with hot hexane and the extract concentrated until crystals formed; yield 95%; mp 129–130°. The product was identified by mass, ^{11}B nmr, and infrared spectra (Tables I–III).

3-Arsa-3-*n*-butyl-1,2-dicarba-*closo*-dodecaborane(12). The addition of a solution of 2.0 g (10 mmol) of n-$C_4H_9AsCl_2$ in diethyl ether to a suspension of 5.4 g (9 mmol) of $Tl_2C_2B_9H_{11}$ in diethyl ether resulted in the formation of TlCl and a clear, light yellow solution. The solution was concentrated under vacuum and the residue distilled. The major fraction distilled at 120° (0.4 mm) as a heavy clear liquid. The ^1H nmr spectrum (Table III) identified the product as n-$C_4H_9AsC_2B_9H_{11}$. The mass, ^{11}B nmr, and infrared spectra (Tables I–III) confirmed its identity; yield ~1.0 g (38%).

Bis(dimethylarsino)-7,8-dicarba-*nido*-undecaborane(13). Method I. A 1.0-g (3-mmol) sample of $TlC_2B_9H_{12}$ was suspended in 100 ml of benzene under a nitrogen blanket at 0° and a solution of 0.54 g (2.9 mmol) of $(CH_3)_2AsBr$ in 20 ml of benzene was added at a moderate rate. The reaction mixture was allowed to warm to room temperature over a 12-hr period. The mixture was filtered and the filtrate was concentrated, yielding a yellow oil. The oily product was next heated to 70° under vacuum in a sublimator; a white solid sublimed out of the reaction flask and was identified by its mass, ^{11}B nmr, and infrared spectra as 7,8-$C_2B_9H_{13}$. The residue was identified by its mass spectrum as $[(CH_3)_2As]_2C_2B_9H_{11}$.

Method **II.** A 5.0-g (0.01-mol) sample of $Tl_2C_2B_9H_{11}$ was weighed into a 250-ml boiling flask and 100 ml of dry benzene was added. The system was purged with nitrogen and a solution of $(CH_3)_2AsBr$ (3.4 g, 0.02 mol) in 50 ml of benzene was added dropwise over a 10-min period. The mixture was allowed to stir for 1 hr after which it was filtered to remove the TlBr, and the filtrate was concentrated to approximately 50 ml. Dry hexane was added slowly to the hot concentrate until cloudiness appeared. On cooling to room temperature a yellow semisolid formed. The mixture was filtered and the semisolid residue was washed with hexane and dried at 50° under vacuum. The resulting off-white waxy solid was sublimed at 150° (0.1 mm) to a −80° cold finger. The product was obtained as a white sublimate, mp 128–130°; yield 2.3 g, 70%. *Anal.* Calcd for $[(CH_3)_2As]_2C_2B_9H_{11}$: C, 21.05; H, 6.77; B, 28.42; As, 43.76. Found: C, 21.23; H, 7.04; B, 28.01; As, 44.11.

Bis(dimethylarsino)-7,8-dimethyl-7,8-dicarba-*nido*-undecaborane(13). A 3.0-g (5.3-mmol) sample of $Tl_2C_2B_9H_9(CH_3)_2$ prepared from thallium acetate and $[(CH_3)_3NH]C_2B_9H_{10}(CH_3)_2$ was placed in a 250-ml boiling flask under a dry nitrogen atmosphere. Benzene (100 ml) was added and the mixture was stirred while a solution of 1.9 g (10.2 mmol) of $(CH_3)_2AsBr$ in 20 ml of benzene was added dropwise over a 10-min period. The reaction was instantaneous as evidenced by the change in color of the solid phase from yellow to white. The mixture was filtered under nitrogen and the filtrate was concentrated to 75 ml. Dry hexane was added until cloudiness occurred. The mixture was then cooled to 0° and a yellow solid precipitated. The mixture was filtered and the filter cake was washed with hexane and dried under vacuum. The product was identified as $[(CH_3)_2As]_2C_2B_9H_9(CH_3)_2$ by its mass, nmr, and infrared spectra (Tables I–III). Attempts to obtain an analytically pure sample *via* sublimation or recrystallization from benzene–hexane were unsuccessful. The melting range was 60–90°. The yield of crude product was quantitative.

Reaction of $[(CH_3)_2As]_2C_2B_9H_{11}$ with Ethanolic Potassium Hydroxide. A 0.5-g sample of $[(CH_3)_2As]_2C_2B_9H_{11}$ was dissolved in approximately 15 ml of an ethanol solution containing 20 g of potassium hydroxide /300 ml of ethanol. The solution was refluxed for 30–60 min. After cooling of the mixture to room temperature the solvent was removed under vacuum and the solid residue was extracted with benzene. Evaporation of the benzene yielded approximately 0.3 g (72%) of a white crystalline solid. This product has not been completely characterized. However, mass spectral and ^{11}B nmr data are consistent with the proposed substitution of a terminally bound $(CH_3)_2As$ group by ethoxide.

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Registry No. $[(CH_3)_3NH]$-7,8-$C_2B_9H_{12}$, 12305-36-1; CH_3AsBr_2, 676-70-0; $CH_3AsC_2B_9H_{11}$, 52175-48-1; $Tl_2C_2B_9H_{11}$, 41721-58-8; $Tl_2C_2B_9H_9(CH_3)_2$, 41721-60-2; $CH_3AsC_2B_9H_9(CH_3)_2$, 52175-47-0; $C_6H_5AsCl_2$, 696-28-6; $C_6H_5AsC_2B_9H_{11}$, 52175-49-2; BBr_3, 10294-33-4; $BrAsC_2B_9H_{11}$, 52175-50-5; n-$C_4H_9AsCl_2$, 692-23-9; n-$C_4H_9AsC_2B_9H_{11}$, 52175-51-6; $TlC_2B_9H_{12}$, 52216-81-6; $(CH_3)_2AsBr$, 676-71-1; ^{11}B, 14798-13-1.

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Nitrile Addition to Polyhedral Boranes in the Presence of Iron(III) Chloride

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The reactions of $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ with $FeCl_3$ in the presence of nitriles were investigated. In addition to $B_{20}H_{18}{}^{2-}$, $B_{24}H_{23}{}^{3-}$, $B_{12}H_{11}Cl^{2-}$, $B_{24}H_{22}Cl^{3-}$, and $B_{12}H_{11}NH_3{}^-$, nitrile adducts were produced in reactions with acetonitrile, ethyl cyanoacetate, malononitrile, and cyanomethyl benzenesulfonate. The adducts were recovered in the partially hydrolyzed form $B_nH_{n-a}(NH_2COR)_a{}^{a-2}$, where $a = 1$ or 2, and R = CH_3, $CH_2COOC_2H_5$, CH_2CONH_2, or $CH_2OSO_2C_6H_5$.

Introduction

Acetonitrile has been used as a solvent in numerous reactions of polyhedral boranes, but at elevated temperatures and under strongly acidic conditions it can also act as a reactant by displacing hydrogen from the boron cage. Monosubstituted derivatives of $B_{10}H_{10}{}^{2-}$ have been obtained from acid-catalyzed reactions with acetonitrile and benzonitrile.[2] The acetonitrile derivative of $B_{12}H_{12}{}^{2-}$ has been prepared in a similar fashion.[3] Whether a second nitrile can be attached to the cage under such conditions has not been reported. A disubstituted derivative, $B_{10}H_8(NCCH_3)_2$, has been made by heating 1,10-$B_{10}H_8(N_2)_2$ in the presence of CH_3CN at 150°.[4]

Since a number of polyhedral boranes having functional groups separated from the cage by several bonds exhibit biological activity,[5] we decided to look for reactions leading to more such compounds. The large number of commercially available substituted nitriles suggested that nitrile addition might lead to such products in a one-step reaction if the other functional group can be protected from loss, decomposition, or direct attachment to the cage. At elevated temperatures and in the presence of protonic acids most functional groups of biological interest, particularly those

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containing oxygen or sulfur, react readily with the polyhedral boron cage.[2,6,7] Though the problem is less serious in the case of diazonium displacement,[4] we were discouraged from pursuing this approach by the very low yield of the diazonium intermediate and the unavailability of a similar derivative of the $B_{12}H_{12}^{2-}$ system.[8]

When copper and iron halides are dissolved in nitriles, they yield a mixture of halo and nitrilo complexes. Therefore we decided to see whether the nitrilo complexes might not facilitate nitrile addition in the absence of protonic acids and at moderate temperatures, in a manner analogous to halogenation by $CuCl_2$ and $FeCl_3$ in nonaqueous solvents.[9,10] Such a nitrile substitution has been reported for a carborane.[11]

Experimental Section

Materials and Techniques. Salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ were prepared by methods described in the literature.[12] The nitriles were obtained from Aldrich Chemical Co., and the inorganic salts from Alfa Inorganics. Analytical reagent grade materials were used whenever available. Ir spectra of samples pressed into KBr pellets were recorded on a Perkin-Elmer Model 237B spectrophotometer, while uv spectra were recorded on a 202 Model. Varian A-60 and T-60 spectrometers were used to record ^1H nmr spectra and the chemical shifts are given in ppm (τ) relative to external Me_4Si. All tlc work was done with Bakerflex PEI-F impregnated cellulose on polyethylene sheets. The most successful eluent contained 20 parts acetonitrile, 17 parts saturated aqueous $NaPF_6$ (or NH_4PF_6), and 3 parts methanol. A 2% solution of aqueous acidic $PdCl_2$ was used to detect the hydroborate derivatives on the tlc plates after elution. The presence of $B_{20}H_{18}^{2-}$ was indicated by its characteristic uv spectrum.[13] Materials which failed to exhibit the B–H stretching band at 2500 Å were discarded. The yields are expressed as per cent of initial borane.

Acetonitrile. $B_{12}H_{11}Cl^{2-}$. Anhydrous $FeCl_3$ (23 g, 142 mmol) was added to 300 ml of acetonitrile containing $Na_2B_{12}H_{12}\cdot 2H_2O$ (5.00 g, 22.4 mmol) and the reaction mixture was stirred at room temperature for 5 days. The resulting brown slurry was separated by filtration into a brown solid and a clear green solution. The brown solid was stirred with water, the water-insoluble portion discarded, and the aqueous solution treated with ammonia. After the hydroxides of iron were removed by filtration, the solution was neutralized with hydrochloric acid and treated with aqueous tetramethylammonium chloride, which precipitated 0.0937 g of $[(CH_3)_4N]_2B_{12}H_{11}Cl$. The green acetonitrile solution was evaporated to dryness under reduced pressure, the solid residue was washed with benzene and ethyl ether until clear washings were obtained, and the washings were saved for later work. The washed solid was dissolved in 100 ml of water and treated with tetramethylammonium chloride, which precipitated 1.30 g of product. After twofold recrystallization from water 1 g (14%) of pure $[(CH_3)_4N]_2B_{12}H_{11}Cl$ was obtained. The product exhibited infrared spectra and tlc characteristics identical with those of authentic material[14] and had equiv wt 161, *vs.* 162 calculated for the salt. A portion of the salt was converted to the corresponding potassium salt with the aid of an ion exchanger.

Anal. Calcd for $K_2B_{12}H_{11}Cl\cdot 1.5H_2O$: K, 27.6; B, 46.0; H, 5.3; Cl, 12.6; equiv wt 141. Found: K, 27.5; B, 45.4; H, 4.8; Cl, 13.5; equiv wt 144.

$B_{24}H_{23}^{3-}$. Removal of the monochloride left a filtrate which after standing for 24 hr in a refrigerator deposited a gummy solid, which was separated from the supernatant liquid by decantation and washed with methanol and acetone. The decantate and the washings were combined and saved. The gummy solid was stirred with boiling water and filtered hot, and the solution was allowed to cool slowly to room temperature to give the first crop of crystals, which were combined with the second crop obtained after the solution was reduced in volume from 250 to 200 ml. These two fractions, which weighed 0.410 g and consisted of the tetramethylammonium salts of $B_{24}H_{23}^{3-}$ and $B_{24}H_{22}Cl^{3-}$ (*vide infra*), were redissolved in boiling water and subjected to fractional crystallization. After removal of several fractions consisting of the two salts mentioned above, 2-propanol was added to the mother liquor to salt out $[(CH_3)_4N]_3B_{24}H_{23}$ (0.117 g, 2.1%). The material was identified by matching its infrared spectra and tlc with those of an authentic sample kindly provided us by Dr. R. L. Middaugh.[3]

$B_{24}H_{22}Cl^{3-}$. The mother liquor (200 ml) remaining after removal of the first two crops of crystals discussed was subjected to further fractional crystallization until the volume was reduced to 100 ml. Fractions 3–5 consisted of $[(CH_3)_4N]_3B_{24}H_{22}Cl$ (0.208 g, 3.4%); fraction 6 contained more of the same but mixed with $(CH_3)_4NB_{12}H_{11}NH_3$ (0.057 g); fraction 7 consisted of pure $(CH_3)_4NB_{12}H_{11}NH_3$ (0.059 g, 1.1%). The remaining 100 ml of mother liquor was saved for later work. With the aid of an ion exchanger the product was converted to the corresponding cesium salt.

Anal. Calcd for $Cs_3B_{24}H_{22}Cl\cdot H_2O$: Cs, 54.5; B, 35.1; H, 3.3; Cl, 4.8; equiv wt 244. Found: Cs, 55.4; B, 33.2; H, 3.3; Cl, 4.7; equiv wt 241.

The combined decantate and washings from the initial separation of $B_{24}H_{23}^{3-}$ were allowed to evaporate at room temperature. After several crops of crystals (1.42 g) containing more than one product were collected, addition of 2-propanol brought down 1.48 g (20.4%) more of $[(CH_3)_4N]_2B_{12}H_{11}Cl$. Ether washings of the solid that was left after the initial evaporation of acetonitrile were evaporated to dryness; the residue was stirred with a water–methanol mixture and filtered; and the filtrate was treated with tetramethylammonium chloride and combined with the mixed crop of crystals mentioned above. The resulting slurry was dissolved in boiling water and filtered; the filtrate was treated with aqueous ammonia and filtered again to remove hydroxides of iron; and the alkaline filtrate was neutralized with hydrochloric acid. As the volume of the solution was gradually reduced, several fractions containing $B_{12}H_{11}Cl^{2-}$ mixed with other products were removed before three fractions consisting of $[(CH_3)_4N]_3B_{24}H_{22}Cl$ were collected (0.246 g, 4.1%). The remaining mother liquor contained many products and was saved for subsequent work.

$B_{12}H_{11}NH_3^-$. Mother liquors saved after the isolation of two crops of the preceding product were combined and allowed to evaporate. After removal of five fractions containing mixtures of at least five compounds, a fraction consisting of pure $(CH_3)_4NB_{12}H_{11}NH_3$ was obtained (0.198 g, 3.8%). Fractions 7 and 8 contained in addition to the amine derivative the parent amide, $B_{12}H_{11}NH_2COCH_3^-$. Addition of methanol to the remaining mother liquor precipitated a white solid which was combined with fractions 7 and 8, and the mixture was recrystallized from water to give 0.450 g (8.7%) more of $(CH_3)_4NB_{12}H_{11}NH_3$. The infrared spectra and the tlc characteristics matched those of the compound made by the method reported in the literature.[15]

Anal. Calcd for $(CH_3)_4NB_{12}H_{11}NH_3\cdot H_2O$: C, 19.3; N, 11.3; B, 52.0; H, 11.3; equiv wt 250. Found: C, 19.5; N, 11.3; B, 49.4; H, 11.0; equiv wt 248.

$B_{12}H_{11}NH_2COCH_3^-$. Evaporation of the benzene washings of the original acetonitrile residue left a gummy solid which was stirred with aqueous methanol and filtered, and the filtrate was treated with tetramethylammonium chloride. The first precipitate consisted of the monochloro and amine derivatives of $B_{12}H_{12}^{2-}$. Evaporation yielded a second precipitate which contained $B_{24}H_{22}Cl^{3-}$ in addition to the products found in the first fraction. The third precipitate consisted of $(CH_3)_4NB_{12}H_{11}NH_2COCH_3$ mixed with a small amount of the other products. Too little material (14 mg) was obtained to permit purification, but the product was identified by the position of its tlc spot and infrared spectrum, which contained all the bands found in an authentic sample of the salt.[3]

In a separate reaction 1.036 g (4.63 mmol) of $Na_2B_{12}H_{12}\cdot 2H_2O$ was allowed to react with $FeCl_3$ (2.47 g, 15.3 mmol) in 35 ml of acetonitrile for 3 days. The reaction mixture was filtered, the solid containing some $B_{12}H_{12}^{2-}$ discarded, and the acetonitrile solution evaporated to dryness under reduced pressure. The yellow residue was stirred with methanol, the insoluble NaCl discarded, and the solution treated with aqueous tetramethylammonium chloride. The

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first precipitate consisted primarily of $[(CH_3)_4N]_2B_{12}H_{11}Cl$ (0.303 g), and after the filtrate was left standing at room temperature for 22 days a strong odor of acetic acid was detected over the solution and a yellow solid accumulated on the surface. The solid was recrystallized twice from 50% aqueous ethanol to give 0.0114 g (0.9%) of $(CH_3)_4NB_{12}H_{11}NH_2COCH_3$. The ^{1}H nmr (DMSO-$d_6$) exhibited peaks at τ 6.87 (s, 4, $(\mathrm{C}H_3)_4\mathrm{N}^+$) and 7.45 (s, 1, $\mathrm{C}H_3\mathrm{CO}$–). The ir spectrum of this and other materials are tabulated in the next section.

Acetonitrile. $B_{10}H_8(NH_2COCH_3)_2$. To a solution of $K_2B_{10}H_{10}$ (1.025 g, 5.23 mmol) in 300 ml of acetonitrile anhydrous ferric chloride (22.4 g, 138 mmol) was added and the mixture stirred at room temperature for 6 hr. The slurry was filtered, a borane-free solid discarded, and the filtrate evaporated to dryness under reduced pressure. The gummy residue was dissolved in methanol, except for a small amount of KCl which was discarded, and when the solution was treated with an equal volume of water, 0.607 g of a tan solid precipitated immediately and was removed by filtration. The filtrate yielded an additional 0.047 g after standing at room temperature for 1 week. The material was free of $B_{20}H_{18}{}^{2-}$ and had only traces of iron salts. It was insoluble in ethanol, ethyl ether, and cyclohexane and soluble in acetone, methanol, acetonitrile, and dimethyl sulfoxide. The solubility in water increased with pH. Recrystallization from a mixture of acetone and ethanol yielded a microcrystalline solid which failed to melt below 300°, exhibited one tlc spot, and had no uv bands above 210 mμ. Larger crystals were obtained when the solid was dissolved in a minimum amount of methanol and the solution was added to a large volume of water. A 0.3-g sample dissolved in 5 ml of methanol yielded 0.2 g of solid when the solution was poured into 50 ml of water. Elemental analyses of materials thus recrystallized gave consistently a carbon:boron ratio well in excess of 4:10 and the nmr indicated retention of a methanolic group even after prolonged vacuum desiccation with pumping. A portion of this solid was dissolved in boiling 95% ethanol and the solution was allowed to cool slowly. After 24 hr a precipitate was collected the tlc spot of which had the same R_f value as that of the parent compound, but whose ir differed in the C–H region. The ^{1}H nmr (DMSO-d_6) consisted of a broad band at τ 2.82 ($-NH_2{}^+-$) and sharper lines at τ 6.23 (s, $\mathrm{C}H_3\mathrm{O}$– or H_2O), 6.55 (quartet, $\mathrm{CH_3C}H_2\mathrm{O}$–), 6.92 (s, $\mathrm{C}H_3\mathrm{CO}$– or $\mathrm{C}H_3\mathrm{C(OR_2}$–), and 8.92 (t, $\mathrm{C}H_3\mathrm{CH_2O}$–).

Anal. Calcd for $B_{10}H_8(NH_2COCH_3)_2 \cdot CH_3OH \cdot C_2H_5OH$: B, 34.6; C, 26.9; N, 9.0; H, 7.7. Found: B, 33.2; C, 26.9; N, 8.5; H, 7.5.

A 0.245-g portion of the first crop (0.607 g) from methanol–water was stirred with 1 *M* NaOH, a small amount of iron hydroxides was removed by filtration, and the filtrate was acidified with 2 *M* HCl after standing at room temperature for 48 hr. Fractional crystallization from the acid solution yielded five indistinguishable fractions the combined weight of which was 0.146 g. The alkaline treatment did not lower the melting point nor alter the solubilities of the product, but it produced drastic changes in the ir spectrum and lowered the R_f value of the tlc spot. The ^{1}H nmr line at τ 6.92 was replaced by one at τ 7.92 (a more reasonable position for $\mathrm{C}H_3\mathrm{CONH_2}$–). When the material was recrystallized from hot aqueous alcohols, it proved very difficult to remove the alcohol from the crystals, but the ^{1}H nmr suggests simple solvation instead of a ketal or hemiketal formation. Thus CH_3OH shows up as a singlet at τ 6.63, and CH_3CH_2OH as a triplet and quartet at τ 8.92 and 6.59, respectively. The ir spectrum will be discussed later.

Anal. Calcd for $B_{10}H_8(NH_2COCH_3)_2$: B, 46.2; C, 20.5; N, 12.0; H, 7.7; equiv wt 117. Found: B, 45.4; C, 20.2; N, 11.2; H, 7.3; equiv wt 116.

Addition of tetramethylammonium chloride to the mother liquor remaining after removal of the five fractions mentioned above yielded a precipitate which was presumed to be $[(CH_3)_4N]_2B_{10}H_8(NHCOCH_3)_2$ on the basis of its infrared spectrum. Addition of tetramethylammonium chloride to the filtrate left after the initial removal of the first two crude fractions precipitated $[(CH_3)_4N]_2B_{20}H_{18}$, identified by its characteristic uv and ir spectra and tlc, mixed with some amide derivatives in the anionic form.

Ethyl Cyanoacetate. Anhydrous $FeCl_3$ (4.5 g, 28 mmol) was added with stirring to a solution of $Na_2B_{12}H_{12} \cdot 2H_2O$ (1.5 g, 6.7 mmol) in 60 ml of ethyl cyanoacetate and the reaction mixture was left stirring for 7 days at room temperature. The slurry was filtered, the solid component discarded, and the filtrate extracted successively with three 200-ml aliquots of a 1:1 benzene–cyclohexane mixture, three 30-ml aliquots of ethyl ether, and four 100-ml aliquots of a 3:1 chloroform–cyclohexane mixture. The ether extract was discarded as it contained no boranes; the others were saved. The brown tarry residue was stirred with 35 ml of methanol, the insoluble component removed by filtration and discarded, and the methanol solution treated with aqueous tetramethylammonium chloride, which precipitated 0.61 g of material containing $B_{12}H_{12}{}^{2-}$ and five derivatives. The filtrate was saved. The precipitate was dissolved in boiling water; the solution was filtered while hot, treated with aqueous ammonia, filtered again to remove hydroxides of iron, and neutralized with hydrochloric acid; and the clear solution was evaporated to dryness under reduced pressure. The residue was washed with acetonitrile, and after the insoluble portion was recrystallized from 95% ethanol, it consisted of $[(CH_3)_4N]_2B_{12}H_{12}$ and $[(CH)_3N]_2B_{12}H_{11}Cl$. The acetonitrile solution was evaporated to dryness, and the residue fractionally crystallized from water. The first two fractions were combined and recrystallized from water to give 22 mg of $[(CH_3)_4N]_3B_{24}H_{23}$, while addition of methanol to the mother liquor salted-out a solid which after recrystallization from water yielded 18 mg of $(CH_3)_4NB_{12}H_{11}NH_3$.

The aqueous filtrate saved after the removal of the first batch of crystals (0.61 g) was allowed to evaporate slowly and several solid fractions were collected. These contained, in addition to the materials identified in the first fraction, a product presumed to be $B_{12}H_{11}NH_2COCH_2COOC_2H_5{}^-$ on the basis of the infrared spectrum, which exhibited two carbonyl bands of almost equal intensity at 1740 and 1650 cm^{-1} and a band at 1220 cm^{-1} attributed to the C–OR bond of the ester.[16] The ^{1}H nmr spectrum contained a peak at τ 8.0 ($\mathrm{-COC}H_2\mathrm{-CO}$). Attempts to isolate and purify this material were unsuccessful as at each step the carbonyl bands diminished while more $B_{12}H_{11}NH_3{}^-$ was produced.

The two organic extracts of the original crude mixture each deposited an oily layer after 24 hr at room temperature. The benzene layer was discarded, while the oil was dissolved in methanol and treated with aqueous $(CH_3)_4NCl$. The resulting precipitate contained a two-carbonyl product resembling the one mentioned above. When the oil left after decantation of the chloroform was treated in the same manner as the benzene residue, it yielded $[(CH_3)_4N]_2B_{12}H_{11}Cl$, which weighed 0.142 g (6.5%) after recrystallization from water. The chloroform decantate was evaporated to dryness, the residue shaken with 100 ml of a chloroform–water mixture (1:1), and the aqueous layer separated. Addition of $(CH_3)_4NCl$ precipitated a solid containing more of the two-carbonyl product.

$\mathbf{H_3NB_{12}H_{10}(NH_2COCH_2SO_3C_6H_5)}$. Anhydrous $FeCl_3$ (4.4 g, 27 mmol) was added to $Na_2B_{12}H_{12} \cdot 2H_2O$ (0.969 g, 4.3 mmol) dissolved in a mixture of cyanomethyl benzenesulfonate (10 ml) and methanol (25 ml). The slurry was refluxed for 3 days and filtered, and the filtrate was flash-evaporated to a gummy residue, which was extracted with ethyl acetate until only a borane-free solid remained undissolved. Evaporation of the filtered extracts left a gummy residue which became powdery after repeated washing with benzene and ether. The washings were discarded and the solid stirred with 50 ml of water and filtered. The water-insoluble fraction contained at least three derivatives (tlc evidence) which proved very difficult to separate and were discarded. Addition of ammonia to the aqueous solution precipitated hydroxides of iron, which were removed, and as the clear filtrate was reduced in volume to 20 ml, a white solid consisting primarily of $C_6H_5SO_3NH_4$ precipitated and was discarded. Continued evaporation left a residue which was dissolved in absolute ethanol, the solution was flash-evaporated, the new residue was stirred with 15 ml of acetonitrile and filtered, and an insoluble solid was discarded. When the acetonitrile was evaporated and the residue was dissolved in water and treated with tetramethylammonium chloride, a gummy solid precipitated. This solid was stirred with 5 ml of acetonitrile, the insoluble portion was discarded, and the filtrate was evaporated to dryness. Recrystallization of the new residue from aqueous acetonitrile (15% by volume) yielded 26 mg (1.4%) of amber-colored crystals. The ^{1}H nmr in CH_3CN-d_6 contained broad peaks at τ 2.35 ($-\mathrm{N}H_3{}^+$, $-\mathrm{N}H_2{}^+-$) and 2.75 ($\mathrm{C_6}H_5$–) and a sharp peak at 7.35 ($-\mathrm{C}H_2-$). The ir spectrum, which is discussed elsewhere, contained all the bands expected for the proposed structure.

Anal. Calcd for $(CH_3)_4NB_{12}H_{10}NH_3(NHCOCH_2SO_3C_6H_5)$: B, 29.2; C, 32.4; N, 9.4; S, 7.2; H, 7.5. Found: B, 29.5; C, 33.7; N, 8.7; S, 6.7; H, 8.0.

Passage of the mother liquor from the recrystallization through an acid ion exchanger and partial evaporation of the acidic effluent yielded 27 mg (1.6%) of $H_3NB_{12}H_{10}NH_2COCH_2SO_3C_6H_5$. The ir spectrum of this solid confirmed the absence of cation and was identical with that obtained when the salt analyzed above was passed through an ion exchanger.

$\mathbf{B_{12}H_{10}(NH_2COCH_2CONH_2)_2}$. To 0.500 g (2.2 mmol) of $Na_2B_{12}H_{12} \cdot 2H_2O$ in 10 ml of malononitrile 2.3 g (14 mmol) of anhydrous ferric chloride was added and the reaction mixture was stirred at 80°

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(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958.

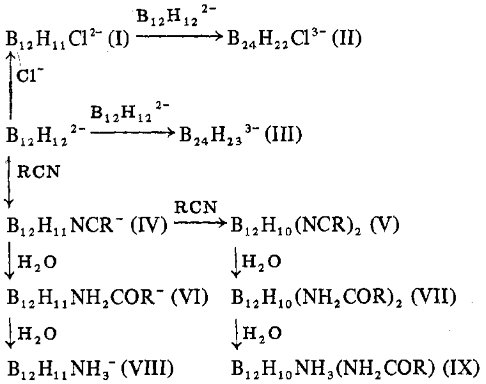
for 40 hr. Addition of absolute ethanol to the solution precipitated a dark brown solid which was isolated but proved difficult to characterize. The nitrile band in the infrared spectrum of this solid was much more intense than the B-H band. Addition of ethanolic tetramethylammonium chloride to the filtrate precipitated a dark brown solid which was removed by filtration, washed with water and ethanol, and dissolved in acetonitrile. Treatment of the acetonitrile solution with aqueous ammonia precipitated hydroxides of iron, which were removed; the filtrate was evaporated to near saturation and passed through an ammonium cation exchanger. The effluent was stirred with decolorizing charcoal (Norit), filtered, and evaporated to dryness under reduced pressure, and the residue was stirred with 10 ml of acetonitrile. An insoluble beige borane-free solid was discarded while the acetonitrile solution was evaporated to dryness and the residue was recrystallized from a hot concentrated aqueous solution of tetramethylammonium chloride. The resulting tetramethylammonium salt was passed through an acid cation exchanger and the effluent was titrated to pH 9 with CsOH. Partial evaporation of the solution followed by addition of ethanol and cooling to 0° yielded 88 mg (6.2%) of $Cs_2B_{12}H_{10}(NHCOCH_2CONH_2)_2 \cdot 2H_2O$. The ir spectrum is reported elsewhere. The ^1H nmr spectrum (DMSO-d_6) contained a sharp peak at τ 7.54 ($-CH_2-$).

Anal. Calcd for $Cs_2B_{12}H_{10}(NHCOCH_2CONH_2)_2 \cdot 2H_2O$: Cs, 41.3; B, 20.1; C, 11.2; N, 8.70; H, 3.76; equiv wt 322. Found: Cs, 39.9; B, 19.2; C, 11.3; N, 8.58; H, 3.65; equiv wt 330.

Results and Discussion

The reactions of both $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ yield a variety of products. The nature of the recovered products depends not only on the type of nitrile used and reaction conditions but also on the conditions and duration of the separation steps, since many of the initial products undergo partial hydrolysis. Scheme I shown for the $B_{12}H_{12}^{2-}$ ion illustrates the various reactions.

Scheme I



In the case of $B_{10}H_{10}^{2-}$ the principal products are derivatives of types III and VII and small amounts of type VI. From the reaction with $B_{12}H_{12}^{2-}$ types I, II, III, VI, and VIII are isolated when R = CH_3; types I, III, and VIII are isolated when R = $CH_2COOC_2H_5$; type IX is isolated when R = $CH_2SO_3C_6H_5$; and type VII is isolated when R = CH_2CN. In the last case both nitriles are hydrolyzed to the amide.

Reactions in Acetonitrile. No detectable amount of $B_{10}H_{10}^{2-}$ remained in reaction mixtures after 6 hr at room temperature. Degradation in this solvent is negligible as no hydrogen was evolved and only negligible amounts of boric acid were found. Nitrile substitution predominated over coupling when the $FeCl_3:B_{10}H_{10}^{2-}$ molar ratio was 26:1; coupling became the dominant process when the ratio was reduced to 14:1; the yield of $B_{20}H_{18}^{2-}$ was quantitative with a 5:1 ratio. In all these runs (a total of nine) the borane concentration was maintained within the 0.015-0.02 *M* range. No chlorinated species have been isolated. The $B_{10}H_8(NH_2COCH_3)_2$ isolated by us differs in several respects from the 1,10-isomer reported in the literature. The latter melts, at 236-238°, has uv bands at 230 and 260 mμ, and is soluble in cyclohexane and ether.[4] The higher melting point and preference for polar solvents of the former indicate a less symmetrical structure, either a diequatorial or an equatorial-apical isomer. The yield of our product is superior to that of the 1,10 isomer, about 22% *vs.* 4-6% of the initial $B_{10}H_{10}^{2-}$.

The $B_{12}H_{12}^{2-}$ ion reacts much more slowly. Most of it can be recovered unchanged when the iron:cage ratio is less than 6:1 or fewer than 5 days is allowed for the reaction at higher ratios. In contrast with $B_{10}H_{10}^{2-}$, chlorination is the dominant process, with nitrile substitution, as indicated by the total yield of VI and VIII, a poor second. Thus under the conditions described in the Experimental Section, the yields of the four principal products were as follows: I, 41-50%; VIII, 13-15%; II, 7-12%; III, 2-6%. Though $B_{10}H_8(NH_2COCH_3)_2$ is more resistant to hydrolysis than $B_{12}H_{11}NH_2COCH_3^-$, an aqueous solution of the former became weakly acidic and acquired the distinct odor of acetic acid after standing for 1 month at room temperature.

The mechanism of oxidative coupling of $B_{10}H_{10}^{2-}$ and of some of its derivatives has been investigated by Middaugh and coworkers.[17] Oxidation by transition metal halides is not likely to generate radical intermediates of the type postulated in the electrochemical process.[17] If the role of $FeCl_3$ were solely that of an oxidant and simple species such as $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ had been produced, the observed effects of $FeCl_3$ concentration on the nature and ratio of products and the radically different behavior of the two cage systems would be difficult to explain.

The precise nature of the reacting species is difficult to ascertain as $FeCl_3$ itself forms a mixture of complexes in nitriles[18]

$$FeCl_3 + RCN \rightleftarrows (RCN)FeCl_3 \overset{RCN}{\rightleftarrows} (RCN)_4FeCl_2^+ + Cl^-$$

Since anionic polyhedral boranes form covalent salts with Cu^+, Ag^+, and Hg^+ ions[19] it is reasonable to assume the possibility of a similar interaction with iron. If some of the ligands of the complexes shown above were displaced by boranes, all of the products isolated by us could be the result of a concerted mechanism in which the charge transfer is rapidly followed by ligand transfer from iron to the cage. This may be one reason why $FeCl_3$ with a standard reduction potential of 1.1 V in CH_3CN[20] couples $B_{12}H_{12}^{2-}$ though 1.45 V is required in the electrochemical coupling.[3] The crystallographic study of $Cu_2B_{10}H_{10}$ revealed that pairs of borons along several polyhedral "edges" can act as bidentate ligands.[21] Consequently a number of complexes with varying metal:cage ratios may be postulated. The formation of metal-rich complexes is probably responsible for the increased solubility of $Ag_2B_{10}H_{10}$ in excess $AgNO_3$(aq).[19] Similarly, the effects of excess $B_{12}H_{12}^{2-}$ on the solubility of $Ag_2B_{12}H_{12}$ suggest the formation of a metal-poor complex. In the latter category one might include $CuB_{10}H_{10}^-$ which has been isolated in this and other laboratories.[22] Therefore, the effects of increased $FeCl_3$ concentration on the relative yields of coupled and substituted species is consistent with a transition from one type of complex to the other.

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(17) R. L. Middaugh and F. Farha, Jr., *J. Amer. Chem. Soc.*, 88, 4147 (1966); A. P. Schmitt and R. L. Middaugh, *Inorg. Chem.*, 13, 163 (1974).

(18) T. C. Waddington, Ed., "Non-aqueous Solvent Systems," Academic Press, London, 1965, p 244.

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(21) R. D. Dobrott and W. N. Lipscomb, *J. Chem. Phys.*, 37, 1779 (1962).

(22) R. L. Middaugh, private communication.

Puzzled by the fact that the yield of $B_{24}H_{22}Cl^{3-}$ (II) exceeded that of $B_{24}H_{23}^{3-}$ (III) we tried to find out whether chlorination precedes or follows coupling. Our data suggest that II arises from the reaction of I and $B_{12}H_{12}^{2-}$. Thus the ratio of I:II which was 8:1 in a reaction mixture stirred for 3 days declined to 3:1 2 days later. Moreover, when $FeCl_3$ and III were stirred for 5 days in CH_3CN, they failed to yield any II.

Reactions in Ethyl Cyanoacetate. The vigorous exothermic reaction with $B_{10}H_{10}^{2-}$ yields primarily boric acid (up to 63%) and $B_{20}H_{18}^{2-}$ (up to 16%). The $(CH_3)_4N^+$ ion also precipitates several substituted species among which one having two types of carbonyl and a tlc spot intermediate between that of $B_{10}H_{10}^{2-}$ and $B_{20}H_{18}^{2-}$ predominates. Attempts to free this product of $B_{20}H_{18}^{2-}$ and iron salts resulted in extensive decomposition. The changes in the ir spectra at various stages of purification leave little doubt that the derivative in question was of type VI or VII. Thus when it was recrystallized from aqueous ammonia, the ester bands at 1750 and 1220 cm^{-1} were replaced irreversibly by bands at 1590 and 1420 cm^{-1}. After repeated recrystallization from water the other carbonyl band at 1660 cm^{-1} was lost too. This suggests the decomposition sequence

$$B\overset{+}{N}H_2COCH_2COOEt \rightarrow B\overset{+}{N}H_2COCH_2COO^- \rightarrow B\overset{+}{N}H_3$$

A similar decomposition of a two-carbonyl derivative of $B_{12}H_{12}^{2-}$ and the isolation of the end product VIII have been described in the Experimental Section. In contrast with $B_{10}H_{10}^{2-}$, the $B_{12}H_{12}^{2-}$ ion reacts more slowly in ethyl cyanoacetate than in acetonitrile and yields the same inorganic derivatives in both solvents, *i.e.*, I, II, III, and VIII. In reactions where the molar iron:cage ratio was below 6:1 about 75% of $B_{12}H_{12}^{2-}$ was recovered unchanged after 1 week at room temperature.

Reactions in Cyanomethyl Benzenesulfonate. Only $B_{20}H_{18}^{2-}$ was isolated from the reaction with $B_{10}H_{10}^{2-}$. After 2 days at reflux $B_{12}H_{12}^{2-}$ was quantitatively converted to three products clearly distinguished by tlc. Separation and purification proved quite arduous so that only one of the three was fully characterized. The anionic conjugate base was written as $B_{12}H_{10}NH_3(NHCOCH_2SO_3C_6H_5)^-$ since the amine function has a greater pK_a than the amide.[2,6] The ^1H nmr spectrum also favors this structure since the peak assignable to the nitrogen protons shows up at τ 2.3 ppm, whereas the amidic $-N^+H_2-$ would have fallen closer to the 2.8 value seen in type VII compounds.

Reactions in Malononitrile. The great variety of products differing widely in the relative intensities of the ir bands attributable to the C≡N, C=O, N–H, B–H–B, and B-H bonds suggest some degree of participation by both nitrile functions. Several of the products had similar elemental composition, but we could not tell readily which were isomers and which were polymers since the equivalent weight determinations were complicated by the presence of several closely spaced inflections on the pH titration curves. Attempts to suppress polymerization by diluting the solvent with ethanol merely reduced the already low yield of product VII.

Infrared Spectra. Bands in the fingerprint region of the ir spectra of compounds I, II, III, and VIII are compared with corresponding bands of related compounds in Table I. It would appear that as in the case of chlorinated $B_{10}H_{10}^{2-}$ species[10] some of the bands show shifts determined by the degree of substitution. The presence of III in a reaction mixture is always revealed by the replacement of a single band in the 700-750-cm^{-1} region by a set of three bands of equal intensities. In the spectra of all except the perchloro ions, the most intense band was the B-H stretching band at 2450-2550 cm^{-1}. The B-H-B bridge absorbs at 2270 cm^{-1} in III and at 2200 cm^{-1} in II. A similar shift, attributable to the electron withdrawal by halogens has been reported by Wiersema and Middaugh.[3] This band though weak and broad is helpful for the detection of II in the presence of I and III.

Table I. Selected Infrared Bands in the 1100–700-cm^{-1} Region[a]

$B_{12}H_{12}^{2-}$	1070 s			720 s
$B_{24}H_{23}^{2-}$ (III)	1050 m	940 w		750, 725, 710 w
$B_{12}H_{11}Cl^{2-}$ (I)	1050 s	960 w	830 s	720 m
$B_{24}H_{22}Cl^{3-}$ (II)	1050 m	960 m	830 m	720 m
$B_{24}H_4Cl_{18}^{4-}$ [b]	1030 s	970	850	700
$B_{12}Cl_{12}^{2-}$	1030 s	1000 sh		
$B_{12}H_{11}NH_3^-$ (VIII)	1060 s	1020 s	890 w	720 m

[a] The relative intensities are for $(CH_3)_4N^+$ and Cs^+ salts. The intensities of most of these bands depend to some extent on the nature of the cation. In salts of Ag^+ and Cu^+ several bands disappear entirely. [b] Reference 3.

The infrared bands of functions separated by more than three atoms from the boron cage were not significantly shifted from their normal position. However, examination of the frequencies listed in Table II reveals that even when a quaternary nitrogen intervenes, the carbonyl band is still shifted well below the frequency expected for a carbonyl adjacent to an electronegative substituent in the absence of formal π conjugation. Depending on the pH of solution, either a normal or a protonated amide may be isolated, and the two species can be easily distinguished by position of the C=O and N–H stretching bands. Moreover, protonation also splits the latter band into two, in analogy with a change from a primary to a secondary amide.[16]

The ir spectra of species isolated when the crude reaction products are initially recovered from alcohols and before they have undergone alkaline hydrolysis are more consistent with an imine structure of the type $B-N^+H=C(OR)CH_3$ than with that of an amide. Such a derivative would arise from incomplete alcoholysis of the nitrile adduct. The structure would explain the single N-H stretching band at 3250 cm^{-1} and the absence of the deformation band near 1600 cm^{-1}. Since imines of the type shown above resemble secondary amides, the weak band at 1480 cm^{-1} and the intense one at 1280 cm^{-1} might represent N-H deformation and C-N stretching, respectively. However, the latter could also represent the C-OR bond. Both bands disappear after alkaline hydrolysis and a new band appears at 1600 cm^{-1}. The C=N bond is hard to distinguish from the C=O since it normally absorbs in the same region of the spectrum.[16]

Chromatography. Since the products were all high-melting solids and most had no uv or visible absorption bands, the ir spectra and tlc were invaluable for following the progress of reaction and purification. The latter was also our principal criterion of purity, since the former is not very sensitive to small amounts of impurities. Frequently the tlc was not a very reliable criterion for estimating the relative amounts of products due to streaking. Large spot size and streaking also made it difficult to get reproducible R_f values, and each sample had to be run beside a $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ standard. In specific cases improvements could be made in the quality of tlc by altering the pH of the eluent, but control experiments were needed to make sure that the compounds were not being altered by the eluent itself. The only useful generalization that we can make is that for derivatives of a given cage, the higher the anion charge the smaller the R_f. For example, the mixture resulting from reactions of $B_{12}H_{12}^{2-}$ in acetoni-

Table II. Selected Infrared Bands in the 3500-1400-cm^{-1} Region

Compd	N–H str	C=O str	N–H def	N–H bend; C–N, C–O str
Primary amides[b]	3350, 3180	1650	1650–1620	1420–1400
Secondary amides[b]	3330–3060	1640	1570–1515	1305–1200
2-$B_{10}H_9NH_3^-$ [c]	3250		1580	1400
$B_{12}H_{11}NH_3^-$	3250, 3200		1590	1400
1-$B_{10}H_9NH_2COCH_3^-$ [d]	3280, 3100	1645		
$B_{10}H_9NH_2COC_6H_5^-$ [d]	3300, 3200	1640	1570	
$B_{10}H_8(NH_2COCH_3)_2 \cdot 2ROH$[a]	3250	1650	1480, 1460	1425, 1280
$B_{10}H_8(NH_2COCH_3)_2$	3440, 3330	1655	1600	1425
$B_{12}H_{11}NHCOCH_3^{2-}$ [e]	3220	1600		
$B_{12}H_{11}NH_2COCH_3^-$	3300, 3100	1640	1590	1420
$B_{12}H_{10}NH_3(NHCOCH_2SO_3C_6H_5)^-$	3430, 3340	1650	1600	1450, 1420
$B_{12}H_{10}NH_3(NH_2COCH_2SO_3C_6H_5)$	3410, 3320, 2900, 2830	1660	1600, 1580	1415
$B_{12}H_{10}(NHCOCH_2CONH_2)_2^{2-}$	3450–3250	1650, 1620	1600, 1570	1450–1425, 1400

[a] See the discussion in the text for alternative assignments of bands in this type of derivative. [b] Reference 16. [c] Reference 15. [d] Reference 2. [e] Reference 3.

trile gave a tlc pattern of spots corresponding to products III, II, $B_{12}H_{12}^{2-}$, I, VIII, and VI in order of ascending R_f.

Conclusion

The work reported in this paper indicates that $FeCl_3$ can be used for the purpose of attaching bifunctional nitriles to polyhedral boranes in a one-step reaction without the loss of the second function. A free ester and amide groups can be converted to a -COOH group and removal of the benzenesulfonate ion will leave behind an alcoholic -OH group. It is noteworthy that a thorough examination of tlc and ir data failed to detect any appreciable amount of either $B_{12}H_{11}OH^{2-}$ or $B_{12}H_{10}(OH)_2{}^{2-}$ among the reaction products. Apparently in the absence of strong protonic acids and at moderate temperatures neither the C=O nor the S=O bonds succeed in establishing a boron-oxygen link to $B_{12}H_{12}^{2-}$, in marked contrast with the reactivity of such bonds in acid-catalyzed additions.[2,7]

Though the yields of organic derivatives were disappointingly low, they compare favorably with the yields of similar compounds synthesized by some of the methods mentioned in the Introduction. Improving the yields of $B_{10}H_{10}^{2-}$ derivatives will be difficult due to the serious competition from coupling and decomposition. Such competition is insignificant in the case of $B_{12}H_{12}^{2-}$. Here the low yields reflect lower reaction rates, which are partly the result of low solubilities of most borane salts in the nitriles. Addition of a common solvent proved counterproductive, since in addition to diluting the reagents most of the highly polar solvents competed with the nitriles and interfered with the reduction of $FeCl_3$. A more promising, though initially tedious, approach involves finding for each nitrile an inert cation capable of solubilizing $B_{12}H_{12}^{2-}$. The separation and purification of monosubstituted derivatives, which accounted for a good portion of the unrecovered reaction products, would have been easier and taken less time in the absence of a large amount of starting material, which tended to coprecipitate with them. Consequent reduction in the length of exposure to aqueous acids and bases would have cut down the losses caused by hydrolysis.

Registry No. $Na_2B_{12}H_{12}$, 12008-78-5; $K_2B_{12}H_{11}Cl$, 52002-73-0; $[(CH_3)_4N]_3B_{24}H_{23}$, 52322-42-6; $Cs_3B_{24}H_{22}Cl$, 52002-75-2; $(CH_3)_4NB_{12}H_{11}NH_3$, 52322-45-9; $(CH_3)_4NB_{12}H_{11}NH_2COCH_3$, 52322-46-0; $B_{10}H_8(NH_2COCH_3)_2$, 12540-58-8; $(CH_3)_4NB_{12}H_{10}NH_3(NHCOCH_2SO_3C_6H_5)$, 52322-47-1; $Cs_2B_{12}H_{10}(NHCOCH_2CONH_2)_2$, 52002-78-5; $B_{12}H_{10}NH_3(NH_2COCH_2SO_3C_6H_5)$, 52322-44-8; $FeCl_3$, 7705-08-0; acetonitrile, 75-05-8; $[(CH_3)_4N]_2B_{12}H_{11}Cl$, 12546-13-3; $[(CH_3)_4N]_3B_{24}H_{22}Cl$, 52322-48-2; $K_2B_{10}H_{10}$, 12447-89-1; ethyl cyanoacetate, 105-56-6; cyanomethyl benzenesulfonate, 10531-13-2; malononitrile, 109-77-3.

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Antipodal Shielding Effects in the Boron-11, Carbon-13, and Phosphorus-31 Nuclear Magnetic Resonance Spectra of Icosahedral Carborane Derivatives

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A long-range shielding effect, possibly similar to that reported previously for B_5H_9 derivatives, has been observed in icosahedral carboranes and their metalloborane derivatives. This perturbation of the chemical shift upon substitution occurs at a position antipodal to the point of substitution and leads to a net shielding of endopolyhedral ^{11}B, ^{13}C, and ^{31}P nmr resonances and a net deshielding of exopolyhedral C-H ^1H nmr resonances.

Introduction

A ^{11}B nmr study of basal boron substituted B_5H_9 derivatives[2] uncovered a long-range shielding effect for the boron resonance trans to the point of substitution. In the case of the closo molecules 1-$CH_3CB_5H_6$[3a] and 1-$ClC_2B_5H_6$[3b] and

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