m/e 244 ($C_{10}H_{16}{}^{10}B_2{}^{11}B_8{}^+$) with isotopic satellites; uv–vis (2,2,4-trimethylpentane) λ_{max} 414 (ϵ 2400), 393 (3140), 377 (2420), 355 (1360), 335 (400), 280 nm (35,000); nmr (CCl_4) δ 6.50 (s, 4, C_6H_4), 6.65 (s, 2, inner ring C*H*). *Anal.* Calcd for $C_{10}H_{16}B_{10}$: C, 49.16; H, 6.60; B, 44.24. Found: C, 49.13; H, 6.62; B, 44.32.

Bromination of Naphthocarborane (1). A 200-mg sample of naphthocarborane (1) in a few milliliters of carbon tetrachloride was treated with bromine until the bromine color persisted. Concentration and sublimation yielded 300 mg (90%) of dibromodihydronaphthocarborane (**5**), confirmed by mixture melting point and nmr.

Naphthocarborane Peroxide Polymer (7). Stirring a 2% solution of naphthocarborane 8 hr under air yielded a white precipitate which would not sublime; mol wt (osmometric in $CHCl_3$) 1700; nmr ($CDCl_3$) δ 7.35 (broad s, 4, C_6H_4), 5.5 (broad s, 2, O–C*H*); mass spectrum *m/e* 276, suggesting the presence of or breakdown to $C_{10}H_{16}B_{10}O_2$. *Anal.* Calcd for $(C_{10}H_{16}B_{10}O_2)_n$: C, 43.5; H, 5.8; B, 39.1. Found: C, 44.06; H, 6.21; B, 35.16.

Adduct 8 of Naphthocarborane with Dimethyl Acetylenedicarboxylate. A Pyrex glass tube was purged with argon, and in it were sealed 244 mg (1 mmol) of naphthocarborane (**1**) and 124 mg (1 mmol) of freshly redistilled dimethyl acetylenedicarboxylate. The mixture was heated at 100° for 8 hr and the tube was then cooled to 25° and opened. Recrystallization from methanol–water yielded 350 mg (91%) of **8**; mp 214–215°; nmr ($CDCl_3$) δ 3.76 (s, 6, OC*H*$_3$), 4.62 (m, 2, bridgehead C*H*); 6.28 (s, 2, inner ring C*H*); 6.59 (m, 2, *H*C=C*H*); ir (KBr) C=O at 1660 cm^{-1}. *Anal.* Calcd for $C_{16}H_{22}B_{10}O_4$: C, 49.73; H, 5.74; B, 27.98. Found: C, 49.62; H, 5.72; B, 29.97.

Adduct 9 of Naphthocarborane with Maleic Anhydride. By the same procedure described for the preparation of **8**, substituting maleic anhydride in place of dimethyl acetylenedicarboxylate, and recrystallizing the product (**9**) from acetone–petroleum ether, an 88% yield was obtained; nmr (DMSO-d_6): δ 3.43 (m, 2, *H*CC=O), 4.07 (m, 2, bridgehead C*H*), 6.48 (m, 2, *H*C=C*H*), 6.85 (s, 2, inner ring C*H*); ir (KBr) 1770 cm^{-1} (C=O). The compound was not analyzed.

Attempted Reactions of Naphthocarborane with Tetracyanoethylene (TCNE). The sealed tube method described for the preparation of **8** and **9** was attempted with TCNE, but the nmr spectrum of the resulting material was that of unconverted naphthocarborane. A mixture of 150 mg of naphthocarborane and 84 mg of tetracyanoethylene in 50 ml of anhydrous tetrahydrofuran immediately turned blue-green, but after 8 hr of reflux under argon only TCNE and naphthocarborane were recovered.

5-Ketodihydronaphthocarborane (6). This compound was isolated from an attempt to debrominate the dibromo compound (**5**) with zinc. A solution of 1.5 g of **5** in 50 ml of freshly distilled dimethylformamide was stirred under nitrogen for 8 hr. The solution immediately turned yellow. The dimethylformamide was distilled under vacuum and the residue was recrystallized from methanol–water, yielding **6**; mp 138–149°; mass spectrum *m/e* 260 ($C_{10}H_{16}{}^{10}B_2{}^{11}B_8O^+$); nmr ($CDCl_3$) δ 3.57 (s, 2, C*H*$_2$), 7.39 (m, 4, C_6H_4), and impurities at 4.62 and 5.89; ir (KBr) 1720 cm^{-1} (C=O). *Anal.* Calcd for $C_{10}H_{16}B_{10}O$: C, 46.13; H, 6.19; B, 41.53. Found: C, 48.64; H, 7.36; B, 41.01.

Registry No. 4, 23810-12-0; **5**, 27120-76-9; 1, 27120-74-7; 7, PM50276-14-7; 8, 27120-77-0; 9, 50276-19-2; **6**, 50276-20-5; dilithio-*o*-carborane, 22220-85-5; α,α'-dibromo-*o*-xylene, 91-13-4; dimethyl acetylenedicarboxylate, 762-42-5; maleic anhydride, 108-31-6.

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Ionic Organoboranes. V. Preparations of Dicarbahemiousenium[1,2] and Dicarbaousenium Cations and a Neutral Ousene[3,4]

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Tropenyl methyl ether reacts with mono- or dilithio salts of *o*- or *m*-carborane to give tropenyl (7-cyclohepta-1,3,5-trienyl) carboranes. Rearrangement to γ-tropenyl (3-cyclohepta-1,3,5-trienyl) carboranes followed by hydride abstraction yields mono- or ditropenyliumylcarboranes (dicarbahemiousenium and dicarbaousenium ions). Electronic, infrared, and ^1H and ^{11}B nmr spectra and nucleophile-exchange studies by nmr demonstrate destabilization of the ring by the $-I$ cage and little π interaction between cage and ring. Unlike most tropenylium ions, these cations form covalent bromides. The syntheses of a neutral $[7.7.10^{2,x}]$ousene and several tropenyliumyl derivatives of the $C_2B_9H_{11}(CH_3)^-$ anion are also reported.

Introduction

As part of a program directed toward the synthesis of ionic polymers based on repeating patterns of carbocyclic cationic rings, polyhedral borane anion cages, and neutral carboranes (Figure 1) we have previously reported on the preparation and properties of the $[7.10^2]$- and $[7.12]$hemiousenide ions[2,6,7] in which a tropenyliumyl[8,9] group is linked to a borane anion cage and report herein on the characterization of a neutral $[7.7.10^{2,x}]$ousene[10] in which the cage is flanked by two cationic rings (Figure 2). These highly colored, zwitterionic compounds show internal charge-transfer absorptions and extensive electron donation from cage to ring.[2]

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(1) The ousene nomenclature has been discussed in detail.[2] In brief, the parent name *ousene* is assigned to a $B_nH_n^{2-}$ closo anion substituted with two aromatic carbocyclic cation rings; the numbers of carbons in the rings and borons in the cage are given in brackets before the name, with the boron number last, and superscript numbers on the boron number designate the position of the rings on the cage. The prefix *hemi* is used for a compound with a single ring on the cage, and the endings *ium* and *ide* are used to indicate cations and anions, respectively. The presence of carbons in the cage is represented by *carba* or *dicarba* in the conventional manner for carboranes. Examples of this nomenclature applied to compounds discussed in the paper are shown in Figure 2.

(2) K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *J. Amer. Chem. Soc.*, 91, 323 (1969).

(3) Work supported by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(4) Reported in part: (a) K. M. Harmon, A. B. Harmon, and B. C. Thompson, *J. Amer. Chem. Soc.*, 89, 5309 (1967); (b) K. M. Harmon, A. B. Harmon, T. Y. Susskind, B. C. Thompson, D. P. Ryan, and T. T. Coburn, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 2, 1971, No. ORGN-183.

(5) To whom inquiries should be addressed at Oakland University.

(6) K. M. Harmon, A. B. Harmon, and A. A. MacDonald, *J. Amer. Chem. Soc.*, 86, 5036 (1964).

(7) A. B. Harmon and K. M. Harmon, *J. Amer. Chem. Soc.*, 88, 4093 (1966).

(8) The tropenyliumyl nomenclature has been discussed.[4a,9]

(9) H. J. Dauben, Jr., and D. F. Rhoades, *J. Amer. Chem. Soc.*, 89, 6764 (1967).

(10) The *x* indicates position of substitution not known.

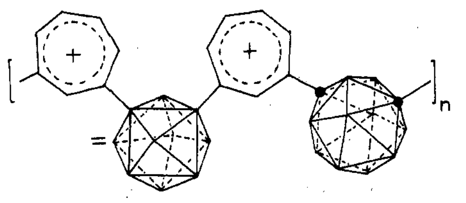


Figure 1. Portion of hypothetical polyousene-type polymer.

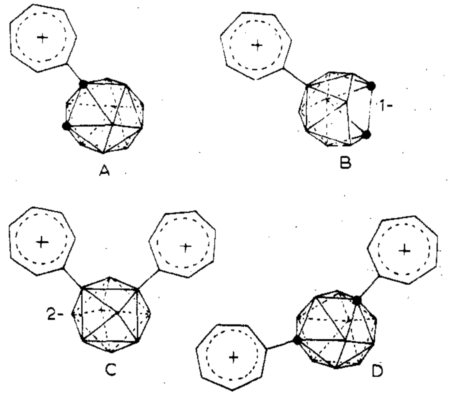
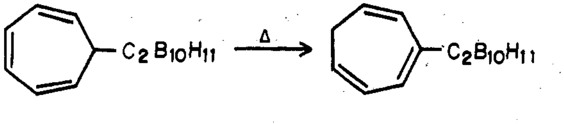


Figure 2. Ousene-type compounds: (A) $[7.12^1]$-1,2-dicarbahemiousenium ion, (B) $[7.11^x]$-*nido*-(3)-1,2-dicarbahemiousene, (C) $[7.7.10^{2,x}]$ousene, and (D) $[7.7.12^{1,7}]$-1,7-dicarbaousenium ion. The positions of the ring in B and of the second ring in C are not known and are drawn as shown for convenience.

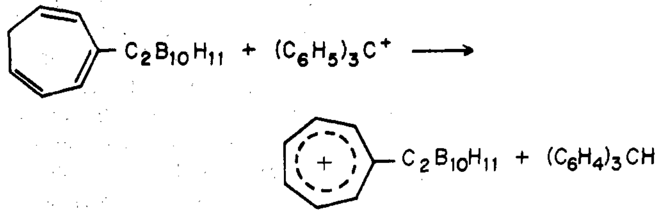
We now wish to report on another class of potential monomers that contains the second type of C–B bond which will link the aromatic moieties in the polymer chain; these compounds include three dicarbahemiousenium cations and one dicarbaousenium dication (Figure 2) in which tropenyliumyl rings are attached to cage carbons in *closo*-1,2- and/or -1,7-dicarbadodecaborane(12).

Results

Closo Carborane Derivatives. Mono- and dilithio salts of carboranes react smoothly with tropenyl methyl ether[11] in hydrocarbon solvent to yield the corresponding mono- or ditropenyl (7-cyclohepta-1,3,5-trienyl) carboranes;[12] these colorless, air-stable compounds are readily purified by conventional means. The tropenylcarboranes were not suitable for conversion to carbonium ions[13-15] and had to be thermally rearranged[16] to γ-tropenyl[17] (3-cyclohepta-1,3,5-trienyl) carboranes prior to hydride abstraction.



The Dauben reaction[18] of mono-γ-tropenylcarboranes with triphenylcarbonium hexafluorometalates in 1,2-dichloroethane proceeds normally to give good yields of carbonium ion salts and triphenylmethane.



Although the cationic ring in these ions is quite acidic, as demonstrated by the nmr nucleophile-exchange studies (see Discussion) the hexafluorometalate salts of the dicarbahemiousenium ions are unaffected by atmospheric moisture and appear to have unlimited shelf life. 1-Methyl$[7.12^1]$-1,2-dicarbahemiousenium fluoroborate, however, is extremely hygroscopic; although the salt is readily prepared, we did not obtain satisfactory analyses for this reason.

The reaction of 1,2-di-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(10) with triphenylcarbonium ion does not give the expected dication; although high yields of triphenylmethane can be isolated from the reaction, the remaining products are intractable tars. We believe that the dication degrades rather than tolerates two cationic rings on adjacent electropositive carbons. Hydride abstraction from 1,7-di-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(10) gives the $[7.7.12^{1,7}]$-1,7-dicarbaousenium ion. This species appears to react with organic solvents, which renders purification difficult; this problem was obviated by conversion to the hexachlorostannate(IV) salt in aqueous solution (see Experimental Section).

Dicarbahemiousenium and dicarbaousenium bromides cannot be prepared *via* reaction with triphenylmethyl bromide in liquid sulfur dioxide, which is the conventional route to tropenylium bromides,[18,19] in part due to the extreme insolubility of the γ-tropenylcarboranes in this solvent. Bromide salts could be prepared, however, by reaction of hexafluorometalate salts with methoxide ion, followed by hydrogen bromide cleavage[11] of the resultant mixture of methyl ethers. 1-Methyl$[7.12^2]$-1,2-dicarbahemiousenium bromide shows unexpected properties. This compound gives the electronic spectrum of the cation in 96% sulfuric acid and shows the expected[19] anion-to-cation charge-transfer color in polar organic solvents; however, unlike other tropenylium bromides,[18,20] this substance dissolves readily in ether or hydrocarbons to give colorless solutions which show the characteristic electronic spectrum of a covalent cycloheptatriene derivative.[19]

Nido Carborane Derivatives. An interesting side reaction was observed in the preparations of 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10). When the reaction is acidified (see Experimental Section), the solution often turns red or purple; the colored material is retained on alumina, from which it is removed by methylene chloride. This material contains two main fractions: a brilliant blue substance soluble in hydrocarbons and an amorphous red solid soluble

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(11) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

(12) Reaction of tropenyl methyl ether with organometallic reagents has been shown to be an excellent source of 7-substituted cycloheptatrienes: (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 5593 (1960); (b) H. J. Dauben, Jr., and R. B. Medz, unpublished work in the Ph.D. thesis of R. B. M., University of Washington, Seattle, Wash., 1964; *Diss. Abstr.*, **25**, 2766 (1964).

(13) Tropenylcarboranes undergo cationic polymerization of the triene rings in the presence of triphenylcarbonium ion; this reaction, which competes to a minor extent with the Dauben reaction of γ-tropenylcarboranes, becomes dominant when hydride transfer is slowed by the bulky, electron-withdrawing carborane substituent in the 7 position.[14]

(14) H. J. Dauben, Jr., R. B. Medz, and T. J. Pratt have observed inhibition of hydride transfer to triphenylcarbonium ion in 7-*tert*-butyl-[12b] and 7-cyanocycloheptatriene.[15]

(15) H. J. Dauben, Jr., and T. J. Pratt, unpublished results in the Ph.D. thesis of T. J. P., University of Washington, Seattle, Wash., 1964; *Diss. Abstr.*, **25**, 4962 (1965).

(16) R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 3527 (1966), and references therein.

(17) The use of γ-tropenyl for the 3 isomer is suggested for convenience and brevity.

(18) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957).

(19) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Amer. Chem. Soc.*, **84**, 3349 (1962).

(20) H. J. Dauben, Jr., and K. M. Harmon, unpublished results in the Ph.D. thesis of K. M. H., University of Washington, Seattle, Wash., 1958; *Diss. Abstr.*, **19**, 1563 (1959).

only in polar organic solvents; both of these have electronic spectra characteristic of ousenes, that is, of compounds in which a tropenyliumyl group is attached to an anionic borane cage.[2] These colored materials have been shown to arise from electrophilic attack of tropenylium ion (generated *in situ* by acid cleavage of excess tropenyl methyl ether) on the 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) anion.

This latter ion may be formed by degradation[21,22] of methylcarborane starting material by methoxide ion liberated in the attack of lithiocarborane on tropenyl methyl ether or by degradation of 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10) to a nido species accompanied by nucleophilic displacement[12] of borane anion from the cycloheptatriene ring by methoxide ion. That the reaction sequence shown in (1)-(3) is a reasonable route to the nido anion is shown

$$\text{1-CH}_3\text{-2-C}_7\text{H}_7\text{-C}_2\text{B}_{10}\text{H}_{10} \xrightarrow{\text{CH}_3\text{O}^-} [\text{1-CH}_3\text{-2-C}_7\text{H}_7\text{-C}_2\text{B}_9\text{H}_{10}]^- \qquad (1)$$

$$[\text{1-CH}_3\text{-2-C}_7\text{H}_7\text{-C}_2\text{B}_9\text{H}_{10}] \xrightarrow{\text{CH}_3\text{O}^-} [\text{1-CH}_3\text{-C}_2\text{B}_9\text{H}_{10}]^{2-} + \text{C}_7\text{H}_7\text{OCH}_3 \qquad (2)$$

$$[\text{1-CH}_3\text{-C}_2\text{B}_9\text{H}_{10}]^{2-} \xrightarrow{\text{H}_2\text{O}} [\text{1-CH}_3\text{-C}_2\text{B}_9\text{H}_{11}]^- \qquad (3)$$

$$[\text{1-CH}_3\text{-C}_2\text{B}_9\text{H}_{11}]^- \xrightarrow{2\text{C}_7\text{H}_7^+} [\text{1-CH}_3\text{-}x\text{-C}_7\text{H}_6\text{-C}_2\text{B}_9\text{H}_{10}]^0 + \text{C}_7\text{H}_8 \qquad (4)$$

by the fact that the triethylammonium salt of this anion is the only species that can be isolated from degradation of preformed 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10) with alkoxide ion.

The reaction of tropenylium ion with the nido anion is strictly analogous to the reaction with $B_{10}H_{10}{}^{2-,2,6}$ in which rapid mixing of the reactants leads to the formation of large quantities of carbon-rich solids resulting from multiple electrophilic attack by tropenylium ion on the cage and a much smaller quantity of more soluble material in which a single cationic ring is substituted on the cage. When tropenylium fluoroborate is added rapidly to a solution prepared by degrading 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10) with methoxide ion, a red amorphous solid is formed, from which 1-methyl$[7.7.11^{x,y}]$-*nido*-(3)-1,2-dicarbaousenium fluoroborate[10] can be isolated by suitable solvent extraction. The solid material remaining after extraction has a carbon to boron ratio of about 3:1; on the assumption that there are at least nine borons per molecule, the material must contain, on the average, more than three rings per cage.

The bright blue, hydrocarbon-soluble 1-methyl$[7.11^x]$-*nido*-(3)-1,2-dicarbahemiousene[10] (Figure 2), which is isolated in low yield as a side product in the reaction above, can be prepared (eq 4) in quantitative yield *via* slow addition of tropenylium ion to an aqueous solution of the 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) anion in a manner analogous to the improved preparation of the $[7.10^2]$hemiousenide ion;[2] with care, formation of the red solids can be completely suppressed.

A Neutral Ousene. Reaction of tropenylium ion with $[7.10^2]$hemiousenide ion gives nearly quantitative yields of cycloheptatriene and a $[7.7.10^{2,x}]$ousene;[10] this highly colored substance is the first characterized example of a parent compound of the ousene system.

The reactions that may occur in a mixture of tropenylium ion and $B_{10}H_{10}{}^{2-}$ ion have been discussed in detail;[2] compound and equation numbers that follow refer to that discussion. The $[7.7.10^{2,x}]$ousene prepared in this work is **3** (eq 4 of ref 2); spectral and solubility properties suggest that it is an isomer of **3′** (eq 6 of ref 2) which is a somewhat more soluble material formed as the main product when tropenylium ion and $B_{10}H_{10}{}^{2-}$ are mixed in concentrated solution. Ousene **3** is an extraordinarily insoluble, highly crystalline, thermally stable substance.

Experimental Section

Foote Mineral Co. *n*-butyllithium, Ozark-Mahoning Co. triphenylcarbonium hexafluoroarsenate and -antimonate, and Eastman White Label trimethylammonium chloride were used as supplied. Tropenyl methyl ether,[11] tri-*p*-tolylmethyl chloride and bromide,[23] and tri-*p*-tolylcarbonium perchlorate[24] were prepared as reported. T. L. Heying of the Olin Mathieson Corp. generously furnished us with samples of *closo*-1,2- and *closo*-1,7-dicarbadodecaborane(12). All solvents were rigorously dried before use, and all reactions were carried out in an atmosphere of dry nitrogen.

Spectra were recorded variously on Cary 13 and Zeiss DMR 21 (electronic), Perkin-Elmer 621 and Beckmann IR-12 (infrared), and Varian A-60 and T-60 (nmr) spectrophotometers. ^{11}B nmr spectra were taken by B. J. Nist on the University of Washington Varian HR-60 instrument at 19.25 MHz.

Analytical data for closo carborane derivatives prepared in this work are shown in Table I. Analyses were performed by the Schwarzkopf Microanalytical Laboratory.

Tropenylcarboranes. A. 1-Methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10). A solution of *n*-butyllithium (34 mmol) in hexane was injected slowly by syringe into a stirred solution of 1-methyl-*closo*-1,2-dicarbadodecaborane(11)[25] (5.18 g, 32.8 mmol) in cyclohexane (60 ml), and the stirred solution was allowed to reflux for 1 hr. Tropenyl methyl ether (4.00 g, 32.8 mmol) in cyclohexane (11 ml) was then added very slowly (30 min) and reflux was maintained overnight. Water (50 ml) was added with caution to the cooled reaction mixture, followed by dilute hydrochloric acid to convert any unreacted tropenyl methyl ether to tropenylium ion. The reaction mixture may turn purple at this point due to the formation of one or more 1-methyl-*x*-tropenyliumyl-*nido*-1,2-dicarbaundecaborate(10)[10] species (see below); this does no harm. The aqueous solution was extracted with pentane (two 25-ml portions) and the combined organic layers were dried over magnesium sulfate, passed through an alumina column with pentane eluent, and concentrated *in vacuo* to yield 93.0% 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10) (7.58 g, 30.5 mmol); white prisms from methanol, mp 57.5-58.0°; electronic spectrum (cyclohexane): $\lambda_{\max}$ 251.5 nm (ϵ 3230).

B. 1-Tropenyl-*closo*-1,2-dicarbadodecaborane(11). A solution of *n*-butyllithium (20.7 mmol) in hexane was diluted with additional hexane (60 ml) and added slowly by syringe to a nearly saturated solution of *closo*-1,2-dicarbadodecaborane(12) (3.00 g, 20.7 mmol) in refluxing hexane (120 ml); a white precipitate formed at once. The reaction was stirred at reflux for 2 days until reaction had ceased as indicated by the absence of a Tyndall effect in the hexane solvent. The flask was cooled to room temperature and a solution of tropenyl methyl ether (2.83 g, 23.4 mmol) in hexane (30 ml) was added slowly with stirring; then the temperature was again raised to reflux and so maintained for 48 hr. The solution was worked up with water and hydrochloric acid as in section A and the aqueous layer extracted with hexane (two 30-ml portions). The combined hexane fractions were dried over Na_2SO_4 and concentrated *in vacuo* to a yellow oil. Sublimation of this oil gave an initial fraction (40°, 0.1 Torr) of unreacted *closo*-1,2-dicarbadodecaborane(12) followed by a second fraction (100°, 0.1 Torr) containing 53.0% 1-tropenyl-*closo*-1,2-dicarbadodecaborane(11) (2.57 g, 11.9 mmol) as white crystals, mp 42°; electronic spectrum (cyclohexane): $\lambda_{\max}$ 252 nm (ϵ 2700).

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(21) R. A. Wiesboeck and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 86, 1642 (1964).

(22) 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).

(23) K. M. Harmon, L. Hesse, L. P. Klemann, C. W. Kocher, S. V. McKinley, and A. E. Young, *Inorg. Chem.*, 8, 1054 (1969).

(24) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 25, 1442 (1960).

(25) (a) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, 2, 1115 (1963); (b) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, 2, 1097 (1963).

Table I. Elemental Analyses of Carborane Derivatives[a,b]

R	R′	Anion	Calcd B	Calcd C	Calcd H	Found B	Found C	Found H
C_7H_7	CH_3		43.55	48.34	8.11	43.29	48.21	8.27
γ-C_7H_7	CH_3		43.55	48.34	8.11	43.41	48.64	7.84
C_7H_7	2-C_7H_7		33.34	59.04	7.46	33.46	59.21	7.45
C_7H_7	7-C_7H_7		33.34	59.04	7.46	33.09	59.27	7.55
$C_7H_6^+$	2-CH_3	AsF_6^-	24.80	27.53	4.35	25.17	27.46	4.62
$C_7H_6^+$	2-CH_3	SbF_6^-	22.39	24.86	3.96	22.29	25.12	4.14
$C_7H_6^+$	2-CH_3	Br^-	33.05	36.68	5.85	33.21	36.58	6.12[c]
$C_7H_6^+$	2-H	SbF_6^-	23.05	23.04	3.65	23.07	23.40	4.23
$C_7H_6^+$	7-H	AsF_6^-	25.63	25.60	4.06	25.79	25.58	4.30
$C_7H_6^+$	7-$C_7H_6^+$	AsF_6^-	15.45	27.44	3.17	15.59	29.68	3.20
$C_7H_6^+$	7-$C_7H_6^+$	$SnCl_6^{2-}$	16.55	29.38	3.39	16.80	29.14	3.10

[a] Analyses by Schwarzkopf Microanalytical Laboratory. [b] Tropenyl- and γ-tropenylcarboranes not listed were identified by nmr and conversion to analyzed salt. [c] Bromine analysis: calcd, 24.41; found, 24.18.

C. 1-Tropenyl-*closo*-1,7-dicarbadodecaborane(11). The reaction was run in a manner identical with section B. Reaction of tropenyl methyl ether (2.41 g, 19.5 mmol) and the lithio salt derived from *closo*-1,7-dicarbadodecaborane(12) (2.74 g, 19.0 mmol) gave, after work-up, an oil which on sublimation gave an initial crop (25°, 0.1 Torr) of unreacted carborane followed by a second fraction (70°, 0.1 Torr) of 1-tropenyl-*closo*-1,7-dicarbadodecaborane(11) in 56% yield (2.49 g, 10.6 mmol) as white crystals, mp 38–39°, with prior sintering; electronic spectrum (cyclohexane): λ_{max} 252.5 nm (ϵ 3420). 1,7-Ditropenyl-*closo*-1,7-dicarbadodecaborane(10), mp 68–72°, could be recovered by recrystallization of the sublimer residues from ethanol.

D. 1,2-Ditropenyl-*closo*-1,2-dicarbadodecaborane(10). A solution of *n*-butyllithium (14.4 mmol) in hexane (10 ml) was added slowly by syringe to a solution of *closo*-1,2-dicarbadodecaborane(12) (1.0 g, 6.9 mmol) in hexane (50 ml) and the solution was refluxed until precipitation of the lithio salt had ceased. Tropenyl methyl ether (1.92 g, 15.6 mmol) in hexane (10 ml) was then added and the mixture maintained at reflux for 60 hr. Water (40 ml) was added; then chloroform was added until all solid materials had dissolved in the organic layer. This layer was washed with water and dilute sulfuric acid, the aqueous washes were back-extracted with chloroform, and the combined organic fractions were dried over sodium sulfate, treated with Norite, and evaporated *in vacuo* to yield 59% crude 1,2-ditropenyl-*closo*-1,2-dicarbadodecaborane(10) (1.33 g, 4.1 mmol); white plates from ethanol, mp 132.5–133.5°; electronic spectrum (cyclohexane): λ_{max} 250.5 nm (ϵ 6400).

E. 1,7-Ditropenyl-*closo*-1,7-dicarbadodecaborane(10) *n*-Butyllithium (33.6 mmol) in hexane (21 ml) was added to a solution of *closo*-1,7-dicarbadodecaborane(12) (1.95 g, 13.5 mmol) in hexane (90 ml) and the mixture was maintained at reflux for 90 hr. The reaction was then cooled, tropenyl methyl ether (4.80 g, 39.0 mmol) in hexane (15 ml) was added, and the reaction was heated at reflux for 48 hr. The flask was then cooled to 0°, the solution was shaken with water and dilute sulfuric acid, and the combined aqueous layers were back-extracted with methylene chloride (two 20-ml portions). The combined organic fractions were dried over sodium sulfate and concentrated *in vacuo* to a yellow oil. This oil was triturated with chilled methanol (30 ml) to precipitate 40% crude 1,7-ditropenyl-*closo*-1,7-dicarbadodecaborane(10) (1.76 g, 5.4 mmol); white prisms from methanol, mp 78.5°; electronic spectrum (cyclohexane): λ_{max} 256 nm (ϵ 6600).

The methanol supernatant was concentrated *in vacuo* to a yellow oil; sublimation (40°, 0.1 Torr) gave a colorless oil shown by infrared and nmr spectra to consist mainly of 1-methoxycycloheptatriene. *Caution*! This material appears toxic and causes severe headaches and dizziness on brief exposure. These effects have been noted by others.[15,26] Continued sublimation (60°, 0.1 Torr) gave a significant yield of 1-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(11).

γ-Tropenylcarboranes.[17] A portion of the appropriate tropenylcarborane was placed in a Pyrex test tube fitted with a ground-glass joint bearing a condenser; a positive pressure of nitrogen was maintained throughout the reaction. Each tropenylcarborane was heated at 165° for 45 min. In every case nmr spectra (Table II) showed quantitative rearrangement to the 3-substituted cycloheptatriene without contaminating by-products.

γ-Tropenylcarboranes prepared include the following ((a) name, (b) form, (c) melting point, (d) electronic spectrum (cyclohexane), (e) ^{11}B nmr spectrum (δ, D_3CCN)[27]): (A) (a) 1-methyl-2-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(10), (b) white needles from methanol, (c) 93–94°, (d) λ_{max} 267 nm (ϵ 6570), (e) d, 121.6 (J = 10.6 Hz); (B) (a) 1-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(11), (b) white prisms from methanol, (c) 27–28.5°; (C) (a) 1-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(11), (b) white solid, (c) about room temperature, (d) λ_{max} 265 nm (ϵ 5390); (D) (a) 1,2-di-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(10), (b) colorless oil; (E) (a) 1,7-di-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(10), (b) colorless oil, (d) λ_{max} 267 nm (ϵ 12,200).

Dicarbahemiousenium Hexafluorometalates. All of these salts were prepared in a similar manner; the directions given in section A will suffice for the other compounds.

A. 1-Methyl[7.12²]-1,2-dicarbahemiousenium Hexafluoroantimonate. 1-Methyl-2-γ-tropenyl-*closo*-1,2-dicarbadodecaborane(10) (0.19 g, 0.77 mmol) and triphenylcarbonium hexafluoroantimonate (0.37 g, 0.77 mmol) were dissolved in dry 1,2-dichloroethane (20 ml) and the mixture was heated at 60° for 12 hr. The solution was allowed to cool and the mother liquor was decanted from a crop of blunt white prisms; these were washed with 1,2-dichloroethane (one 5-ml portion) and ether (two 10-ml portions) and dried *in vacuo*. A second crop of crystals was precipitated from the reaction solvent by addition of ether; the combined crops yielded 99.5% 1-methyl[7.12²]-1,2-dicarbahemiousenium hexafluoroantimonate (0.372 g, 0.77 mmol); white, air-stable prisms from slow addition of ether to minimum acetonitrile, no melting point below 300°; electronic spectrum (96% sulfuric acid): λ_{max} 224.5 (ϵ 33,400), 287 (sh), 294.5 (ϵ 6360), and 302 nm (sh); electronic spectrum (acetonitrile): λ_{max} 231 (ϵ 32,400), 287 (sh), and 292.5 nm (ϵ 6490); ^{1}H nmr spectrum (τ, D_3CCN):[28] m, 0.45 (2 H); s, 0.65 (4 H); s, 8.15 (3 H); ^{11}B nmr spectrum (δ, D_3CCN):[27] d, 122.0 (J = 11.8 Hz). Work-up of the mother liquors gave 96.9% triphenylmethane (0.181 g, 0.745 mmol), mp 93.5–94°.

Other dicarbahemiousenium hexafluorometalates prepared include the following ((a) name, (b) per cent yield, (c) form, (d) melting point, (e) electronic spectrum, (f) ^{1}H nmr spectrum (τ, D_3CCN)[28]): (B) (a) 1-methyl[7.12²]-1,2-dicarbahemiousenium hexafluoroarsenate, (b) 69%, (c) white needles, (d) dec pt >230°, (e) see A, (f) see A; (C) (a) [7.12¹]-1,2-dicarbahemiousenium hexafluoroantimonate, (b) 63%, (c) white prisms, (d) 197–198°, (e) (acetonitrile) λ_{max} 233 (ϵ 36,100) and 293 nm (6490), (f) s, 0.68 (6 H); s, 6.25 (1 H); (D) (a) [7.12¹]-1,7-dicarbahemiousenium hexafluoroarsenate, (b) 91%, (c) white prisms, (d) 235°, (e) (96% sulfuric acid) λ_{max} 232.5 (ϵ 38,300), 296.5 (7750), and 302.5 nm (7900); (f) ss, 0.73 (6 H); s, 5.64 (1 H).

[7.7.12^{1,7}]-1,7-Dicarbaousenium Hexafluoroarsenate. A solution of 1,7-di-γ-tropenyl-*closo*-1,7-dicarbadodecaborane(10) (0.326 g, 1.00 mmol) in methylene chloride (1 ml) was added all at once to a sample of triphenylcarbonium hexafluoroarsenate (0.432 g, 1.00 mmol) covered with methylene chloride (5 ml). The remaining triphenylcarbonium salt dissolved in about 1 min with swirling, and a white precipitate began to form; after 1 hr a considerable quantity of white crystals had been deposited. The solution was filtered and the crystals washed on the filter with several small portions of methylene chloride and dried *in vacuo* to yield 76.4% [7.7.12^{1,7}]-1,7-dicarbaousenium hexafluoroarsenate (0.534 g, 0.764 mmol) as white prisms, mp >200° dec; electronic spectrum (96% sulfuric acid): λ_{max} 234

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(26) E. Weth and A. S. Drieding, *Proc. Chem. Soc., London*, 59 (1964).

(27) ^{11}B nmr spectra are given in ppm (δ) relative to triethylboron = 0.

(28) ^{1}H nmr spectra are given in ppm (τ) relative to TMS = 10.

Table II. ^{1}H Nmr Spectra of Tropenyl- and γ-Tropenylcarboranes[a-c]

Carborane	Ring protons: 3 Position	Ring protons: 2-Position	Ring protons: 1-Position	Ring protons: 7 Position	Cage protons: *C*-H	Cage protons: *C*-CH_3
			Monotropenylcarboranes			
1-CH_3-2-	t, 3.21, 3.36, 3.31, 2 H	m, 3.60–3.93, 2 H	q, 4.55–4.80, 2 H	t, 8.22, 8.33, 8.43, 1 H		s, 8.22, 3 H
1,2-	t, 3.28, 3.33, 3.39, 2 H	m, 3.66–4.05, 2 H	q, 4.56–4.89, 2 H	t, 7.97, 8.07, 8.15, 1 H	bs, 6.45, 1 H	
1,7-	t, 3.20, 3.25, 3.30, 2 H	m, 3.58–4.00, 2 H	q, 4.58–4.83, 2 H	t, 8.13, 8.25, 8.33, 1 H	bs, 7.05, 1 H	
			Ditropenylcarboranes			
1,2-	t, 3.33, 3.38, 3.44, 4 H	m, 3.76–4.00, 4 H	q, 4.74–5.00, 4 H	t, 8.43, 8.53, 8.63, 2 H		
1,7-	t, 3.28, 3.33, 3.38, 4 H	m, 3.68–4.02, 4 H	q, 4.56–4.95, 4 H	t, 8.15, 8.24, 8.35, 2 H		
			Mono-γ-tropenylcarboranes			
1-CH_3-2-	d, 2.81, 2.90, 1 H	q, 3.62–3.87, 2 H	m, 4.18–4.87, 2 H	t, 7.70, 7.83, 7.94, 2 H		s, 8.28, 3 H
1,2-	d, 3.02, 3.11, 1 H	q, 3.70–3.95, 2 H	m, 4.26–4.79, 2 H	t, 7.70, 7.82, 7.94, 2 H	bs, 6.16, 1 H	
1,7-	d, 3.04, 3.15, 1 H	m, 3.58–3.94, 2 H	m, 4.22–4.83, 2 H	t, 7.61, 7.73, 7.84, 2 H	bs, 6.96, 1 H	
			Di-γ-tropenylcarboranes			
1,2-	d, 2.95, 3.05, 2 H	m, 3.62–4.05, 4 H	m, 4.32–5.04, 4 H	t, 7.90, 8.02, 8.13, 4 H		
1,7-	d, 3.13, 3.22, 2 H	t, 3.76, 3.92, 4.04, 4 H	m, 4.36–4.88, 4 H	t, 7.75, 7.86, 7.98, 4 H		

[a] In $CDCl_3$. [b] Values in ppm (τ) relative to TMS = 10. [c] Symbols: t, triplet; m, multiplet; q, quartet; s, singlet; bs, broad singlet.

(ε 73,700), 284 (sh), 292 (14,800), and 301 nm (14,300); electronic spectrum (acetonitrile): λ_{max} 235 (ε 77,300), 285 (sh), 291 (13,900), and 297.5 nm (sh); ^{1}H nmr spectrum (τ, D_3CCN):[28] ss, 0.70. Addition of benzene (10 ml) followed by cyclohexane (10 ml) to the reaction mother liquor gave 10.3% additional yield (0.069 g, 0.106 mmol) for an overall yield of 86.7%.

Recrystallization of this salt from acetonitrile, nitromethane, or methylene chloride by addition of ether or cyclohexane gave initial crops of snow white crystals; however, these always darkened before they could be separated from the solutions and decomposed if left in contact with organic solvents.

$[7.7.12^{1,7}]$-1,7-Dicarbaousenium Hexachlorostannate. A portion of the hexafluoroarsenate (above) was triturated with boiling 12 *N* hydrochloric acid to effect partial solution and filtered while hot. An equal volume of a saturated solution of stannic chloride pentahydrate in 12 *N* hydrochloric acid was added to the hot filtrate with the immediate formation of a white precipitate. The solution was allowed to cool, the solid was collected on fritted glass, washed with a small portion of 12 *N* hydrochloric acid, and dried *in vacuo* over sodium hydroxide pellets to give $[7.7.12^{1,7}]$-1,7-dicarbaousenium hexachlorostannate as white prisms, mp >300°.

1-Methyl$[7.12^2]$-1,2-dicarbahemiousenium Bromide. 1-Methyl-$[7.12^2]$-1,2-dicarbahemiousenium hexafluoroarsenate (1.48 g, 3.40 mmol) was partially dissolved in methanol (3 ml) and a solution of 0.34 *M* sodium methoxide in methanol (11 ml) was added slowly. This solution was flooded with water until opaque and then extracted with methylene chloride (four 15-ml portions). The methylene chloride was then dried over magnesium sulfate and concentrated *in vacuo* to a colorless oil (0.827 g) presumed to be a mixture of methyl ethers. Hydrogen bromide (about 10 ml) was condensed onto the oil; the resulting orange solution was evaporated to a slush at room temperature and then dried *in vacuo*, and the resulting solid was sublimed (90°, 0.1 Torr) to yield 87.0% 1-methyl$[7.12^2]$-1,2-dicarbahemiousenium bromide (0.970 g, 2.96 mmol) as pale yellow crystals, mp 103–105°; electronic spectrum (96% sulfuric acid): λ_{max} 224 (ε 33,200), 287 (sh), 294 (6350), and 302 nm (sh).

$[7.7.12^{1,7}]$-1,7-Dicarbaousenium Bromide. $[7.7.12^{1,7}]$-1,7-Dicarbaousenium hexafluoroarsenate (0.36 g, 0.54 mmol) was treated as above; concentration of the dried methylene chloride extracts *in vacuo* gave 100% $[7.7.12^{1,7}]$-1,7-dicarbaousenium bromide (0.26 g, 0.54 mmol); scarlet microcrystals from 1,2-dichloroethane; electronic spectrum (96% sulfuric acid): λ_{max} 284 (sh), 292 (ε 14,700), and 301 nm (sh); this shows the salt to contain 66.4% cation by weight; the amount calculated for $C_{16}H_{22}B_{10}Br_2$ was 66.86% cation.

$[7.7.10^{2,x}]$Ousene.[9] A solution of cesium $[7.10^2]$hemiousenide[2] (0.099 g, 0.290 mmol) in water (250 ml) was added dropwise over a period of 5 hr to a stirred solution of tropenylium bromide[19] (0.510 g, 2.98 mmol) in water (250 ml). After this time the solution was light red, dark crystals had formed, and the odor of cycloheptatriene was apparent. The reaction mixture was stirred for 3 hr more and then was extracted once with cyclohexane and filtered to yield 35 mg of purple microcrystals. The solution was stored in the refrigerator overnight and a second crop of 43 mg of deep purple, dichroic single needles was collected by filtration for a combined yield of 90.5% $[7.7.10^{2,x}]$ousene (0.078 g, 0.263 mmol); no melting point or change on heating in air to 360°; electronic spectrum (acetonitrile): λ_{max} 261.5 and 481 nm; ^{1}H nmr spectrum ($(CD_3)_2CO$):[29] m, 1.03–2.51 (4 H); d, 2.72, 2.89 (2 H); infrared spectrum (KBr pellet):[30] 3000 (w) (C–H stretch), 2485 and 2450 (s) (B–H stretch), 1482 and 1472 (vs) (aromatic ring C–C), 1230 and 1190 (m) (ring in-plane C–H wag), 852 (w), and 735 cm^{-1} (w).

Anal. Calcd for $C_{14}H_{20}B_{10}$: C, 56.71; H, 6.80; B, 36.49. Found: C, 56.21; H, 7.15; B, 36.43.

An identical reaction was carried out with cesium $[7.10^2]$hemiousenide (0.0435 g, 0.125 mmol) and tropenylium bromide (0.231 g, 1.36 mmol); during the reaction the solution was covered with pentane. Quantitative electronic spectral analysis[19] of the pentane solution showed the presence of 96.5% cycloheptatriene, λ_{max} 262 nm.

1-Methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) Anion. A. Potassium Salt by Direct Synthesis.[31] A mixture of 1-methyl-*closo*-1,2-dicarbadodecaborane(11) (7.02 g, 44.3 mmol), potassium hydroxide (5.00 g), and anhydrous ethanol (50 ml) was stirred at room temperature for 30 min and then heated at reflux for 20 hr; the solution was then cooled and solid carbon dioxide (40 g) was added with stirring. The solution was filtered to remove potassium carbonate and concentrated *in vacuo*, and the syrupy residue taken up in dry ether. The ether solution was filtered to remove additional potassium carbonate and concentrated *in vacuo*. The material was then dissolved in the minimum amount of anhydrous ethanol, benzene (60 ml) was added, and the solvent was removed by distillation until the temperature reached 80°. The cooled solution deposited white crystals which were washed with benzene and dried *in vacuo* to yield 94.5% potassium 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) (7.80 g, 41.8 mmol); ^{1}H nmr spectrum (τ, D_2O):[28] bs, 8.06 (1 H); s, 8.57 (3 H); infrared spectrum (KBr pellet and Nujol mull):[30,32] 2935 (m) (cage C–H stretch), 2830 (w) (methyl C–H stretch), 2520 (vs) (B–H stretch), and 1040 cm^{-1} (s) (cage deformation).

B. Trimethylammonium Salt by Degradation of 1-Methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10).[33] A sample of the tropenylcarborane (4.52 g, 19 mmol) was added to a solution of potassium hydroxide (2.0 g) in ethanol (50 ml) and the reaction was held at reflux for 22 hr. Carbon dioxide gas was bubbled through the cooled solution for 2 hr, potassium carbonate was removed by filtration, the filtrate was concentrated *in vacuo*, and the resulting syrupy material was taken up in hot distilled water and treated with trimethylammonium chloride (1.78 g, 18.6 mmol); concentration and cooling of the solution afforded 100% trimethylammonium 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) (4.0 g, 19 mmol) as

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(29) We are indebted to Mr. B. J. Nist, who determined this spectrum on the University of Washington Varian HR-60 spectrometer with 49-scan CAT signal enhancement.

(30) Principal bands only.

(31) Directions kindly furnished by M. F. Hawthorne and K. Callahan.

(32) The assignments of the cage C–H stretch and the methyl C–H stretch are based on a comparison with 1-methyl-*closo*-1,2-dicarbadodecaborane, in which the cage C–H band is much more intense and lies about 100 cm^{-1} to the high-energy side of the methyl band. Should our assignment be reversed it will not affect arguments advanced herein, since both bands are retained in the nido ousene type compounds.

(33) With P. A. Wegner and G. A. Fisher.

white microcrystals, mp 253–254°; ^{1}H nmr spectrum (τ, D_3CCN):[28,31] s, 7.92 (9 H); bs, 8.22 (1 H); s, 8.83 (3 H); infrared spectrum (Nujol mull):[30] 3220 (s) (N–H stretch),[34] 2520 (vs) (B–H stretch), 1040 (s) (cage deformation), and 985 cm^{-1} (vs) (C–N stretch). A number of additional small peaks in the 1200–800 cm^{-1} region are identical in the spectra of this salt and the potassium salt above.

1-Methyl[7.7.11^{x,y}]-*nido*-(3)-1,2-dicarbaousenium Fluoroborate.[10] A solution of the 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) anion was prepared by refluxing 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10) (0.90 g, 3.61 mmol) with sodium methoxide (2.1 g) in methanol (60 ml) for 24 hr. Water (35 ml) was added, the solution was made slightly acidic with sulfuric acid, and tropenylium fluoroborate[19] (2.57 g, 14.4 mmol) was added in one portion; the mixture turned purple at once, the odor of cycloheptatriene was apparent, and a dark red precipitate formed. The mixture was extracted twice with cyclohexane (bright blue) and once with methylene chloride (purple) and filtered on a glass frit. The reddish black solids on the frit were dried *in vacuo* and leached with acetonitrile; concentration of this acetonitrile *in vacuo* afforded a small quantity of 1-methyl-[7.7.11^{x,y}]-*nido*-(3)-1,2-dicarbaousenium fluoroborate as dark red prisms; electronic spectrum (methylene chloride): λ_{max} 263, 340, 525 nm (A_{263}:A_{340}:A_{525}::1.76:0.60:1.00); infrared spectrum (KBr pellet):[30,32] 2920 (m) (cage C–H stretch), 2850 (w) (methyl C–H stretch), 2540 (vs) (B–H stretch), 1480 (s) (aromatic ring C–C), 1400 (m, b), and 1080 cm^{-1} (vs) (BF_4^-).[35]

Anal. Calcd for $C_{17}H_{24}B_{10}F_4$: C, 49.50; H, 5.86; B, 26.21. Found: C, 49.78; H, 5.94; B, 26.13.

1-Methyl[7.11^x]-*nido*-(3)-1,2-dicarbahemiousene.[10] A solution of tropenylium fluoroborate[19] (0.1604 g, 0.901 mmol) in water (66 ml) was added dropwise over 4 hr to a stirred solution of potassium 1-methyl-*nido*-(3)-1,2-dicarbaundecaborate(11) (0.04 g, 0.2 mmol) in water (244 ml), which was covered throughout the reaction with a layer of methylene chloride (150 ml);[36] 20 min after the addition had been started a faint pink color appeared in the methylene chloride layer. The reaction was allowed to stir for 24 hr; after this time the methylene chloride layer was deep purple and the water layer colorless. The methylene chloride was concentrated *in vacuo* and the residue dried (0.1 Torr, 25°) for 4 hr to remove water and cycloheptatriene; this afforded a quantitative yield of presumed 1-methyl[7.11^x]-*nido*-(3)-1,2-dicarbahemiousene (0.05 g, 0.2 mmol) as a red microcrystalline powder; electronic spectrum (methylene chloride): λ_{max} 260 nm (ϵ 6710) and 529 (8480); electronic spectrum (cyclohexane): λ_{max} 260 and 570 nm (A_{260}:A_{570}::1.25: 1.00); infrared spectrum (film on NaCl):[30,32] 2930 (m) (cage C–H stretch), 2860 (w) (methyl C–H stretch), 2550 (vs) (B–H stretch), 1480 (s) (aromatic ring C–C), 1370 (m, b), 1295 and 1335 (m) (ring in-plane C–H wag); and 1030 cm^{-1} (cage deformation); ^{1}H nmr spectrum (τ, D_3CNO_2):[28] m, 0.67–1.22 (2 H); ss, 1.68 (4 H); s, 8.18; s, 8.35; s, 8.37; s, 8.45 (3 H).[37] This material is sensitive to oxygen; the solid turns white on exposure to air, and solutions in cyclohexane or methylene chloride are rapidly rendered colorless when air is bubbled through them.

Nmr Exchange Studies. The general method is that of Freedman, Young, and Sandel.[38,39] Weighed samples of 1-methyl[7.12^2]-1,2-dicarbahemiousenium hexafluoroarsenate and either tri-*p*-tolylmethyl chloride or bromide were mixed in an nmr sample tube and dissolved in methylene chloride to which a small amount of acetonitrile-d_3 had been added to ensure solution of the hemiousenium salt; the chemical shift of the tolyl group methyl protons was used to measure the equilibrium position of the time-averaged spectrum. A representative set of data is as follows: (a) tri-*p*-tolylcarbonium perchlorate, −168.1 Hz;[40] (b) tri-*p*-tolylmethyl chloride or bromide, −140.0 Hz; (c) mixture of 1-methyl[7.12^2]-1,2-dicarbahemiousenium hexafluoroarsenate (0.0131 g, 0.0301 mmol) and tri-*p*-tolylmethyl bromide (0.0114 g, 0.0304 mmol), −154.5 Hz; (d) mole fraction B/(B + D) (see eq 5), 0.325; (e) K_{eq} for (5), 4.84; (f) $\Delta G_{(5)}$, −0.99 kcal/mol.

$$\underset{A}{[7.12^2]^+AsF_6^-} + \underset{B}{Tol_3CBr} = \underset{C}{[7.12^2]Br} + \underset{D}{Tol_3C^+AsF_6^-} \qquad (5)$$

Numerous runs gave an average $\Delta G_{(5)} = 1.00 \pm 0.22$ kcal/mol at 309°K.[41,42]

Discussion

Dicarbahemiousenium and Dicarbaousenium Ions. The carborane cages are recognized[43,44] as substituents with strong $-I$ and weak $+T$ electronic effects, and these effects are respectively stronger and weaker in the 1,2 than in the 1,7 isomer. The spectral properties of the dicarbahemiousenium and dicarbaousenium ions reflect these substituent effects clearly.

The electronic spectra of these ions lie midway between the type I substituted tropenylium ion spectra,[45] which result when an inert substituent lowers the ring symmetry from D_{7h} to C_{2v}, and type II spectra in which polarization by (but not charge transfer from) a $+T$ substituent breaks down the degeneracy of both ring bands and makes the previously symmetry-forbidden $^1E_{3u}$ band allowed along the axis of the ring-substituent bond. Both the [7.12^1]-1,7-dicarbahemiousenium and [7.7.12^{1,7}]-1,7-dicarbaousenium ions show more type II character than the [7.12^1]-1,2-dicarbahemiousenium ion. Similarly, the infrared spectra of these ions (Table III; Figure 3) are quite similar except for the enhancement of the C–H in-plane wag in the 1,7 derivatives; such enhancement has been correlated with increased electronic interaction between substituent and ring.[2,45] As previously discussed[4a] the ^{1}H nmr spectra of the ring protons in these ions are typical of tropenylium ions bearing a simple $-I$ substituent, and the similarity of the ^{11}B nmr spectra of 1-methyl-2-tropenyl-*closo*-1,2-dicarbadodecaborane(10) and the cation derived from it show that the cage is little perturbed by the tropenyliumyl substituent. Neither the electronic, infrared, nor nmr spectra of the [7.7.12^{1,7}]-1,7-dicarbaousenium ion indicate significant interaction between the two cationic rings.

[7.7.10^{2,x}]Ousene. In the neutral ousene, unlike the dicarbaousenium ion described above, there is spectroscopic evidence for interaction between the two tropenyliumyl substituents. Comparison of the position of the substituent-to-ring charge-transfer band in the type III spectra[45] of this compound with that of the [7.10^2]hemiousenide ion[2] shows that the cage is a weaker donor when the second ring is attached. The infrared spectrum of the ousene is generally similar to that of the hemiousenide ion; however, the ring absorptions are increased in intensity relative to those of the cage, and the C–C aromatic ring region shows less conjugation with the substituent cage.[2,45] The ^{1}H nmr spectrum resembles that of methoxy- or hydroxytropenylium ion, in which the doublet assigned to the two protons adjacent to the substituent are upfield from the multiplet of the remaining four protons. In contrast, this doublet is downfield from the

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(34) The sharp N–H stretching band shows little if any hydrogen bonding to the anion.

(35) Ring C–H wag and cage deformation bands masked by anion absorption.

(36) If cyclohexane is used for extraction instead of methylene chloride, it can be shown that the only product under these reaction conditions is blue, hydrocarbon-soluble material; no red, water-insoluble solid is formed. The blue material is, however, much less soluble in cyclohexane than in methylene chloride, and repeated extractions are necessary to render the aqueous solution colorless.

(37) The methyl region consists of a group of one large and three very small singlets; the peak at τ 8.35 is much larger than the others combined.

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(41) The temperature of the probe was determined by the methanol shift method of Van Geet.[42]

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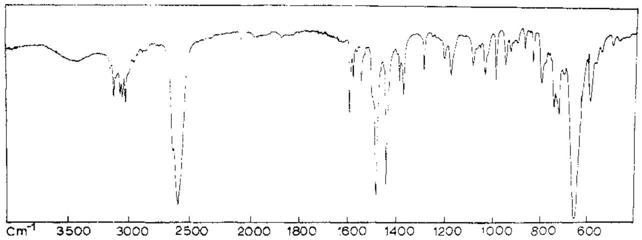

Figure 3. Infrared spectrum (KBr pellet) of 1-methyl[7.12^2]-1,2-dicarbahemiousenium hexafluoroantimonate.

Table III. Infrared Spectra of Dicarbahemiousenium and Dicarbahousenium Salts[a-c]

R′[d]	C–H	B–H	C–C aromatic	C–H[e]	Anion
2-CH_3	3160–2950	2590	1595, 1548, 1488, 1445, 1390[f]	[g]	650 SbF_6^-
2-H	3170–3000	2590	1600, 1545, 1490, 1440, 1380		650 SbF_6^-
7-H	3160–2990	2610	1605, 1545, 1493, 1450, 1382	1245, 1210	695 AsF_6^-
7-$C_7H_6^+$	3160–2980	2610[h]	1600, 1550, 1490, 1449, 1382	1240, 1205	695 AsF_6^-

[a] KBr pellets. [b] Values in cm^{-1}. [c] Intensities very similar to those in the spectrum shown in Figure 3, except for the dication. [d] First substituent in all cases 1-$C_7H_6^+$. [e] In-plane wag. [f] Methyl bending at 1372 cm^{-1} also. [g] If the structure at 1205 and 1178 cm^{-1} (Figure 3) is the in-plane C-H wag, it is at lower frequencies than normally found; shape and relative intensity, however, are reasonable. [h] The B–H band in this ion is approximately half as intense relative to bands due to cationic ring or AsF_6^- anion when compared to the spectrum of the [7.12^1]-1,7-dicarbahemiousenium ion.

four-proton multiplet in the ^1H nmr spectrum of the [7.10^2]-hemiousenide ion. It is possible that rearrangement has occurred and that the rings are apical in this ousene, not equatorial as the ring is known to be in the [7.10^2]hemiousenide ion.[46,47] This would give a highly symmetrical structure which would be in accord with the extreme crystallinity, high melting point, and low solubility of this material. Structural studies on this ousene are in progress.

Nido Carborane Derivatives. Although the 1-methyl[7.11^x]-*nido*-(3)-1,2-dicarbahemiousene prepared in this work was not subjected to elemental analyses due to its ready reaction with oxygen and its apparent instability in the solid state or in concentrated solutions, the electronic, infrared, and nmr spectra and mode of formation are all consonant with the assigned formulation. The electronic and infrared spectra are markedly similar to those of the 1-methyl[$7.7.11^{x,y}$]-*nido*-(3)-1,2-dicarbaousenium cation, for which satisfactory analyses were obtained, except that the absorptions ascribed to the ring are less intense in the monosubstituted nido dicarbahemiousene. Since the cage C–H band is retained in the infrared spectrum, the substitution is presumed to be on boron. The appearance of the infrared and nmr spectra of this compound suggest that it may consist of a mixture of very similar substances, presumably positional isomers. In all preparations, however, a single isomer (as judged by the ^1H nmr spectrum; see Experimental Section) predominates.

In its general spectral properties the nido dicarbahemiousene resembles a hemiousenide ion;[2] the ground-state shielding of the ring protons by electron donation from the cage is similar to that in the [7.12] hemiousenide ion, while the cage-to-ring charge-transfer band in methylene chloride (525 nm) lies at slightly lower energy than that of the [7.10^2] hemiousenide ion (520 nm) in this solvent.

The most remarkable property of this compound is its solubility. The neutral [$7.7.10^{2,x}$]ousene is completely insoluble in hydrocarbons and dissolves to only a slight extent in polar organic solvents; however the neutral 1-methyl[7.11^x]-*nido*-(3)-1,2-dicarbahemiousene dissolves readily in all polar solvents and to a reasonable extent in hydrocarbons such as cyclohexane. The solubility of the nido dicarbahemiousene in hydrocarbons is enhanced if they are not completely dry; no such effect is noted with the closo ousene.

The solubility of the nido dicarbahemiousene in hydrocarbons, coupled with its ready reaction with oxygen, suggested that the compound might be a diradical, in which an electron has been transferred from the cage to the ring, rather than a zwitterionic species. This possibility is ruled out by the positive slope of the Kosower Z value[2,48] plot of the cage-to-ring charge-transfer band and by the fact that the compound fails to show any esr signal[49] either at room temperature in solvent or at liquid nitrogen temperature in hydrocarbon glass. An alternative explanation of the properties of this compound is that the polarity is reduced by delocalization of electrons from cage to ring through molecular orbitals encompassing both moieties; such electrons would remain paired and thus show no esr signal.

Nmr Measurements of the Stability of the 1-Methyl[7.12^2]-1,2-dicarbahemiousenium Ion. When solutions of the 1-methyl[7.12^2]-1,2-dicarbahemiousenium ion in 12 N hydrochloric acid are treated with stannic chloride pentahydrate, a white, crystalline complex salt is formed. This material gives the infrared and electronic spectra expected for the dicarbahemiousenium cation, and in addition the infrared spectrum shows the characteristic band[23] of the hexachlorostannate(IV) anion.

Since the hexachlorostannate(IV) anion forms in the presence of the 1-methyl[7.12^2]-1,2-dicarbahemiousenium ion, this ion must be at least 1.85 kcal/mol more stable than the triphenylcarbonium ion;[23] however the fact that it also forms a covalent bromide indicates that it is less stable—or more acidic—than the trianisylcarbonium ion, which forms[50] an ionic bromide. The ion thus lies in a range of stability that should be amenable to quantitative study by the nmr nucleophile exchange technique developed by Freedman, Young, and Sandel.[38,39] Nmr measurement of the fast halide exchange between the 1-methyl[7.12^3]-1,2-dicarbahemiousenium ion and the tri-p-tolylcarbonium ion in methylene chloride-acetonitrile-d_3 solution gives reproducible equilibrium values and shows this hemiousenium ion to be only 3.6 kcal/mol more stable than the triphenylcarbonium ion. This represents a destabilizing effect of about 9 units in pK_{R^+}[51] relative to the unsubstituted tropenylium ion.

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Polyhedral Expansion of Metallocarboranes

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New metallocarboranes of general formulas $(C_5H_5)_2Co_2C_2B_nH_{n+2}$ and $(C_5H_5)_3Co_3C_2B_nH_{n+2}$ can be directly prepared by the reduction of the closo metallocarboranes 2,1,6-$C_5H_5CoC_2B_7H_9$, 1,2,3-$C_5H_5CoC_2B_8H_{10}$, 1,2,4-$C_5H_5CoC_2B_8H_{10}$, and 3,1,2-$C_5H_5CoC_2B_9H_{11}$ with Na in the presence of naphthalene followed by addition of $CoCl_2$ and NaC_5H_5. The preparation, characterization, and proposed structures of these metallocarboranes are discussed.

The general reaction sequence involving the reduction of a carborane with subsequent or concomitant complexation with a transition metal to produce a monometallocarborane has been established.[1-7] The primary objective of this polyhedral expansion[2] reaction was the synthesis of a polyhedral monometallocarborane one vertex larger than the starting carborane

$$C_2B_nH_{n+2} \xrightarrow{2e^-} [C_2B_nH_{n+2}]^{2-} \xrightarrow[NaC_5H_5]{MCl_2} C_5H_5MC_2B_nH_{n+2}$$

and this was usually the principal product observed. The achievement of this goal was enhanced, however, by the simultaneous formation of a wealth of side products. Monometallic species including $C_5H_5MC_2B_{n+1}H_{n+3}$, $C_5H_5MC_2B_{n-1}H_{n+1}$, $C_5H_5MC_2B_nH_{n+1}(C_2B_nH_{n+1})$, and $C_5H_5MC_2B_nH_{n+1}(C_{10}H_7)$ were formed as well as several new bimetallic compounds, $(C_5H_5)_2M_2C_2B_nH_{n+2}$ where $n = 4, 5, 6$, and 8. The isolation of these bimetallic species suggested that the polyhedral expansion reaction could be extended to metallocarboranes to provide not only an improved preparative route to known bimetallocarboranes but also a direct synthesis of new bimetallic species

$$C_5H_5MC_2B_nH_{n+2} \xrightarrow{3e^-} \xrightarrow[2.\ [O]]{1.\ M'Cl_2,\ NaC_5H_5} (C_5H_5)_2MM'C_2B_nH_{n+2}$$

We report here the results of the polyhedral expansion of 2,1,6-$C_5H_5CoC_2B_7H_9$,[8,10] 1,2,3-$C_5H_5CoC_2B_8H_{10}$,[2,11] 1,2,4-$C_5H_5CoC_2B_8H_{10}$,[12] and 3,1,2-$C_5H_5CoC_2B_9H_{11}$[13] to form *inter alia* the first eleven- and thirteen-vertex bimetallic metallocarboranes and the first trimetallic metallocarborane.[14]

General Procedure

Each metallocarborane was treated in tetrahydrofuran (THF) with 3 equiv of sodium metal in the presence of naphthalene. This may be formally viewed as a M(III) → M(II) reduction followed by an additional two-electron reduction to form an anionic nido metallocarborane species. While reduction times varied depending upon the metallocarborane, in each case the THF solution gradually darkened to near opacity with deposition of material on the sides of the reaction vessel. When the reduction was complete, excess NaC_5H_5 and $CoCl_2$ were added and the air-oxidized reaction mixture was chromatographed on silica gel. As in the polyhedral expansion of carboranes,[5] variations in reaction times and temperatures affected the yield and nature of the products. The primary products obtained from the most representative reactions for each metallocarborane enumerated above are reported here.

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