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Benzodicarbollide and Dihydrobenzodicarbollide Ions and Their Complexes with Manganese, Cobalt, and Nickel

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(1,4-Dihydrobenzo)carborane (1) has been brominated to (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (7), which on treatment with excess base yields the hydrogen benzodicarbollide ion (5). Benzocarborane (4) has been degraded with base in another preparation of 5, and 1 has been converted to the hydrogen (1,4-dihydrobenzo)dicarbollide ion (2). Several unsuccessful attempts to convert the dibromo compound 7 to benzocarborane (4) and the products obtained are described. Deprotonation of the monoanions 2 and 5 with sodium hydride has yielded the (1,4-dihydrobenzo)dicarbollide ion (3) and benzodicarbollide ion (6). The conversion of 3 to manganese and cobalt complexes and of 6 to manganese, cobalt, and nickel complexes has been accomplished. The nmr and electronic spectra of benzodicarbollide derivatives are consistent with a slight degree of aromatic character in the carbocyclic ring.

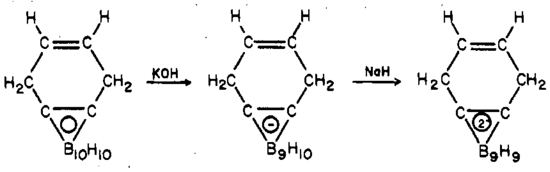
Introduction

Benzocarborane, which has a benzene ring and an *o*-carborane cage fused along one edge, is a very stable compound but shows little evidence of aromatic character in the carbocyclic ring.[2] Naphthocarborane is highly reactive and essentially nonaromatic.[3] Conversion of benzocarborane to a dicarbollide anion[4] should increase the degree of π bonding between the cage and the ring[5] and also lead to dicarbollyl complexes of transition metals.

Our synthesis of benzocarborane[2] is somewhat inconvenient, and in the present work we have succeeded in finding a shorter route to the benzodicarbollide anion, though not to benzocarborane itself. We have also investigated the synthesis of transition metal complexes of (1,4-dihydrobenzo)dicarbollide ion for comparison with the benzodicarbollide complexes. We have synthesized benzodicarbollylmetal complexes and examined their nmr and electronic spectra for evidence of ring-cage conjugation.

Results

Syntheses of Benzodicarbollide and Related Ions. Following one of Hawthorne's procedures for degrading the carborane cage,[6] (1,4-dihydrobenzo)carborane (1) reacted with ethanolic potassium hydroxide to form the hydrogen (1,4-dihydrobenzo)dicarbollide monoanion (2), which on deprotonation with sodium hydride[7] yielded the (1,4-dihydrobenzo)dicarbollide dianion (3). Benzocarborane (4) (Figure 1) was degraded with piperidine[7] to the monoanion (5) (not illustrated, but like 6 with a proton added to the pentagonal face), which with sodium hydride yielded the benzodicarbollide dianion (6) (Figure 1). The systematic names of these compounds are cumbersome and difficult to define precisely,[8] and we find it more convenient to extend Hawthorne's dicarbollide nomenclature to cover all of these ions in a self-consistent way.



1 2 3

The only deficiency in the foregoing route to the benzodicarbollide ion (6) lies in the inefficiency of the prerequisite preparation of benzocarborane (4). The conversion of (1,4-dihydrobenzo)carborane (1) to benzocarborane (4) requires an allylic bromination followed by a dehydrobromination.[2b] Purification of the allylic bromination products (two isomers) is difficult, and the unconverted (1,4-dihydrobenzo)carborane (1) that remains in the bromination products also persists in the benzocarborane (4) itself until a special purification procedure is carried out.[2b] We therefore sought a better route to benzocarborane.

We have previously reported that dihydrobenzocarborane (1) is inert toward bromine,[2b] but D. S. M. was skeptical enough to repeat the experiment and careless enough to cap the flask with aluminum foil. The aluminum bromide from corrosion of the aluminum foil proved a sufficient and necessary catalyst for completion of the bromination in about 1 hr, and the resulting (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (7) was obtained in better than 90% yield and proved easy to purify.

If the dibromo compound (7) could be dehydrobrominated, it should yield benzocarborane (4), but the reaction with base does not go that way. Instead, the first step is degradation of the carborane cage to the hydrogen (2,3-dibromo-1,2,3,4-tetrahydrobenzo)dicarbollide ion (8), which can be

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(1) (a) National Aeronautics and Space Administration Fellow, 1966-1969. (b) This work was supported in part by U. S. Public Health Service Grant No. CA-05513 from the National Cancer Institute. (c) Abstracted from the Ph.D. thesis of R. E. G., Washington State University, 1970.

(2) (a) N. K. Hota and D. S. Matteson, *J. Amer. Chem. Soc.*, 90, 3570 (1968); (b) D. S. Matteson and N. K. Hota, *ibid.*, 93, 2893 (1971).

(3) (a) D. S. Matteson and R. A. Davis, *Chem. Commun.*, 669 (1970); (b) D. S. Matteson and R. A. Davis, *Inorg. Chem.*, in press.

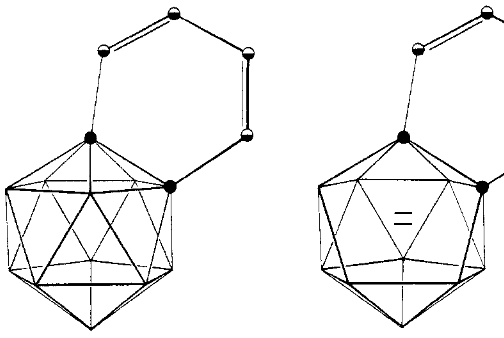
(4) M. F. Hawthorne, *Accounts Chem. Res.*, 1, 281 (1968).

(5) See for example L. I. Zakharkin, V. N. Kalinin, B. A. Kvasov, E. I. Fedin, and A. P. Snyakin, *Dokl. Akad. Nauk SSSR*, 184, 854 (1969).

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

(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, *J. Amer. Chem. Soc.*, 90, 879 (1968).

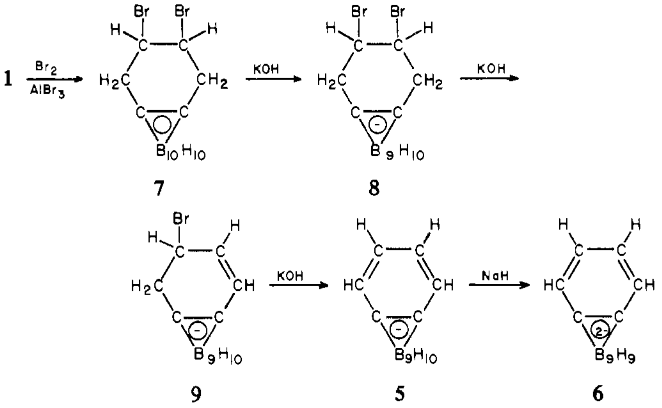
(8) For example, a systematic name for benzocarborane (4) might be benzo-1,2-dicarba-*closo*-dodecaborane(12), provided it is assumed the ring-cage juncture must contain the two cage carbon atoms. If this restriction is lifted, the edge of the cage could be specified by a letter insert, as in complex heterocycles: benzo-[*a*]-1,2-dicarba-*closo*-dodecaborane(12). This becomes ambiguous for higher numbered edges of the icosahedron in the absence of any established convention, and it would be clearer to use a numerical prefix: 1,2-benzo-1,2-dicarba-*closo*-dodecaborane(12). The monoanion (5) is either 7,8-benzo-7,8-dicarba-*nido*-undecaborate(12)(1−) or 7,8-benzododecahydro-7,8-dicarba-*nido*-undecaborate(1−), and the dianion (6) is 7,8-benzo-7,8-dicarba-*nido*-undecaborate(11)(2−), etc. The "dicarbollide" nomenclature proposed by Hawthorne lacks a term for the 7,8-dicarba-*nido*-undecaborate(12)(1−) ion, and we have adopted "hydrogen dicarbollide" to fill the gap.



4 6

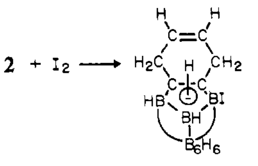
Figure 1. Structure diagrams of benzocarborane (4) and the benzodicarbollide ion (6). Darkened circles represent C, half-filled circles CH, and unmarked line junctions BH.

isolated as the tetramethylammonium salt if the base treatment is mild enough. Further base treatment dehydrobrominates **8** to the allylic bromo compound **9**, which was not isolated but detected by nmr, and **9** is dehydrobrominated to the hydrogen benzodicarbollide ion (**5**). Thus, this route makes the benzodicarbollide ion (**6**) more conveniently available than benzocarborane (**4**).



We also briefly investigated the halogenation of the hydrogen 1,4-dihydrobenzodicarbollide monoanion (**2**). The double bond is not affected, but iodine attacks the cage. From the work of Olson and Hawthorne on the halogenation of hydrogen dicarbollide ion $(C_2B_9H_{12}^-)$,[9] the iodine atom should be attached to a boron atom in the pentagonal face adjacent to carbon, and our product is therefore the hydrogen (1,4-dihydrobenzo)-4-iodo-(3)-1,2-dicarbollide ion (**10**), which might be named systematically as 7,8-(2,3-cyclohexeno)-9-iodo-7,8-dicarba-*nido*-undecaborate(12)(1−).

We still wanted a better synthesis of benzocarborane (**4**) itself, and we made several more attempts to prepare it from (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (**7**). Refluxing **7** with lithium chloride in dimethylformamide led to an unsaturated chloro compound which from its nmr spectrum appeared to be (2-chloro-1,4-dihydrobenzo)carborane (**11**). Substitution of chloride for bromide is an unexpected result, whether it takes place directly on **7** or subsequently on an initially formed vinylic bromide. It might seem easier to rationalize the formation of an isomeric allylic chloride such as **12**, but **12** would probably dehydrochlorinate in refluxing dimethylformamide, and the nmr data are also inconsistent with structure **12**.



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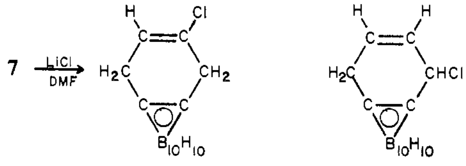
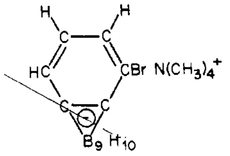


11 12 (not found)

Pyrolysis of the dibromo compound (**7**) did result in some dehydrobromination to benzocarborane (**4**) but also yielded an approximately equal amount of debromination to dihydrobenzocarborane (**1**), and the difficulty of separating these two compounds[2] makes this approach useless.

In earlier work,[2a] we had noted the presence of a by-product believed to be (1-bromobenzo)carborane in our benzocarborane preparation. This compound disappeared when the dehydrobromination in dimethylformamide was adopted.[2b] Evidently its fate is to undergo cage degradation in hot dimethylformamide. When we added tetramethylammonium chloride to aqueous extracts from the preparation of benzocarborane from impure bromodihydrobenzocarboranes,[2b] we obtained not the benzodicarbollide salt (**5**) but a compound believed to be tetramethylammonium hydrogen (1-bromobenzo)dicarbollide (**13**). The possibility that it is the 2-bromo isomer cannot be excluded.



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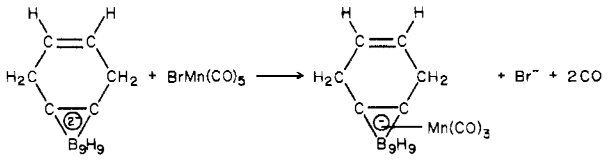
Synthesis of Metal Complexes. We have converted the (1,4-dihydrobenzo)dicarbollide ion (**3**) and the benzodicarbollide ion (**6**) to manganese and cobalt complexes by standard methods.[4,7]

Bromomanganese pentacarbonyl reacts with benzodicarbollide ion (**6**) to form benzodicarbollylmanganese(I) tricarbonyl monanion (**14**) (Figure 2), which was isolated as the tetramethylammonium salt. (1,4-Dihydrobenzo)dicarbollide ion (**3**) was similarly converted to its manganese tricarbonyl derivative (**15**).



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Anhydrous cobalt(II) chloride in tetrahydrofuran reacts with benzodicarbollide ion (**6**) to form the bis(benzodicarbollyl)cobaltate(III) monoanion (**16**) (Figure 3), which was isolated as the tetramethylammonium salt. The reaction with dihydrobenzodicarbollide ion (**3**) was more sluggish and required refluxing diglyme [bis(2-methoxyethyl) ether] as solvent in order to produce a fair yield of the bis((1,4-

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[9] F. P. Olson and M. F. Hawthorne, *Inorg. Chem.*, 4, 1839 (1965).

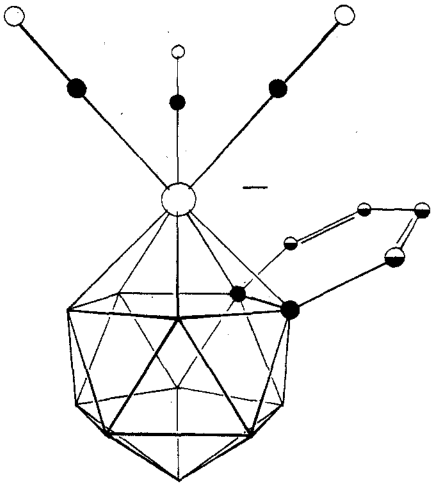


Figure 2. Structure diagram of the benzodicarbollylmanganese(I) tricarbonyl ion (**14**). The large open circle represents Mn; small open circles represent O, darkened circles C, half-filled circles CH, and unmarked line junctions BH.

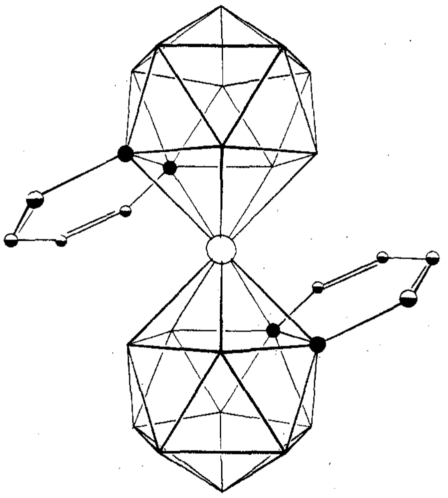
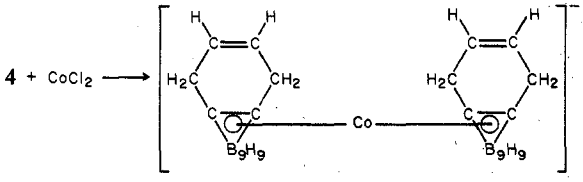


Figure 3. Structure diagram of the bis(benzodicarbollyl)cobaltate(III) ion (**16**). The large open circle represents Co; darkened circles represent C, half-filled circles CH, and unmarked line junctions BH. The relative rotational orientations of the two cages were chosen to show both rings clearly and do not necessarily represent a preferred conformation.



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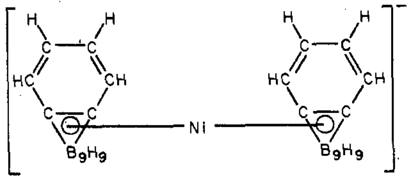
dihydrobenzo)dicarbollyl)cobaltate(III) salt (**17**). The presence of a small amount of unsubstituted dicarbollide ion, $C_2B_9H_{11}{}^{2-}$, in the sample of **4** led to the formation of a minor by-product, tetramethylammonium dicarbollyl((1,4-dihydrobenzo)dicarbollyl)cobaltate(III), $(C_2B_9H_{11})Co(C_6B_9H_{15})$ (**18**).

Analogous metal derivatives of cyclopentenodicarbollide ion have been described by Hawthorne and coworkers.[10]

We expended considerable effort trying to make a nickel complex of the benzodicarbollide ion (**6**), with results that are partly inconclusive but interesting enough to warrant further investigation. Reaction of **6** with nickel(II) iodide in diglyme at 110° in the presence of a catalytic amount of piperidine led to what appears to be tetramethylammonium bis(benzodicarbollyl)nickelate(III) (**19**). The spectra and carbon, hydrogen, and nitrogen analyses support structure **19**, but the boron analysis is too low and the nickel too high to be consistent with any reasonable structure, suggesting perhaps an unanticipated interference between these elements in the analysis.

We also obtained a neutral, diamagnetic purple by-product which we tentatively formulate as the dimer of benzodicarbollylnickel(II) (**20**). The nmr spectrum shows the typical A_2B_2 pattern of benzocarborane[2] but at an unusually high field, δ 1.54, which is nearly 4 ppm upfield from the corresponding multiplet of the benzodicarbollide anion itself. This strongly suggests that the nickel is complexed with the diene system of benzodicarbollide anion. The nmr spectrum shows no tetramethylammonium ion, and the infrared spectrum is similar to that of benzocarborane itself. Again, the carbon and hydrogen analyses support the proposed structure, but the boron and nickel analyses are inconsistent with anything reasonable. Structure **20** is proposed as having the correct number of bonding electrons and is consistent with the spectral data.



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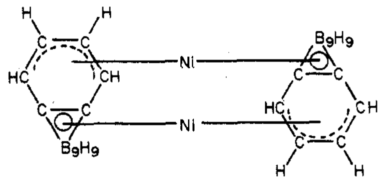

20 (tentative)

Reactions of a Manganese Complex (15). (1,4-Dihydrobenzo)dicarbollylmanganese(I) tricarbonyl anion (**15**) was the most accessible of our dicarbollyl complexes, and we made a brief study of its reactivity. Photolysis of cyclopentadienylmanganese tricarbonyl in the presence of olefins is known to lead to replacement of one carbon monoxide with an olefinic ligand.[11,12] We thought that the double bond of **15** might be in a position to coordinate internally with the manganese atom but were disappointed by the results of ultraviolet photolysis of its tetramethylammonium salt in methanol in a quartz flask. A light yellow solution resulted, which immediately turned orange on exposure to oxygen. Concentration of the solution yielded an acetone-insoluble tan solid which showed only B–O and O–H absorptions in the infrared spectrum, indicating destruction of the cage. The volatile fraction was found to react with bromine, and gas chromatography revealed the presence of cyclohexene. In addition to these decomposition products, a 49% yield of tetramethylammonium hydrogen (1,4-dihydrobenzo)dicarbollide (**2**) was isolated. When a solution of **2** was irradiated under similar conditions, 75% of its was recovered unchanged, and no cyclohexene was found in the volatile fraction.

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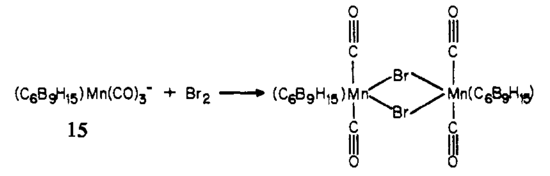
[10] D. A. T. Young, T. E. Paxson, and M. F. Hawthorne, *Inorg. Chem.*, 10, 789 (1971).

[11] W. Strohmeier, *Angew. Chem., Int. Ed. Engl.*, 3, 730 (1964).

[12] M. L. Ziegler, *Inorg. Chem.*, 4, 1230 (1965).

We also tried to replace a carbonyl group of **15** by prolonged (60-100 hr) refluxing in ethanol with diphenylacetylene or triphenylphosphine but recovered the starting materials in each case.

The manganese complex (**15**) has several sites that might be attacked by bromine, including the carborane cage, the manganese atom, and the double bond. The manganese turned out to be the most easily attacked. The analysis indicated replacement of one carbon monoxide by bromine, but since the nmr spectrum shows that the product is diamagnetic, it must be formulated as the bis((1,4-dihydrobenzo)dicarbollylbromomanganese dicarbonyl) dianion (**21**).



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Physical Measurements. Polarographic reduction of bis(benzodicarbollyl)cobaltate(III) (**16**) showed a two-electron wave at −1.14 V. Bis(benzodicarbollyl)nickelate(III) (**19**) yielded one-electron waves at −0.72 and −1.14 V. For comparison, the one-electron potential for $Co(C_2B_9H_{11})_2^-$ is −1.42 V, for the *C*-methyl compound $Co[(C_2(CH_3)_2B_9H_9]_2^-$ is −1.13 V, and for $Ni(C_2B_9H_{11})_2^-$ is −0.56 V.[7] The one-electron potential for a *B*-bromo compound $Co(C_2B_9H_9Br_3)_2^-$ is −0.48 V, and the second electron is accepted at −1.58 V. We were unable to oxidize our nickel(III) complex **19** with ferric chloride to form the nickel(IV) complex, which indicates that oxidation is more difficult than usual.[7]

The nmr spectra of the various benzocarborane derivatives each showed an A_2B_2 pattern characterisitic of the -CH=CH—CH=CH- group. The chemical shifts are of interest in connection with the question of the possible aromaticity of the ring and are summarized in Table I.

We have measured the ultraviolet-visible spectra of most of our new compounds. The complete details are in the Experimental Section, but some useful comparisons of absorption band positions are summarized in Table II.

Discussion

The synthetic work described is straightforward and needs little comment. We did find it more difficult to make metal complexes from dihydrobenzodicarbollide ion (**3**) and benzodicarbollide ion (**6**) than from unsubstituted dicarbollide ion, but this is typical of substituted dicarbollides.[4] For example, aqueous hydroxide suffices to generate dicarbollide ion for preparation of the cobalt complex but fails with substituted dicarbollides[4] and fails with benzodicarbollide. Our cyclic compounds appeared less reactive than most, and we failed to obtain any iron complexes under the usual conditions,[4] though we did not vary the conditions as we did in order to obtain the benzodicarbollylnickel complex (**19**).

We made a few attempts to prepare diene complexes of benzocarborane (**4**) with palladium chloride, dicobalt octacarbonyl, or triiron dodecacarbonyl but recovered unchanged benzocarborane (**4**) in each case, under conditions where the metal carbonyls began to decompose. The extreme steric hindrance by the BH groups to either side of the plane of the ring[3] accounts for these negative results.

We had originally hoped to find some evidence for conjugation between the fused benzene ring and carborane cage. The conjugation is weak partly because the molecular orbitals of the carborane cage are at much lower energy levels than the benzene π orbitals,[2b] and bonding is always weak in such situations. The energy levels in the dicarbollide ion should be somewhat higher and conjugation with the ring should therefore be stronger. Similar effects have been noted in physical organic studies of aryl-substituted carboranes and dicarbollides.[5] The energy levels of the cage electrons in dicarbollylmetal complexes relative to those in the carborane cage itself are not predictable on the basis of simplified theories.

Table I. Chemical Shifts of Centers of -CH=CH—CH=CH- A_2B_2 Multiplets in Benzocarborane and Benzodicarbollides

Compd	Solvent	Chem shift, δ, ppm
Benzocarborane (**4**)	CCl_4	6.38
$C_6B_9H_{14}^-$ (**5**)	DMSO-d_6	5.76
$C_6B_9H_{13}^{2-}$ (**6**)	THF	5.48
$Co(C_6B_9H_{13})_2^-$ (**16**)	DMSO-d_6	6.42
$(C_6B_9H_{13})Mn(CO)_3^-$ (**14**)	DMSO-d_6	6.11
$[Ni(C_6B_9H_{13})]_2$ (**20**)	DMSO-d_6	1.54

Table II. Electronic Spectral Bands of Selected Carborane and Dicarbollyl Compounds

Compd	Band positions, nm
Benzocarborane (**4**)	220, 260, 270[a]
$C_6B_9H_{14}^-$ (**5**)	208, 240, 250, 318
$C_6B_9H_{16}^-$ (**2**)	217, 232
$Co(C_2B_9H_{11})_2^-$	216, 293, 345, 445[b]
$(C_2B_9H_{11})Co(C_6B_9H_{15})^-$ (**18**)	212, 281, 329
$Co(C_6B_9H_{13})_2^-$ (**16**)	246, 279, 418, 576
$(C_2B_9H_{11})Mn(CO)_3^-$	212, 346[b]
$(C_6B_9H_{15})Mn(CO)_3^-$ (**15**)	218, 264 sh, 354, 520 w
$(C_6B_9H_1)Mn(CO)_3^-$ (**14**)	216, 260 sh, 368
$Ni(C_2B_9H_{11})_2^-$	237, 337, 435[b]
$Ni(C_6B_9H_{13})_2^-$ (**19**)	204, 210, 248, 330, 380, 428, 472

[a] Reference 2. Benzocarborane also has weaker peaks at 252 and 282 nm. [b] Reference 7.

The nmr spectra do reveal some evidence for ring-cage conjugation in the hydrogen benzodicarbollide ion (**5**) and the benzodicarbollide ion (**6**). These -CH=CH—CH=CH- groups absorb at significantly higher field (by 0.62 and 0.90 ppm, respectively) than does benzocarborane (**4**) (Table I), evidently because the negative charge is significantly delocalized to the ring. (The increase in aromatic character of the benzenoid ring should cause some downfield shift, but it is reasonable that this should be overruled by the electron density effect.) Much less effect is seen on converting (1,4-dihydrobenzo)carborane (**1**) (δ 3.0 and 5.65) to the corresponding monoanion **2** (δ 2.79 and 5.55). The cobalt and manganese complexes of both benzodicarbollide ion (**6**) and dihydrobenzodicarbollide ion (**3**) all show very little shift from the corresponding parent icosahedral carboranes.

Electronic excited states would do the most to overcome the effect of the ring-cage energy level differences. Three of the bands of the bis(benzodicarbollyl)cobaltate(III) ion (**16**) (Table II) show substantial bathochromic shifts; one does not, compared to the unconjugated compounds $Co(C_2B_9H_{11})_2^-$ and $(C_2B_9H_{11})Co(C_6B_9H_{15})^-$ (**18**). The 368-nm band of the benzodicarbollylmanganese tricarbonyl ion (**14**) shows a small bathochromic shift compared with the corresponding bands of the unconjugated analogs. Bis(benzodicarbollyl)nickelate(III) (**19**) shows a far more complex spectrum than the unsubstituted analog.

At first glance, it might seem strange that the benzenoid ring absorptions of benzocarborane (**4**) appear at longer wavelengths than those of the hydrogen benzodicarbollide anion (**5**), but the excitation in question probably occurs parallel to the line of ring–cage junction. Excited-state stabilization by ring–cage conjugation requires excitation perpendicular to this line (but in the plane of the ring). Perhaps the rather weak (ϵ 975) additional band at 318 nm in the spectrum of **5** is due to such an excitation. In any case, it is clear that not all of the bands should undergo bathochromic shift when ring–cage conjugation is introduced or enhanced in a series of compounds.

Any aromatic character in the benzenoid ring will result in a tendency to withdraw electron density from the cage, the ring being a very electron-deficient one,[2b] and complexed metals should be stabilized in lower oxidation states. The limited oxidation–reduction data seem consistent with this idea.

In summary, all of our data are consistent with a small degree of conjugation between the ring and the cage and a small amount of aromatic character in the carbocyclic ring of benzocarborane, benzodicarbollylmetal complexes, and benzodicarbollide ion.

Experimental Section

Trimethylammonium Hydrogen (1,4-Dihydrobenzo)dicarbollide (2). The procedure is based on one by Hawthorne and coworkers.[6] A 2.63-g (13.4-mmol) portion of (1,4-dihydrobenzo)carborane (**1**) was added to a solution of 1.50 g (26.7 mmol) of potassium hydroxide in 50 ml of absolute ethanol under nitrogen, stirred 1 hr at 25°, and refluxed 12 hr. The solution was cooled to 25°, diluted with 50 ml of absolute ethanol, saturated with carbon dioxide, and filtered to remove potassium carbonate; the solid was washed with more ethanol, and the filtrate was concentrated under vacuum to yield an oil which crystallized on standing. The crude salt was dissolved in 40 ml of hot water, cooled, and washed with two 20-ml portions of ether. A solution of 2.55 g (26.7 mmol) of trimethylammonium chloride in 10 ml of water was added to the aqueous solution and the trimethylammonium hydrogen (1,4-dihydrobenzo)dicarbollide (**2**) separated either as a precipitate or as a colorless oil which crystallized on cooling to 0°. The crude salt was recrystallized from hot water to yield 3.00 g (91%) of **2**, plates, mp 104–105°. Ir (KBr): 3106 (s), 3021 (m), 2976 (w), 2882 (w), 2841 (m), 2747 (m), 2513 (vs, BH), 1639 (w, C=C), 1460 (s), 1427 (s), 1404 (m), 1374 (m), 1245 (w), 1230 (w), 1215 (w), 1152 (m), 1008 (s), 997 (s), 876 (w), 831 (w), 672 (m) cm^{-1}. Nmr (DMSO-d_6): δ 2.79 (single peak, 13, N–CH_3 + C–CH_2–CH), 5.55 (broadened single peak, 2, –CH=CH–). Uv (methanol): 217 nm (ϵ 4620), 232 nm (sh, ϵ 3384). *Anal.* Calcd for $C_9H_{26}B_9N$: C, 44.00; H, 10.68; B, 39.65; N, 5.72. Found: C, 44.24; H, 10.69; B, 39.46; N, 5.48.

(2,3-Dibromo-1,2,3,4-tetrahydrobenzo)carborane (1). A small amount of aluminum foil (~1 cm^2) was added to a solution of 4.82 g (24.6 mmol) of (1,4-dihydrobenzo)carborane in 50 ml of methylene chloride, followed by 5.80 g (37 mmol) of bromine. The mixture was stirred under nitrogen for 75 min, filtered, and concentrated under vacuum. The residue was crystallized from methanol–water and sublimed at 180° (0.05 mm), yielding 9.05 g (93%) of (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (**7**), mp 193–195°. The analytical sample was recrystallized from *m*-xylene. Ir (CCl_4): 3115 (m), 2985 (w), 2950 (m), 2874 (w), 2618 (vs), 1449 (m), 1351 (w), 1250 (w), 1212 (w), 1188 (m), 1143 (w), 1031 (m), 961 (m), 935 (w), 892 (m), 870 (m), 757 (s) cm^{-1}. Nmr (CCl_4): δ 3.19 (d, J = 5 Hz, 4, CH_2), 4.07 (t, J = 5 Hz, 2, CHBr). Uv (methanol): 245 nm (ϵ 378). Mass spectrum: *m/e* 354 (mol wt), 275 (base peak), 230, 195, with boron isotope patterns. *Anal.* Calcd for $C_6H_{16}B_{10}Br_2$: C, 20.23; H, 4.52; B, 30.35; Br, 44.87. Found: C, 20.32; H, 4.75; B, 30.15; Br, 44.69.

Tetramethylammonium Hydrogen Benzodicarbollide (5) from Benzocarborane (4). A 200-mg (1.03-mmol) sample of benzocarborane (**4**) was mixed with 1 ml of piperidine. An exothermic reaction occurred immediately, and the sample was warmed to 60–80° for a few minutes until a homogeneous solution was formed. The solution was diluted with 10 ml of methanol and treated with 2.0 g (18 mmol) of tetramethylammonium chloride in 7 ml of water, followed by 30 ml of water to complete the precipitation of the tetramethylammonium salt of **5**. The precipitate was recrystallized from hot water to yield 268 mg (101%) of plates which did not melt below 300°. The analytical sample recrystallized from methanol–water. *Anal.* Calcd for $C_{10}H_{26}B_9N$: C, 46.62; H, 10.17; B, 37.77; N, 5.44. Found: C, 46.99; H, 10.02; B, 37.98; N, 5.25.

Tetramethylammonium Hydrogen Benzodicarbollide (5) from (2,3-Dibromo-1,2,3,4-tetrahydrobenzo)carborane (7). A solution of 200 mg (0.561 mmol) of **7** and 120 mg (1.8 mmol) of 85% potassium hydroxide in 25 ml of absolute ethanol was stirred 1 hr at 25° and refluxed 2 hr under nitrogen. Potassium bromide was removed by filtration and washed with ethanol. The combined filtrate was concentrated to ~20 ml and treated with 1.0 g of tetramethylammonium chloride in 10 ml of water; then the mixture was diluted further with water to precipitate the product. Recrystallization from hot water yielded 138 mg (9.5%) of **5**. Ir (KBr): 3030 (m), 2941 (w), 2907 (w), 2558 (vs), 1555 (m), 1481 (s), 1447 (w), 1416 (m), 1393 (w), 1284 (w), 1230 (m), 1175 (w), 1149 (m), 1031 (m), 1010 (m), 944 (s), 902 (w), 778 (w), 741 (w), 702 (w) cm^{-1} (same as analytical sample). Nmr (DMSO-d_6): δ 3.12 (s, 12, NCH_3), 5.76 (m, 4, CH=CH–CH=CH–. Uv (methanol): 208 nm (ϵ 9500), 240 nm (ϵ 6395), 250 nm (ϵ 5160), 318 nm (ϵ 975).

Tetramethylammonium Hydrogen (2,3-Dibromo-1,2,3,4-tetrabenzo)dicarbollide (8). A solution of 0.356 g (1.0 mmol) of (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (**7**) and 0.170 g (4 mmol) of lithium chloride in 50 ml of acetone was refluxed 4 hr under nitrogen. The mixture was cooled, filtered, and concentrated, and the residue was recrystallized from methanol–water to yield 0.276 g (78%) of unconverted **7**, identified by nmr. The filtrate was treated with tetramethylammonium chloride and the precipitate was recrystallized from methanol–water; yield 0.075 g (18%) of **8**; mp 195–196°. Nmr (DMSO-d_6): δ 3.17 (s, 12, NCH_3), 3.67 (apparent s, 4, CH_2), 4.43 (m, 2, CHBr). Ir (KBr): 3021 (w), 2915 (w), 2849 (w), 2513 (vs), 1481 (s), 1449 (w), 1431 (w), 1416 (w), 1284 (w), 1205 (w), 1181 (w), 1096 (w), 1071 (w), 1022 (w), 946 (s), 837 (w), 794 (w), 762 (w) cm^{-1}. Uv (methanol): 206 nm (ϵ 4055), 242 nm (sh, ϵ 879). *Anal.* Calcd for $C_{10}H_{28}B_9Br_2N$: C, 28.70; H, 6.75; B, 23.20; Br, 28.10; N, 3.34. Found: C, 28.50; H, 6.04; B, 23.13; Br, 28.56; N, 3.41.

Reaction of (2,3-Dibromo-1,2,3,4-tetrahydrobenzo)carborane (7) with a Deficient Amount of Potassium Hydroxide. A solution of 356 mg (1.0 mmol) of **7** and 132 mg (2.0 mmol) of 85% potassium hydroxide in 50 ml of absolute ethanol was refluxed 4 hr under nitrogen, concentrated under vacuum, and treated with water, which did not precipitate any carboranes. Addition of excess tetramethylammonium chloride precipitated the product mixture, which was recrystallized from methanol–water to yield 300 mg (100%) of a mixture of tetramethylammonium and (2,3-dibromo-1,2,3,4-tetrahydrobenzo)dicarbollide (**8**) (22%) by nmr analysis. Similar treatment of 1 mmol of **7** and 0.056 g (0.9 mmol) of potassium hydroxide led to isolation of 190 mg (54%) of unchanged **7**, mp 193–195°, whose identity was checked by nmr, and 140 mg (~43%) of a mixture of **5** (50%), **9** (28%), and **8** (22%).

Tetramethylammonium Hydrogen *B*-Iodo(1,4-dihydrobenzo)dicarbollide (10). A solution of 490 mg (2 mmol) of trimethylammonium hydrogen (1,4-dihydrobenzo)dicarbollide and 132 mg (2 mmol) of potassium hydroxide in 10 ml of methanol was heated on a steam bath to drive out trimethylamine, cooled to 25°, and stirred during the dropwise addition of 254 mg (2 mmol) of iodine in 10 ml of methanol. The iodine color was discharged immediately. The solution was concentrated under vacuum to ~10 ml and mixed with a solution of 1 g (9 mmol) of tetramethylammonium chloride in 100 ml of water. The precipitate was recrystallized from ethanol–water, yielding 0.48 g (62%) of *B*-iodo(1,4-dihydrobenzo)dicarbollide, mp 158° dec. Ir (KBr): 3021 (m), 2959 (w), 2890 (w), 2825 (w), 2513 (vs), 1664 (w, C=C), 1481 (s), 1429 (m), 1412 (m), 1284 (w), 1224 (w), 1151 (w), 1063 (w), 1018 (m), 991 (m), 945 (s), 877 (w), 812 (m), 756 (w), 671 (w) cm^{-1}. Nmr (DMSO-d_6): δ 3.11 (single peak, 16, N–CH_3 + C–CH_2–CH), 5.58 (broadened single peak, 2, –CH=CH–). Uv (methanol): 219 nm (ϵ 3430), 277 nm (sh, ϵ 29), 295 nm (ϵ 24). *Anal.* Calcd for $C_{10}H_{27}B_9IN$: C, 31.15; H, 7.06; B, 25.24; I, 32.92; N, 3.63. Found: C, 31.72; H, 7.34; B, 27.22; I, 30.70; N, 3.74.

(2-Chloro-1,4-dihydrobenzo)carborane (11). A solution of 200 mg (0.56 mmol) of (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (**7**) and 85 mg (2 mmol) of lithium chloride in 10 ml of dimethylformamide was refluxed under nitrogen for 8 hr. The dimethylformamide was distilled under vacuum, the residue was triturated with carbon tetrachloride, and the lithium salts were removed by filtration. The carbon tetrachloride was removed under vacuum, the residue was dissolved in methanol, and the product was crystallized by adding water; yield 51 mg (39%) of **11**. It was then recrystallized from methanol–water and sublimed; mp 88–90°. Nmr (CCl_4): δ 3.17 (unresolved s + d, 4, CH_2 + CH_2CH=), 5.80 (t, J = 3 Hz, 1, CH_2CH=). Mass spectrum: *m/e* 230 ($C_6H_{15}{}^{10}B_2{}^{11}B_8{}^{35}Cl^+$) and isotopic satellites, *m/e* 195 (strongest peak). Uv (methanol): 204 nm (ϵ 2030), 241 nm (sh, ϵ 86), 284 nm (ϵ 46). Ir (KBr): 2959 (w), 2915 (w), 2825 (w), 2591 (s), 2577 (s), 2558 (s), 1669 (w), 1429 (w), 1350 (w), 1340 (w), 1295 (w), 1256 (w), 1193 (w), 1024 (s), 980 (m), 970 (m), 898 (w), 824 (m), 769 (w), 736 (w), 726 (m), 698 (m) cm^{-1}. *Anal.* Calcd for $C_6H_{15}B_{10}Cl$: C, 31.23; H, 6.55; B, 46.85; Cl, 15.36. Found: C, 32.69; H, 6.61; B, 47.85; Cl, 13.99.

Thermolysis of (2,3-Dibromo-1,2,3,4-tetrahydrobenzo)carborane (7). A 200-mg sample of 7 was placed in a glass tube and heated under argon at atmospheric pressure with a flame for several minutes until the melted sample began to reflux. The blackened sample solidified on cooling and was triturated with carbon tetrachloride and filtered. The nmr spectrum indicated that the sample consisted of 76% unconverted 7, 12% benzocarborane (4), and 12% (1,4-dihydrobenzo)carborane (1). Sublimation of another 200-mg sample of 7 under argon at atmospheric pressure at 300° yielded a sublimate which was 50% unchanged 7, 12% 4, and 38% 1.

Sodium Hydride and (2,3-Dibromo-1,2,3,4-tetrahydrobenzo)carborane (7). A solution of 155 mg (0.435 mmol) of 7 in 25 ml of tetrahydrofuran with 500 mg (21 mmol) of sodium hydride was refluxed 4 hr under nitrogen. By nmr analysis the product consisted of 80% unchanged 7, 10% benzocarborane (4), and 10% (1,4-dihydrobenzo)carborane (1).

Tetramethylammonium Hydrogen (1-Bromobenzo)dicarbollide (13). From a preparation of benzocarborane in the usual manner,[2b] the aqueous solution remaining after extraction of the benzocarborane was treated with excess tetramethylammonium chloride and the precipitate of 13 was recrystallized from methanol–water; mp 193–195°. Nmr (DMSO-d_6): δ 3.12 (s, 12, NCH_3), 6.04 (m, 3, =*CH*–*CH*–*CH*–). Ir (KBr): 3030 (w), 2513 (vs), 1610 (m), 1481 (s), 1418 (w), 1284 (w), 1220 (m), 1156 (w), 1058 (w), 1026 (m), 984 (w), 943 (s), 816 (m), 741 (w) cm^{-1}. Uv (methanol): 220 nm (ϵ 9370), 242 nm (ϵ 6170), 331 nm (ϵ 673). *Anal.* Calcd for $C_{10}H_{25}B_9BrN$: C, 35.69; H, 7.48; B, 28.91; Br, 23.74; N, 4.16. Found: C, 35.14; H, 7.42; B, 28.54; Br, 23.21; N, 4.22.

Disodium (1,4-Dihydrobenzo)dicarbollide (3). This was prepared by the method of Hawthorne and coworkers[7] from 2 mmol of trimethylammonium hydrogen (1,4-dihydrobenzo)dicarbollide and 8 mmol of sodium hydride in 50 ml of tetrahydrofuran.

Tetramethylammonium Salt of (1,4-Dihydrobenzo)dicarbollylmanganese(I) Tricarbonyl (15). A solution of 8 mmol of disodium (1,4-dihydrobenzo)dicarbollide (3) in 200 ml of tetrahydrofuran was added dropwise to 2.60 g (8 mmol) of bromomanganese pentacarbonyl in 100 ml of anhydrous tetrahydroduran under nitrogen; the mixture was then refluxed 8 hr. The sodium bromide was removed by filtration and the solvent was distilled under vacuum. The brown oily residue was extracted with 200 ml of hot water and filtered; the filtrate was concentrated to 100 ml under vacuum. A solution of 1.75 g (16 mmol) of tetramethylammonium chloride in 15 ml of hot water was added, the yellow precipitate was collected and dissolved in acetone, 50 ml of water was added, and the product was crystallized by slow removal of the acetone at reduced pressure, yielding 1.94 g (61%) of pale yellow **15**, mp 252° dec, an air-stable but light-sensitive compound. Ir (KBr): 3300 (w), 2907 (w), 2841 (w), 2618 (w), 2551 (s), 2500 (s), 2463 (s), 1988 (vs), 1890 (vs), 1473 (m), 1425 (m), 1410 (w), 1295 (w), 1280 (w), 1124 (w), 1029 (w), 1018 (m), 970 (w), 943 (m), 729 (w), 677 (m), 657 (m), 639 (m) cm^{-1}. Nmr (DMSO-d_6): δ 2.92 (single peak, 16, NCH_3 + C–CH_2CH), 5.52 (broadened single peak, 2, –*CH*=*CH*–). Uv (methanol): 218 nm (ϵ 24,100), 264 nm (sh, ϵ 8420), 354 nm (ϵ 2160), 520 nm (ϵ 324). *Anal.* Calcd for $C_{13}H_{27}B_9MnNO_3$: C, 39.39; H, 6.86; B, 24.50; Mn, 13.82; N, 3.53. Found: C, 39.15; H, 6.87; B, 24.70; Mn, 14.04; N, 3.30.

Tetramethylammonium Salt of Bis(1,4-dihydrobenzo)dicarbollylbromomanganese(II) Dicarbonyl) Anion (21). A solution of 640 mg (4 mmol) of bromine in 50 ml of methanol was added dropwise under nitrogen to a solution of 400 mg (1 mmol) of the tetramethylammonium salt of (1,4-dihydrobenzo)dicarbollylmanganese(I) tricarbonyl anion in 50 ml of methanol. The bromine color was discharged immediately. The solution was stirred overnight under nitrogen and concentrated under vacuum. The yellow-brown residue was dissolved in acetone; the solution was filtered and added to 25 ml of water, and the acetone was evaporated slowly under reduced pressure, yielding 120 mg (23%) of yellow microcrystalline **21**, mp 253° dec. The analytical sample was chromatographed on silica gel with 1:1 methylene chloride–acetonitrile and recrystallized from acetone–water and again from acetonitrile–water. Ir (KBr): 3030 (w), 2907 (w), 2849 (w), 2597 (vs), 2519 (vs), 2000 (vs), 1890 (vs), 1481 (s), 1445 (m), 1418 (w), 1332 (w), 1285 (w), 1217 (w), 1163 (w), 1125 (w), 1015 (m), 991 (w), 943 (s), 917 (w), 808 (w), 789 (s), 770 (s), 746 (w), 718 (w), 687 (w), 670 (s), 661 (s), 642 (s) cm^{-1}. Nmr (DMSO-d_6): δ 2.78 (broadened single peak, 8, C–CH_2–CH), 3.12 (s, 24, NCH_3), 5.57 (broadened single peak, 4, –*CH*=*CH*–). Uv (methanol): 216 nm (ϵ 23,150), 360 nm (ϵ 2040). *Anal.* Calcd for $C_{24}H_{54}B_{18}Br_2Mn_2N_2O_4$: C, 32.06; H, 6.05; B, 21.65; Br, 17.78; Mn, 12.22; N, 3.12. Found: C, 32.36; H, 5.65; B, 21.92; Br, 17.84; Mn, 12.32; N, 2.86.

Photolysis of the Tetramethylammonium Salt of (1,4-Dihydrobenzo)dicarbollylmanganese(I) Tricarbonyl (15). A solution of 0.4 g of **15** in 50 ml of methanol in a quartz flask was irradiated with a "Mineralight" ultraviolet lamp under nitrogen for 24 hr. Distillation under vacuum yielded a methanol solution which decolorized bromine and yielded a peak having the same retention time as cyclohexene on gas chromatography. From the residue, half the starting material (15) was recovered, together with some acetone-insoluble material which appeared to be boric acid or related material from its infrared spectrum (3200- and 1351-cm^{-1} bands prominent).

Tetramethylammonium Bis(1,4-dihydrobenzo)dicarbollyl)cobaltate(III) (17). A solution of 0.36 g (1.5 mmol) of cobalt(II) chloride hexahydrate and 1.87 g (18 mmol) of 2,2-dimethoxypropane in 50 ml of anhydrous diglyme was refluxed under nitrogen overnight. The acetone, methanol, and excess 2,2-dimethoxypropane were removed by distillation, and the resulting cobalt(II) chloride solution in diglyme was added dropwise under nitrogen to a stirred solution of 2 mmol of disodium (1,4-dihydrobenzo)dicarbollide in diglyme and the mixture was refluxed overnight. The cobalt metal was removed by filtration and the diglyme was distilled under vacuum. The dark red residue was extracted with 50 ml of hot water, filtered, and treated with a solution of 0.44 g (4 mmol) of tetramethylammonium chloride in 10 ml of water. After cooling to 5°, the red-brown precipitate was collected and recrystallized from hot water to yield 0.18 g (30%) of **17** as the pentahydrate, mp 125° dec. Ir (KBr): 3571 (s), 3030 (w), 2959 (w), 2841 (w), 2545 (vs), 1613 (m), 1473 (s), 1425 (m), 1253 (m), 1215 (w), 1089 (m), 979 (w), 943 (m), 876 (w), 832 (m), 746 (m), 656 (w) cm^{-1}. Nmr (DMSO-d_6): δ 31.0–3.19 (two roughly equal peaks, 20, NCH_3 + C–CH_2–CH), 5.66 (broadened single peak, 4, –*CH*=*CH*–). *Anal.* Calcd for $C_{12}H_{52}B_{18}CoNO_5$: C, 32.50; H, 8.85; B, 32.85; Co, 9.95; N, 2.37. Found: C, 32.58; H, 8.96; B, 32.91; Co, 10.01; N, 2.39.

Tetramethylammonium Dicarbollyl((1,4-dihydrobenzo)dicarbollyl)cobaltate(III) (18). This was isolated in 30-mg (6%) yield as a result of contamination by dicarbollide ion in the (1,4-dihydrobenzo)dicarbollide from the preceding preparation of **17**. Compound **18** was found in the water-insoluble residue and was recrystallized from methanol–water; it did not melt up to 300°. Ir (KBr): 3030 (w), 2907 (w), 2849 (w), 2525 (vs), 1481 (s), 1466 (w), 1416 (w), 1357 (w), 1269 (w), 1220 (w), 1111 (m), 1042 (m), 1010 (m), 980 (m), 943 (s), 909 (w), 873 (w), 741 (w), 714 (w) cm^{-1}. Uv (methanol): 212 nm (ϵ 8490), 281 nm (ϵ 18,200), 329 nm (ϵ 7140). *Anal.* Calcd for $C_{12}H_{38}B_{18}CoN$: C, 32.03; H, 8.51; B, 43.24; Co, 13.09; N, 3.11. Found: C, 30.60; H, 8.54; B, 40.70; Co, 13.63; N, 3.10.

Potassium Sodium Benzodicarbollide (6). A solution of 2 mmol of potassium hydrogen benzodicarbollide (5) in ethanol, prepared from either benzocarborane (4) or (2,3-dibromo-1,2,3,4-tetrahydrobenzo)carborane (7) and potassium hydroxide as outlined in the preparations of the tetramethylammonium salt of 5, was treated with carbon dioxide to remove the potassium hydroxide and then filtered and concentrated. The residue of potassium hydrogen benzodicarbollide (5) was dissolved in 50 ml of anhydrous tetrahydrofuran or diglyme, then mixed with a stirred suspension of 1 g (40 mmol) of sodium hydride in the same solvent, and refluxed (THF) or heated at 110° (diglyme) for 0.5 hr. The yellow solution of potassium sodium benzodicarbollide (6) was withdrawn with a syringe and used directly in subsequent reactions. The nmr spectrum in THF consists of an A_2B_2 multiplet of nine peaks centered at δ 5.48.

Tetramethylammonium Bis(benzodicarbollyl)cobaltate(III) (16). A solution of 2 mmol of potassium sodium benzodicarbollide (6) in 75 ml of tetrahydrofuran was added to 357 mg (1.5 mmol) of anhydrous cobalt(II) chloride and refluxed under nitrogen for 2 hr, then cooled, and filtered to remove cobalt metal. The solvent was removed under vacuum, the brown residue was dissolved in a minimum amount of methanol, and 2 g of tetramethylammonium in 10 ml of water was added, followed by more water to complete the precipitation. The solid was recrystallized from methanol–water to yield 246 mg (50%) of **16** as red-brown plates, which did not melt below 300°. The product was recrystallized from dichloromethane–hexene. Nmr (DMSO-d_6): δ 3.30 (s, 12, NCH_3), 6.42 (m of A_2B_2 type, 8, *CH*=*CH*–*CH*=*CH*). Uv–vis (methanol): 246 nm (ϵ 12,710), 279 nm (ϵ 16,250), 418 nm (ϵ 5080), 576 nm (ϵ 750). Ir (KBr):

3030 (w), 2915 (w), 2545 (vs), 1481 (m), 1466 (w), 1449 (w), 1418 (w), 1370 (w), 1285 (w), 1266 (w), 1203 (w), 1149 (w), 1018 (s), 944 (m), 765 (w), 735 (w), 704 (m) cm^{-1}. *Anal.* Calcd $C_{16}H_{38}B_{18}CoN$: C, 38.58; H, 7.69; B, 39.07; Co, 11.83; N, 2.81. Found: C, 38.62; H, 7.72; B, 38.76; Co, 11.58; N, 3.12.

Tetramethylammonium Tricarbonyl(benzodicarbollyl)manganate(I) (14). A solution of 2 mmol of potassium sodium benzodicarbollide (6) in 75 ml of tetrahydrofuran was added to 650 mg (2 mmol) of bromomanganese pentacarbonyl. After stirring, the mixture was filtered and the solvent was evaporated under vacuum. The orange residue was dissolved in a minimum amount of methanol and 2 g of tetramethylammonium chloride in 10 ml of water was added, followed by more water to complete the precipitation. The precipitated product was collected and dried in air and then chromatographed on silica gel using acetonitrile as the eluent. The yellow band was collected and crystallized from acetonitrile–water to yield 561 mg (88%) of 14 as bright yellow plates, mp 285° dec. The product was recrystallized from acetone–water. Nmr (DMSO-d_6): δ 3.11 (s, 12, NCH_3), 6.11 (m of A_2B_2 type, 4, CH=CH–CH=CH). Uv–vis (methanol): 216 nm (ϵ 23,800), 260 nm (sh, ϵ 6950), 368 nm (ϵ 1650). *Anal.* Calcd for $C_{13}H_{25}B_9MnNO_3$: C, 39.47; H, 6.37; B, 24.59; Mn, 13.88; N, 3.54. Found: C, 39.38; H, 6.36; B, 24.31; Mn, 13.66; N, 3.35.

Tetramethylammonium Bis(benzodicarbollyl)nickelate(III) (19). A solution of 2 mmol of potassium sodium benzodicarbollide and 0.08 mmol of piperidine in 75 ml of diglyme was added to 1 mmol of anhydrous nickel(II) iodide and was heated 22 hr at 110° under nitrogen. The mixture was filtered through Celite and the solvent was evaporated under vacuum. The residue was dissolved in a small amount of methanol and filtered and then treated with excess tetramethylammonium chloride and water. The 335 g of crude material contained a large proportion of tetramethylammonium hydrogen benzodicarbollide. Chromatography on silica gel with 5% acetonitrile in methylene chloride led to the elution of a purple band of 20, the work-up of which is described in the following paragraph. The product (19) was eluted with 10% acetonitrile in dichloromethane. The solvent was removed under vacuum and the brown residue was dissolved in a minimum amount of methanol and filtered. Addition of water and then sodium chloride crystallized the product (19); 75 mg (15%). Ir (KBr): 3021 (w), 2915 (w), 2849 (w), 2519 (vs), 1481 (s), 1441 (w), 1418 (w), 1200 (w), 1183 (w), 1142 (w), 1064 (w), 1007 (s), 968 (w), 941 (m), 905 (w), 762 (w), 714 (m), 694 (m) cm^{-1}. Uv–vis (methanol): 204 nm (ϵ 12,210), 210 nm (ϵ 12,460), 248 nm (ϵ 9998), 330 nm, (ϵ 5820), 380 nm (ϵ 5700), 428 nm (sh, ϵ 3320), 472 nm (sh, ϵ 2023). The analytical sample was again chromatographed on silica gel and recrystallized from methanol–water. *Anal.* Calcd for $C_{16}H_{38}B_{18}NNi$: C, 38.60; H, 7.69; B, 39.09; N, 2.81; Ni, 11.79. Found: C, 38.77; H, 7.65; B, 35.36; N, 3.11; Ni, 15.60.

Bis(benzodicarbollyl)dinickel(II) (20). The solution of the rapidly eluted purple band from the chromatography of the nickel(III) salt 19 was concentrated and the residue was triturated with methanol to yield 27 mg (5%) of **20** as dark purple crystals, which did not melt below 300°. Nmr (DMSO-d_6): δ 1.54 (m, A_2B_2 pattern, CH=CH–CH=CH). Ir (KBr): 3333 (w), 2865 (w), 2597 (vs), 2525 (vs), 1418 (w), 1364 (w), 1212 (m), 1136 (m), 1002 (s), 927 (w), 911 (w), 887 (w), 849 (m), 830 (w), 824 (w), 791 (w), 758 (w), 723 (m) cm^{-1}. Uv–vis (acetonitrile): 224 nm (ϵ 13,080), 248 nm (sh, ϵ 9920), 265 nm (ϵ 11,000), 283 nm (sh, ϵ 9830), 388 nm (ϵ 6380), 468 nm (ϵ 2500), 552 nm (ϵ 1840). *Anal.* Calcd for $C_{12}H_{26}B_{18}Ni_2$: C, 29.88; H, 5.43; B, 40.34; Ni, 24.34. Found: C, 30.09; H, 5.64; B, 28.10; Ni, 26.26.

Registry No. 1, 20505-39-9; 2, 39472-28-1; 3, 39472-25-8; 4, 20505-38-8; 5, 39472-24-7; 6, 39472-22-5; 7, 49564-22-9; 8, 39472-27-0; 10, 39472-26-9; 11, 49564-23-0; 13, 39472-23-6; 14, 49564-26-3; 15, 49613-21-0; 16, 49613-22-1; 17, 49564-25-2; 18, 49664-78-0; 19, 49564-27-4; 20, 49683-29-6; 21, 49564-24-1; bromomanganese pentacarbonyl, 14516-54-2.

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Electron Paramagnetic Resonance Spectrum of Dinitratotris(pyridine)copper(II) Doped into Single Crystals of Dinitratotris(pyridine)zinc(II) and -cadmium(II). Electronic Structure of Dinitratotris(pyridine)copper(II)

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The electron paramagnetic resonance spectra of dinitratotris(pyridine)copper(II) doped into single crystals of the analogous zinc and cadmium complexes have been studied at room and liquid nitrogen temperatures. At liquid nitrogen temperature, hyperfine splittings from the ^{14}N nuclei of the pyridine ligands as well as the ^{63}Cu and ^{65}Cu nuclei are easily resolved. The principal values of the g and copper hyperfine tensors exhibit a very pronounced rhombic symmetry. An analysis of the hyperfine and g values suggests that the ground state can be described as mostly d_{z^2} with a small admixture of $d_{x^2-y^2}$. Detailed considerations of the copper and ligand hyperfine tensors indicate the unpaired electron is delocalized from the metal to the pyridine ligands to the extent of 25–30%. The orientation of g and hyperfine tensors can easily be rationalized in terms of the known crystal and molecular structures of the dinitratotris(pyridine) complexes.

Introduction

There has been considerable interest in complexes which contain coordinated nitrate ions. Crystallographic studies have shown that nitrate ions can function as monodentate,[1,2] bidentate,[3] or bridging[4] ligands. Pyridine complexes of divalent transition metal nitrates have been known for some time, but the first systematic attempt to characterize these complexes was made by Haendler and coworkers.[5-7] More recently, Cameron and coworkers have determined the crystal structures of a number of the pyridine–metal(II) nitrate complexes.[1,2,4,8,9] The tris(pyridine) complexes in particular

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