Preparation and Characterization of the Bis-π-(3)-1,7-dicarbollylcobalt(III) Ion. The existence of an isomeric series of cobalt(III) complexes was demonstrated by the preparation of the bis-π-(3)-1,7-dicar-

---

(21) We are indebted to Dr. A. Zalkin and Professor D. H. Templeton for the preliminary communication of these, as yet, unpublished results.

Table XII. Elemental Analyses, Molecular Weights, and Yields of Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylnickel Derivatives

Compound		% B	% C	% H	% Ni	% N	Mol wt[a]	Yield, %
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{11})_2Ni]$	Calcd	48.97	24.14	8.62	14.76	3.52	397.72	74,[c] 76[d]
	Found	49.35	24.02	8.68	14.48	3.78	399	
$(1,2\text{-}B_9C_2H_{11})_2Ni$	Calcd	60.17	14.84	6.85	18.14	...	323.63	90[b]
	Found	60.33	15.13	6.85	17.84	...	309	
$(CH_3)_4N[(1,7\text{-}B_9C_2H_{11})_2Ni]$	Calcd	48.97	24.14	8.62	14.76	3.52	397.72	78[c]
	Found	47.34	24.59	8.61	14.12	3.34	422	
$(1,7\text{-}B_9C_2H_{11})_2Ni$	Calcd	60.17	14.84	6.85	18.14	...	323.63	85[b]
	Found	59.87	15.11	7.05	18.23	...	355	

[a] Osmometric: the salts in acetone solution, the neutral derivatives in benzene. [b] From the corresponding Ni(III) compound. [c] Nonaqueous preparation. [d] Aqueous preparation.

bollylcobalt(III) ion using the standard preparative methods in tetrahydrofuran solvent and in aqueous media. Tables VII–XI record the characterization and properties of this ion.

A single-crystal X-ray diffraction study[21] of the cesium salt of the bis-π-(3)-1,7-dicarbollylcobalt(III) ion confirmed the presence of sandwich bonding although the carbon atoms were not specifically located. These results and the confirmed sandwich bonding[21] in the hexabromo derivative of the bis-π-(3)-1,2-dicarbollylcobalt(III) ion indicate that all the cobalt derivatives are similarly bonded. As in the case of the 1-phenyl-(3)-1,2-dicarbollyliron system, only one of the two possible sandwich-bonded bis-1-phenyl-(3)-1,2-dicarbollylcobalt(III) stereoisomers appears to have been isolated. Again, the stereochemistry of the isolated product remains undetermined at the present time.

π-Cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III). The reaction of a mixture of cyclopentadienide ion and the (3)-1,2-dicarbollide ion with cobalt(II) chloride proceeded as in the case of the corresponding iron system to afford, in low yield, an uncharged, diamagnetic cobalt(III) complex containing one π-C_5H_5 group and a π-(3)-1,2-dicarbollyl group.[2b] The over-all reaction was accompanied by the formation of cobalt metal.

$$C_5H_5^- + (3)\text{-}1,2\text{-}B_9C_2H_{11}^{-2} + 1.5CoCl_2 \longrightarrow (\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}] + 0.5Co + 3Cl^-$$

Although the 19.3-Mc/sec ^{11}B nmr spectrum of this compound was not informative with regard to structure, the ^1H nmr spectrum contained a sharp singlet of intensity 5 at -5.70 ppm and a broad singlet of intensity 2 at -4.26 ppm relative to tetramethylsilane. The former resonance clearly signified the presence of a π-C_5H_5 ring. On the basis of this observation and the equivalence of the two carborane C–H protons, we have assigned the same sandwich-bonded structure to this compound as was determined for the corresponding iron(III) species. Tables VII–XI present the characterization data associated with this compound.

π-(3)-1,2- and π-(3)-1,7-Dicarbollylnickel Derivatives. Preparation and Properties of the Bis-π-(3)-1,2-dicarbollylnickel System. The reaction of nickel(II) salts with the (3)-1,2-dicarbollide ion generated in tetrahydrofuran or in strong aqueous base produced (after air oxidation) a paramagnetic complex which we have tentatively designated bis-π-(3)-1,2-dicarbollylnickel(III)[6] since no X-ray diffraction studies have been completed with this species. Oxidation of this species with 1 equiv of ferric ion in aqueous solution afforded the corresponding species which contained nickel in the formal +4 oxidation state.[6] The latter compound was uncharged and diamagnetic. Reduction of the nickel(III) complex afforded the air-sensitive, paramagnetic nickel(II) species (two unpaired electrons, $\mu_{eff} = 2.90$ BM). The nickel(III) complex contained one unpaired electron ($\mu_{eff} = 1.76$ BM). Both polarographic and chemical redox reactions have shown that all interconversions of formal oxidation states are reversible.

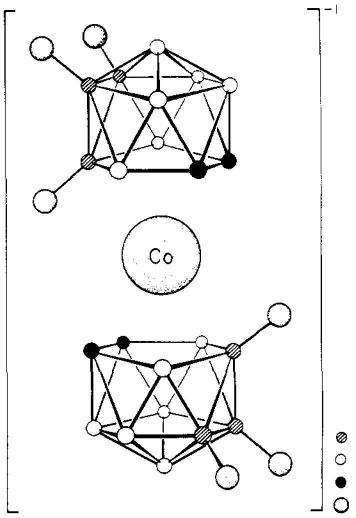

Figure 5. Schematic drawing of the hexabromobis-π-(3)-1,2-dicarbollylcobalt(III) ion structure.

Tables XII–XV present the characterization and spectroscopic data associated with these species. Proton nmr data were obtained with the diamagnetic nickel(IV) compound in benzene and consisted of a broad singlet resonance at -2.94 ppm relative to tetramethylsilane. The mass spectrum of the sublimable nickel(IV) complex exhibited a parent peak at m/e 330.270 (calculated for $^{62}Ni(^{11}B_9{}^{12}C_2{}^1H_{11})_2$: 330.268) and confirmed the assigned molecular composition.[22] The 19.3-Mc/sec ^{11}B nmr spectra of the paramagnetic nickel(II) and nickel(III) complexes, as in the case of the corresponding iron(III) complex, exhibited large paramagnetic contact and psuedo-contact shifts. No interpretation has yet been placed upon these spectra. The 19.3-Mc/sec ^{11}B nmr spectrum of the nickel(IV) compound was undramatic and resembled the envelope of

(22) The peak at mass number 330 calibrated against $C_6F_{13}^+$. Further confirmation that this was the parent peak was deduced from an analysis of the intensities in the multiplets arising from the distribution of ^{10}B, ^{11}B, and five isotopes of nickel.

Table XIII. Infrared Spectral Data (cm^{-1}) for Bis-(3)-1,2- and Bis-(3)-1,7-dicarbollylnickel Derivatives (Nujol Mulls)

$[(C_2H_5)_4N]_2[(1,2\text{-}B_9C_2H_{11})_2Ni]$	2500 (s), 2420 (s), 1393 (m), 1303 (m), 1180 (s), 1152 (w), 1077 (m), 1030 (s), 1001 (m), 970 (s), 930 (w), 874 (w), 789 (s), 720 (m), 686 (w)
$(CH_3)_4N[(1,2\text{-}B_9C_2H_{11})_2Ni]$	3037 (w), 2527 (s), 1245 (m), 1160 (m), 1098 (s), 1063 (w), 1047 (m), 997 (s), 968 (s), 924 (m), 893 (w), 872 (w), 783 (w), 755 (m), 743 (m)
$(1,2\text{-}B_9C_2H_{11})_2Ni$	3028 (w), 2595 (s), 1233 (m), 1133 (w), 1098 (m), 1079 (s), 1008 (m), 963 (s), 926 (m), 913 (m), 888 (m), 742 (s), 717 (s)
$(CH_3)_4N[(1,7\text{-}B_9C_2H_{11})_2Ni]$	2545 (s), 1140 (w), 1097 (s), 1051 (s), 1014 (s), 968 (s), 942 (s), 869 (m), 730 (m), 693 (m)
$(1,7\text{-}B_9C_2H_{11})_2Ni$	2580 (s), 2558 (m), 1137 (m), 1100 (m), 1040 (w), 1009 (s), 958 (w), 902 (w), 858 (w), 843 (w), 787 (w), 741 (w), 728 (m), 685 (w)

Table XIV. Electronic Spectral Data for Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylnickel Derivatives

λ_{max}, mμ (ε)			
$(CH_3)_4N$-$[(1,2\text{-}B_9C_2\text{-}H_{11})_2Ni]$ (CH_3CN)	$(1,2\text{-}B_9C_2\text{-}H_{11})_2Ni$ (cyclohexane)	$(CH_3)_4N$-$[(1,7\text{-}B_9C_2\text{-}H_{11})_2Ni]$ (CH_3OH)	$(1,7\text{-}B_9C_2\text{-}H_{11})_2Ni$ (cyclohexane)
237 (8580)	297 (37,100)	275 (5000)^a	296 (39,500)
337 (21,400)	425 (2050)	324 (17,400)	
435 (3600)^a		409 (5000)^a	
		860 (263)	

^{a} Shoulder.

Table XV. Reduction Potentials for the Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylnickel Derivatives

		$E_{1/2}$ *vs.* sce	
Compound	Method	$M^{IV} + e^- \rightarrow M^{III}$	$M^{III} + e^- \rightarrow M^{II}$
$(1,2\text{-}B_9C_2H_{11})_2Ni$	Polarography^a	...	−0.63
	Cyclic voltammetry^b	+0.25	−0.59
$(1,7\text{-}B_9C_2H_{11})_2Ni$	Cyclic voltammetry^b	+0.55	−0.91

^{a} Done in 50% acetone–water, 0.1 *N* $LiClO_4$ supporting electrolyte using a dropping mercury electrode. ^{b} Done in acetonitrile solution, 0.1 *N* $(C_2H_5)_4NClO_4$ supporting electrolyte; half-peak reduction potentials reported.

the corresponding diamagnetic iron(II) and cobalt(III) species. Spectroscopic evidence showed the extremely air-sensitive Ni(II) complex to be free from oxidized products, in spite of the rather poor elemental analysis (see Experimental Section).

Preparation and Properties of the Bis-π-(3)-1,7-dicarbollylnickel System. The (3)-1,7-dicarbollide ion and nickel(II) acetylacetonate reacted in tetrahydrofuran to produce a red complex which was air-oxidized to the bis-π-(3)-1,7-dicarbollylnickel(III) ion. As in the case of the corresponding (3)-1,2-dicarbollyl system, no structural data are available, and we have assumed the presence of a π-bonded arrangement of the ligands about formal nickel(III). On the basis of polarographic data (Table XV) and the work-up procedure employed, it is reasonable to assume that the initially formed red complex is the corresponding complex which contains formal nickel(II). The nickel(III) complex was easily oxidized by ferric ion to an uncharged and sublimable complex which contained formal nickel(IV). The mass spectrum of this compound produced a parent peak of *m/e* 330.280 (calculated 330.268).

The nickel(III) complex was paramagnetic (μ_{eff} = 1.74 BM) and exhibited contact and psuedo-contact shifts in its ^{11}B nmr spectrum. The corresponding diamagnetic nickel(IV) complex gave a ^{11}B nmr spectrum which resembled that of the corresponding cobalt(III) derivative. Its ^1H nmr spectrum in benzene consisted of a broad singlet resonance at −3.20 ppm relative to tetramethylsilane.

Tables XII–XV present the characterization and spectroscopic data associated with the bis-π-(3)-1,7-dicarbollylnickel system. The major difference between the (3)-1,2- and the (3)-1,7-dicarbollide complexes was found to be the greater stability of the former.

The Bis-π-(3)-1,2-dicarbollylcopper(II) Complex. Preparation. The addition of copper(II) salts to solutions of the (3)-1,2-$B_9C_2H_{12}^-$ ion in strongly basic aqueous media resulted in the formation of a deep blue copper(II) complex which could be precipitated by the addition of a large cation. The resulting salts were unstable in the air and not characterized by conventional means. Air oxidation of the copper(II) complex in the presence of aqueous acid resulted in the formation of a red diamagnetic ion which may contain copper in the formal oxidation state +3.

Structure. Wing[23] has carried out a single-crystal X-ray diffraction study of the tetraethylammonium salt of the blue copper(II) complex. This study proved that two (3)-1,2-dicarbollyl ions were sandwich bonded to copper(II) and that the resulting complex contained parallel dicarbollide ligands which had "slipped" about 0.6 Å with respect to the molecular axis which lies perpendicular to the plane of the open faces of the ligands. Figure 6 presents a schematic view of this structure. It can be seen that the three boron atoms present in the open face of each (3)-1,2-dicarbollide ion ligand are closer to copper than the carbon atoms. Wing[23] has rationalized this observation in terms of a π-allylic type of interaction between each ligand and copper. We believe, however, that a complete molecular orbital treatment will be required to fully explain the bonding in this compound. Aside from this point, it is interesting to note that no corresponding bis-π-cyclopentadienylcopper complex is known although a cyclopentadienylcopper(I) triethylphosphine derivative has been reported with σ bonding.[24,25]

[23] R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

[24] (a) G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2**, 32 (1956); (b) T. S. Piper and G. Wilkinson, *ibid.*, **3**, 104 (1956).

[25] G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).

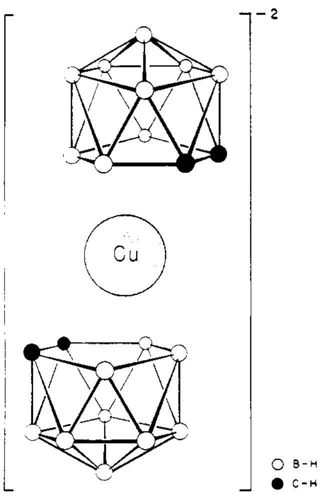

Figure 6. Schematic drawing of the bis-π-(3)-1,2-dicarbollylcopper(II) dianion structure showing "slippage" of ligands with respect to one another.

π-Tetraphenylcyclobutadienyl-π-(3)-1,2-dicarbollylpalladium(II). Although the reaction of the (3)-1,2-dicarbollide ion with simple platinum and palladium salts was not successful, the synthesis of the π-tetraphenylcyclobutadienyl-π-cyclopentadienylpalladium(II) cation by Maitlis and coworkers[26] suggested that an analogous derivative might be prepared in which the (3)-1,2-dicarbollide ion replaces the π-C_5H_5 anion. Such a material was prepared and fully characterized.[5]

Preparation and Properties. The dimer of π-tetraphenylcyclobutadienylpalladium(II) dichloride[27] was prepared by the method of Maitlis and coworkers. The reaction of this substrate with the (3)-1,2-dicarbollide ion resulted in the displacement of 2 equiv of chloride ion and the formation of the desired compound in approximately 10% yield. The 1,2-dimethyl derivative was prepared in low yield in an analogous fashion. In both cases the principal reaction product was a black solid which ignited in the air.

$$[\pi\text{-}C_4(C_6H_5)_4PdCl_2]_2 + 2[(3)\text{-}1,2\text{-}B_9C_2H_{11}]^{-2} \longrightarrow 2[\pi\text{-}C_4(C_6H_5)_4]Pd[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}] + 4Cl^-$$

The infrared spectra of the unsubstituted and 1,2-dimethyl derivatives contained a B–H stretching band at 2500 cm^{-1} and a strong monosubstituted phenyl absorption at 700 cm^{-1}. The ^{1}H nmr spectrum of the unsubstituted compound in methylene chloride contained phenyl resonances centered at −7.45 ppm (relative intensity 10) as well as a broad singlet due to carborane C–H at −2.69 ppm (relative intensity 1) relative to tetramethylsilane. Relative to the same standard, the 1,2-dimethyl derivative exhibited a phenyl resonance centered at −7.60 ppm (relative intensity 20) and a methyl resonance at −1.47 ppm (relative intensity 6). The ^{11}B nmr spectra of these two derivatives were essentially featureless at 19.3 Mc/sec and uninterpretable.

Pettersen, Zalkin, and Templeton[28] have confirmed the sandwich structure of the 1,2-dimethyl derivative by means of an X-ray diffraction study. This structure is reproduced in Figure 7. It should be noted that the methyl groups unequivocally label the two carbon atoms in the (3)-1,2-dicarbollide ion.

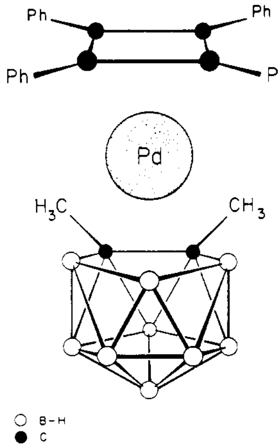

Figure 7. Schematic drawing of the π-tetraphenylcyclobutadienyl-π-(3)-1,2-dicarbollylpalladium(II) structure.

π-(3)-1,2-Dicarbollyl Derivatives of Metal Carbonyls. The ability of the (3)-1,2-dicarbollide ion to form a variety of sandwich-bonded transition metal derivatives was further illustrated by the synthesis of several derivatives related to metal carbonyls.

Preparation and Properties of π-(3)-1,2-Dicarbollylmanganese and -rhenium Tricarbonyl Anions. Bromomanganese pentacarbonyl and the isoelectronic bromorhenium pentacarbonyl reacted rapidly at room temperature with tetrahydrofuran solutions of the (3)-1,2-dicarbollide ion to produce bromide ion and no carbon monoxide. When such reaction mixtures were heated to the reflux temperature, 2 moles of CO was evolved and the relatively stable π-(3)-1,2-dicarbollyl metal tricarbonyl monoanions resulted.[4] These anions are analogs of the well-known $[\pi\text{-}C_5H_5]Mn(CO)_3$.[29] The rapid formation of bromide ion suggests that the initial product of the over-all reaction is a σ-bonded (3)-1,2-dicarbollyl derivative which is converted to the π-bonded derivative, with loss of CO, when heated. No attempts were made to isolate the presumed intermediate.

$$(3)\text{-}1,2\text{-}B_9C_2H_{11}^{-2} + BrMn(CO)_5 \xrightarrow{\text{fast}} [\sigma\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mn(CO)_5^- + Br^-$$

$$[\sigma\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mn(CO)_5^- \xrightarrow[\text{heat}]{\text{slow}} 2CO + [\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]Mn(CO)_3^-$$

The infrared spectra (Nujol mull) of the tetramethylammonium salts contained a B–H stretching band at 2500 cm^{-1} and two carbonyl stretching bands between 2150 and 1850 cm^{-1} (manganese, 2020 and 1908 cm^{-1}; rhenium, 1988 and 1880 cm^{-1}). The manganese derivative exhibited electronic transitions at 212 mμ (ϵ 33,300) and 346 mμ (ϵ 2500). The rhenium derivative exhibited corresponding transitions at 210 mμ (ϵ 24,000) and 272 mμ (ϵ 2900). Although the ^{11}B nmr spectra of the anions were not interpretable, the ^{1}H nmr spectra contained broad carborane C–H singlets at (Mn) −2.48 and (Re) −2.90 ppm, relative to tetramethylsilane.

---

(26) P. M. Maitlis, A. Efraty, and M. L. Games, *J. Am. Chem. Soc.*, **87**, 719 (1965).

(27) P. M. Maitlis and M. L. Games, *Can. J. Chem.*, **42**, 183 (1964).

(28) We are indebted to these workers for the preliminary results of their investigation received prior to publication.

(29) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

Table XVI. Elemental Analyses for the π-(3)-1,2 Dicarbollylmolybdenum and -tungsten Carbonyl Derivatives

Compound		% B	% C	% H	% N	% Mo	%W
$[(CH_3)_4N]_2(B_9C_2H_{11})Mo(CO)_3$	Calcd	21.12	33.89	7.67	6.08	20.82	
	Found	21.01	33.70	7.67	6.28	20.59	
$[(CH_3)_4N]_2(B_9C_2H_{11})W(CO)_3$	Calcd	17.73	28.46	6.44	5.11		33.51
	Found	17.53	28.21	6.65	4.86		33.50
$[(CH_3)_4N]_2(B_9C_2H_9(CH_3)_2)Mo(CO)_3$	Calcd	19.90	36.86	8.06	5.73	19.63	
	Found	19.90	36.67	8.25	6.00	19.31	
$[(CH_3)_4N]_2(B_9C_2H_{11})W_2(CO)_8$	Calcd	11.15	24.78	4.04	3.21		42.14
	Found	11.73	24.55	5.38	3.40		44.80
$[(CH_3)_4N]_2(B_9C_2H_9(CH_3)_2)Mo_2(CO)_8$	Calcd	13.43	33.15	5.42	3.87	26.48	
	Found	14.29	32.11	6.19	4.12	28.96	
$[(CH_3)_4N]_2(B_9C_2H_{11})MoW(CO)_8$	Calcd	12.40	27.56	4.50	3.57	12.23	23.43
	Found	12.32	26.60	4.67	3.71	9.73	29.38
$[(CH_3)_4N]_2(B_9C_2H_{11})WMo(CO)_8$	Calcd	12.40	27.56	4.50	3.57	12.23	23.43
	Found		27.64	5.08	3.89	13.12	24.88
$(CH_3)_4N[(B_9C_2H_{11})W(CO)_3CH_3]$	Calcd	19.87	24.53	5.36	2.86		37.56
	Found	20.09	24.78	5.53	3.06		37.99
$(CH_3)_4N[(B_9C_2H_{11})Mo(CO)_3CH_3]$	Calcd	24.23	29.91	6.54	3.49	23.89	
	Found	24.24	30.09	6.67	3.56	24.13	

The structure of the rhenium derivative was determined by X-ray diffraction studies,[30] and that structure is reproduced in Figure 8. The observed C–Re and B–Re distances were 2.31 and 2.35 Å, respectively. The published structure[30] should be consulted for further details.

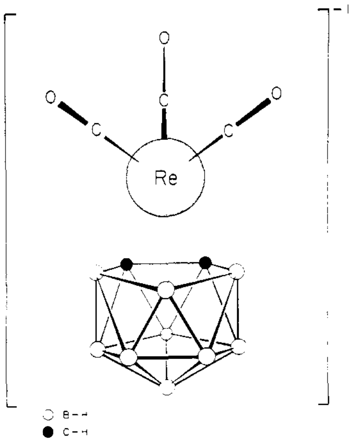

Figure 8. The structure of the π-(3)-1,2-dicarbollylrhenium tricarbonylate ion in schematic form.

Preparation and Properties of π-(3)-1,2-Dicarbollyltungsten and -molybdenum Tricarbonyl Dianions and Related Binuclear Species. The simple displacement of carbon monoxide from $W(CO)_6$ and $Mo(CO)_6$ by the (3)-1,2-dicarbollide ion was not successful when carried out by simply heating the reactants in tetrahydrofuran solution. However, the accumulation of a large number of photochemical displacement reactions of the desired type[31] suggested the photolysis of $W(CO)_6$ and $Mo(CO)_6$ in the presence of the (3)-1,2-dicarbollide ion.

When $W(CO)_6$ was added to a solution of the (3)-1,2-dicarbollide ion in tetrahydrofuran at room temperature, no apparent reaction occurred. Upon exposure of the reaction mixture (quartz vessel) to ultraviolet radiation, carbon monoxide evolution commenced at once and the solution became yellow. After treating the reaction mixture with water, a pale yellow tetramethylammonium salt was precipitated and purified in an inert atmosphere. Analytical data supported the formulation of this product as $[\pi\text{-(3)-1,2-}B_9C_2H_{11}]W(CO)_3^{-2}$ (Table XVI). Other compounds prepared in an analogous manner were obtained from the (3)-1,2-dicarbollide ion and $Mo(CO)_6$ and from the 1,2-dimethyl-(3)-1,2-dicarbollide ion and $Mo(CO)_6$. Although evolved carbon monoxide was not quantitatively accounted for, the general overall reaction is in agreement with the following equation.

$$\text{(3)-1,2-}B_9C_2H_{11}^{-2} + W(CO)_6 \xrightarrow{h\nu} [\pi\text{-(3)-1,2-}B_9C_2H_{11}]W(CO)_3^{-2} + 3CO$$

The tetramethylammonium salts of these anions were not stable in air and were insoluble in most organic solvents except acetone and acetonitrile.

Solution infrared spectra (Table XVII) of the three dianions each exhibited two strong bands in the carbonyl region near 1750 and 1880 cm⁻¹. Attempts to obtain ^1H and ^{11}B nmr spectra were frustrated by the solubility and sensitivity of the products toward decomposition. On the basis of their mode of formation and certain reactions coupled with an X-ray diffraction study (*vide infra*) of a derivative, the structure of these dianions appears to be analogous to that of the π-(3)-1,2-dicarbollylrhenium tricarbonyl anion (Figure 8).

Table XVII. Infrared Absorptions (cm⁻¹) in the Carbonyl Stretching Region for π-(3)-1,2-Dicarbollylmolybdenum and -tungsten Carbonyl Derivatives

$[(CH_3)_4N]_2(B_9C_2H_{11})Mo(CO)_3{}^a$	1890 (s), 1754 (s)
$[(CH_3)_4N]_2(B_9C_2H_{11})W(CO)_3{}^a$	1876 (s), 1828 (w), 1748 (s)
$[(CH_3)_4N]_2(B_9C_2H_9(CH_3)_2)Mo(CO)_3{}^a$	1879 (s), 1828 (w), 1748 (s)
$[(CH_3)_4N]_2(B_9C_2H_{11})W_2(CO)_8{}^b$	2004 (m), 1961 (w), 1905 (s), 1887 (s), 1845 (m), 1795 (s)
$[(CH_3)_4N]_2(B_9C_2H_9(CH_3)_2)Mo_2(CO)_8{}^b$	2012 (m), 1953 (w), 1901 (s), 1885 (m), 1799 (s)
$[(CH_3)_4N]_2(B_9C_2H_{11})WMo(CO)_8{}^b$	2012 (m), 1953 (w), 1898 (s), 1855 (m), 1798 (s)
$[(CH_3)_4N]_2(B_9C_2H_{11})MoW(CO)_8{}^b$	2004 (m), 1905 (s), 1886 (s), 1848 (m), 1795 (s)
$(CH_3)_4N(B_9C_2H_{11})W(CO)_3CH_3{}^b$	1992 (s), 1898 (s)
$(CH_3)_4N(B_9C_2H_{11})Mo(CO)_3CH_3{}^b$	1996 (s), 1905 (s)
$(CH_3)_4N(B_9C_2H_{11})Mo(CO)_3H^c$	2041 (s), 1946 (s)

[a] Acetonitrile solution. [b] Tetrahydrofuran solution. [c] Methylene chloride solution.

---

(30) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *Inorg. Chem.*, 5, 1189 (1966).

(31) See a recent review by W. Strohmeier, *Angew. Chem. Intern. Ed. Engl.*, 3, 730 (1964).

Nucleophilic Reactions of π-(3)-1,2-Dicarbollyltungsten and -molybdenum Tricarbonyl Dianions. Assuming that the products of the photolysis reactions were indeed $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3^{-2}$ ions analogous to the $\pi\text{-C}_5\text{H}_5\text{M(CO)}_3^-$ anions containing Mo, W, and Cr, one might expect the dicarbollyl derivatives to give reactions characteristic of the latter species. Acccordingly, the protonation and alkylation reactions described by Piper and Wilkinson[32] and Fischer and Hafner[33] were applied to the dianions.

Treatment of $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3^{-2}$ with anhydrous hydrogen chloride produced a red compound which was not sufficiently stable to give an accurate elemental analysis. However, the protonated product as its tetramethylammonium salt was titrated as a monoprotic acid with an equivalent weight of 392 (theory for $(\text{CH}_3)_4\text{N}[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3\text{H}$, 389) in aqueous acetone. The infrared spectrum of the protonated product exhibited carbonyl stretching bands at 2041 and 1946 cm^{-1} in methylene chloride solution which correspond to the 2030 and 1949 cm^{-1} bands observed[32,33] in the case of $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{H}$.

When methyl iodide was allowed to react with $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{W(CO)}_3^{-2}$ ion in tetrahydrofuran, a methylated monoanion was isolated as its tetramethylammonium salt which gave the proper elemental analysis for $(\text{CH}_3)_4\text{N}[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{W(CO)}_3\text{CH}_3$. The solution infrared spectrum of this material contained carbonyl stretching bands at 1992 and 1898 cm^{-1}. An analogous product was formed in the molybdenum system which exhibited carbonyl stretching bands at 1996 and 1905 cm^{-1} in its solution infrared spectrum. Tetrahydrofuran was employed as the infrared solvent. The ^1H nmr spectra of the methylated products contained methyl resonances at -0.54 and -0.49 ppm for the tungsten and molybdenum system, respectively. Piper and Wilkinson[32] report -0.17 and -0.10 ppm for $\pi\text{-C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ and $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{CH}_3$, respectively, relative to tetramethylsilane. The ^{11}B nmr spectra were essentially featureless at 19.3 Mc/sec.

The reaction of the (3)-1,2-dicarbollide ion with 2 moles of W(CO)_6 or Mo(CO)_6 was carried out in tetrahydrofuran at the reflux temperature. After quenching the reaction mixture with water, tetramethylammonium salts of the products were obtained. Elemental analyses indicated that these anions had the empirical formula $(\text{B}_9\text{C}_2\text{H}_{11})\text{M}_2(\text{CO})_x^{-2}$ where $x = 7$ or 8. Products of the same type were obtained from the reaction of W(CO)_6 or Mo(CO)_6 with $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{W(CO)}_3^{-2}$ or $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3^{-2}$. The complex infrared spectra exhibited by this new family of dianions (Table XVII) contained five or six carbonyl stretching bands and indicated that their structures were of low symmetry.

The binuclear carbonyl dianions were found to be considerably more stable than the simple mononuclear tricarbonyl dianions. They may be exposed to air, as solids, for several days without appreciable decomposition, but in solution they decomposed rapidly. It was possible, however, to obtain nmr spectra which showed carborane C–H resonances in the region of -2.5 to -2.8 ppm relative to tetramethylsilane. Attempts to obtain useful ^{11}B nmr spectra were unsuccessful.

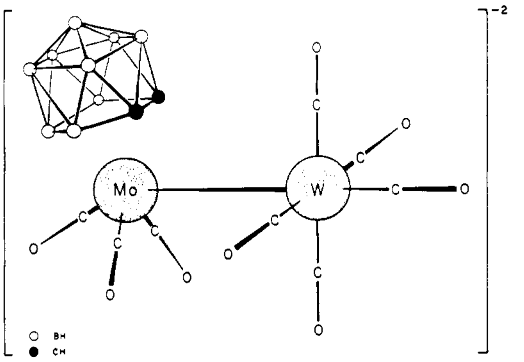

Figure 9. Proposed structure of binuclear carbonylate ion containing Mo–W σ bond and (3)-1,2-dicarbollyl ligand.

The tetramethylammonium salt of the dianion generated from W(CO)_6 and $[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3^{-2}$ was subjected to an X-ray diffraction study by Wing and Callahan.[34] Preliminary results of this study suggest the presence of eight carbonyl groups in the dianion and a Mo–W bond. The tentative structure is presented in Figure 9. It is apparent from these results that the π-(3)-1,2-dicarbollylmolybdenum tricarbonyl dianion most likely does contain the assigned π-bonded (3)-1,2-dicarbollyl ligand and that the tricarbonyl dianion serves as a nucleophile toward W(CO)_6.

$$[\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3^{-2} + \text{W(CO)}_6 \longrightarrow [\pi\text{-(3)-1,2-B}_9\text{C}_2\text{H}_{11}]\text{Mo(CO)}_3\text{W(CO)}_5^{-2} + \text{CO}$$

Conclusion

The results reported above represent our initial studies in the area of hybrid transition metal–boron hydride chemistry, and additional investigations will be reported in the near future. Recent work by Knoth[13] and Todd[12] has extended this research to include the transition metal derivatives of the (3)-1-carbollide ion ($(3)\text{-1-B}_{10}\text{CH}_{11}^{-3}$), and Hertler, Klanberg, and Muetterties[35] have obtained similar results in their recent discovery of the metallothiaboranes. These derivatives are generated from a transition metal ion and two $\text{B}_{10}\text{SH}_{10}^{-2}$ ions. The latter species is believed to be an 11-particle icosahedral fragment isostructural and isoelectronic with the $\text{B}_9\text{C}_2\text{H}_{11}^{-2}$ ions. The sulfur atom is believed to be in the periphery of the open face, and derivatives such as $(\text{B}_{10}\text{SH}_{10})_2\text{Fe}^{-2}$ are easily formed.

Experimental Section

Physical Measurements. Ultraviolet–visible spectra were measured with a Cary Model 14 spectrophotometer. Infrared spectra were determined using a Beckman IR5 infrared spectrophotometer and a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Proton nmr spectra were obtained by means of a Varian A-60 spectrometer and ^{11}B nmr spectra with a Varian HR60 spectrometer at 19.3 Mc/sec. Molecular weights were determined with a Mechrolab Model 301A osmometer. Titrations were carried out using a Leeds and Northrup Model 7664 pH meter with a saturated calomel reference electrode and a Beckman Model 1190-80 glass electrode. Polarographic measurements were made with a Sargent Model XXI polarograph with a dropping mercury electrode and a saturated calomel reference electrode. Controlled-potential cyclic voltammetry was carried out using an instrument based on the design of Alden, Chambers, and Adams.[36] Magnetic suscepti-

---

(32) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

(33) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 140 (1955).

(34) We thank Dr. R. M. Wing for the preliminary results of this investigation received prior to publication.

(35) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, **6**, 1696 (1967).

(36) J. R. Alden, J. Q. Chambers, and R. A. Adams, *J. Electroanal. Chem.*, **5**, 152 (1963).

bilities were measured utilizing an Alpha Scientific Laboratory, Inc., Model AL7536 water-cooled electromagnet with Models AL7500 and AL7500R power supply and current regulator, and a Metler analytical balance with sensitivity of 0.05 mg. Mass spectra were determined with a CEC Type 21-103B mass spectrometer.

Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. The preparation of the dicarbadodecahydroundecaborate(−1) ions, (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$, and their carbon-substituted derivatives was described in a preceding communication.[9] Nickel acetylacetonate and the manganese, rhenium, molybdenum, and tungsten carbonyls were obtained from Alfa Inorganics, Inc. Palladium chloride and anhydrous sublimed ferric chloride were obtained from Matheson Coleman and Bell. Tetraphenylcyclobutadienepalladium dichloride was prepared by the method of Maitlis[27] and the bromomanganese and rhenium pentacarbonyls were prepared by the method of Abel and Wilkinson.[37] Sodium hydride as a 56% dispersion in mineral oil was obtained from Metal Hydrides, Inc. Hydrogen-reduced iron powder (100 mesh) was obtained from Mallinckrodt Chemical Co.

All tetrahydrofuran was freshly distilled from lithium aluminum hydride and collected under nitrogen. Acetonitrile was dried by distillation from calcium hydride. Ultraviolet and visible spectra were measured in Spectrograde solvents, and the cyclic voltammetry measurements were made in Spectrograde acetonitrile.

Nonaqueous Preparation of the Dicarbollide Dianions. (a) Disodium (3)-1,2-Dicarbollide, Na_2(3)-1,2-$B_9C_2H_{11}$. A solution of 5.0 g (25.9 mmoles) of $(CH_3)_3NH$(3)-1,2-$B_9C_2H_{12}$ in 75 ml of tetrahydrofuran was added slowly to a stirring suspension of sodium hydride, 1.51 g (63 mmoles, (2.70 g of a 56% dispersion in mineral oil which had been washed twice with 30 ml of tetrahydrofuran), in 90 ml of the same solvent. The reaction mixture was stirred at reflux temperature under nitrogen for 3 hr. Complete removal of trimethylamine was achieved by passing a stream of nitrogen over the solution and through the condenser during the final 30 min of the reflux period. Stirring was then stopped and the reaction mixture allowed to cool to room temperature. When the excess sodium hydride had settled, the clear tetrahydrofuran solution of Na_2(3)-1,2-$B_9C_2H_{11}$ was decanted under nitrogen for use in subsequent reactions.

(b) Disodium 1,2-Dimethyl-(3)-1,2-dicarbollide, Na_2(3)-1,2-$B_9C_2H_9(CH_3)_2$, Disodium 1-Phenyl-(3)-1,2-dicarbollide, Na_2(3)-1,2-$B_9C_2H_{10}(C_6H_5)$, Disodium (3)-1,7-Dicarbollide, Na_2(3)-1,7-$B_9C_2H_{11}$. Tetrahydrofuran solutions of these compounds were obtained from the corresponding trimethylammonium dicarbadodecahydroundecaborate(−1) salts using the procedure described above for Na_2(3)-1,2-$B_9C_2H_{11}$. In some instances, the potassium salts of the various $B_9C_2H_{12}^-$ monoanions were employed as starting materials. However, the mixed sodium–potassium salt of the 1-phenyl-1,2-dicarbollide dianion as well as the mixed sodium–cesium salts of all the dicarbollide dianions were found to be only sparingly soluble in tetrahydrofuran.

Nonaqueous Preparation of the π-(3)-1,2-Dicarbollyliron(III) Derivatives. (a) $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe$. To a stirred suspension of 55.5 mmoles of ferrous chloride in tetrahydrofuran (150 ml), prepared by the method of Wilkinson,[38] was added under nitrogen a tetrahydrofuran solution of Na_2(3)-1,2-$B_9C_2H_{11}$ (25.9 mmoles, from 5.0 g of $(CH_3)_3NH$(3)-1,2-$B_9C_2H_{12}$). The resulting dark red mixture was stirred for 1 hr at room temperature under nitrogen. The initially formed Fe(II) complex was converted to the Fe(III) compound by stirring the reaction solution for 45 min in the presence of air, and the solvent then was removed *in vacuo*. The dark red residue was dissolved with agitation in 250 ml of water and the solution filtered. The light red solid that precipitated upon addition of excess 50% aqueous tetramethylammonium chloride to the filtrate was collected and washed with water. Crystallization was achieved by dissolving the solid in a mixture of 200 ml of acetone and 80 ml of water and slowly removing the acetone at room temperature under reduced pressure. Red plates of $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe$ (3.12 g, 7.9 mmoles, 61%), mp >300°, were obtained. This material was sufficiently pure for most synthetic purposes. Successive crops of product, which may have been contaminated with $(CH_3)_4N$(3)-1,2-$B_9C_2H_{12}$, were obtained by further removal of solvent giving a total yield of crude product of 3.74 g (73%). Further purification was effected by alternate recrystallization from acetone–water and acetone–hexane mixtures by allowing the solvent to slowly evaporate at ambient conditions until crystallization occurred.

The bulk molar magnetic susceptibility, χ_m, was measured for $(CH_3)_4N[\pi$-(3)-$B_9C_2H_{11}]_2Fe$ and its carbon-substituted derivatives in acetone solution (4–6%) using the Gouy method as described by Figgis and Lewis.[39] Diamagnetic corrections were made using Pascal's constants. An effective "spin-only" magnetic moment, μ_{eff}, of 2.10 BM was obtained for the unsubstituted complex.

(b) $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_9(CH_3)_2]_2Fe$. Using a similar procedure as described above, 40 mmoles of Na_2(3)-1,2-$B_9C_2H_9(CH_3)_2$ was heated at the reflux temperature for 2 hr with an excess of ferrous chloride in tetrahydrofuran. The mixture was filtered, the solvent removed *in vacuo*, and the residue shaken with a mixture of 500 ml of diethyl ether and *ca.* 25 ml of dilute aqueous hydrochloric acid. The red ether phase was filtered and the solvent removed *in vacuo*. The residue was taken up in water, from which the tetramethylammonium salt, $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_9(CH_3)_2]_2Fe$, 7.13 g (15.8 mmoles, 79%), was obtained as red crystals (mp 247–249°) in the manner described above for the unsubstituted derivative. The molar magnetic susceptibility measured on the tetramethylammonium salt in acetone solution gave a spin-only magnetic moment of 1.99 BM (corrected for diamagnetism).

(c) $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_{10}(C_6H_5)]_2Fe$. Using the procedure described above for the 1,2-dimethyl derivative, 40 mmoles of Na_2(3)-1,2-$B_9C_2H_{10}(C_6H_5)$ gave 7.40 g (13.5 mmoles, 68%) of red $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_{10}(C_6H_5)]_2Fe$ (mp >300°, μ_{eff} 1.87 BM).

(d) $(\pi$-$C_5H_5)Fe[\pi$-(3)-1,2-$B_9C_2H_{11}]$. A tetrahydrofuran solution of 1.32 g (20 mmoles) of freshly cracked cyclopentadiene and 3.86 g (20 mmoles) of $(CH_3)_3NH$(3)-1,2-$B_9C_2H_{12}$ was treated with excess sodium hydride as described above for the preparation of Na_2(3)-1,2-$B_9C_2H_{11}$. The resulting solution of NaC_5H_5 and Na_2(3)-1,2-$B_9C_2H_{11}$ was added under nitrogen to a mixture of 28.5 mmoles of ferrous chloride in refluxing tetrahydrofuran. After heating for an additional 15 min, the red solution was cooled and filtered, and the solvent was removed *in vacuo*. The residue was extracted with a mixture of 75 ml each of benzene and water, and the solvents were separated. Addition of 150 ml of pentane to the benzene extract (dried over magnesium sulfate) precipitated purple needles of $(\pi$-$C_5H_5)Fe[\pi$-(3)-1,2-$B_9C_2H_{11}]$. Further purification was effected by recrystallization from cyclohexane–benzene to yield 1.25 g (4.95 mmoles, 25%) of the complex, mp 181–182°. Evaporation of the benzene–pentane filtrate to dryness followed by recrystallization of the residue from methanol gave ferrocene, 1.55 g (8.35 mmoles, 42%), identified by its infrared spectrum. The aqueous layer from the extraction was treated with excess tetramethylammonium chloride, and the precipitated salt was recrystallized from acetone–water to give $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe$, 0.95 g (2.4 mmoles, 12%), identified by its infrared spectrum.

The analytical data, infrared spectra, electronic spectra, and polarographic data for the π-(3)-1,2-dicarbollyliron(III) derivatives are given in Tables I–IV.

Aqueous Preparation of the Bis-π-(3)-1,2-dicarbollyliron(III) Anion. To 5.0 g of $(CH_3)_3NH$(3)-1,2-$B_9C_2H_{12}$ (25.8 mmoles) was cautiously added 50 ml of a freshly prepared hot aqueous 40% sodium hydroxide solution. Most of the liberated trimethylamine was carefully removed under reduced pressure, and the remaining solution was added with vigorous stirring to a slurry of 50 mmoles of ferrous hydroxide from 10.0 g of $FeCl_2 \cdot 4H_2O$ in 100 ml of hot 40% aqueous sodium hydroxide solution. This mixture was heated at 100° for 15 min with stirring, allowed to cool to room temperature, and extracted (without filtering) with *ca.* 1.5 l. of diethyl ether. During the course of the extraction, the pink Fe(II) complex was air-oxidized to the red Fe(III) derivative which was extracted into the ether. The ether was removed *in vacuo* and the residue dissolved in 130 ml of water and filtered. The filtrate was made slightly acidic with hydrochloric acid and treated with a trace of $FeCl_3 \cdot 6H_2O$ to convert any remaining Fe(II) to the Fe(III) derivative. The addition of 2.3 g of cesium chloride (13.7 mmoles) to the heated red solution gave upon cooling black crystals of $Cs[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe$ (3.30 g, 7.3 mmoles, 56%).

Attempts to employ the aqueous procedure to prepare the carbon-substituted derivatives of $[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe^-$ were not successful.

Preparation of the π-(3)-1,2-Dicarbollyliron(II) Derivatives. (a) $[(CH_3)_4N]_2[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe$. A solution of 1 g of $(CH_3)_4N[\pi$-(3)-1,2-$B_9C_2H_{11}]_2Fe$ in 150 ml of a 2:1 acetone–water mixture

---

[37] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

[38] G. Wilkinson, *Org. Syn.*, **36**, 31 (1956).

[39] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 6.

was shaken with excess sodium amalgam in the absence of air until the color had changed from red to deep pink. A 50% aqueous solution of tetramethylammonium chloride was then added under a stream of nitrogen until precipitation occurred. The precipitate was filtered, dried under vacuum, and stored in an inert atmosphere. Purification was effected by allowing an acetone–toluene solution of the complex to slowly evaporate under ambient conditions in a drybox. An almost quantitative yield of pure $[(CH_3)_4N]_2[\pi-(3)-1,2-B_9C_2H_{11}]_2Fe$ was obtained.

(b) $[(CH_3)_4N]_2[\pi-(3)-1,2-B_9C_2H_9(CH_3)_2]_2Fe$. The reduction of $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_9(CH_3)_2]_2Fe$ was carried out in the same manner as described above for the unsubstituted derivative, the red going to deep lavender blue for the Fe(II) species.

(c) $[(CH_3)_4N]_2[\pi-(3)-1,2-B_9C_2H_{10}(C_6H_5)]_2Fe$. Using the same procedure as described above, the deep blue 1-phenyl Fe(II) complex was obtained from the corresponding red Fe(III) derivative.

(d) $(CH_3)_4N(\pi-C_5H_5)Fe[\pi-(3)-1,2-B_9C_2H_{11}]$. A solution of the neutral Fe(III) species in acetone was shaken with excess sodium amalgam in the absence of air, the color changing from deep red to orange. The acetone solution was diluted with water, the acetone removed under reduced pressure, and the resulting aqueous solution treated with tetramethylammonium chloride solution to give an orange precipitate which could be crystallized from ethanol to yield orange plates of $(CH_3)_4N(\pi-C_5H_5)Fe[\pi-(3)-1,2-B_9C_2H_{11}]$ (mp 158°). *Anal.* Calcd for $(CH_3)_4N(C_5H_5)Fe(B_9C_2H_{11})$: Fe, 17.05; B, 29.73; C, 40.33; N, 4.28; H, 8.61. Found: Fe, 17.86; B, 29.44; C, 37.47; N, 4.74; H, 8.55. In contrast to the above Fe(II) derivatives, this compound was stable to oxidation by air. The infrared spectrum (Nujol mull) included absorptions at 2503 (s), 2370 (w), 1653 (w), 1302 (w), 1105 (s), 1025 (m), 1010 (m), 992 (m), 953 (s), 882 (m), 828 (m), 820 (s), and 770 (w) cm^{-1}.

The ^1H nmr data and the electronic spectra of the π-(3)-1,2-dicarbollyliron(II) derivatives are given in Tables V and VI.

Equivalent Weights of the Bis-π-(3)-1,2-dicarbollyliron(III) Anion Derivatives. Approximately 0.133 mmole of the pure tetramethylammonium or cesium salts of the bis-π-(3)-1,2-dicarbollyliron(III) derivatives was dissolved in the minimum amount of acetone and washed onto an acid ion-exchange column (1 in. × 18 in.) of Dowex resin (Dowex 50W-X12, 50–100 mesh, J. T. Baker Co.). The materials were eluted with 10 ml of 60:40 water–acetone mixture and then with distilled water. The acetone was removed from the solutions under reduced pressure, and the resulting solutions were titrated with standard sodium hydroxide solution. All the titration curves were typically those of strong acids. The results are tabulated in Table I.

Base Degradation of the Bis-π-(3)-1,2-dicarbollyliron(III) Anion Derivatives. A sample of 1,2-dimethyl complex, $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_9(CH_3)_2]_2Fe$ (0.500 g, 1.11 mmoles), was ion exchanged to the hydronium salt as described above. To the resulting aqueous solution was added 0.5 g (8.9 mmoles) of potassium hydroxide and the mixture refluxed under nitrogen for 4 hr. The red color of the iron complex was completely discharged. After cooling, the mixture was filtered, the precipitate dissolved in hydrochloric acid, and the iron content analyzed by the standard dichromate method[40]: iron content, calculated, 1.11 mmoles; found, 1.08 mmoles (97.8%). The colorless filtrate was treated with tetramethylammonium chloride, and the resulting white precipitate was isolated and dried to give 0.495 g (2.11 mmoles, 95%) of $(CH_3)_4N(3)-1,2-B_9C_2H_{10}(CH_3)_2$, as identified by its infrared spectrum.

Using the same procedure, 1.67 mmoles of the 1-phenyl derivative, $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_{10}(C_6H_5)]_2Fe$, gave 3.00 mmoles (90%) of $(CH_3)_4N(3)-1,2-B_9C_2H_{11}(C_6H_5)$ and 1.58 mmoles of iron (94.5%).

When a sample of the unsubstituted complex, $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_{11}]_2Fe$ (1.00 g, 2.54 mmoles), was subjected to the procedure described above, the color of the complex was not discharged over a 4-day period. The solution was diluted to 1 l. with distilled water, and using the characteristic 444-mμ (ϵ 585) band in the visible spectrum, no degradation could be detected.

Nonaqueous Preparation of π-(3)-1,2- and π-(3)-1,7-Dicarbollylcobalt(III) Derivatives. (a) $Cs[\pi-(3)-1,2-B_9C_2H_{11}]_2Co$. To a stirred suspension of 1.20 g (9.2 mmoles) of anhydrous cobaltous chloride in dry tetrahydrofuran (50 ml) was added under nitrogen a tetrahydrofuran solution of $Na_2(3)-1,2-B_9C_2H_{11}$ (5.2 mmoles). The resulting black mixture was refluxed for 2 hr under nitrogen, cooled, and filtered to remove the cobalt metal and sodium chloride. After removal of the solvent *in vacuo*, the residue was extracted with hot water, the resulting aqueous solution filtered, and the orange filtrate treated with cesium chloride. The yellow-orange precipitate was recrystallized from aqueous acetone to yield 0.84 g (1.85 mmoles, 72%) of dark yellow $Cs[\pi-(3)-1,2-B_9C_2H_{11}]_2Co$, mp >300°.

(b) $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_9(CH_3)_2]_2Co$. The 1,2-dimethyl derivative was prepared from 9.05 mmoles of $Na_2(3)-1,2-B_9C_2H_9(CH_3)_2$ and 19.2 mmoles (2.5 g) of anhydrous $CoCl_2$ in the manner described for the corresponding iron compound with the one exception that *in situ* oxidation by $CoCl_2$ renders the air-oxidation step unnecessary. The crude product was recrystallized from aqueous acetone to give 1.29 g (2.85 mmoles, 63%) of $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_9(CH_3)_2]_2Co$ as red plates, mp 273–275°.

(c) $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_{10}(C_6H_5)]_2Co$. Using the procedure described above, 11.1 mmoles of $Na_2(3)-1,2-B_9C_2H_{10}(C_6H_5)$ gave 3.9 mmoles (70%) of $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_{10}(C_6H_5)]_2Co$ as large red crystals from aqueous acetone, mp 290–293°.

The equivalent weights of the three bis-π-(3)-1,2-dicarbollylcobalt(III) derivatives were determined by the same procedure employed with the iron complexes. These results are given in Table VII.

(d) $(\pi-C_5H_5)Co[\pi-(3)-1,2-B_9C_2H_{11}]$. The same procedure used for the analogous iron derivative was employed with the mixed cobalt complex. A mixture of 15.5 mmoles of $Na_2(3)-1,2-B_9C_2H_{11}$ and 23.3 mmoles of NaC_5H_5 was allowed to react under nitrogen with 23.0 mmoles of anhydrous cobaltous chloride in tetrahydrofuran. The benzene extract of the reaction products was chromatographed on silica gel, eluting with 1:1 benzene–hexane. The product was recrystallized from methylene chloride–hexane to give yellow crystals of $(\pi-C_5H_5)Co[\pi-(3)-B_9C_2H_{11}]$, 0.60 g (2.34 mmoles, 15%), mp 246–248°.

(e) $Cs[\pi-(3)-1,5-B_9C_2H_{11}]_2Co$. Using the procedure described for the unsubstituted bis-1,2 derivative, a tetrahydrofuran solution of $Na_2-1,7-B_9C_2H_{11}$ (5.17 mmoles) treated with excess cobaltous chloride gave 0.945 g (2.07 mmoles, 80%) of $Cs[\pi-(3)-1,7-B_9C_2H_{11}]_2Co$ as tan-colored plates from aqueous acetone (mp >350°).

The analytical data, infrared absorptions, electronic spectra, and polarographic and ^1H nmr data for the π-(3)-1,2- and π-(3)-1,7-dicarbollylcobalt(III) derivatives are given in Tables VII–XI.

Aqueous Preparation of the Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylcobalt(III) Anions. (a) $[\pi-(3)-1,2-B_9C_2H_{11}]_2Co^-$. Using the procedure employed in the aqueous iron dicarbollide preparation, 20.0 g (103.4 mmoles) of $(CH_3)_3NH(3)-1,2-B_9C_2H_{12}$ was treated with 500 ml of freshly prepared 40% aqueous sodium hydroxide and 40 g (168 mmoles) of $CoCl_2 \cdot 6H_2O$. The mixture solidified on cooling and 500 ml of water was added before extracting with ethyl ether. The organic phase was separated, the solvent removed *in vacuo*, and the residue taken up in 1.5 l. of water and treated with 7.0 g (58 mmoles) of rubidium chloride, giving upon cooling 15.8 g (38.7 mmoles) of yellow-orange needles of $Rb[\pi-(3)-1,2-B_9C_2H_{11}]_2Co$. The filtrate was treated with 1.0 g of cesium chloride to give 0.90 g (2.0 mmoles) of the less soluble $Cs[\pi-(3)-1,2-B_9C_2H_{11}]_2Co$. The total yield was 78.7%.

(b) $[\pi-(3)-1,7-B_9C_2H_{11}]_2Co.^-$ A mixture containing 1.00 g (5.18 mmoles) of $(CH_3)_3NH(3)-1,7-B_9C_2H_{12}$, 2.00 g (8.42 mmoles) of $CoCl_2 \cdot 6H_2O$, and 40 ml of a freshly prepared 50% sodium hydroxide solution was treated as described above and heated at 100° for 6 hr under nitrogen with stirring. Upon cooling, the mixture was diluted to 100 ml with distilled water and worked up as above. Addition of an excess of cesium chloride to the aqueous solution of the sodium salt of the complex gave 1.064 g (2.34 mmoles, 90%) of tan $Cs[\pi-(3)-1,7-B_9C_2H_{11}]_2Co$, which was recrystallized from aqueous acetone.

Bromination of the Bis-π-(3)-1,2-dicarbollylcobalt(III) Anion. To a solution of 0.999 g (2.44 mmoles) of $Rb[\pi-(3)-1,2-B_9C_2H_{11}]_2Co$ in glacial acetic acid (60 ml) was added 10.0 g (3.4 ml, 62.5 mmoles) of bromine. The resulting mixture was heated at reflux temperature for 2 hr. The total volume was then reduced to *ca.* 20 ml, 150 ml of water added, and the mixture filtered. The filtrate was treated with excess aqueous tetramethylammonium chloride; the resulting yellow-orange precipitate was filtered and recrystallized from aqueous acetone at ambient temperature to give 1.636 g (1.88 mmoles, 77%) of orange, crystalline $(CH_3)_4N[\pi-(3)-1,2-B_9C_2H_8Br_3]_2Co$. The compound appeared to decompose in aqueous acetone, slowly at room temperature or rapidly if the solution was heated. Characterization data for the brominated derivative are given in Tables VII–XI.

Nonaqueous Preparation of the Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylnickel(III) Anions. (a) $(CH_3)_4N[\pi-(3)-1,7-B_9C_2H_{11}]_2Ni$. A solution of nickel acetylacetonate (0.667 g, 2.59 mmoles,

---

(40) W. C. Pierce, E. L. Haenisch, and D. T. Sawyer, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1958, p 317.

in tetrahydrofuran (35 ml)) was added dropwise under nitrogen to a stirred solution of Na$_2$(3)-1,7-B$_9$C$_2$H$_{11}$ (5.17 mmoles) prepared in the manner described above. The red mixture was heated at 35° under nitrogen for 3 hr, with stirring. Oxygen was then bubbled through the solution until it turned green (*ca.* 10 min). The mixture was filtered, the solvent removed *in vacuo*, the residue extracted with ether, and the ether evaporated to dryness. The residue was taken up in 50 ml of water and the resulting green aqueous solution treated with tetramethylammonium chloride. The product was recrystallized from aqueous acetone to give 0.804 g (2.02 mmoles, 78%) of olive-green (CH$_3$)$_4$N[π-(3)-1,7-B$_9$C$_2$H$_{11}$]$_2$Ni, mp >300°. The molar magnetic susceptibility was measured on the solid using the Faraday technique,[39] using copper sulfate pentahydrate as standard. A spin-only magnetic moment of 1.74 BM (corrected for diamagnetism using Pascal's constants) was obtained for this derivative.

(b) (CH$_3$)N$_4$[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni. Using the procedure described above, 5.45 mmoles of Na$_2$(3)-1,2-B$_9$C$_2$H$_{11}$ gave 0.80 g (2.01 mmoles, 84%) of yellow-brown (CH$_3$)$_4$N[π-(3)-1,2-B$_9$C$_2$H$_{11}$]Ni, mp >300°. The magnetic susceptibility measured on the solid by the Faraday technique gave a corrected spin-only magnetic moment of 1.76 BM.

Aqueous Preparation of the Bis-π-(3)-1,2-dicarbollylnickel(III) Anion. A mixture of 10.0 g (51.8 mmoles) of (CH$_3$)$_3$NH(3)-1,2-B$_9$C$_2$H$_{12}$, 20.0 g (84 mmoles) of NiCl$_2$.6H$_2$O, and 250 ml of freshly prepared 40% aqueous sodium hydroxide solution was treated as described in the aqueous iron dicarbollide preparation. The brown residue from the ether extraction was taken up in 300 ml of water, filtered, warmed to *ca.* 70°, and treated with 5.0 g (41.3 mmoles) of rubidium chloride. Upon cooling, 7.99 g (19.6 mmoles, 76%) of Rb[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni was obtained as black crystals with a greenish luster.

Preparation of Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylnickel(IV). (a) [π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni. A solution of 1.32 g of FeCl$_3\cdot$6H$_2$O (4.89 mmoles) in 250 ml of water was added slowly to a freshly prepared solution of 2.00 g (4.89 mmoles) of Rb[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni in 1 l. of warm water. The yellow precipitate formed was filtered, washed with water, and dried under vacuum. Further purification of this crude material (1.58 g) was achieved by column chromatography on silica gel with a 1:1 benzene–hexane mixture as the eluent. The solvents were reduced to a low volume *in vacuo* and heptane was added. Slow removal of the remaining benzene from the solution at room temperature under reduced pressure left orange crystals of pure [π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni, 1.43 g (4.43 moles, 90.5%). The compound decomposed at *ca.* 265°. The pure compound was sublimed unchanged at 150° under high vacuum.

(b) [π-(3)-1,7-B$_9$C$_2$H$_{11}$]$_2$Ni. The 1,7-dicarbollylnickel(IV) derivative was prepared in the same manner as the 1,2 isomer. The Rb[π-(3)-1,7-B$_9$C$_2$H$_{11}$]$_2$Ni (0.852 g, 2.09 mmoles) was obtained from a nonaqueous preparation, substituting rubidium chloride for tetramethylammonium chloride as the precipitating agent. The Ni complex was then treated with FeCl$_3\cdot$6H$_2$O (0.563 g, 2.08 mmoles) as described above. The crude, dried product was purified by column chromatography on silica gel with *n*-pentane as the eluent to give 0.575 g (1.78 mmoles, 85%) of [π-(3)-1,7-B$_9$C$_2$H$_{11}$]$_2$Ni as orange needles. Further purification was effected by rapid recrystallization from hot acetonitrile and by sublimation at 150° under high vacuum. The bis-1,7 compound was much less stable in solution than its bis-1,2 isomer.

The analytical data, infrared absorptions, electronic spectra, and polarographic data for the bis-π-(3)-1,2- and bis-π-(3)-1,7-dicarbollylnickel(III) and -(IV) derivatives are given in Tables XII–XV.

Reduction of Bis-π-(3)-1,2- and Bis-π-(3)-1,7-dicarbollylnickel(IV). A 0.502-g (1.55 mmoles) sample of [π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni was stirred under nitrogen for *ca.* 10 hr with mossy cadmium in 50 ml of reagent acetone. The acetone solution was treated with aqueous tetramethylammonium chloride and the acetone removed under reduced pressure to give 0.617 g (1.53 mmoles, 98.7%) of brown (CH$_3$)$_4$N[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni. The amount of cadmium consumed was 1.616 mequiv.

Similarly, 0.527 mmole of [π-(3)-1,7-B$_9$C$_2$H$_{11}$]$_2$Ni was reduced with mossy zinc metal to give 0.444 mmole (84%) of green (CH$_3$)$_4$N[π-(3)-1,7-B$_9$C$_2$H$_{11}$]$_2$Ni, 0.494 mequiv of zinc being consumed.

Preparation of the Bis-π-(3)-1,2-dicarbollylnickel(II) Dianion. To a solution of 2.00 g (4.89 mmoles) of Rb[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni in 120 ml of warm water were added 15 ml of 85% hydrazine and 15 g of potassium hydroxide (solid). The brown solution was stirred for several minutes until gas evolution ceased and then cooled. A cold, slightly basic solution containing 1.50 g (7.15 mmoles) of tetraethylammonium bromide was added to this with stirring. The pale yellow precipitate was filtered, washed once with deoxygenated ice–water, and dried under vacuum. This crude material was crystallized in a drybox under a dry nitrogen atmosphere by slowly dripping dry, degassed heptane into a concentrated dry, degassed acetone solution of the compound with stirring. Pale brown needles of [(C$_2$H$_5$)$_4$N]$_2$[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Ni formed, 1.72 g (2.95 mmoles, 60.3%). Because of the extreme air sensitivity of the salt, a satisfactory elemental analysis was not obtained. *Anal.* Calcd for [(C$_2$H$_5$)$_4$N]$_2$(B$_9$C$_2$H$_{11}$)$_2$Ni: Ni, 10.05; N, 33.32; C, 41.13; N, 4.80; H, 10.70. Found: Ni, 11.24; N, 32.19; C, 37.51; N, 4.69; H, 11.60. The ^{11}B nmr of the compound *in acetone solution showed no resonances due to the nickel(III)* species. The molar magnetic susceptibility was measured on the solid using the Faraday technique. A spin-only magnetic moment of 2.90 BM (corrected for diamagnetism, as above) was obtained for the complex. The infrared spectrum of the tetraethylammonium salt is given in Table XIII.

Preparation of the Bis-π-(3)-1,2-dicarbollylcopper(II) Dianion. The preparation of the copper complex utilized the standard aqueous procedure, with the following modification. A 1.00-g (5.17 mmoles) sample of (CH$_3$)$_3$NH(3)-1,2-B$_9$C$_2$H$_{12}$ was treated with 30 ml of freshly prepared 40% sodium hydroxide solution as described above. This was then cooled to 0° before adding a cooled aqueous solution of CuSO$_4\cdot$5H$_2$O (1.50 g, 6.0 mmoles). The intense blue mixture was stirred at 0° and filtered, and the filtrate was diluted to approximately twice its volume with cold distilled water. A cooled, slightly basic solution containing 1.0 g (4.76 mmoles) of (C$_2$H$_5$)$_4$NBr was added with stirring. The blue precipitate was filtered, washed with ice–water, dried under vacuum, and crystallized in the same manner as the nickel(II) complex. The yield of deep blue crystalline [(C$_2$H$_5$)$_4$N]$_2$[π-(3)-1,2-B$_9$C$_2$H$_{11}$]$_2$Cu was 0.917 g (1.56 mmoles, 60.4%). The infrared spectrum (Nujol mull) of the compound contained absorptions at 2053 (s), 2044 (m), 1306 (m), 1240 (w), 1135 (s), 1122 (w), 1082 (m), 1066 (m), 1032 (s), 1016 (m), 1008 (m), 972 (s), 953 (m), 944 (m), 923 (m), 908 (m) 880 (s), 795 (s), 763 (m), and 736 (m) cm^{-1}.

Preparation of π-Tetraphenylcyclobutadienyl-π-(3)-1,2-dicarbollylpalladium(II) Derivatives. (a) [π-C$_4$(C$_6$H$_5$)$_4$]Pd[π-(3)-1,2-B$_9$C$_2$H$_9$(CH$_3$)$_2$]. A tetrahydrofuran solution containing 3.94 mmoles of Na$_2$(3)-1,2-B$_9$C$_2$H$_9$(CH$_3$)$_2$ was added slowly under nitrogen to a stirred suspension of 2.10 g (3.94) mmoles) of [π-C$_4$(C$_6$H$_5$)$_4$]PdCl$_2$ dimer[27] in 100 ml of tetrahydrofuran. The reaction mixture was stirred under nitrogen at room temperature for 3 hr and filtered, the solvent removed *in vacuo*, and the residue extracted with benzene. The benzene extract was chromatographed on a silica gel column. Elution with 60:40 benzene–hexane gave a red material as the major fraction. The yield of red [π-C$_4$(C$_6$H$_5$)$_4$]Pd[π-(3)-1,2-B$_9$C$_2$H$_9$(CH$_3$)$_2$] after crystallization from methylene chloride–hexane was 0.16 g (0.257 mmole, 6.5%). *Anal.* Calcd for C$_4$(C$_6$H$_5$)$_4$Pd[B$_9$C$_2$H$_9$(CH$_3$)$_2$]: Pd, 17.12; B, 15.61; C, 61.70; H, 5.62; mol wt, 622.9. Found: Pd, 17.17; B, 15.62; C, 61.66; H, 5.53; mol wt, 652 (osmometric in benzene). The electronic spectrum in methylene chloride solution gave λ_{max}, mμ (ϵ): 440 (3600), 363 (76,100), 300 (36,900), 252 (25,100). The infrared spectrum (Nujol mull) contained absorptions at 2515 (s), 1588 (w), 1302 (w), 1179 (w), 1073 (m), 1021 (m), 996 (m) 920 (w), 858 (m), 779 (s), 756 (m), 750 (s), 733 (m), 708 (s), 700 (s), and 687 (m) cm^{-1}.

(b) [π-C$_4$(C$_6$H$_5$)$_4$]Pd[π-(3)-1,2-B$_9$C$_2$H$_{11}$]. The unsubstituted derivative was prepared in the manner described above for the 1,2-dimethyl derivative. The reaction between 9.0 mmoles each of π-C$_4$(C$_6$H$_5$)$_4$PdCl$_2$ and Na$_2$(3)-1,2-B$_9$C$_2$H$_{11}$ gave 0.9 mmole (10%) of red [π-C$_4$(C$_6$H$_5$)$_4$]Pd[π-(3)-1,2-B$_9$C$_2$H$_{11}$], dec pt 310°. *Anal.* Calcd for C$_4$(C$_6$H$_5$)$_4$Pd(B$_9$C$_2$H$_{11}$): Pd, 17.90; B, 16.30; C, 60.60; H, 5.24; mol wt, 595.5. Found: Pd, 18.42; B, 16.09; C, 60.46; H, 5.42; mol wt, 571 (osmometric in benzene). The electronic spectrum in methylene chloride solution gave λ_{max}, mμ (ϵ): 433 (3360), 355 (64,300), 294 (30,600), 250 (19,800). The infrared spectrum (Nujol mull) contained absorptions at 2515 (s), 1588 (w), 1311 (w), 1181 (m), 1084 (m), 1028 (w), 1016 (w), 1002 (w), 976 (m), 924 (w), 785 (s), 752 (s), 706 (s), 696 (s), and 686 (m) cm^{-1}.

Preparation of the π-(3)-1,2-Dicarbollylmanganese and -rhenium Tricarbonyl Anions. (a) Cs[π-(3)-1,2-B$_9$C$_2$H$_{11}$]Mn(CO)$_3$. A tetrahydrofuran solution containing 5.18 mmoles of Na$_2$(3)-1,2-B$_9$C$_2$H$_{11}$ was added under nitrogen to a tetrahydrofuran solution of 1.42 g (5.18 mmoles) of BrMn(CO)$_5$. The mixture was refluxed under nitrogen for 4 hr and filtered, the solvent removed *in vacuo*, and the residue taken up in 50 ml of water. The aqueous solution was treated with cesium chloride, and the resulting precipitate crystallized from warm water to give 1.16 g (2.87 mmoles, 55.5%) of pale yellow Cs[π-(3)-1,2-$B_9C_2H_{11}$]Mn$(CO)_3$. *Anal.* Calcd for Cs($B_9C_2H_{11}$)Mn$(CO)_3$: Mn, 13.60; B, 24.10; C, 14.85; H, 2.74; Cs, 32.90; equiv wt, 404.4. Found: Mn, 13.19; B, 24.15; C, 14.72; H, 3.17; Cs, 32.88; equiv wt, 410.8. The equivalent weights of π-(3)-1,2-dicarbollylmanganese and -rhenium tricarbonyl anions were obtained using the same procedure employed for the bis-π-1,2-dicarbollyliron(III) and -cobalt(III) derivatives. The electronic spectrum in methanol solution gave λ_{max}, mμ (ϵ): 212 (33,300), 346 (2500). The infrared spectrum (Nujol mull) included absorptions at 2535 (s), 2345 (m), 2015 (s), 1905 (s), 1875 (s), 1215 (w), 1153 (w), 1133 (w), 1111 (w), 1028 (m), 997 (m), and 670 (m) cm^{-1}.

(b) Cs[π-(3)-1,2-$B_9C_2H_{11}$]Re$(CO)_3$. Using the same procedure as described above, 5.18 mmoles of Na_2(3)-1,2-$B_9C_2H_{11}$ in tetrahydrofuran was heated at reflux under nitrogen with 2.1 g (5.18 mmoles) of BrRe$(CO)_5$ for 6 hr. The product was isolated as the cesium salt and crystallized from water. The yield of very pale yellow Cs[π-(3)-1,2-$B_9C_2H_{11}$]Re$(CO)_3$ was 1.164 g (2.17 mmoles, 42%). *Anal.* Calcd for Cs($B_9C_2H_{11}$)Re$(CO)_3$: Re, 34.80; B, 18.22; C, 11.23; H, 2.07; Cs, 24.78; equiv wt, 535.65. Found: Re, 35.27; B, 18.00; C, 11.70; H, 2.15; Cs, 24.04; equiv wt, 548. The electronic spectrum in methanol solution gave λ_{max}, mμ (ϵ): 210 (24,000) and 272 (2900). The infrared spectrum (Nujol mull) included absorptions at 2520 (s), 2140 (m), 1988 (s), 1880 (s), 1853 (s), 1213 (w), 1028 (w), and 1013 (w) cm^{-1}.

Preparation of the π-(3)-1,2-Dicarbollylmolybdenum and -tungsten Tricarbonyl Dianions and Related Binuclear Species. (a) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$. To a tetrahydrofuran solution (100 ml) of 15.0 mmoles of Na_2(3)-1,2-$B_9C_2H_{11}$ in a quartz tube was added 5.28 g (15.0 mmoles) of tungsten hexacarbonyl; the tube was flushed with nitrogen and kept under a slight static pressure of the gas. The tungsten hexacarbonyl did not dissolve immediately and the mixture was stirred. The tube was irradiated with a Hanovia, Type A, 500-w mercury lamp for 37 hr. The solution immediately turned yellow with evolution of carbon monoxide upon irradiation, which was stopped when there was no more evolution of gas. The orange-yellow solution was poured into 1.5 l. of water and an excess of a 50% aqueous solution of tetramethylammonium chloride was added. The copious yellow precipitate was collected by filtration and dried under vacuum, yield 6.5 g (11.9 mmoles, 79%) of crude $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$. The product was recrystallized three times from acetone by slow evaporation of the solvent under reduced pressure. All recrystallization operations were performed in a drybox in an inert atmosphere. The infrared spectrum (Nujol mull) included absorptions at 2551 (s), 2463 (s), 1858 (s), 1730 (s), 1375 (m), 1096 (w), 1070 (w), 1032 (w), 980 (w), 948 (m), and 856 (w) cm^{-1}.

(b) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$. In the manner described above, 20 mmoles of Na_2(3)-1,2-$B_9C_2H_{11}$ and 5.28 g (20 mmoles) of molybdenum hexacarbonyl in 100 ml of tetrahydrofuran were irradiated for 24 hr. The yield of $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$ was 7.7 g (16.7 mmoles, 83.6%). The product was recrystallized three times under an inert atmosphere by precipitation with benzene from an acetone solution. The final product consisted of shiny metallic gray plates. The infrared spectrum (Nujol mull) included absorptions at 2545 (s), 2457 (s), 1860 (s), 1750 (s), 1288 (m), 1192 (w), 1093 (w), 1068 (w), 1027 (m), 1018 (m), 959 (s), and 902 (w) cm^{-1}.

(c) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_9(CH_3)_2$]Mo$(CO)_3$. Irradiation of 20 mmoles of Na_2(3)-1,2-$B_9C_2H_9(CH_3)_2$ and 6.28 g (20 mmoles) of molybdenum hexacarbonyl in 100 ml of tetrahydrofuran under nitrogen for 36 hr gave 7.5 g (15.4 mmoles, 77%) of $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_9(CH_3)_2$]Mo$(CO)_3$ using the procedure described above. The product was recrystallized five times under an inert atmosphere by precipitating from acetone with benzene–pentane (75:25 v/v), giving a pale yellow microcrystalline compound. The infrared spectrum (Nujol mull) included absorptions at 2469 (s), 2445 (s), 1864 (s), 1724 (s), 1286 (w), 1153 (w), 1068 (m), 1013 (m), 948 (s), 892 (w), 856 (m), and 767 (w) cm^{-1}.

(d) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$W$(CO)_5$. A mixture of 30 mmoles of Na_2(3)-1,2-$B_9C_2H_{11}$ and 24.64 g (70 mmoles) of tungsten hexacarbonyl in 250 ml of tetrahydrofuran was refluxed under nitrogen for 60 hr. The mixture was poured into 2 l. of water, and an excess of an aqueous 50% tetramethylammonium chloride solution was added. An orange oil was obtained which solidified when the supernatant liquid was decanted and water added. The product was collected by filtration and dried under vacuum. The yield of $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$W$(CO)_5$ was 17.7 g (20.3 mmoles, 67.6%). The compound was recrystallized five times under an inert atmosphere by precipitation from acetone with benzene. Benzene of crystallization (evident from the ^{1}H nmr) was removed by dissolving the compound in acetone and adding pentane. The oil obtained could be solidified by decanting the supernatant and triturating with fresh pentane. The infrared spectrum (Nujol mull) included absorptions at 2551 (s), 2506 (s), 1997 (s), 1874 (s), 1852 (s), 1777 (s), 1280 (w), 1222 (w), 1092 (m), 1023 (w), 974 (m), 947 (s), 895 (w), and 742 (m) cm^{-1}.

(e) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_9(CH_3)_2$]Mo$(CO)_3$Mo$(CO)_5$. A solution of 20 mmoles of Na_2(3)-1,2-$B_9C_2H_9(CH_3)_2$ in 150 ml of tetrahydrofuran was heated under nitrogen with 13.2 g (50 mmoles) of molybdenum hexacarbonyl for 18 hr. The reaction mixture was worked up as described above. The yield of yellow $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_9(CH_3)_2$]Mo$(CO)_3$Mo$(CO)_5$ was 11.9 g (16.5 mmoles, 82.3%). The product was recrystallized five times as above from acetone with benzene–pentane (75:25 v/v). The infrared spectrum (Nujol mull) contained absorptions at 2506 (m), 2012 (s), 1882 (s), 1835 (s), 1760 (s), 1004 (w), and 947 (m).

(f) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$Mo$(CO)_5$. A solution of 20 mmoles of Na_2(3)-1,2-$B_9C_2H_{11}$ in 100 ml of tetrahydrofuran was photolyzed under nitrogen in the presence of 20 mmoles of tungsten hexacarbonyl as described above. Molybdenum hexacarbonyl, 7.92 g (30 mmoles), was added and the mixture refluxed under nitrogen for 24 hr, after which it was worked up as described above. The yield of orange-yellow $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$Mo$(CO)_5$ was 13.5 g (17.2 mmoles, 85%). The product was recrystallized five times from acetone–benzene–pentane and once from acetone–pentane as described above. The infrared spectrum (Nujol mull) contained absorptions at 2540 (s), 2500 (s), 1990 (s), 1892 (s), 1852 (s), 1778 (s), 1582 (w), 1308 (w), 1286 (w), 1178 (m), 1150 (m), 1085 (m), 1037 (m), 1003 (w), 977 (w), 948 (s), and 862 (w) cm^{-1}.

(g) $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$W$(CO)_5$. The reaction mixture from the photolysis of 20 mmoles of Na_2(3)-1,2-$B_9C_2H_{11}$ with 20 mmoles of molybdenum hexacarbonyl for 24 hr was refluxed under nitrogen with 30 mmoles of tungsten hexacarbonyl for 48 hr. The yield of $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$W$(CO)_5$ was 15.5 g (19.8 mmoles, 99%). The material was recrystallized as described above. The infrared spectrum (Nujol mull) included absorptions at 2540 (s), 2506 (s), 1996 (s), 1892 (s), 1853 (s , 1790 (s), 1575 (m), 1312 (w), 1284 (w), 1180 (s), 1152 (m), 1086 (m), 1037 (m), 1003 (w), 973 (m), 948 (s), 858 (m), and 743 (m) cm^{-1}.

Preparation of Methylated π-(3)-1,2-Dicarbollylmolybdenum and -tungsten Tricarbonyl Anions. (a) $(CH_3)_4N$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3CH_3$. To a tetrahydrofuran solution (100 ml) containing 20 mmoles of Na_2[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3$, prepared as described above, was added methyl iodide (14.2 g, 100 mmoles), and the mixture was heated to 40° under nitrogen for 24 hr. The reaction mixture was poured in 1 l. of water and treated with an excess of 50% aqueous tetramethylammonium chloride. An oil separated from which the supernatant was decanted. When the oil was triturated with water, it solidified. The product was dried under vacuum, giving 9.7 g (19.8 mmoles, 99%) of $(CH_3)_4N$[π-(3)-1,2-$B_9C_2H_{11}$]W$(CO)_3CH_3$. The material was recrystallized three times under an inert atmosphere by precipitation from acetone with 2:1 ethyl ether–pentane, and the pale greenish yellow product was dried under vacuum. The infrared spectrum (Nujol mull) contained absorptions at 2506 (s), 1988 (s), 1873 (s), 1283 (w), 1178 (w), 1098 (m), 1062 (w), 1026 (m), 1012 (w), 983 (m), 948 (s), 767 (w), and 743 (m) cm^{-1}.

(b) $(CH_3)_4N$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3CH_3$. A tetrahydrofuran solution of 20 mmoles of Na_2[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$ was treated with 100 mmoles of methyl iodide as described above. The yield of tan $(CH_3)_4N$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3CH_3$ was 6.1 g (15.2 mmoles, 76%). The infrared spectrum (Nujol mull) contained absorptions at 2506 (s), 1996 (s), 1892 (s), 1636 (w), 1160 (w), 1093 (w), 1027 (w), 982 (m), and 947 (m) cm^{-1}.

Protonation of the π-(3)-1,2-Dicarbollylmolybdenum Tricarbonyl Dianion. All of the following operations were carried out under an inert atmosphere. Dry hydrogen chloride was passed through a solution of 2.0 g (4.35 mmoles) of $[(CH_3)_4N]_2$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$ in 200 ml of dry acetonitrile for 1 hr during which time the initially green solution became red. The solvent and excess hydrogen chloride were removed under high vacuum. The residue was extracted with dry acetone giving a red solution which was separated from the insoluble tetramethylammonium chloride by filtration. The solvent was removed *in vacuo*, and the red oily residue solidified upon trituration with pentane, yielding a red solid, 1.1 g (2.85 mmoles, 65.4% based on $(CH_3)_4N$[π-(3)-1,2-$B_9C_2H_{11}$]Mo$(CO)_3$H). A 0.2007-g sample was titrated with standard base in 125 ml of 50% aqueous acetone, giving an equivalent weight of 392 (calculated for $(CH_3)_4N(B_9C_2H_{11})$Mo$(CO)_3$H, 389).

The infrared spectrum (Nujol mull) of the solid included absorptions at 2519 (s), 2048 (s), 1940 (s), 1022 (w), 982 (w), and 948 (m) cm^{-1}.

Analytical data and solution infrared absorptions in the carbonyl region for the π-(3)-1,2-dicarbollylmolybdenum and -tungsten carbonyl derivatives are given in Tables XVI and XVII.

Acknowledgment. The authors wish to express their gratitude to the Army Research Office (Durham) and to the donors of the Petroleum Research Fund administered by the American Chemical Society for their generous support of this research.

The Reconstruction of the 1,2-Dicarbaclovododecaborane(12) Structure by Boron-Atom Insertion with (3)-1,2-Dicarbollide Ions

M. Frederick Hawthorne and Patrick A. Wegner

Contribution from the Department of Chemistry, The University of California, Riverside, California. *Received August 18, 1967*

Abstract: A series of (3)-1,2-dicarbollide ions were employed with phenylboron dichloride or ethylboron dichloride to reconstitute the 1,2-dicarbaclovododecaborane(12) icosahedron. This boron insertion reaction yields B-substituted 1,2-dicarbaclovododecaborane(12) derivatives which were further degraded to 6-substituted (3)-1,2-dicarbadodecahydroundecaborate(−1) ions. The latter ions were converted to the corresponding (3)-1,2-dicarbollide ions which were employed in subsequent insertion reactions and in the formation of a representative transition metal derivative.

Previous reports of the chemistry of the (3)-1,2-dicarbollide ion[1–7] and its carbon-substituted derivatives have dealt with the formation of transition metal complexes which resemble the π-bonded metallocenes. We now wish to amplify our earlier report[8] of the reaction of the (3)-1,2-dicarbollide ion with phenylboron dichloride which led to the first synthesis of B-aryl derivatives of the 1,2-dicarbaclovododecaborane(12) system by boron-atom insertion. The only previously reported derivatives of 1,2-dicarbaclovododecaborane(12) which bear an organic substitutent on boron were 8- and 9-ethyl-1,2-dicarbaclovododecaborane(12) which were obtained as a mixture from the reaction of 1- and 2-ethyldecaborane(14) with acetylene and not separated.[9]

Results and Discussion

Phenylboron dichloride and the (3)-1,2-dicarbollide ion reacted in tetrahydrofuran (THF) solution to produce 3-phenyl-1,2-dicarbaclovododecaborane(12) (I) according to eq 1. The yields of I were 80–85%, while

$$C_6H_5BCl_2 + Na_2B_9C_2H_{11} \xrightarrow[THF]{} 2NaCl + \underset{\text{I}}{C_6H_5B_{10}C_2H_{11}} \quad (1)$$

the recovery of sodium chloride based upon the above equation was quantitative. Other B-phenyl derivatives of substituted 1,2-dicarbaclovododecaborane(12) were prepared in analogous reactions. The 1,2-dimethyl-(3)-1,2-dicarbollide and the 1-phenyl-(3)-1,2-dicarbollide ions reacted with phenylboron dichloride to produce 3-phenyl-1,2-dimethyl-1,2-dicarbaclovododecaborane(12) (II) and 1,3-diphenyl-1,2-dicarbaclovododecaborane(12) (III) in 55 and 38% yield, respectively. A B-ethyl derivative, 3-ethyl-1,2-dicarbaclovododecaborane(12) (IV), was formed in 49% yield from ethylboron dichloride and the (3)-1,2-dicarbollide ion.

The preparation of compounds I–IV illustrated that the insertion reaction was successful using the (3)-1,2-dicarbollide ion and its carbon-substituted derivatives with both aryl- and alkylboron dichlorides. The B-phenyl-substituted derivatives (I–III) were sublimable, white crystalline solids, while the B-ethyl derivative was a viscous liquid. The B-substituted derivatives, in general, have physical properties comparable to those of the corresponding B-unsubstituted 1,2-dicarbaclovododecaborane(12) derivatives.

The characterization data for I–IV are presented in Table I. An osmometric molecular weight determination of I was in good agreement with theory (calculated 220, found 227). The infrared spectra of I–IV contained B–H stretching bands in the 2550–2580-cm^{-1} region of the infrared spectrum. Compounds I, II, and III contained absorption bands characteristic of a monosubstituted phenyl ring near 700 cm^{-1} while I, III, and IV contained an absorption band due to the carboranyl carbon–hydrogen stretch at 3000 cm^{-1}.

The ^1H nmr spectra of I–IV presented in Table II confirmed their formulation as B-substituted 1,2-dicarbaclovododecaborane(12) derivatives. Integration of these spectra proved that the original substituents on the carbon atoms of the precursor (3)-1,2-dicarbollide ion

---

(1) M. F. Hawthorne, D. C. Young, and P. A. Wegner, *J. Am. Chem. Soc.*, **87**, 1818 (1965).

(2) M. F. Hawthorne and R. L. Pilling, *ibid.*, **87**, 3987 (1965).

(3) M. F. Hawthorne and T. D. Andrews, *Chem. Commun.*, 443 (1965).

(4) M. F. Hawthorne and T. D. Andrews, *J. Am. Chem. Soc.*, **87**, 2496 (1965).

(5) P. A. Wegner and M. F. Hawthorne, *Chem. Commun.*, **861** (1966).

(6) L. F. Warren and M. F. Hawthorne, *J. Am. Chem. Soc.*, **89**, 470 (1967).

(7) 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, *ibid.*, **90**, 879 (1968).

(8) M. F. Hawthorne and P. A. Wegner, *ibid.*, 87, 4392 (1965).

(9) T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).