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

Acknowledgment.—The author is indebted to Mr. A. Fronzaglia for experimental assistance and to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-64.

CONTRIBUTION NO. 1104 FROM THE CENTRAL RESEARCH
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Stereochemical Nonrigidity in PF_3Cl_2 and PF_3Br_2

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Received July 6, 1965

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

TABLE I

F^{19} N.M.R. PARAMETERS AND EXCHANGE DATA[a]

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

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

Line-width analysis[4] of the transition region where the high-temperature doublet is undergoing broadening (-70 to $+20°$) 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

$$PF_3Cl_2 \rightleftharpoons PF_3Cl\cdot + Cl\cdot$$

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

$$PF_3X_2 \rightleftharpoons PF_3 + X_2$$

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.

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CONTRIBUTION NO. 1070 FROM THE CENTRAL RESEARCH
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Quadrupole Coupling in Boron Cage Compounds

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Received March 18, 1965

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

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