

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

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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-

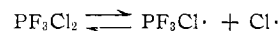
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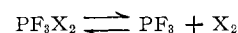
(3) R. R. Holmes, R. P. Carter, Jr., and G. E. Peterson, *ibid.*, **3**, 1748 (1964).

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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.

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Quadrupole Coupling in Boron Cage Compounds

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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

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