Table I[a]

B, M	$\log h_p$	$\log B$	$m \log h_p$	$\log K^*$
0.100	−1.61	−1.000	−3.22	−2.22
0.050	−1.75	−1.250	−3.50	−2.25
0.010	−2.11	−2.000	−4.22	−2.22
0.005	−2.25	−2.250	−4.50	−2.25
0.001	−2.59	−3.000	−5.18	−2.18

[a] $m = 2$; $\log K^*$ (average) = $-(2.20 \pm 0.03)$. Evaluation of precipitate composition and $\log K^*$ is from the experimental data of Figure 1.

initial curvature indicates that small amounts of soluble hydrolysis products can still be present in the solutions.

In order to check the mechanism of formation of this new phase in a more quantitative way and to calculate m and K^* in our ionic medium, equilibrium 6 can be looked upon as a precipitation reaction. For this purpose the values of (Fe^{3+}) and $(H^+)_p$ at the precipitation point must be available. They are easily obtained by setting $(Fe^{3+}) = B$ (before the solubility product is reached all the iron is assumed to be unhydrolyzed) and calculating $(H^+)_p$ from the intercept of the nearly vertical lines of the plot Z *vs.* $-\log h$ of Figure 1. These values are reported in Table I.

Differentiation of eq 5 gives then

$$\frac{d \log (Fe^{3+})}{d \log (H^+)_p} = \frac{d \log B}{d \log h_p} = m \qquad (7)$$

Figure 2 shows that the plot of $\log B$ *vs.* $\log h_p$ is rectilinear with a slope $m = 2$. Equation 2 can then be treated as

$$Fe(NO_3)^{2+} + 2OH^- \rightarrow Fe(NO_3)(OH)_2(s)$$

and $\log K^*$ can then be easily obtained from $\log K^* = 2 \log h_p - \log B$. The calculated averaged value of $\log K^*$ is -2.20 ± 0.03 (see also Table I).

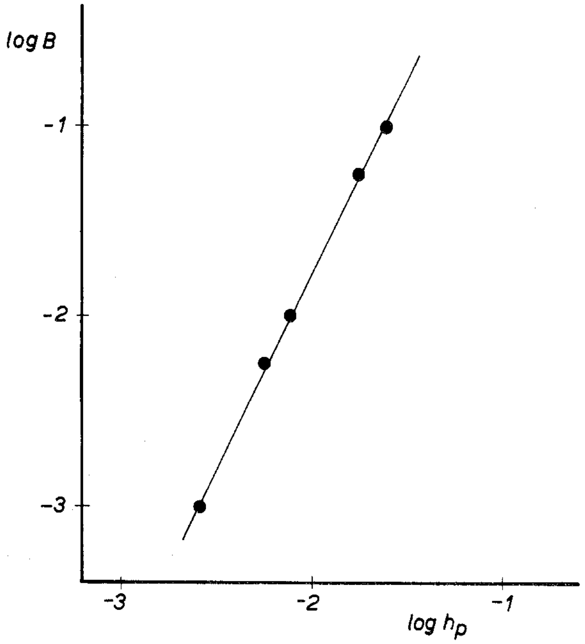

Figure 2. Logarithm of total iron(III) concentration ($\log B$) *vs.* the logarithm of equilibrium hydrogen ion concentration at the precipitation point ($\log h_p$). $\log h_p$ is obtained as the intercept of the dashed lines on the $-\log h$ scale of Figure 1.

The results we have found are in good agreement with the previous finding[4] that the final product of the hydrolysis process is a basic salt precipitate, $Fe(OH)_{2.70}Cl_{0.30}$, with $\log K^* = -3.04$. In our case the different stoichiometry of the basic salt precipitated as well as the different $\log K^*$ value can be ascribed to the different nature and concentration of the ionic medium. It seems moreover, from the long time required to reach equilibrium, that the previously identified[16,17] low molecular weight species such as $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_3(OH)_4^{5+}$, and $Fe_2(OH)_2^{2+}$ are probably initially unstable products of the hydrolysis reaction which ends in precipitation of a basic salt (probably polymeric in character) with composition and solubility product value depending on the concentration and nature of the supporting electrolyte.

Registry No. $Fe(NO_3)_3$, 10421-48-4; $Fe(OH)_2(NO_3)$, 39900-57-7.

(16) B. Hedstrom, *Ark. Kemi*, 6, 1 (1953).

(17) G. Biedermann and G. Schindler, *Acta Chem. Scand.*, 11, 731 (1957).

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Studies in Boron Hydrides. X. Substituent Effects in the Decahydrodecaborate(2−) Ion

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The ^{11}B nmr chemical shifts in two series of phenyl-substituted aryldiazoboranes of the types $XAr{-}N_2H{-}B_{10}H_9^-$ and $XAr{-}N_2{-}B_{10}H_9^{2-}$ are linearly related to the σ_m and σ_p constants for the substituent groups. These relationships indicate a resonance interaction between the two apical positions in the B_{10} polyhedron. Inductive and resonance effects may operate in the equatorial positions.

Introduction

Previously, we have employed ^{11}B nuclear magnetic resonance spectroscopy to elucidate substituent effects in pentaborane(9) and phenylboronic acid.[2] We now report results which extend our observations to include substituent effects in the decahydrodecaborate(2−) ion, $B_{10}H_{10}^{2-}$.

The one truly definitive piece of evidence regarding elec-

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(1) To whom correspondence may be addressed at the Department of Commerce, National Bureau of Standards, Washington, D. C. 20234.

(2) A. R. Siedle and G. M. Bodner, *Inorg. Chem.*, 11, 3108 (1972).

tron delocalization in a polyhedral borane is an esr study of the anion radical $B_8H_8{}^{\cdot -}$.[3] Kaczmarczyk and coworkers[4,5] obtained evidence for aromaticity in $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ from studies of polarizability and magnetic susceptibilities. Of greater relevance to the study at hand are the investigations by Knoth[6] of the electronic spectra of 1,10-disubstituted derivatives of $B_{10}H_{10}{}^{2-}$ which indicated the presence of an apical-apical electronic interaction.[7] Notwithstanding a common belief that electronic interactions, reminiscent of resonance effects in organic chemistry, exist in $B_{10}H_{10}{}^{2-}$ and in other polyhedral boranes and carboranes, direct experimental evidence has been lacking. Our approach to the study of electronic effects in $B_{10}H_{10}{}^{2-}$ involves the introduction of substituents at one of the apical positions in the boron cage and observing the effect of the substituent upon the ^{11}B nmr chemical shift of other boron positions.

Experimental Section

The aryldiazo-substituted $B_{10}H_{10}{}^{2-}$ derivatives were prepared by the method of Hawthorne and Olsen[8] and isolated as the protonated tetramethylammonium salts. Recrystallization was accomplished by slow evaporation of aqueous acetone solutions containing a few drops each of 3 *N* hydrochloric acid and aqueous tetramethylammonium chloride. All of these compounds were found to be pure by ^{11}B nmr spectroscopy and thin-layer chromatography. Elemental analyses for new derivatives are given in Table I. We were unable to prepare crystalline samples of the base forms of these compounds which did not contain small amounts of the acid forms as impurities. These impurities were easily detected in the visible spectra of the compounds. Consequently, the base forms of the aryldiazoboranes were prepared directly in nmr tubes by the addition of a 2 *M* solution of sodium methoxide in methanol until the characteristic end point color change of red to yellow occurred. Further addition of sodium methoxide did not alter the chemical shifts of the base forms.

All ^{11}B nmr chemical shifts were measured at 70.6 MHz on a Varian HR-220 spectrometer with a digitized frequency sweep. The field instability was estimated[9] to be <±5 Hz. The spectra were referenced to external $BF_3{\cdot}O(C_2H_5)_2$ and the shifts are believed to be accurate to within ±0.1 ppm. The chemical shifts were found not to be sensibly concentration dependent. ^{19}F nmr spectra were measured on a Varian HA-100 spectrometer operating at 94.1 MHz and were referenced to internal fluorobenzene. Reagent grade acetonitrile was employed as the solvent in all cases.

Results

Aryldiazonium salts couple with $B_{10}H_{10}{}^{2-}$ to give apically substituted aryldiazoboranes of the general formula $Ar\text{-}N_2\text{-}B_{10}H_9{}^{2-}$ (referred to herein as the base form). Treatment of these compounds with aqueous mineral acid affords a protonated or acid form, $Ar\text{-}N_2H\text{-}B_{10}H_9{}^{-}$, whose proposed structure is shown in Figure 1. The site of protonation is not known with certainty but is believed to be one of the nitrogen atoms.[8]

The 70.6-MHz ^{11}B nmr spectra of meta- and para-substituted aryldiazoboranes are substantially like those reported by Hawthorne and Olsen and are indicative of apical substitution. In both forms, two structurally distinct apical boron resonances may be readily discerned. In the acid form, resonances due to the two nonequivalent sets of equatorial boron nuclei are well resolved. There was no convenient way of making a further structural assignment of these resonances and so they are simply referred to as the high-field and low-field equatorial positions. The equatorial positions in the base forms have nearly identical chemical shifts and could not be cleanly resolved even with white noise ^{1}H decoupling.

Table I. Analytical Data for New Aryldiazoboranes

	% C		% H		% N	
X	Calcd	Found	Calcd	Found	Calcd	Found
Para CN	40.99	40.31	8.07	8.14	17.39	17.26
Meta F	38.10	38.43	8.25	8.30	13.33	14.00
Para F	38.10	39.23	8.25	8.10	13.33	12.76
Meta Br	31.91	32.18	6.91	6.90	11.17	11.06
Meta CH_3	42.44	42.88	9.33	9.05	13.50	14.09
Para CF_3	36.16	36.31	7.12	7.42	11.51	11.48

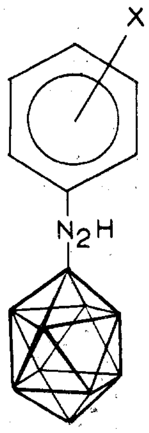

Figure 1. Proposed structure for $XAr\text{-}N_2H\text{-}B_{10}H_9{}^{-}$.

The chemical shifts of all boron positions in the acid form change significantly as the substituent X on the phenyl ring is varied. In the base forms, the range of chemical shifts, particularly of the substituted apical position, is much smaller relative to the experimental error. Consequently, a less satisfactory treatment of the chemical shift data may be anticipated in this series.

If a shielding parameter $\int_{H}{}^{X}$ be defined as the change in ^{11}B nmr chemical shift at a position of interest in the polyhedral framework when a hydrogen in the phenyl ring is replaced by a substituent X, then one may attempt to account for this change in terms of what is known about the electronic properties of X. In this manner, information might be obtained about how the substituent interacts with the different positions in the boron polyhedron.

The data may be analyzed by use of a modified Hammett equation

$$\int_{X}{}^{H} = \sigma_{m,p}\rho \tag{1}$$

where $\sigma_{m,p}$ is the appropriate σ_m or σ_p value for X.[10] The optimal value for the slope ρ is calculated by a χ^2 minimization of the difference between the experimental shielding parameters and those calculated on the basis of eq 1.[1] This slope may be taken to be a measure of the sensitivity of a site to the electronic effects of X. The results of this analysis, along with the linear correlation coefficients, $\bar{r}$, and the chemical shift data for each position, are given in Tables II and III. Figure 2 shows a plot of the ^{11}B nmr shielding parameters for the unsubstituted apical position in the acid *vs.* the Hammett σ parameters. It may be seen that the ^{11}B nmr chemical shifts for all boron positions are linearly sensitive

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(3) F. Klanberg, D. R. Eaton, L. J. Guggenberger, and E. L. Muetterties, *Inorg. Chem.*, 6, 1271 (1967).

(4) A. Kaczmarczyk and G. B. Kolski, *J. Phys. Chem.*, 68, 1227 (1964).

(5) A. Kaczmarczyk and G. B. Kolski, *Inorg. Chem.*, 4, 665 (1965).

(6) W. H. Knoth, *J. Amer. Chem. Soc.*, 88, 935 (1966).

(7) These and other lines of evidence have been summarized by E. L. Muetterties and W. H. Knoth in "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968.

(8) M. F. Hawthorne and F. P. Olsen, *J. Amer. Chem. Soc.*, 87, 2366 (1965).

(9) A. O. Clouse, private communication.

(10) These values are tabulated in J. P. Jesson and E. L. Muetterties, "Chemical and Physical Data for Chemists," Marcel Dekker, New York, N. Y., 1971.

Table II. ^{11}B Nmr Chemical Shifts for Acid Forms of Substituted Aryldiazoboranes, $XAr-N_2H-B_{10}H_9^-$

X	Apical Unsub-stituted	 Substi-tuted	Equatorial Low-field	 High-field
Para CN	−26.0	−18.5	15.9	21.6
Para Br	−20.7	−15.8	17.9	23.3
Meta OCH_3	−19.4	−14.7	18.7	23.8
Para CH_3	−17.6	−14.4	19.4	24.3
H	−17.8	−15.2	19.2	24.1
Meta CH_3	−18.8	−15.0	18.9	23.8
Para CF_3	−25.0	−18.2	16.2	21.9
Meta F	−22.1	−16.5	17.3	22.7
Meta Br	−21.9	−16.2	17.4	22.8
Para F	−19.3	−15.1	18.7	23.6
Meta CF_3	−21.9	−16.2	17.5	22.9
Para OCH_3	[a]	[a]	20.4	24.8
ρ	−11.8	−4.2	−4.9	−3.5
r	96.5	94.1	98.1	97.5
ρ'	−10.7	−4.9	−4.2	−3.0
r	93.4	92.4	96.9	94.7

[a] These two resonances are badly overlapped and could not be resolved.

Table III. ^{11}B Nmr Chemical Shifts of Base Forms of Substituted Aryldiazoboranes, $XAr-N_2-B_{10}H_9^{2-}$

X	Apical Substituted	 Unsubstituted
Meta F	−19.3	−3.0
Para CN	−19.6	−4.4
Para CF_3	−19.4	−3.6
Para Br	−19.4	−2.9
Para F	−19.2	−2.4
Para OCH_3	−18.7	−2.0
Meta OCH_3	−19.2	−2.0
Para CH_3	−19.2	−2.0
Meta CH_3	−19.2	−2.1
H	−19.2	−2.3
Meta CF_3	−19.6	−3.0
ρ	−0.7	−1.7
r	83	90
ρ'	−0.7	−1.9
r	58	91

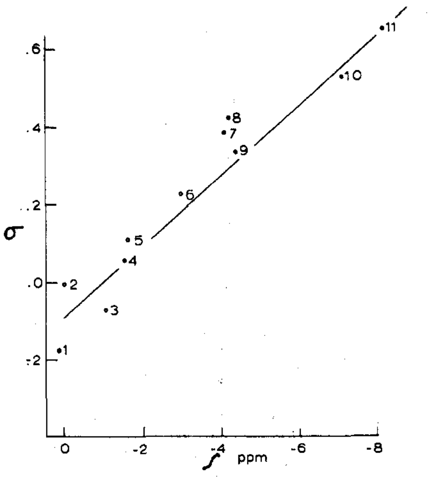

Figure 2. Plot of the Hammett $\int$ substituent parameters for X *vs.* the ^{11}B nmr shielding parameters of the unsubstituted apical position in the acid form. X: 1, para CH_3; 2, H; 3, meta CH_3; 4, para F; 5, meta OCH_3; 6, para Br; 7, meta Br; 8, meta CF_3; 9, meta F; 10, para CF_3; 11, para CN.

to the electronic effects of X as judged by the excellent correlations between the shielding parameters and $\sigma_{m,p}$ and by the large ρ values which obtain.

Discussion

On the basis of the observed correlations, it may be concluded that there are, in both the acid and base forms of the aryldiazoboranes, large and significant resonance and inductive interactions between X and the substituted apical boron position. When X is in a meta position in the benzene ring, inductive effects, *i.e.*, σ_m, suffice to account for the trends in chemical shifts. However, when X is in a para position, σ_p parameters must be used to correlate the chemical shift data. Use of σ_p constants requires that explicit cognizance be taken of resonance effects. A similar line of reasoning demonstrates that there must also be both inductive and resonance interactions between X and the unsubstituted apical boron position and therefore between the two apical positions in the B_{10} cage. This is consistent with the earlier work of Knoth.[6]

Additional evidence that large resonance effects prevail in these $B_{10}H_{10}^{2-}$ derivatives may be obtained by application of eq 2. The left-hand term is the difference in chemical shift

$$\int_{\text{meta X}}^{\text{para X}} = \sigma_R{}^0 \rho' \qquad (2)$$

at a position of interest between analogous meta- and para-substituted aryldiazoboranes and $\sigma_R{}^0$ is the pure resonance substituent parameter for X derived from ^{19}F nmr chemical shift data.[11] The slope, ρ', and the linear correlation coefficients resulting from this treatment are given in Tables II and III for each position in the B_{10} cage. The magnitude of ρ' should be a measure of the sensitivity of each position to resonance effects alone. Use of this equation does in fact yield large correlation coefficients and ρ' values which parallel the trends seen in ρ. These results support the conclusion that resonance effects operate between the apical positions in the B_{10} polyhedron.

It is manifest that substituent effects influence the ^{11}B nmr chemical shifts of the equatorial positions in the acid forms of the aryldiazoboranes. What is not obvious is the manner in which these effects operate. It has already been shown that the substituent X can affect the electron density at the substituted position by a resonance mechanism. A fraction of this change in electron density could propagate to other positions by either an inductive or resonance mechanism or both. For positions where ρ' is greater than at the substituted position, as it is at the unsubstituted apical position, resonance effects are necessarily operative. However, ρ' for the two equatorial positions is comparable to or less than the substituted position, and this is compatible with either an inductive or a resonance effect. If the equatorial boron atoms are considered to be analogous to the meta carbons in benzene, then only an inductive effect would be anticipated.

The ρ values for the unsubstituted apical and the two equatorial positions do not appear to exhibit the r^{-1} attenuation with distance from X that would be expected if only an inductive mechanism were operative in transmitting electronic effects through the boron polyhedron. In fact, just the opposite is true: if only meta substituents are considered, the unsubstituted apical position still has the largest span of chemical shifts and ρ is still about 4 times that for the substituted position. The electron density at the unsubstituted boron is probably greater than at the opposite apex as a result of formal replacement of H^- by the more electronegative $XArN_2H$ group. The greater sensitivity of the unsubstituted apical position could be accounted for if it were supposed that greater polarizability attended this greater charge density. Consistent with such reasoning is the observation.

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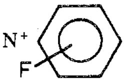
(11) P. R. Wells, S. Ehrenson, and R. W. Taft, Jr., *Progr. Phys. Org. Chem.*, 6, 147 (1968). These authors also discuss the separation of resonance and inductive effects in aromatic systems.

Table IV. Electronic Properties of Some Aryldiazo Derivatives

	$\delta_{\text{meta F}}$	$\delta_{\text{para F}}$	$\sigma_R{}^0$	σ_I
$[(CH_3)_4N^+]_2$  $-N_2-B_{10}H_9{}^{2-}$	−0.40	+1.89	−0.08	−0.14
$(CH_3)_4N^+$  $-N_2H-B_{10}H_9{}^-$	−2.83	−9.42	+0.22	+0.48
 $-N_2{}^+BF_4{}^-$	−9.46	−29.3	+0.67	+1.49
 $-N_2-C_6H_5$	−0.78[a]	−3.17[a]	+0.08	+0.19

[a] Values taken from G. W. Parshall, *J. Amer. Chem. Soc.*, 87, 2133 (1965).

that, as inferred from the relative magnitude of ρ, apical–apical interactions in the acid forms of the aryldiazoboranes appear stronger than in the base forms. This could be a consequence of the greater electronegativity of $XArN_2H$ than of $XArN_2{}^-$. The correlations observed for the apical–apical interactions in the base forms are less satisfactory owing to the smaller span of chemical shifts relative to the error involved in their measurement. Thus, the *relative* sensitivity of the various positions in the B_{10} cage to substituent effects need not be an intrinsic property of the polyhedral framework but may depend in part upon the way in which the ground-state electron distribution is perturbed by the substituents.

The ^{19}F nmr chemical shifts of the *m*- and *p*-fluorophenyldiazoboranes were used to calculate σ_I and $\sigma_R{}^0$ for the $(B_{10}H_9-N_2-)^{2-}$ and $(B_{10}H_9-N_2H-)^-$ groups. These parameters, along with those for some related groups, are given in Table IV. The σ values for the aryldiazoborane moieties should be used with some caution for these groups are ionic and highly polar solvents, *e.g.*, acetonitrile, had to be used to dissolve the salts. The substituent properties of the $(B_{10}H_9-N_2-)$ group are much like those of the $C_6H_5-N_2-$ function. This may reflect small perturbations of the electronic properties of the diazo linkage by the phenyl and $B_{10}H_9$ groups.

In benzene derivatives, substituent effects are usually separable into inductive and resonance components involving σ and π bonding, respectively. While the bonding in $B_{10}H_{10}{}^{2-}$ may not be so neatly factored according to symmetry type, our results show that significant resonance interactions do occur in the boron cage between positions which are not directly bonded to one another. These interactions could arise from the extensive multicenter bonding characteristic of the nominally electron-deficient boron hydrides and would be the three-dimensional analogs of the interactions involving delocalized π orbitals in benzenoid compounds. Insofar as they may be estimated by ^{11}B nmr chemical shift measurements, these interactions may be satisfactorily accounted for by the same substituent parameters which have proved so useful in organic chemistry. Finally, the conclusions concerning resonance interactions in $B_{10}H_{10}{}^{2-}$ derivatives are consistent with the chemical behavior of this ion. The preternatural kinetic stability of $B_{10}H_{10}{}^{2-}$ to hydrolysis and oxidation, as well as its propensity to undergo substitution reactions, is indicative of a substantial delocalization energy and aromatic character.

Registry No. $Me_4N^+[p\text{-}NC-Ar-N_2H-B_{10}H_9{}^-]$, 39291-45-7; $Me_4N^+[m\text{-}F-Ar-N_2H-B_{10}H_9{}^-]$, 39291-34-4; $Me_4N^+[p\text{-}F-Ar-N_2H-B_{10}H_9{}^-]$, 39291-35-5; $Me_4N^+[m\text{-}Br-Ar-N_2H-B_{10}H_9{}^-]$, 39291-30-0; $Me_4N^+[m\text{-}Me-Ar-N_2H-B_{10}H_9{}^-]$, 39291-48-0; $Me_4N^+[p\text{-}(F_3-Ar-N_2H-B_{10}H_9{}^-]$, 39291-42-4; $p\text{-}Br-Ar-N_2H-B_{10}H_9{}^-$, 39291-31-1; $m\text{-}MeO-Ar-N_2H-B_{10}H_9{}^-$, 39291-51-5; $p\text{-}CH_3-Ar-N_2H-B_{10}H_9{}^-$, 39291-53-7; $Ph-N_2H-B_{10}H_9{}^-$, 39291-39-9; $m\text{-}CF_3-Ar-N_2H-B_{10}H_9{}^-$, 39291-43-5; $p\text{-}MeO-Ar-N_2H-B_{10}H_9{}^-$, 39291-52-6; $m\text{-}F-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-33-3; $p\text{-}NC-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-44-6; $p\text{-}CF_3-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-41-3; $p\text{-}Br-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-29-7; $p\text{-}F-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-32-2; $p\text{-}CH_3O-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-50-4; $m\text{-}CH_3O-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-49-1; $p\text{-}CH_3-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-47-9; $m\text{-}CH_3-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-46-8; $Ph-N_2-B_{10}H_9{}^{2-}$, 39291-38-8; $m\text{-}CF_3-Ar-N_2-B_{10}H_9{}^{2-}$, 39291-40-2; $[(CH_3)_4N^+]_2[m\text{-}F-Ar-N_2-B_{10}H_9{}^{2-}]$, 39291-37-7; $[(CH_3)_4N^+]_2[p\text{-}F-Ar-N_2-B_{10}H_9{}^{2-}]$, 39291-36-6; boron-11, 14798-13-1.

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