

a weaker reducing agent at least toward metal carbonyl systems than the free alkali metals.

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Stereochemical Nonrigidity in PF_3Cl_2 and PF_3Br_2

BY W. MAHLER AND E. L. MUETTERTIES

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In two earlier papers^{1,2} we described an intramolecular rearrangement of fluorine atoms in PF_3Cl_2 . We have examined PF_3Cl_2 as well as PF_3Br_2 in more detail and with greater precision and can now characterize these two phosphoranes as stereochemically nonrigid molecules.

The F^{19} n.m.r. spectra of PF_3Cl_2 and PF_3Br_2 below -120° reveal two fluorine atom environments in each molecule. (The geometry is probably a C_{2v} trigonal bipyramid.¹⁻³) At room temperature, there is just one fluorine atom environment with chemical shifts and P-F coupling constants (Table I) of the weighted average of the low-temperature values. These data

TABLE I
 F^{19} N.M.R. PARAMETERS AND EXCHANGE DATA^a

	PF_3Cl_2	PF_3Br_2
J_{PF_2}	1023	1141
J_{PF_e}	1085	1143
J_{FF}	142	124
δ_{F}	-144	-181
δ_{F_e}	-36	-43
$J_{\text{PF(av)}} 25^\circ$	1050	1130
$J_{\text{PF(av)}} \text{ calcd.}$	1044	1124
$\delta_{\text{F(av)}} 25^\circ$	-112	-135
$\delta_{\text{F(av)}} \text{ calcd.}$	-108	-135
Exchange activation energy	7.2	7.2
$\tau_{\text{F}} (-50^\circ)$	$\sim 10^{-1}$	$\sim 10^{-2}$

^a J in c.p.s., δ in p.p.m. from CF_3COOH , ΔH_a in kcal./mole, τ in sec.

demonstrate that no molecular change (*e.g.*, dimerization) occurs as a function of temperature.

Line-width analysis⁴ of the transition region where the high-temperature doublet is undergoing broaden-

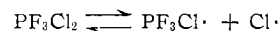
(1) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(2) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964).

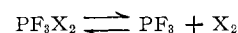
(3) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *ibid.*, **3**, 1748 (1964).

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 222.

ing (-70 to $+20^\circ$) gives a value for the activation energy for the fluorine exchange process of 7.2 ± 0.5 kcal./mole for both PF_3Cl_2 and PF_3Br_2 . Since P-F coupling is maintained in the temperature region where the fluorine atoms lose their positional identity, the exchange process cannot involve P-F bond breaking. There is no difference in the n.m.r. transition region between liquid PF_3Cl_2 and a 25% solution of PF_3Cl_2 in petroleum ether. This insensitivity of exchange rate strongly supports an intramolecular process. Since the petroleum ether does not inhibit the exchange, a radical dissociative process



is excluded. In addition, mixed solutions of PF_3Cl_2 and PF_3Br_2 display the sum of the individual, characteristic n.m.r. patterns at 20° . Since the two halides maintain their integrity, the possibility of the other dissociative process



is eliminated.

The above observations establish a low-energy intramolecular fluorine exchange for PF_3Cl_2 and PF_3Br_2 . Exchange through vibrational excitation is the only plausible process.^{1,2,5,6} Since the exchange barriers are identical for PF_3Cl_2 and PF_3Br_2 , the barrier must largely reflect anharmonic motion of the fluorine atoms.

(5) S. Berry, *J. Chem. Phys.*, **32**, 933 (1960), discusses exchange in PF_6 .

(6) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965).

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Quadrupole Coupling in Boron Cage Compounds

BY D. R. EATON

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Recently a number of boron hydrides and their derivatives have been shown to possess cage structures. The electronic structure of these compounds presents a problem of some interest. The B^{11} quadrupole coupling constants constitute a relevant piece of information since such constants are proportional to the electric field gradient at the boron nucleus and therefore serve as a probe for the electron distribution. The magnitudes of these quadrupole coupling constants are accessible from n.m.r. experiments rather than by means of pure quadrupole resonance.¹ It is, in fact, in favorable cases, possible to obtain estimates of these parameters from the broad-line n.m.r. spectra of powdered, polycrystalline samples.²⁻⁵ Application of this method

(1) M. H. Cohen and F. Reif, *Solid State Phys.*, **5**, 322 (1957).

(2) A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **29**, 984 (1958).

(3) A. H. Silver and P. J. Bray, *ibid.*, **31**, 247 (1959).

(4) A. H. Silver and P. J. Bray, *ibid.*, **32**, 288 (1960).

(5) A. H. Silver and T. Kushido, *ibid.*, **38**, 865 (1963).

TABLE I
 QUADRUPOLE COUPLING IN BORON CAGE COMPOUNDS

Compound	Order of spectrum	eqQ , Mc./sec.	Compound	Order of spectrum	eqQ , Mc./sec.
$\text{Na}_2\text{B}_{12}\text{H}_{12} \cdot 2\text{H}_2\text{O}$	1st	0.070	$\text{Cs}_2\text{B}_{10}\text{H}_{10}$	Intermediate	...
$\text{Cs}_2\text{B}_{12}\text{H}_{12}$	1st	~ 0	$(\text{NH}_4)_2\text{B}_{10}\text{H}_{10} \cdot x\text{H}_2\text{O}$	2nd	2.0
$[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{D}_{12}$	1st	< 0.003	$[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_{10}$	Intermediate	...
$[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{B}_{12}\text{H}_{12}$	2nd	2.2	$\text{Cs}[1\text{-B}_{10}\text{H}_6\text{S}(\text{CH}_3)_2]$	2nd	2.3
$[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{Cl}_{12}$	1st	0.022	$\text{Cs}[2\text{-B}_{10}\text{H}_6\text{S}(\text{CH}_3)_2]$	2nd	2.0
$[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{H}_{11}\text{I}$	1st	0.160	$\text{B}_{10}\text{H}_8(\text{N}_2)_2$	2nd	1.9
$[(\text{CH}_3)_4\text{N}]_2\text{B}_{12}\text{D}_{11}\text{I}$	1st	0.170	$\text{B}_{10}\text{H}_6(\text{CO})_2$	Intermediate	...
			$[(\text{CH}_3)_4\text{N}]_2\text{B}_{10}\text{H}_6\text{I}_4$	2nd	1.8

to a number of metallic borides,⁵ other simple inorganic boron compounds,⁴ and boron-containing glasses² has been reported. In the present note the results of broad-line n.m.r. studies of a number of ten-membered^{6,7} and twelve-membered^{8,9} boron cage compounds are presented.

The theory of quadrupolar coupling has been presented in the excellent monograph of Das and Hahn¹⁰ and the use of the n.m.r. method in a review article by Cohen and Reif.¹ All nuclei with spin greater than $1/2$ possess quadrupole moments and will interact with any electric field gradient produced by the surrounding electrons and positively-charged nuclei. This interaction is characterized by two parameters, the quadrupole coupling constant (eqQ), which depends on the magnitudes of the nuclear quadrupole moment and the electric field gradient, and the asymmetry parameter (η), which is a measure of the deviation of the field gradient from axial symmetry. The gross appearance of the n.m.r. spectrum depends on the relative magnitude of the quadrupole coupling and the magnetic splitting ($g\beta H$), and the resulting line shapes have been discussed by several authors.^{1,2,11} Briefly, if the quadrupole coupling is small, the spectrum comprises a central component arising from the unperturbed $m = -1/2 \rightarrow m = 1/2$ transition and two satellites arising from the $-3/2 \rightarrow -1/2$ and $1/2 \rightarrow 3/2$ transitions. The splitting of these satellites arises from a first-order perturbation of the magnetic energy by the quadrupolar terms and in the case that $\eta = 0$ is equal to $1/2 eqQ$. If the quadrupole coupling is rather larger, the satellites become broadened beyond the point of observation, but the central component undergoes a second-order shift and broadening which gives rise to an apparent splitting into two components. If $\eta = 0$, this splitting is equal to $25(eqQ)^2/192\nu_0$, where ν_0 is the frequency of the n.m.r. experiment. There is also an intermediate region in which the satellites have been lost, but the central line has not been clearly separated into two components. For cases in which $\eta \neq 0$ the line shape is

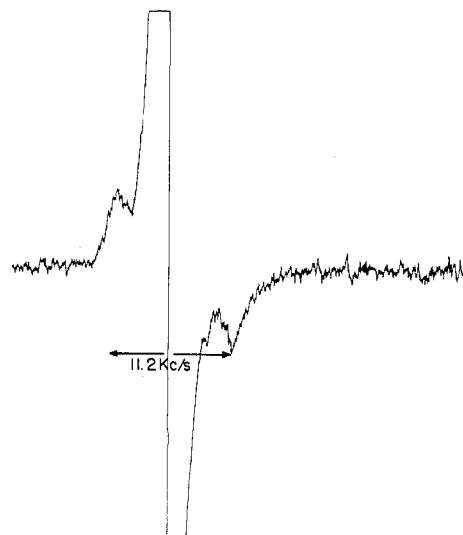


Figure 1.— B^{11} spectrum of $[\text{N}(\text{CH}_3)_4]_2\text{B}_{12}\text{Cl}_{12}$ as a polycrystalline powder; 14.2 Mc./sec.

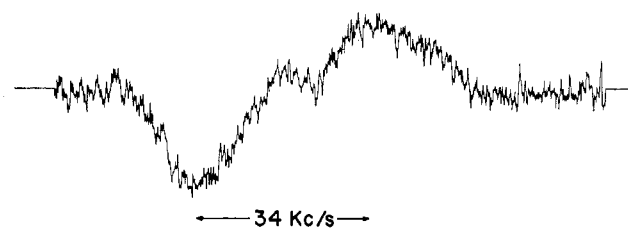


Figure 2.— B^{11} spectrum of $(\text{NH}_4)_2\text{B}_{10}\text{H}_{10}$ as a polycrystalline powder; 14.2 Mc./sec.

more complex, and although it is possible in principle to analyze the spectrum² to obtain both eqQ and η , this is not usually feasible. Even in such cases it is possible, though, to classify the spectra as first-order, second-order, or intermediate and obtain a rough estimate of the quadrupole coupling constant.

Figures 1 and 2 show two spectra (obtained at 14.2 Mc./sec.) of boron cage compounds, the first of which is clearly first-order and the second, second-order. In Table I the results obtained with a number of twelve-membered and ten-membered cage compounds are collected. This table also includes estimates of eqQ obtained on the assumption that $\eta = 0$. It may be noted that the ten-membered cages contain two different types of boron atoms and for the equatorial boron $\eta \neq 0$ by symmetry. Additional structure corresponding possibly to these different environments was seen in some cases. The measurements were made on the

(6) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(7) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, **3**, 444 (1964).

(8) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

(9) H. C. Miller, N. E. Miller, and E. L. Muetterties, *ibid.*, **85**, 3885 (1963).

(10) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Supplement 1 to "Solid State Physics," Academic Press, New York, N. Y., 1958.

(11) J. F. Hon and P. J. Bray, *Phys. Rev.*, **110**, 624 (1958), and references therein.

most intense peaks which presumably arose from the equatorial borons.

Although these results are of necessity more qualitative than quantitative, several interesting trends are apparent. All of the ten-membered cages give second-order or intermediate spectra whereas all the twelve-membered cages except one give first-order spectra. The quadrupole coupling is not independent of the cation present. The coupling constant is not therefore a reliable quantitative measure of the electron distribution within the boron cage. The unsymmetric cation $(C_2H_5)_3NH^+$ produces a sufficiently large field gradient at the boron of the twelve-membered cage to give rise to a second-order spectrum. In the twelve-membered cages with the small coupling constants the introduction of a substituent (iodine) distorts the electron distribution sufficiently to produce a significant increase in coupling. If, however, the symmetry is maintained, as in $B_{12}Cl_{12}^{2-}$, a small coupling again results.

The most interesting of these observations is the pronounced difference between the ten-membered and twelve-membered cages. This difference is of the same order as the difference between boron in a tetrahedral environment (eqQ ranges from ~ 0 in $NaBH_4^4$ to 104 kc./sec. in $NaBF_4^4$ and up to 570 kc./sec. for BO_4^- in some glasses^{2,12,13}) and boron in a planar environment (eqQ is 2.96 Mc./sec. in boron nitride⁴ and 2.76 Mc./sec. for BO_3 in glasses^{2,12,13}). These results are usually discussed in terms of the occupancy of the boron 2p orbitals. Thus, in a symmetric tetrahedral environment all three 2p orbitals are equally occupied, giving rise to zero field gradient at the nucleus so that in the absence of fields arising from external ions eqQ will be zero. On the other hand, for a planar boron forming three sp^2 bonds two of the p orbitals (p_x and p_y) are occupied, but p_z is empty. It may be readily shown

that the quadrupole coupling constant expected for this situation is just that of a free boron atom^{2,14} (5.39 Mc./sec.). The observation of lower values than this (in boron nitride, for example) has been rationalized in terms of donation of electrons into the p_z orbital by π bonding. It is of interest therefore to see whether these results for boron cage compounds can be similarly interpreted in terms of inequalities in the populations of the boron 2p orbitals. With this in view, extended Hückel calculations similar to those reported by Hoffman and Lipscomb¹⁵ on these cage compounds have been made. These calculations indicate a difference of about 0.03 in the populations of the different p orbitals of the twelve-membered cage borons and of about 0.17 for the equatorial borons of the ten-membered cages. These population differences would give quadrupole coupling constants agreeing in order of magnitude with the experimental results. There are several reasons why this type of calculation cannot be regarded as being particularly reliable. The most important of these are the well-known inadequacy of the Hückel type of approximation for predicting charge distributions and the uncertainty regarding the directions of the principal axes of the quadrupole coupling tensor. The results may, however, be taken as providing at least a suggestive indication of the nature of the differences in boron bonding in the two types of cage compound.

Experimental

All spectra were obtained at 14.2 Mc./sec. using a Varian broad-line instrument. The samples were examined in the form of compressed pellets. The preparation of these compounds has been described previously.^{7,9}

Acknowledgments.—The author is indebted to Dr. W. R. Hertler, who kindly provided the boron cage compounds used in this study, and to Mr. Lee Stone of the Engineering Department for computing facilities.

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 (13) P. J. Bray, M. Leventhal, and H. O. Hooper, *ibid.*, **4**, 47 (1963).

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 (15) R. Hoffman and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2872 (1962).

Correspondence

Stereochemistry of the Base Hydrolysis of Cobalt(III) Complexes

Sir:

There is now considerable evidence in support of the conjugate base dissociation mechanism ($SN1CB$) for the base hydrolysis of halogenoamminecobalt(III) complexes.¹⁻³ However, the most detailed attempt to explain the stereochemistry of this reaction was done on the basis of a bimolecular displacement ($SN2$) mechanism.⁴ We wish to show that the available

stereochemical data can be better explained on the basis of a dissociation process and to propose two stereochemical rules that must be obeyed if the mechanism postulated is correct.

Since a tetragonal pyramidal structure with water entering at the position vacated by the leaving group can only result in retention of configuration, the initial assumption is that the five-coordinated intermediate has a trigonal-bipyramidal structure. This is in accord with the hypothesis that this structure is stabilized by the π bonding of the electron pair on the amido nitrogen, which must be in the same trigonal plane as the vacant $d_{x^2-y^2}$ orbital on Co(III).⁵ Assuming that a

(1) For discussion and references see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 124; F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 25 (1960).

(2) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).
 (3) R. B. Jordan and A. M. Sargeson, *ibid.*, **4**, 433 (1965).

(4) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **194**, 344 (1962).

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