ligand transition in the π_v orbitals.[6] A similar band appears at 29,500 cm.$^{-1}$ in the spectrum of bis(methylthio)maleonitrile; finally, the very intense band at 37,000 cm.$^{-1}$ is assigned as the strongly allowed ligand (σ^b) to metal (σ^*) charge transfer.

The electronic spectra of the $Pd(MNT)_2{}^{2-}$, $Pt(MNT)_2{}^{2-}$, and $Au(MNT)_2{}^-$ complexes are similar to the spectrum of $Ni(MNT)_2{}^{2-}$, and the observed transition energies are consistent with the above assignments.

(6) The $\pi_h \to 6\pi_v$ transitions, which are expected to appear somewhat higher than 31,700 cm.$^{-1}$, are "perpendicular" and thus much less intense than the strongly allowed bands. These transitions are probably buried under the $\sigma \to \sigma^*$ band at 37,000 cm.$^{-1}$.

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Diazonium and Carbonyl Derivatives of Polyhedral Boranes

Sir:

We have now established the scope of $B_{10}H_{10}{}^{-2}$ and $B_{12}H_{12}{}^{-2}$ derivative chemistry[1] to be comparable to that of aromatic hydrocarbon chemistry. The key to this advance has been the preparation of several important intermediates, namely, the inner diazonium salt $B_{10}H_8(N_2)_2$ and the dicarbonyls $B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$

The diazonium derivative is prepared from $B_{10}H_{10}{}^{-2}$ by reaction with a large excess (10–12 mole equiv.) of aqueous nitrous acid followed by reduction of a precipitated intermediate with $NaBH_4$ in methanol.[2]

Figure 1.

the corresponding $B_{10}H_8(ligand)_2$ species. A similar displacement occurs with amides but the stereochemistry of these products is uncertain. Minor amounts ($<5\%$) of other isomers of $B_{10}H_8(CO)_2$ have been separated by gas chromatography; the presence of corresponding amounts of the analogous isomers of $B_{10}H_8(N_2)_2$ would not be detectable by boron n.m.r. because of the chemical shifts and line widths encountered in B^{11} n.m.r. spectroscopy.

$B_{10}H_8(CO)_2$ has been the most thoroughly studied of the ligand displacement products. It is best prepared from $B_{10}H_8(N_2)_2$ and carbon monoxide at 120–140°, in the absence of a solvent, although iron carbonyl can

TABLE I

ANALYSES OF REPRESENTATIVE SPECIES

Species	% Calcd.					% Found				
	B	C	H	N	Misc.	B	C	H	N	Misc.
$B_{10}H_8(N_2)_2$	62.8	..	4.6	32.6	Mol. wt. 172	62.1	..	4.9	33.3	169
$B_{10}H_8(CO)_2$	62.8	14.0	4.6	..	Mol. wt. 172	62.9	14.2	4.8	..	186
$B_{10}Cl_8(CO)_2$	24.1	5.4	0.0	..	Cl 63.3	24.2	6.2	0.9	..	63.3
$Cs_2B_{10}Cl_8(N_3)_2$	14.6	..	...	11.3	Cl 38.2	14.6	..	..	11.1	38.7
					Cs 35.8					35.8
$(Me_4N)_2B_{10}Cl_8(COC_6H_4NMe_2)_2$	18.0	19.9	5.0	4.6	...	17.6	19.9	4.6	4.7	...
$B_{12}H_{10}(CO)_2$	66.1	12.2	5.0	..	Mol. wt. 196	65.8	12.1	5.0	..	204
$(Me_4N)_2B_{12}H_{10}(NCO)_2$	34.9	32.3	9.2	15.0	...	34.8	32.3	9.1	15.2	...
$(Me_4N)_2B_{12}H_{10}(COOCH_3)_2$	32.0	35.5	9.9	6.9		31.9	35.1	10.0	6.9	...

$B_{10}H_8(N_2)_2$ is a colorless solid which decomposes slowly at about 125° without melting and which can be sublimed at 90–100° under vacuum. It is not shock sensitive. *However, the unreduced intermediate is exceedingly shock sensitive and should be handled with extreme caution, preferably never in the dry state.* $B_{10}H_8(N_2)_2$ is 1,10 (bisapical, see Fig. 1 for B_{10} numbering system) substituted within the detection limits of boron n.m.r. This configuration is maintained throughout reactions with amines, nitriles, ammonia, and carbon monoxide in which nitrogen is lost at 115–140° to give

(1) For an initial report on this subject see: W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, J. C. Sauer, and E. L. Muetterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

(2) This two-step synthesis of $B_{10}H_8(N_2)_2$ may be mechanistically related to the direct introduction of diazonium groups into organic aromatic species by excess nitrous acid. In the organic system, however, a reduction step is not necessary. See: J. M. Tedder and G. Theaker, *Tetrahedron*, **5**, 288 (1959).
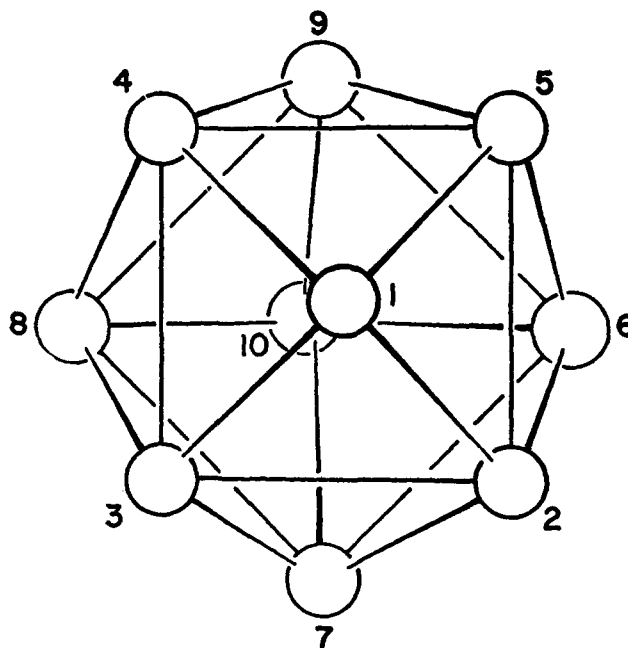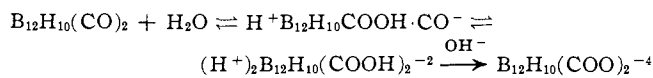
be used. If the reaction is run in the presence of cyclohexane, $C_6H_{11}B_{10}H_7(CO)_2$ and $(C_6H_{11})_2B_{10}H_6(CO)_2$ are formed, suggesting a free radical mechanism. The reaction of $B_{12}H_{12}{}^{-2}$ with carbon monoxide under acidic conditions has given $B_{12}H_{11}CO^-$ and $B_{12}H_{10}(CO)_2$; the latter consisting of at least two isomers according to preliminary gas chromatographic studies. The dicarbonyls of $B_{10}H_{10}{}^{-2}$ and $B_{12}H_{12}{}^{-2}$ have very intense carbonyl stretching frequencies at 2140 and 2250 cm.$^{-1}$, respectively. These volatile compounds are easily purified by sublimation at *ca.* 100° under vacuum and do not readily undergo thermal dissociation. $B_{10}H_8(CO)_2$ (m.p. in sealed tube 155–156°) was unchanged after 2 hr. at 200° in an evacuated sealed tube, although there was evidence of decomposition at 250°.

In water the carbonyls are in equilibrium with carboxylic acid derivatives, which can be isolated as

$$B_{12}H_{10}(CO)_2 + H_2O \rightleftharpoons H^+B_{12}H_{10}COOH \cdot CO^- \rightleftharpoons$$

$$(H^+)_2B_{12}H_{10}(COOH)_2{}^{-2} \xrightarrow{OH^-} B_{12}H_{10}(COO)_2{}^{-4}$$

salts. Acidity function studies indicate carboxyl proton ionization constants of $\sim 10^{-9}$.

The chemistry of the dicarbonyls is of extremely broad scope. Some of their reactions are outlined below for the B_{10} system; analogous reactions occur with the B_{12} dicarbonyl.

$$B_{10}H_8(CO)_2 + \begin{cases} 2CH_3OH \rightleftharpoons (H^+)_2B_{10}H_8(COOCH_3)_2{}^{-2} \\ 4NH_3 \longrightarrow (NH_4{}^+)_2B_{10}H_8(CONH_2)_2{}^{-2} \\ LiAlH_4 \longrightarrow B_{10}H_8(CH_3)_2{}^{-2} \\ NaN_3 \longrightarrow B_{10}H_8(NCO)_2{}^{-2} \\ H_2O + H_2NOSO_3H \longrightarrow B_{10}H_8(NH_3)_2 + 2CO_2 \end{cases}$$
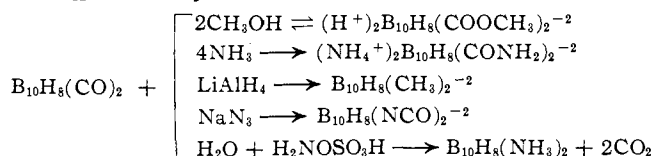
The $B_{10}H_8(NH_3)_2$ prepared in this fashion is identical with that prepared from $B_{10}H_8(N_2)_2$ and NH_3. In water the following equilibria exist.

$$B_{10}H_8(NH_3)_2 \rightleftharpoons H^+B_{10}H_8NH_2 \cdot NH_2{}^- \rightleftharpoons (H^+)_2B_{10}H_8(NH_2)_2{}^{-2}$$
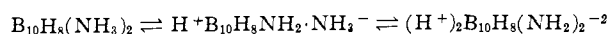
Dehydration of $Cs_2B_{10}H_8(CONH_2)_2$ is effected by heating to about $300°$. We have not encountered a

$$Cs_2B_{10}H_8(CONH_2)_2 \longrightarrow Cs_2B_{10}H_8(CN)_2$$
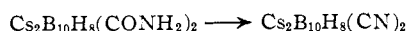
change in stereochemistry in any of the reactions of $B_{10}H_8(CO)_2$.

Halogenated carbonyls (e.g., $B_{10}Cl_8(CO)_2$, $B_{10}Br_8(CO)_2$) have been prepared by aqueous halogenation of $B_{10}H_8(CO)_2$ and $B_{12}H_{10}(CO)_2$ followed by dehydration, at elevated temperatures, of the resulting halogenated carboxylic acids. These halogenated carbonyls are even more thermally stable than the perhydro carbonyls, e.g., there was no evidence of decomposition after heating $B_{10}Cl_8(CO)_2$ at $300°$ in an evacuated sealed tube for 1 hr. A diverse chemistry based on halogenated carbonyls has been demonstrated. For example, $B_{10}Cl_8(CO)_2$ reacts with sodium borohydride to give the bishydroxymethyl species $B_{10}Cl_8(CH_2OH)_2{}^{-2}$ and couples with dimethylaniline to give $B_{10}Cl_8(COC_6H_4-NMe_2)_2{}^{-2}$. $B_{10}Cl_8(CO)_2$ is converted to $B_{10}Cl_8(NH_3)_2$ by reaction with aqueous hydroxylamine-o-sulfonic acid. Diazotization of this chlorinated diamine readily gives $B_{10}Cl_8(N_2)_2$ which, in turn, can be converted to $B_{10}Cl_8(N_3)_2{}^{-2}$ by reaction with sodium azide or to $B_{10}Cl_8(SH_2)_2$ by reaction with hydrogen sulfide.

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An Electromotive Force Cell for Carbonium Ion Stabilization Energies[1]

Sir:

Substituent effects on thermodynamic properties afford one of the principal building blocks of theoretical organic chemistry. The accepted standard, both for application of theoretical analysis and for analysis of reaction rates, is the substituent effect on the equilibrium process.[2] However, there has been an inherent dilemma in the application of such standards. For convincing tests of applications of basic theory to essentially complex organic molecules, substituent effects of substantial (optimum) magnitude are required. Variation of equilibrium constants through

many powers of ten is simply unfeasible by direct experimental determination. Resort has been made, therefore, to such devices as the use of acidity functions, for example, in proton transfer equilibria, to estimate the effects of changing acid medium. No direct experimental data have been available to test the accuracy of the acidity function method over wide ranges (corresponding to many powers of ten in equilibrium constant), and indeed recent evidence leads to certain serious questions of this usage.[3]

We report herein the determination of reversible electrode reduction potentials in acetonitrile solution at $25°$ which provide quantitative measures of the (large) substituent effects on the standard free energy change of a process[3a] which gives relative cation stabilization energies,[4] i.e.

$$R^+ + e \rightleftharpoons \tfrac{1}{2}R-R \qquad (1)$$
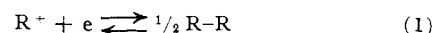
In this process, the widely delocalized charge of R^+ becomes essentially localized (for most practical purposes) in the nonpolar C–C bond. For general R^+, important steric effects on formation of R–R may be involved. In the present report, however, we have restricted R^+ to p-substituted triphenylmethyl (trityl) cations so that steric interactions in the hexaphenylethane derivatives are essentially constant.

The cell, Pt $\mid R_{2(CH_3CN)}$, $R^+BF_4{}^-_{(CH_3CN)}$ $\mid$ Ag^+-$NO_3{}^-_{(CH_3CN)}$ $\mid$ Ag, is prepared on a vacuum line with a weighed amount of $R^+BF_4{}^-$ [5] into which highly purified acetonitrile[6] is distilled. The e.m.f. cell contains a volumetric compartment enabling a measured volume of known concentration of the $R^+BF_4{}^-$ acetonitrile solution to be withdrawn, reduced (to the equilibrium mixture of R_2 and $R\cdot$) by metallic zinc, and titrated into the solution in contact with the Pt electrode. Contact between the two electrode compartments is obtained by use of an asbestos fiber. The e.m.f. measurements are made with an L. and N. K-3 potentiometer and are reproducible to ± 0.002 v. The e.m.f. values are stable over time intervals of a few minutes up to at least 2 hr. to the same precision. Variation of (R^+) from 0.6×10^{-2} M to 2.6×10^{-2} M and of (R_2) from 0.10×10^{-2} M to 0.80×10^{-2} M gives e.m.f. values which follow the equation
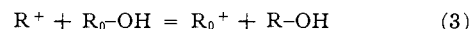
$$E = E^0 - \frac{RT}{n\mathfrak{F}} \ln\left[\frac{(R_2)^{1/2}(Ag^+)}{(R^+)}\right]$$

to a precision of ± 0.003 v.

The standard free energy change, $\Delta F_2°$, for the reaction

$$R^+ + \tfrac{1}{2}(R_0-R_0) = R_0{}^+ + \tfrac{1}{2}(R-R) \qquad (2)$$
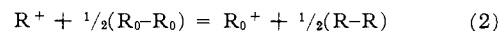
where R_0 designates unsubstituted trityl cation and R the p-substituted derivative, is obtained from E^0 corresponding to this cell reaction (which is negligibly affected by the liquid junction potential). Table I lists values of E^0, K_{equil}, and $\Delta F_2°$ for reaction 2. Also listed in Table I are $\Delta F_3°$ values for the reaction

$$R^+ + R_0-OH = R_0{}^+ + R-OH \qquad (3)$$

obtained through the application of the H_R acidity function.[7]

(2) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., 1940, Chapters 3, 4, 7, and 9.

(3) E. M. Arnett, in "Progress in Physical Organic Chemistry," Vol. I, Editors, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, Inc., 1963, p. 223.

(3a) J. B. Conant, et al., J. Am. Chem. Soc., **47**, 1959 (1925); **55**, 3752 (1933).

(4) Cf. N. Muller and R. S. Mulliken, ibid., **80**, 3489 (1958).

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

(6) J. F. Coetzee, G. P. Cunningham, D. R. McGuire, and G. R. Padmanabhan, Anal. Chem., **34**, 1139 (1962).

(7) (a) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, J. Am. Chem. Soc., **77**, 3044 (1955); (b) N. C. Deno and A. Schriesheim, ibid., **77**, 3051 (1955); (c) N. C. Deno and W. L. Evans, ibid., **79**, 5804 (1957).