SYNTHESIS AND PROPERTIES OF (TRIFLUOROMETHYL)PHOSPHINOHYDRAZINES AND RELATED SYSTEMS

by

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ABSTRACT

The reactions of BX_3 (X=Me, F, Cl) with $MeNHNH_2$, Me_2NNH_2, Me_2NNHMe and Me_2NNMe_2 were investigated. On the basis of an analysis of NMR spectral data for $Me_2NNH_2.BX_3$ and $Me_2NNHMe.BX_3$, the structures of the adducts were deduced. The reactions of BX_3 with $MeNHNH_2$ and Me_2NNMe_2 are discussed in terms of adduct formation, and reactions leading to hydrazinoboranes. Infrared data are reported.

The reactions of CH_2Cl_2 and CCl_4 with $MeNHNH_2$, and CH_2Cl_2 with Me_2NNH_2 were investigated. The reaction between $MeNHNH_2$ and CCl_4 is discussed in terms of a free radical mechanism leading to the major products, N_2 and CH_4. The reaction between $MeNHNH_2$ and CH_2Cl_2 was observed to give $MeNHN{=}CH_2$ (II), which dimerizes to $(\text{-}MeNNHCH_2\text{-})_2$ (I). $Me_2\overset{+}{N}(CH_2Cl)NH_2\ \ Cl^-$ was isolated from the reaction between Me_2NNH_2 and CH_2Cl_2. Infrared, NMR and mass spectral, and other physical data are reported.

The reactions between $(CF_3)_nPI_{(3-n)}$ (n=1, 2, 3), and H_2NNH_2, $MeNHNH_2$, Me_2NNH_2 and Me_2NNHMe were investigated. $(CF_3)_2PI$ was found to react with the methylhydrazines to give the new compounds, $(CF_3)_2PNHNMe_2$ (IV), $(CF_3)_2PNMeNMe_2$ (V), $(CF_3)_2PNMeNH_2$ (VI), and$(CF_3)_2PNHNHMe$ (VII), while products isolated from the separate reactions between

CF_3PI_2 and the methylhydrazines in ether, yielded, $CF_3P(NHNMe_2)_2$ (VIII), $CF_3P(NMeNMe_2)_2$ (IX), and two isomers of $CF_3P(NMeNH)_2PCF_3$ (X, XI). Reactions of HCl with IV and V are reported. Physical properties, and infrared, NMR, and mass spectral data are reported. Significant features of the NMR data are discussed.

BX_3 (X = Me, F, Cl) adducts were prepared for some (trifluoromethyl)phosphinohydrazines. NMR spectral data and the stereochemistry of the adducts are discussed.

To Pamela

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CHAPTER I INTRODUCTION

A. Phosphorus Nitrogen Chemistry and the Formation of the P-N bond

Phosphorus nitrogen chemistry is an extensive field, including the phosphonitrilic polymers (1-5) and large classes of phosphorus nitrogen compounds, the aminophosphines $(R_2P)_nNR^1_{3-n}$ and $R_nP(NR^1_2)_{3-n}$, phosphonic amides, $R_nP(O)(NR^1_2)_{3-n}$, phosphoric amides, $(RO)_nP(O)(NR^1_2)_{3-n}$ phosphine imines, $R_3P=NR^1$, azophosphoric esters $(RO)_2P(O)-N=N-R$, phosphazines, $R_3P=N-N=X$ ($X=PR_3$, CR_2 etc.), phosphorus azides, R_2PN_3, and phosphorus hydrazines and hydrazides, $R_nP(NRNR^1_2)_{3-n}$ and $R_nP(O)(NRNR^1_2)_{3-n}$ (6,7). Our basic interests have been in the study of trivalent phosphorus and its compounds with nitrogen; recent comprehensive treatments of the pentavalent phosphorus - nitrogen system of compounds have been included in articles by Fluck (6) and Nielsen (7).

The formation of the P-N bond has been accomplished using a variety of reactions, but the majority of aminophosphines, $R_nP(NR^1_2)_{3-n}$ and $(R_2P)_nNR_{3-n}$, have been prepared by aminolysis of the phosphorus halogen bond. (Eqn.1-1).

$$R_nPX_{3-n}+2(3-n)HNR_2 \rightarrow R_nP(NR_2)_{3-n}+(3-n)R_2NH.HX \qquad (1-1)$$

The use of this reaction has facilitated the preparation of a range of compounds of the types from $P(NR_2)_3$ to $(R_2P)_3N$. Included in Table I-1 are representative examples of some aminophosphines and phosphorus (V) nitrogen compounds prepared by the aminolysis of the phosphorus halogen bond. Other routes to the formation of the P-N bond include a variety of displacement reactions (Table I-2), and addition reactions (Table I-3).

Table I-1. Formation of the P-N Bond, by the Aminolysis of the Phosphorus-Halogen Bond

Compound	Preparation		Reference
$P(NH_2)_3$	$PCl_3 + NH_3$		p.296 of ref.6
$\{(RN)P(NHR)\}_2$	$PCl_3 + H_2NR$	R=aryl R=alkyl	8, 9 10
$P_4N_6Me_6$	$PCl_3 + H_2NMe$		11
$P(NR_2)_3$	$PCl_3 + HNR_2$		12, 13, 14
F_2PNMe_2	$PF_3 + HNMe_2$		15
Cl_2PNR_2	$PCl_3 + HNR_2$		12, 13, 14
$ClP(NR_2)_2$	" "		16
$RP(NHR)_2$	$RPCl_2 + H_2NR$		17
$CF_3P(NHMe)_2$	" "		21
$RP(NR_2)_2$	$RPCl_2 + HNR_2$		p.315 of ref.6, 17
$RP(Cl)(NR'_2)$	" "		18, 19, 20
$(CF_3)_2PNH$	$R_2PCl + NH_3$		22
$\{(CF_3)_2P\}_2NH$	" "	$+ Et_3N$	23

$(CF_3)(CH_3)PNH_2$	$R_2PCl + NH_3$	24
$\{(CF_3)(CH_3)P\}_2NH$	" "	24
R_2PNHR	$R_2PCl + H_2NR$	25
$(CF_3)_2PNHMe$	" "	22
$\{(CF_3)_2P\}_2NMe$	" " + Et_3N	23
$(CF_3)(CH_3)PNHMe$	" "	24
$\{(CF_3)(CH_3)P\}_2NMe$	" "	24
R_2PNR_2	$R_2PCl + HNR_2$	13, 17, 25, 26
$(CF_3)_2PNMe_2$	" "	22
$(CF_3)(CH_3)PNMe_2$	" "	24
$OP(NH_2)_3$	$OPCl_3 + NH_3$	27, 28
$RP(O)(NH_2)_2$	$RP(O)Cl_2 + NH_3$	29
$OP(NHR)_3$	$OPCl_3 + H_2NR$	10
$OP(Cl)_n(NR_2)_{3-n}$	$OPCl_3 + HNR_2$	30, 31
$(CF_3)_2P(O)NMe_2$	$(CF_3)_3PO + Me_2NH$	32

Table I-2

Formation of the P-N Bond, Displacement Reactions

$3PCl_3 + 3\ EtN(SiMe_3)_2 \rightarrow (EtNPCl)_3 + 6Me_3SiCl$	33
$\{(CF_3)_2P\}_2NNa + (CF_3)_2PCl \rightarrow \{(CF_3)_2P\}_3N + NaCl$	23
$(CF_3)_2NCl + (CF_3)_3P \rightarrow CF_3Cl + (CF_3)_2NP(CF_3)_2$	34
$(CF_3)_2NCl + (CF_3)_2NP(CF_3)_2 \rightarrow \{(CF_3)_2N\}_2PCF_3 + \{(CF_3)_2N\}_3P$	34

$Ph_2P(O)Cl + NaN_3 \rightarrow Ph_2P(O)N_3 + NaCl$ 35

$(EtO)_2P(O)H + CCl_4 + NH_3 \rightarrow (EtO)_2P(O)NH_2 + NH_4Cl + CHCl_3$ 36

$RNH_2 + Ph_3P + X_2 \rightarrow RN{=}PPh_3 + HX$ (X = halogen) 37

Table I-3 Formation of the P-N Bond, Addition Reactions

$Ph_nPCl_{3-n} + RN_3 \rightarrow Ph_nP(Cl)_{3-n}{=}NR + N_2$ 38, 39

$R_3PBr_2 + H_2NR \xrightarrow{base} (R_3PNHR)^+Br^- + HBr$ 40

$R_3P + R_2NCl \rightarrow (R_2NPR_3)^+Cl^-$ 41, 46

$PhP(NRNMe_2)_2 + NH_2Cl \rightarrow \{PhP(NH_2)(NRNMe_2)_2\}^+Cl^-$ 47, 48

$RN(PPh_2)_2 + NH_2Cl + NH_3 \rightarrow RN\{P(=NH)(Ph_2)\}\{PNH_2Ph_2\}^+Cl^-$ 49

From the heat of formation of $P(NEt_2)_3$, the P-N bond dissociation energy has been calculated to be 66.8 Kcal/mole (50) (cf. H_2NNH_2, ΔH_{diss} N-N, 57.1 Kcal/mole (51), $H_3C\text{-}CH_3$, ΔH_{diss} C-C, 84 Kcal/mole (52)), but due to its polarity, it is readily cleaved by HCl (6, 13, 53), and in some cases, by BF_3 (54), and BCl_3 (11, 54); alcoholysis of $(R_2N)_3P$ gives the respective amine and trialkylphosphite $(RO)_3P$ (6). For the aminophosphines, the donor site to boron (p.323 of ref. 6, 55, 56, 57, 58), aluminum (59, 60),

phosphorus (61) and carbonium ion (13, 14, 17, 41, 42) species, is always the phosphorus atom. This has been taken to suggest (p-d)π interaction between the lone pair on nitrogen and the empty 3d orbitals on phosphorus lessens the availability of the nitrogen lone pair, while enhancing the basicity of phosphorus (42). Coordination of aminophosphines to transition metals is also believed to occur through phosphorus (16, 62, 63, 64, 65, 66); the stability of this arrangement is discussed in terms of the hard-soft concept of Chatt (67) and Pearson (68, 69) in which the 3d orbitals of phosphorus are able to accept electrons from the d orbitals of the metal (62, 63, 70).

The reaction of aminophosphines with dilute H_2O_2(or O_2) or elemental sulphur, leads to the respective amino-phosphine-oxides and -sulphides, $(R_2N)_3P{=}X$ (X=O,S) (6, 10, 11, 12, 26).

B. Some Aspects of the Chemical and Stereochemical Properties of Substituted Hydrazines

Hydrazine and substituted hydrazines present a number of interesting chemical and stereochemical properties. Listed in Table I-4 are some structural parameters for some hydrazine derivatives. Investigations to date suggest that methylhydrazines have a gauche structure (71 - 77), while F_2NNF_2 is half gauche and half trans (78), and $(CF_3)_2NN(CF_3)_2$ (79) and $(SiH_3)_2NN(SiH_3)_2$ (80, 81) are approximately described as having D_{2d} symmetry. $(SiH_3)_2NN(SiH_3)_2$ and $(SiH_3)_3N$ are analagous with respect to skeletal planarity at the nitrogen atom(s) (80, 81, 82) and non-basic character (83, 84); these properties have been taken to suggest the presence of N-Si dative π bonding (80, 82, 83, 84).

The weakness of the N-N bond in F_2NNF_2 has been discussed in terms of radical stability (95) while the planarity and long N-N bond length of N_2O_4 has been suggested to be a result of π, with little or no σ bonding character between the nitrogen atoms (p.61 of ref.96).

Table I-4

Some Structural and Chemical Parameters of some Substituted Hydrazines

Compound	Structure	N-N Å	X-N Å	< NNX°	< XNX°
H_2NNH_2	gauche (72,77)(d,e,f)	1.453±0.003 (77)(d) 1.449±0.004 (94)(a)			
$MeNHNH_2$	gauche (71,73)(d,e,f)				
Me_2NNH_2	gauche (75)(d,e,f)	1.45±0.03 (93)(a)	1.47±0.03 (93)(a)	110 ±4 (93)(a)	110 ±4 (93)(a)
MeNHNHMe	gauche (74)(d.e.f)	1.45±0.03 (93)(a)	1.47±0.03 (93)(a)		
Me_2NNHMe	gauche (76)(d,e,f)				
Me_2NNMe_2	gauche (85,80)(d,e)				
F_2NNF_2	47% gauche 53% trans (78)(a)	1.489±0.004 (78)(a)	1.375±0.004 (78)(a)	100-104 gauche 100.6±0.6 trans(78)(a)	105.1±1.5 gauche 102.9±1.0 trans(78)(a)
$(CF_3)_2NN(CF_3)_2$	gauche ≃ D_{2d} (79)(a)	1.40±0.02 (79)(a)	1.433±0.01 (79)(a)	119.0±1.5 (79)(a)	121.2±1.5 (79)(a)
$(SiH_3)_4N_2$	D_{2d}(80,81)(a) NNSi planar	1.457±0.016 (81)(a)	1.731±0.004 (81)(a)		129.7±0.7 (81)(a)
O_2NNO_2	planar(91)(a)	1.75 (91)(a)	1.180(91)(a)		133.7(91)(a)

Compound	N-N ΔH disc			pKa (88)
H_2NNH_2	57.1	(51)	(c)	
	60	(86)	(b)	8.07
	38	(87)	(b)	
$MeNHNH_2$	51.9	(51)	(c)	
	67	(86)	(b)	7.87
Me_2NNH_2	49.6	(51)	(c)	
	72	(86)	(b)	7.21
MeNHNHMe	74	(86)	(b)	7.52
Me_2NNHMe	80	(86)	(b)	6.56
Me_2NNMe_2	85	(86)	(b)	
	50	(87)	(b)	6.30
F_2NNF_2	19.2	(89)	(b)	
	21	(90)		
O_2NNO_2	12.9	(92)	(f)	

Method: (a) electron diffraction, (b) electron impact, (c) pyrolysis, (d) infrared spectroscopy, (e) Raman spectroscopy, (f) thermodynamic entropy calculations.

This is not supported by spectroscopic data (96 p.45), but other bonding schemes involving mostly N-N π bonding interactions have been invoked to explain the structure of O_2NNO_2 (96 p.62). The surprisingly short N-N bond length in $(CF_3)_2NN(CF_3)_2$ has led Bartell and Higginbotham (79) to postulate the presence of π as well as σ bonding interaction across the N-N bond.

The N-N bond dissociation energies of the methylhydrazines, obtained from electron impact studies, have been shown to increase with increasing methyl substitution (86, 87), while studies of the pyrolysis of methylhydrazines indicate the reverse order (51), in keeping with the trend noted for substituted C-C and O-O systems (51, 87). The low N-N dissociation energies for F_2NNF_2 (89,90) and O_2NNO_2 (92), are in accord with their long N-N bond lengths. In contrast the N-N bond of $(CF_3)_2NN(CF_3)_2$ has been found quite stable towards thermal cleavage (97).

The decrease in base strengths of the alkyhydrazines with increasing alkyl substitution (88) is in contrast to the amine series (98), $Me_2NH > MeNH_2 > Me_3N \simeq NH_3$. This apparently anomalous behavior has been attributed to loss of hydration energy (99).

Hydrazine forms complexes with most of the transition metals (100) and has a variety of possible modes of

coordination. The few structural studies completed on transition metal hydrazine complexes, indicate possible M-N-N-M bridging,  bidentate, and M-N-N monodentate functions for hydrazine (101-105).

C. Hydrazine Derivatives of the Main Group Elements

1. Hydrazine Derivatives of the Group III Elements

(a) Hydrazinoboranes

The preparation of hydrazinoborane, $H_2BNHNHBH_2$ was first attempted in the early 1950's (106, 107), but the successful isolation of hydrazinoborane was not reported until 1961 (108). Since then a number of hydrazinoboranes have been prepared, by the pyrolysis of hydrazine-borane adducts (109-111), and by the hydrazinolysis, (a) of the B-Cl bond (108, 109, 112), (b) of aminoboranes (109), and (c) of trialkylborates (113). In Table I-5 are collected a representative sample of known hydrazinoboranes.

Chemically, the hydrazinoboranes differ only slightly

Table I-5
Hydrazinoboranes

Compound	Preparation	Reference
$H_2BNHNHBH_2$	$H_2NNH_2.BH_3$ pyrolysis	108
$(NH_2NH)_3B$	$BCl_3 + H_2NNH_2$	112
$Me_2BNHNMe_2$	$Me_2BCl + Me_2NNH_2$	109
$B(NHNMe_2)_3$	$B(NMe_2)_3 + Me_2NNH_2$	109
$(RO)_2BNHNH_2$	$B(OR)_3 + H_2NNH_2$	113

from the aminoboranes; HCl is observed to cleave the B-N bond in some hydrazinoboranes (109) yielding the chloroborane and hydrazine hydrochloride (equation 1-2), but the reaction of HCl with $(Me_2NNH)_3B$ gives the simple adduct $B(NHNMe_2)_3.3HCl$ (109).

$$R_2BNHNHPh + 2HCl \rightarrow R_2BCl + PhNHNH_2.HCl \qquad (1\text{-}2)$$

(b) Hydrazinoalanes

The hydrazinolysis of the Al-Cl bond has yielded a variety of hydrazinoalane dimers and higher polymers (112), and reactions of R_3Al (114-117) and $R_3Al.NR_3$ (114, 115) with substituted hydrazines, have given similiar results (equations 1-3 and 1-4).

$$R_3Al + R^1_2NNH_2 \rightarrow (R_2AlNHNR^1_2)_2 + RH \qquad (1\text{-}3)$$

$$R_3Al.NR^1_3 + R^{11}_2NNH_2 \rightarrow (R_2AlNHNR^{11}_2)_2 + RH + NR^1_3 \qquad (1\text{-}4)$$

Notably, in reactions of alkylhaloalanes with 1,1-dimethylhydrazine, the aluminum-carbon, rather than the aluminum-halogen bond is cleaved (117) (equation 1-5).

$$Et_2AlCl + Me_2NNH_2 \rightarrow (EtAlClNHNMe_2)_2 + EtH \qquad (1\text{-}5)$$

The dimeric hydrazinoalanes are easily converted to polymeric

materials by pyrolysis (117). Table I-6 includes a representative sample of the hydrazinoalanes that have been prepared.

Table I-6 Hydrazinoalanes

Compound	Preparation	Reference
$(EtAlClNHNMe_2)_2$	$Et_2AlCl + Me_2NNH_2$	117
$(Et_2AlNHNMe_2)_2$	$Et_3Al + Me_2NNH_2$	116
$(-Al(HNNHMe)NHNMe-)_n$	$AlH_3 + MeNHNH_2$	115
$(-MeAlNHNMe-)_n$	$Me_3Al + MeNHNH_2$	114

2. Hydrazine Derivates of the Group IV Elements

The Group IV elements other than carbon, for which hydrazine derivatives have been prepared, include silicon, germanium and tin. Carbon-hydrazine chemistry forms a large area of study in itself (118).

(a) Silylhydrazines (hydrazinosilanes)

The extent of silylhydrazine chemistry has been due in no small measure to the work of U. Wannagat (119), who has prepared and studied the chemistry of a large number of silylhydrazine compounds. The preparatinn of silyl hydrazines has been effected, by the hydrazinolysis of a silicon halogen bond (84, 119-124) (equation 1-6), and by the hydrazinolysis of silylamines (119) (equation 1-7).

1,1-bis(silyl)hydrazines, on the other hand, have been prepared by the reaction between a halosilane and the lithium salt of a silylhydrazine (119, 122) (equation 1-8).

$$2R_2NNH_2 + Me_3SiCl \rightarrow Me_3SiNHNMe_2 + R_2NNH_2.HCl \quad (1\text{-}6)$$

$$2RNHNH_2 + (Me_3Si)_2NH \rightarrow 2RNHNHSiMe_3 + NH_3 \quad (1\text{-}7)$$

$$R_2NN(Li)SiMe_3 + Me_3SiCl \rightarrow R_2NN(SiMe_3)_2 + LiCl \quad (1\text{-}8)$$

Representative compounds are presented in Table I-7.

Substitution of a silyl group on a monosubstituted hydrazine seems to occur at the unsubstituted nitrogen (119), although there has been some controversy over this interpretation (125). The Si-N bond is readily cleaved solvolytically by dilute acid, and by anhydrous HCl (119); $(SiH_3)_2NN(SiH_3)_2$ detonates in dry air (84). Silylamines are generally thermally stable against decomposition at room temperature (126).

Reactions of CO_2 and CS_2 with silylamines lead to the carbamates and thiocarbamates, $R_3Si\text{-}Y\text{-}\underset{\underset{Y}{\|}}{C}\text{-}NR_2$ (Y=O, S) analagous products are noted in the reactions of silyl-hydrazines with CO_2 and CS_2 (128).

(b) Germyl- and stannyl-hydrazines

Whereas the hydrazinolysis of a silicon-halogen bond has led to the preparation of silylhydrazines (119), the equivalent reaction does not occur with Me_3GeBr; instead,

Table I-7 Silylhydrazines

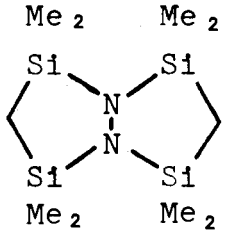
Compound	Preparation	Reference
$Me_3SiNMeNMeSiMe_3$	Me_3SiCl + MeNHNHMe	122
$Me_3SiNHNHSiMe_3$	$Me_3SiCl + H_2NNH_2$	121, 123
$(Me_3Si)_2NNH_2$	" "	121, 123
$(Me_3Si)_2NNMe_2$	$Me_3SiCl + Me_2NN(Li)H$	122
$Me_3SiNHNMe_2$	$Me_3SiCl + Me_2NNH_2$	122
$(SiH_3)_2NN(SiH_3)_2$	$H_3SiI + H_2NNH_2$	84
	$ClSi(Me_2)CH_2Si(Me_2)Cl + H_2NNH_2$	124
$Si(NHNMe_2)_4$	$SiCl_4 + Me_2NNH_2$	120

Table I-8 Germylhydrazines

$Ph_2Ge(NPhNPh)_2GePh_2$	$Ph_2GeCl_2 + Li_2(PhN{=}NPh)$	130
$Me_3GeN(R)NMe_2$	$Me_3GeBr + Me_2NN(Li)R$	128

R=H, Me, $GeMe_3$, $SiMe_3$

a hydrazinegermane adduct is formed (128). Germyl-hydrazines have been prepared however, utilizing the

reaction between triphenylgermyllithium and azobenzene (129) (equation 1-9), or between trimethylbromogermane and lithium 1,1-dimethylhydrazide (128) (equation 1-10).

$$Ph_3GeLi + PhN{=}NPh \rightarrow Ph_3GeN(Ph)N(Li)(Ph) \xrightarrow{H_2O} Ph_3GeN(Ph)NHPh \qquad (1\text{-}9)$$

$$Me_3GeBr + Me_2NN(Li)H \rightarrow Me_3GeNHNMe_2 + LiBr \qquad (1\text{-}10)$$

Table I-8 includes a representative sample of known germylhydrazines.

The Ge-N bond is easily cleaved by protic reagents (128, 131) and electron deficient molecules such as BF_3 (128), as is usually found for the aminosilanes (83). However, for $Me_2NN(SiMe_3)(GeMe_3)$, the analysis of products from reactions with protic solvents, and analysis of mass spectral data, suggest that the Ge-N bond is preferentially cleaved over the Si-N bond (128).

Reactions with CY_2 (Y=O,S) give products of the type $R_2NN(R^1)-\underset{\underset{Y}{\|}}{C}-Y-GeMe_3$ (128). These reactions parallel the behavior of the $Si-NR_2$ (127), $Ge-NR_2$ (132) and $Sn-NR_2$ (133) systems.

The preparation of stannylhydrazines has received little attention; however, the reaction between $SnCl_4$ and H_2NNH_2 has been reported to give an octahedrally coordinated complex of trichlorostannylhydrazine, $SnCl_3N_2H_3.2N_2H_4$(134).

3. Hydrazine Derivatives of Phosphorus and Arsenic

(a) Arsinohydrazines

While aminoarsines, $R_nN(AsR^1_2)_{3-n}$ (R=H, alkyl, aryl; R^1=alkyl, aryl) are a well established class of nitrogen arsenic compounds (135), few arsinohydrazines have been prepared. The hydrazinolysis of $(CF_3)_2AsCl$ and $(CF_3)_3As$ yield $(CF_3)_2AsNHNHMe$ and $(CF_3)_2AsNHNMe$ (136, 137), and the reaction between $(CF_3)_2AsCl$ and Me_2NNHMe gives $(CF_3)_2AsNMeNMe$ (137). The(trifluoromethyl)arsinohydrazines were found to be unstable with respect to elimination of CF_3H and N_2 at room temperature, restricting an examination of their chemistry, but HCl was found to cleave the As-N bond in $(CF_3)_2AsNHNMe_2$ quantitatively to give $(CF_3)_2AsCl$ and $Me_2NNH_2.HCl$ (136).

(b) Phosphorus-hydrazine Compounds

The majority of phosphorus-hydrazine compounds prepared to date are those containing phosphorus in the pentavalent state; interest in their preparation stems partly from their possible biological activity (138,139).

Phosphorus-hydrazine compounds have been synthesized, generally following the routes used in the preparation of aminophosphines; (a) by hydrazinolysis of a phosphorus-halogen bond and various other elimination reactions, (b) by transamination reactions, and (c) by addition reactions. Listed in Table I-9 are representative examples of phosphorus(V)-hydrazine compounds, while in Table I-10 the phosphinohydrazine compounds prepared to date are tabulated.

The chemistry of phosphorus(V)-hydrazine compounds has been described in an excellent article by Fluck (6). Notable features of these compounds are their thermal stability, and resistance to basic hydrolysis of the P-N bond (6), although acid hydrolysis generally cleaves the P-N bond (6, 138). Reactions of phenylphosphonic dihydrazide, $PhP(O)(NHNH_2)_2$, with aldehydes and ketones, give the hydrazones, $PhP(O)(NHN{=}CR_2)_2$, and with stoichiometric quantities of HCl in ethanol solution, give the dihydrochloride salt (140). These reactions parallel those found for substituted hydrazines (118). Hydrazidophosphoric diphenylester, $(PhO)_2P(O)N_2H_3$, gives analogous products with aldehydes and ketones, but cleavage of the P-N bond occurs in aqueous solution (138). All of the phosphinohydrazines prepared to date (Table I-10), were obtained by the hydrazinolysis of a phosphorus-halogen bond, except for bicyclic $P(NMeNMe)_3P$

Table I-9. Phosphorus(V)-hydrazine Compounds

Compound	Preparation	Reference
$YP(NHNH_2)_3$	$YPCl_3 + H_2NNH_2$	141, 142, 143
$YP(NHNHR)_3$	$YPCl_3 + RNHNH_2$	143, 144
$PhP(Y)(NHNH)_2P(Y)Ph$	$RP(Y)Cl_2 + H_2NNH_2$	140,145
$ROP(Y)(NHNH_2)_2$	$ROP(Y)Cl_2 + H_2NNH_2$	141, 142, 146
$ROP(Y)(NHNR_2)_2$	$ROP(Y)Cl_2 + R_2NNH_2$	147
$ROP(Y)(NHNHR)_2$	$ROP(Y)Cl_2 + RNHNNH_2$	147, 148
$R_2P(Y)NHNH_2$	$R_2P(Y)Cl + H_2NNH_2$	149, 150
$R_2P(Y)NHNHP(Y)PR_2$	$R_2P(Y)Cl + H_2NNH_2$	140, 140, 151, 152
$(RO)_2P(Y)NHNH_2$	$(RO)_2P(Y)Cl + H_2NNH_2$	138, 141, 142, 153
$RP(Y)(NH_2)(NHNH_2)$	$RP(Y)(NH_2)_2 + H_2NNH_2$	29
$(R_3PNHNH_2)^+Br^-$	$R_3PBr_2 + H_2NNH_2$	154
$(R_3PNHNHPR_3)Cl_2$	$R_3PCl_2 + N_2H_4.2HCl$	154
$RP(Y)(NHNH_2)_2$	$RP(Y)(OC_6H_4SO_2NHNH_2) + N_2H_4$	155
$(PN(NHNH_2)_2)_3$	$(PNCl_2)_3 + H_2NNH_2$	156
$Cl_2P(Y)NHNHP(Y)Cl_2$	$PCl_5 + H_2NNH_2 + H_2O$	157

Y = O, S

Table I-10

Phosphinohydrazines

Product	Procedure	Reference
$P(NMeNMe)_3P$	$(Me_2N)_3P + HNMeNMeH.HCl$	158
$ClP(NMeNMe)_2PCl$	$PCl_3 + P(NMeNMe)_3P$	158
$Ph_2PNRNMe_2$	$Ph_2PCl + HNRNMe_2$ R=H, Me, Et.	48, 159

$PhP(NRNMe_2)_2$	$PhPCl_2$ + $HNRNMe_2$ R=H, Me	48, 159
$P(NMeNMe_2)_3$	PCl_3 + $HNMeNMe_2$	48
$(Ph_2P)_2NNMe_2$	Ph_2PCl + H_2NNMe_2 + Et_3N	159
$Ph_2PNHNHPPh_2$	Ph_2PCl + H_2NNH_2 + Et_3N	149, 159
$(Ph_2P)_2NNMe(PPh_2)$	Ph_2PCl + $MeNHNH_2$ + Et_3N	159
$P_4(NNMe_2)_6$	PCl_3 + H_2NNMe_2	160
$(Me_2N)_2PNHNHP(NMe_2)_2$	$(Me_2N)_2PCl$ + H_2NNH_2	149
$X_2PNMeNMe_2$ (X=Cl, F)	X_2PCl + Me_2NNHMe (X=F; NaF + $Cl_2PNMeNMe_2$)	161
$XP(NMeNMe)_2$ (X= Cl, F)	$XPCl_2$ + Me_2NNHMe (X=F; NaF + $ClP(NMeNMe_2)_2$)	161
$Ph_2PNHNPh_2$	Ph_2PCl + H_2NNPh_2	162
$(CF_3)_2PNHNMe_2$	$(CF_3)_2PI$ + Me_2NNH_2	163
$CF_3P(NHNMe_2)_2$	CF_3PI_2 + Me_2NNH_2	164
$(CF_3)_2PNMeNMe_2$	$(CF_3)_2PI$ + Me_2NNHMe	164
$(CF_3)_2PNMeNH_2$ $(CF_3)_2PNHNHMe$	$(CF_3)_2PI$ + $MeNHNH_2$	165

and cyclic $ClP(NMeNMe)_2PCl$, which were prepared by the **transamination** reaction between $(Me_2N)_3P$ and HNMeNMeH.HCl, and by the reaction of stoichiometric quantities of PCl_3 and $P(NMeNMe)_3P$, respectively (158). Although the P-N-N arrangement offers three adjacent electron lone pairs, and

might be expected to show differences in reactivity towards electrophilic species as compared to the aminophosphines, the chemistry of the alkyl and aryl phosphinohydrazines is strikingly similar to that of the alkyl and aryl aminophosphines. Thus, the phosphinohydrazines are oxidized by oxygen (158, 159) and sulphur (158, 159) at the phosphorus atom to give the respective hydrazinophosphine-oxides and -sulphides. Adduct formation with boron (158) and carbonium ion (158, 166) species occurs at phosphorus. Surprisingly, the terminal nitrogen of the P-N-N system is unreactive towards electrophilic species (166); the reaction of various (aryl) phosphinohydrazines with chloramine give products indicating that reaction occurs at the phosphorus atom. Subsequent chloramination of either of the nitrogen atoms does not occur (47, 48, 166).

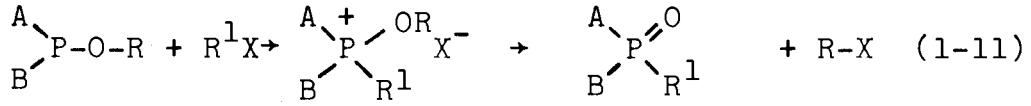
In contrast to the silyl- and germyl-hydrazine systems, reactions of phosphinohydrazines with CS_2 are not expected to give products resulting from an insertion reaction. The $(CF_3)_nP(NR_2)_{3-n}$ compounds do not react with CS_2 (22), and Nielsen et. al. (166) suggested that the initial product from the reaction between $Ph_2PNHNMe_2$ and CS_2 is an adduct, in which the CS_2 molecule is coordinated to the phosphorus atom through

carbon. This rearranges to give $Ph_2PN(CSSH)NMe_2$.

The possibility exists for the phosphinohydrazines to undergo an Arbuzov rearrangement (167) to give species of the type $R_2P(NR)NR_2$, although this reaction has not been observed except at high temperatures (200°C); pyrolysis of $PhP(NHNMe_2)_2$ gives $\left[\begin{matrix} Ph \\ -P=N- \\ NMe_2 \end{matrix}\right]_n$ (168).

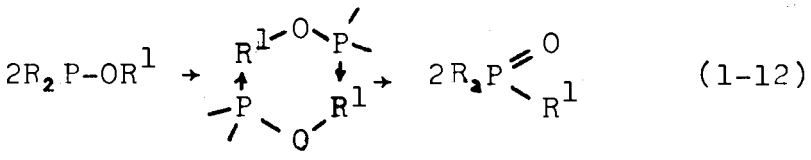
D. $(CF_3)_nPX_{(3-n)}$: The Influence of Trifluoromethyl Substituents on the Chemistry of Trivalent Phosphorus

The Michaelis-Arbuzov reaction has been widely used to effect the formation of carbon-phosphorus bonds, classically involving the reaction of an alkyl halide with an ester of trivalent phosphorus. The reaction proceeds stepwise according to equation 1-11. (167).



(1-11)

Thus, if a phosphine has good nucleophilic properties at the phosphorus atom, a rearrangement can occur as in equation 1-12.



(1-12)

This rearrangement previously prevented the isolation of many R_2P-OR and R_2P-SR phosphines (172). Compounds of the type $(CF_3)_2$POR {R=Me (169), H (170) -C(O)Me and $-C(O)CF_3$ (173), $SiMe_3$ (171), $P(CF_3)_2$ (169)} , and $(CF_3)_2$PSR {R=CH_3 , H, Bu^t, $P(CF_3)_2$ (174, 175) } , have been found to be stable with respect to an Arbuzov rearrangement, and together with compounds of the type $(CF_3)_2PNR_2$ and $\{(CF_3)_2PBH_2\}_3$, represent series of compounds whose properties suggest strong (p-d) interaction across the P-M (M=O,S,N, "B-H" bond (56, 172)).

The key to the existence and to the particular properties of these compounds lies in the function of the CF_3 groups on phosphorus.

Alkyl and aryl phosphines readily display nucleophilic reactivity, as evidenced in the Michaelis-Arbuzov reaction, and in the formation of stable complexes with Lewis acids (56, 176, 177). In this respect they function much like their nitrogen analogues through σ donation of a lone pair. However, phosphorus can show π-acceptor properties as well; the extent to which the σ-donor π-acceptor interactions of phosphorus is manifest, is dependent on the stereochemical and electronic properties of its substituents. Electronegative substituents, through an inductive effect, decrease the availability of the phosphorus lone pair for σ donation; electron releasing substituents, which donate electrons into the phosphorus d orbitals, reduce its capability as a π acceptor. The electronegative CF_3 group {F > CF_3 > Cl (172)}, while reducing phosphorus σ donor properties, is unable to offer π electrons to compete with π donor ligands; thus the trifluoromethylphosphines function as good π acceptors (63). But with the CF_3 substituents, σ donor properties are severely reduced. (62, 172, 178).

Barlow, Nixon and Webster (63), through observation of the carbonyl stretching frequencies in $L_nMo(CO)_{(6-n)}$

compounds, have suggested a series in which π acceptor ability decreases in the order:

$CF_3PF_2 \sim (CF_3)_2PF > PF_3 > CCl_3PF_2$

$> ClCH_2PF_2 \sim PhPF_2 > ROPF_2$

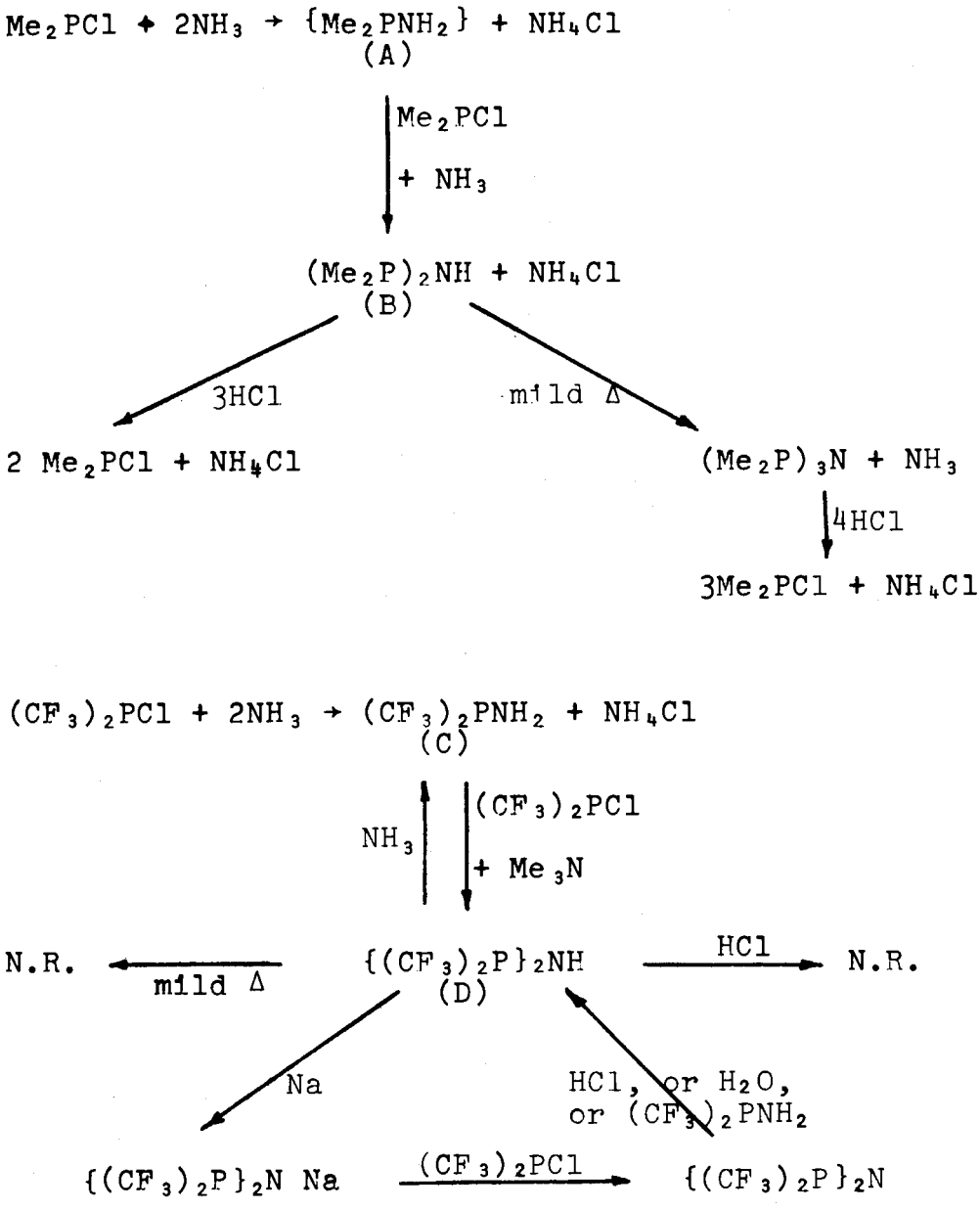
$> R_2NPF_2 > RPFNR \sim (R_2N)_2PF$

$>>> R_3P.$

It is suggested that the trifluoromethyl phosphines are third only to CO and NO in π acceptor ability. Thus, in the trifluoromethylphosphinoamines, $\{(CF_3)_2P\}_{3-n}NR_n$, Np-Pd π bonding should be more extensive than in the analagous alkylated phosphinoamines. Evidence for a (p-d) π interaction in these systems comes from both chemical and physical investigations.

Attempts to prepare Me_2PNH_2 (A) have led only to $(Me_2P)_2NH$ (B) (13), while the ammonolysis of $(CF_3)_2PCl$ readily gives $(CF_3)_2PNH_2$ (C) (22). $\{(CF_3)_2P\}_2NH$ (D) is prepared only by the reaction of (C) with excess $(CF_3)_2PCl$ in the presence of Me_3N as the hydrogen chloride acceptor (23). $\{(CF_3)_2P\}_2NMe$ (E) is prepared by the same method. Moreover, whereas the P-N bonds in (B) are easily cleaved by HCl, the P-N bonds in (D) and (E) do not undergo fission in this manner. The reaction schemes are shown in Figure I-11.

Figure I-1. Effect of Trifluoromethyl Substituents on Phosphorus(III) Chemistry



It is argued (23, 172) that in (D), HCl does not cleave the P-N bond because the nitrogen lone pairs are fully employed. (D) does react with NH_3 to give $(CF_3)_2PNH_2$ (C) indicating that the phosphorus atom acts, in this reaction as a σ acceptor (23).

Auxiliary π bonding between phosphorus and nitrogen might be expected to show evidence of a rotational barrier about the P-N bond. H^1 and F^{19} NMR studies on compounds of the type $RP(X)NR^1_2$ (R = $ClCH_2$, $CHCl_2CF_2$, Pr^i, Ph; R^1 = CH_3; X = Cl, F), indicate rotational isomers at -50°C and below, depending on R and X (20, 179).

E. Research Proposal

A number of factors suggested the synthesis and study of (trifluoromethyl)phosphino hydrazines. As noted earlier, substituted hydrazines appear to present some anomalous chemical and stereochemical properties; increasing alkyl substitution causes a decrease in basicity, relative to hydrazine (88), a trend contrary to that observed for alkylamines (98), and the effect on the basicity, stability and stereochemistry of hydrazine with other substituents such as CF_3 (79), F, (89), and SiH_3 (84) is quite complex. As well, whether the N-N bond dissociation energy increases (86), or decreases (51) with methyl substitution is still uncertain.

The preparation of the P-N-N linkage is a natural extension of aminophosphine chemistry, but while the latter has two potential basic sites, the phosphinohydrazine offers three sites to which a Lewis acid or metal ion may co-ordinate. The factors influencing the basicities of the phosphorus and nitrogen atoms in the phosphinohydrazine backbone are of interest. Whereas alkyl and aryl phosphinoamines, (13,17,42) and aryl phosphinohydrazines (166) undergo reactions indicating phosphorus to be the most basic atom, it might be expected that the presence of CF_3 groups attached to phosphorus would diminish the availability of the phosphorus lone pair, and enhance nitrogen

to phosphorus (p-d)π bonding. Experiments were designed to test these possibilities. The modifying effects due to the electronegative CF_3 groups may change the coordination characteristics of the phosphorus, and may also determine the molecular configuration and hence, the potential chelating properties of the (trifluoromethyl)phosphinohydrazine molecule.

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CHAPTER II

EXPERIMENTAL SECTION

A. Physicochemical Measurements

1. Infrared Spectra

Infrared measurements were determined using either a Perkin-Elmer 457, a Beckman I.R. 12 or, in one instance, a Unicam S.P. 200 infrared spectrophotometer. Samples were prepared as KBr disks, or as mulls in nujol or halo oil,as noted. Where possible, gas phase samples were run, using 10 cm. gas phase cells having either NaCl or KBr windows. All spectra were calibrated with polystyrene film.

2. Mass Spectra

Mass spectral measurements were determined using a Hitachi Perkin-Elmer R.M.U.-6E mass spectrometer. Samples were generally introduced through the gas phase sample receiving system, and all were ionized at a chamber voltage of 80 ev.

3. Nuclear Magnetic Resonance Spectra

NMR measurements were made using a Varian A56/60 NMR spectrometer. H^1 chemical shifts were measured relative to tetramethylsilane as internal reference, while F^{19} chemical shifts were measured relative to $CFCl_3$ as internal reference. The spectrometer was fitted with a Varian V-6057, variable temperature accessory system, allowing spectral measurements from -60^{o}

to +200°C. Temperature calibration was achieved using methanol (low temperature range), or ethylene glycol (high temperature range).

4. Vapour Phase Molecular Weight Determination

Where compounds display reasonably high vapour pressures at room temperature (>5mm), the determination of molecular weight by gas density measurement is practical. By measuring the pressure that a weighed sample of gas exerts in a known volume, the molecular weight can be calculated from the ideal gas law.

$$M = \frac{wt}{PV} RT$$

wt = Weight of sample
R = Gas constant
T = Temperature (°K)
P = Pressure
V = Volume
M = Molecular weight

This measurement was used, to verify the presence of postulated reaction products, to determine the mole ratios of mixtures of two known gases, to check for possible intermolecular association in the gas phase, and to determine the molecular weights of new compounds.

5. Melting Point Determination

The majority of melting points were determined on samples sealed under vacuum into glass capillaries. The capillaries were then suspended in a variable temperature oil bath equipped with an electric stirrer and heating unit.

The sample was viewed through a glass plate in the side of the bath as the temperature was raised. Melting points are reported as the temperature at which the sample just begins to melt, to the temperature at which the last crystals melt. The melting points of compounds melting below 25°C were obtained using an unsilvered dewar vessel as the bath; the temperature of a suitably cooled liquid was gradually raised by bubbling nitrogen gas through the bath. Temperatures were measured with a calibrated thermometer.

6. Saturated Vapour Pressure Measurements

Saturated vapour pressures were measured using a mercury tensimeter. The tensimeter was rigidly clamped in a Tamson TV40 thermostatic bath filled with paraffin oil (max. temp. variation ± 0.005°C to 100°C, ± 0.01°C over 100°; capacity 40 litres). Vapour pressures were calculated from the difference in mercury levels within the tensimeter, as measured by a cathetometer. The maximum permissible difference in mercury levels within the tensimeter was 100 mm Hg; pressures greater than this were compensated by bleeding nitrogen into the vacuum side of the tensimeter, and measuring this quantity with an auxiliary manometer. Pressures were measured during both rising and falling temperature runs as a check against measurement errors, and to detect possible thermal decomposition of the compounds under investigation. The vapour pressures reported are uncorrected for the variation of Hg density with T.

B. Materials

Hydrazine, methylhydrazine, and 1,1-dimethylhydrazine, obtained from K & K, were dried over anhydrous barium hydroxide, and purified either by low temperature column distillation under nitrogen, or by vacuum fractionation. Trimethylhydrazine and tetramethylhydrazine were prepared and purified by the method of Class et.al.(1); the reaction sequences are noted in equations (2-1) and (2-2).

Trimethylhydrazine:

$$Me_2NNH_2 \xrightarrow{HCHO} Me_2NN{=}CH_2 \xrightarrow{LiAlH_4} Me_2NN\begin{matrix}Me\\H\end{matrix} \qquad (2\text{-}1)$$

Tetramethylhydrazine:

$$N_2H_4 \cdot H_2SO_4 \xrightarrow{HCOONa} \underset{H}{\overset{OHC}{}}\!\!>\!\!N\!\!-\!\!N\!\!<\!\!\underset{H}{\overset{CHO}{}} \xrightarrow{Me_2SO_4} \underset{Me}{\overset{OHC}{}}\!\!>\!\!N\!\!-\!\!N\!\!<\!\!\underset{Me}{\overset{CHO}{}}$$

$$\underset{Me}{\overset{OHC}{}}\!\!>\!\!N\!\!-\!\!N\!\!<\!\!\underset{Me}{\overset{CHO}{}} \xrightarrow{LiAlH_4} Me_2NNMe_2 \qquad (2\text{-}2)$$

Infrared spectra (2) and vapour pressure measurements (3) (4) (5) were made,and where applicable, N.M.R. spectra were used, to verify purity and composition. The pure hydrazines were stored as liquids in sealed tubes.

Trimethylboron was prepared by the method of Brown (6) utilizing the reaction between methylmagnesium bromide and boron trifluoride. (equation 2-3)

$$3MeMgBr + BF_3 \rightarrow Me_3B + 3MgBrF \qquad (2\text{-}3)$$

The product was purified by vacuum fractionation and stored as a gas in the vacuum system. Boron trifluoride (Allied Chemicals) and boron trichloride (K&K), were purified by vacuum fractionation and stored within the system as gases. Infrared spectra of Me_3B, BF_3 and BCl_3 were consistent with those reported in the literature (7,8,9).

Methylene chloride, chloroform, and carbon tetrachloride (Fisher Scientific) were purified by vacuum fractionation, stored in stoppered flasks over anhydrous calcium sulphate, and refractionated just prior to use; deuterated chloroform (Stohler Isotope Chemicals) was stored over anhydrous calcium sulphate as obtained and fractionated before use.

Tetramethylsilane (Stohler Isotope Chemicals)was purified by vacuum fractionation and stored as a gas within the system. Gaseous trichlorofluoromethane (Matheson, Coleman and Bell) was found to be readily soluble in the vacuum stopcock grease, which soon deteriorated, allowing seepage of air into the system: it was kept as a liquid in a tightly sealed metal container, and samples were fractionated before use. D_2O (Stohler Isotope Chemicals) was used as received.

Anhydrous hydrogen chloride was prepared by the dropwise addition of concentrated hydrochloric acid to concentrated sulphuric acid, purified by vacuum fractionation, and stored as a gas within the system.

The preparation of the trifluoromethylhalophosphines, $(CF_3)_n PI_{(3-n)}$ followed the procedure of Bennett et.al.(10), utilizing the reaction between iodine (Fisher Scientific),

red phosphorus (Fisher Scientific), and trifluoroiodomethane at moderately high pressure (≈ 9 atmos.) and temperature (≈200 - 220°C). Trifluoroiodomethane was prepared from the reaction of silver trifluoroacetate with iodine (11) (12); silver trifluoroacetate was obtained from the reaction between trifluoroacetic acid (Eastman Organic Chemicals), and either silver carbonate (Fisher Scientific), or silver oxide (Fisher Scientific) (11) (12). The above reaction sequences are noted in equations (2-4), (2-5), (2-6) and (2-7).

Silver trifluoroacetate:

$$Ag_2CO_3 + 2CF_3COOH \longrightarrow 2CF_3COOAg + CO_2 + H_2O \qquad (2\text{-}4)$$

$$Ag_2O + 2CF_3COOH \longrightarrow 2CF_3COOAg + H_2O \qquad (2\text{-}5)$$

Trifluoroiodomethane:

$$CF_3COOAg + I_2 \longrightarrow CF_3I + CO_2 + AgI \qquad (2\text{-}6)$$

Trifluoromethyliodophosphines:

$$CF_3I(xs) + P + I_2 \xrightarrow[4\ \text{days}]{200\text{-}220^\circ C} CF_3PI_2 + (CF_3)_2PI + (CF_3)_3P \qquad *(2\text{-}7)$$

* Mole ratios of products depends on the temperature employed (10); PI_3 and/or P_2I_4 is also formed.

Solvents used, diethyl ether, chlorobenzene, cyclohexane, tetrachloroethlyene, (Fisher Scientific), dibutyl ether, (Eastman Organic Chemicals), were dried rigourously by standard procedures, and purified by vacuum fractionation, discarding all but constant vapour pressure fractions. Purified solvents for later use were stored in sealed tubes. Infrared, NMR, and vapour pressure measurements were used to confirm purity and composition.

C. Borane Adducts of Methylhydrazines

1. Experimental Procedure

Reactions between BX_3 (X = Me, F, Cl) and methyl-, 1,1-dimethyl-, trimethyl-, and tetramethyl-hydrazine, both in the presence and in the absence of solvent, were carried out in a 75 ml. pyrex tube fitted with a B-14 cone. Typically, reactions in solution were effected according to the following procedure: (a) the alkyl hydrazine, followed by the solvent, was condensed into a tube immersed in liquid nitrogen, (b) the tube was warmed to room temperature, allowing the components to mix, (c) the solution was refrozen in liquid nitrogen and the borane was condensed into the tube, and (d) the system was allowed to come to room temperature. After a few hours at room temperature, products were fractionated across a five trap vacuum system to effect the separation of solvent, unused reagents and new products.

Reactions in the absence of a solvent were executed in a different manner: (a) the alkyl hydrazine was condensed into a reaction tube surrounded by liquid nitrogen, (b) the liquid nitrogen bath was moved to a higher level on the reaction tube, and the borane was then allowed to condense on a different section of the tube, (c) the liquid nitrogen bath was replaced by a bromobenzene slush bath at $-33^{o}C$, and the system allowed to equilibrate, and (d) after one hour the system was brought to room temperature. Products were then fractionated through a five trap system to remove any unreacted species.

Products from these reactions were usually volatile and transfer within the vacuum system was achieved by cooling the accepting section in liquid nitrogen; products were transferred in this manner into N.M.R.tubes, modified to be easily attached to,and removed from, the system.

In early experiments, N.M.R. tubes fitted with B-14 cones, were sealed off under vacuum after transfer of products. Reuse of the N.M.R. tube however, involved the removal of the sealed section, and the resultant shortening of the tube restricted the number of times it could be used. Added sections of equivalent diameter pyrex tubing preserved the length of the tube through subsequent use, but usually caused poor spinning in the N.M.R. spectrometer. A tube having good spinning characteristics, and which could be used any number of times, was constructed by attaching a B-7 cone directly to the tube. The top half of the cone was cut off to decrease weight (improving spinning qualities), and to allow a small syringe cap to be inserted as a plug. A B-7 to B-14 adapting section was used to attach the tube to the vacuum system. Products and a suitable solvent were condensed into the tube, allowed to warm to room temperature, and dry nitrogen gas was added to bring the pressure to one atmosphere. The tube was then disengaged from the system and a tightly fitting syringe cap was used as a plug. Removal of a few millilitres of gas by syringe, was facilitated through the cap, and was done as a precaution against breakage of the tube at the running

temperature of the NMR spectrometer (≈39°C).

Nonvolatile products were transferred to NMR tubes by syringe. Reaction tubes including such products were filled with dry nitrogen gas to one atmosphere and disconnected from the system. A suitable solvent was then introduced by a syringe fitted with a plastic tubing adapter and a length of Intramedic polyethylene tubing (Clay Adams). The solution was then drawn out, injected into an NMR tube previously flushed with dry nitrogen, and capped.

NMR studies at temperatures other than the operating temperature of the spectometer required syringe transfer of solutions in the same manner. The Varian A 56/60 spectometer was fitted with a Varian V-6057 variable temperature accessory which required that a pressure cap be fitted over the NMR sample tube to enable the air spinner to function. This restricted the length of the NMR tube used, but the above transferring procedures to a shortened NMR tube proved satisfactory.

2. The Formation of Adducts.

(a) Reaction of $MeNHNH_2$ with BMe_3

$MeNHNH_2$ (2.40 m.moles), followed by 2.43 m.moles of BMe_3 were condensed into a reaction tube and allowed to equilibrate at -33°C for one hour before bringing to room temperature. The product was observed as a white crystalline volatile solid, melting at about 20°C; NMR (Table II.4) and infrared measurements (Table II.7) indicated the product to be the adduct $MeNHNH_2.BMe_3$. The adduct was soluble in $CDCl_3$ and CH_2Cl_2.

(b) Reaction of $MeNHNH_2$ with BF_3

In a typical experiment, $MeNHNH_2$ (2.29 m.moles and BF_3 (2.31 m.moles) were allowed to react at -33°C for one hour. At room temperature, the product was observed initially as a viscous oil, which slowly crystallized to a white solid m.p.≈50°C). Products were volatile enough to be transferred slowly in vacuo, and were insoluble in $CDCl_3$ and CH_2Cl_2. DMSO-d^6 , and D_2O solutions gave H^1 and F^{19} NMR spectra (Table II.4) indicating more than one product had been formed. The infrared spectrum of the products is given in Table II.8.

(c) Reaction of $MeNHNH_2$ with BCl_3

$MeNHNH_2$ (3.25 m.moles), followed by 3.16 m.moles of BCl_3 were condensed into a reaction tube open to a mercury manometer. The nitrogen bath was removed, and a -45° bath placed around the tube. Immediately, there was a sudden rise in the pressure of the system followed by a second rise shortly thereafter. After one hour, products were fractionated across a five trap vacuum system. Products recovered were HCl (0.83 m.moles) and BCl_3(1.49 m.moles). A white involatile solid remained in the reaction vessel. Infrared spectra of the solid (Table II.9) together with analysis of the reaction stoiciometry suggested a number of products had been formed.

(d) Reaction of Me_2NNH_2 with BMe_3

Me_2NNH_2 (1.47 m.moles), followed by 1.49 m.moles of BF_3 were condensed into a reaction flask and brought to -33°C

for one hour before allowing the system to come to room temperature. The product was observed as a volatile white solid which was easily transferred in vacuo to an NMR tube. NMR (Table II.3) and infrared (Table II.11) measurements suggested the product to be $Me_2NNH_2.BMe_3$.

(e) Reaction of Me_2NNH_2 with BF_3

Me_2NNH_2 (1.63 m.moles), followed by 1.62 m.moles of BF_3 were condensed into a reaction tube, and the system allowed to equilibrate for one hour at $-33^{\circ}C$ before it was allowed to come to room temperature. The product, soluble in $CDCl_3$ and CH_2Cl_2, was observed as a white crystalline solid. NMR (Table II.3) and infrared measurements (Table II.12) suggested the product to be the adduct, $Me_2NNH_2.BF_3$. Reactions in cyclohexane gave identical results.

(f) Reaction of Me_2NNH_2 with BCl_3

Reactions between Me_2NNH_2 and BCl_3 in the absence of solvent gave a mixture of white and yellow solids. Products from solution reactions however suggested the formation of an adduct $Me_2NNH_2.BCl_3$. 2.23 m.moles of Me_2NNH_2 followed by 1.6642 g. of cyclohexane were condensed into a reaction tube and allowed to mix at room temperature. After refreezing in liquid nitrogen, 2.24 m.moles of BCl_3 were added and the system was allowed to come to room temperature. After one hour, removal of the cyclohexane in vacuo yielded a white solid which was insoluble in both $CDCl_3$ and CH_2Cl_2. DMSO-d^6 solutions required transfer to NMR tubes by syringe. After long standing,

a white solid precipitated from these solutions. NMR data (Table II.3) suggested that the initial product was the adduct, $Me_2NNH_2.BCl_3$. The infrared spectrum is given in Table II.13.

(g) Reaction of Me_2NNHMe with BMe_3

Me_2NNHMe (1.72 m.moles), followed by 1.84 m.moles of BMe_3 were condensed into a reaction tube and the system allowed to equilibrate at -33°C for one hour. After products were brought to room temperature, the most volatile fraction was removed, which showed the characteristic infrared spectrum for BMe_3 = (0.14 m.moles). The product, a colorless liquid at room temperature, was soluble in $CDCl_3$ and CH_2Cl_2. NMR (Table II.3) and infrared measurements (Table II.15) indicated the product to be $Me_2NNHMe.BMe_3$.

(h) Reaction of Me_2NNHMe with BF_3

Me_2NNHMe (1.38 m.moles), followed by 0.3380 g. of cyclohexane were condensed into a reaction tube and the components were allowed to mix. After refreezing the solution, 1.41 m. moles of BF_3 were added and the system allowed to come to room temperature. The product, a clear liquid, separated from the cyclohexane quite rapidly, comprising the bottom layer. The cyclohexane was removed in vacuo and the product transferred to an NMR tube. NMR spectra of $CDCl_3$ and CH_2Cl_2 solutions (Table II.3) as well as infrared measurements (Table II.16) suggested the product to be the adduct $Me_2NNHMe.BF_3$. Reactions in the absence of solvent gave equivalent results.

(i) Reaction of Me_2NNHMe with BCl_3

Me_2NNHMe (0.72 m.moles), followed by BCl_3(0.72 m.moles), were condensed into a reaction tube, and the system allowed to react at -33°C for one hour before bringing to room temperature. The product, a clear viscous oil, could be transferred very slowly by vacuum distillation, hence NMR tubes were filled with $CDCl_3$ solutions of the compound by the syringe method. NMR spectra (Table II.3) suggested that the initial product was the adduct $Me_2NNHMe.BCl_3$. The infrared spectrum is given in Table II.17.

(j) Reaction of Me_2NNMe_2 with BMe_3

Me_2NNMe_2 (1.25 m.moles), was condensed into a reaction tube followed by 1.24 m.moles of BMe_3, and the system was allowed to equilibrate at -33°C for one hour before bringing to room temperature. Transfer of products by vacuum distillation to an NMR tube was rapid, and as a precaution against the possibility of free BMe_3 remaining in the vapour phase, the most volatile component was condensed into a trap on the vacuum system. The NMR spectrum of the remaining component was that of uncomplexed Me_2NNMe_2 . The most volatile fraction showed the infrared spectrum for BMe_3. Thus, at room temperature, BMe_3 does not form an adduct with Me_2NNMe_2.

(k) Reaction of Me_2NNMe_2 with BF_3

Me_2NNMe_2 (1.25 m.moles), followed by 1.26 m.moles of BF_3 were condensed into a reaction flask and allowed to equilib-

rate at -33°C for one hour before bringing to room temperature. The products were observed as a clear non volatile liquid, which quickly turned pale yellow (15 min.). The products were insoluble in $CDCl_3$ and CH_2Cl_2, but dissolved in DMSO-d^6 ; solutions of the latter were transferred to an NMR tube by syringe. H^1 and F^{19} NMR spectra (Table II.4) indicated that an initially formed $Me_2NNMe_2.BF_3$ adduct undergoes further reaction. After three weeks, the DMSO (d^6) solution of products turned dark brown.

(1) Reaction of Me_2NNMe_2 with BCl_3

Me_2NNMe_2 (1.22 m.moles), followed by 1.23 m.moles of BCl_3 were condensed into a reaction tube. No reaction was observed at -78°C, but as the tube was warmed to -33°C, a rather violent reaction occurred, yielding a dark orange viscous liquid, which was insoluble in $CDCl_3$ and CH_2Cl_2: DMSO-d^6 solutions were transfered to an NMR tube by syringe. The H^1 NMR showed a single peak at 7.18τ (Table II.4).

3. NMR Data

(a) Preparation of 10% $Me_2NNH_2.BX_3$ and $Me_2NNHMe.BX_3$ Solutions for NMR Studies

Reactions of $MeNHNH_2$ and Me_2NNMe_2 gave results indicating other than simple adduct formation with some boranes; only the $Me_2NNHMe.BX_3$ and $Me_2NNH_2.BX_3$ series were used for the comparison of deshielding effects at the NMe protons caused by adduct formation with BX_3. To minimise the effects of

concentration on the NMe proton chemical shifts, 10% by weight solutions were prepared for NMR study. The quantities of reactants and solvents are noted in Tables II.1 and II.2. The NMR data for $Me_2NNH_2.BX_3$ and $Me_2NNHMe.BX_3$ as 10% solutions in CH_2Cl_2 are shown in Table II.3. The NMR data for the $MeNHNH_2.BX_3$ and $Me_2NNMe_2.BX_3$ systems are shown in Table II.4.

4. Infrared Data

(a) Preparation of $RR^1NNR^{11}R^{111}.BX_3$ Samples for Infrared Spectroscopic Measurements

Infrared measurements of the $R_2NNR_2.BX_3$ adducts were made on samples prepared by reaction between R_2NNR_2 and BX_3 at -33^oC, in the absence of solvent. In most cases, products were liquid, and could be run on the sample pressed between NaCl plates. In one instance ($Me_2NNH_2.BMe_3$) the product displayed a vapour pressure suitable for a good vapour phase spectrum. Solid samples were run as KBr pellets. Quantities of reactants employed in the preparation of these samples are shown in Table II.5. The infrared data for the hydrazineborane systems are shown in Tables II.6 to II.7.

Table II.1 Reactant and Solvent Quantities for "10% Solutions" of $Me_2NNH_2.BX_3$

Me_2NNH_2	BMe_3	BF_3	BCl_3	Solvent		
# m.moles	# m.moles	# m.moles	# m.moles	CH_2Cl_2 grams	$CDCl_3$ grams	% Adduct in Solvent
1.342					0.7385	(9.8%)
1.378				0.7114		(10.4%)
1.223	1.226				1.2794	10.0%
0.974	0.975			1.0275		9.9%
1.083		1.035			1.2503	10.2%
1.112		1.115		1.2738		10.3%
2.227			2.239		DMSO (d^6)	

Table II.2 Reactant and Solvent Quantities for "10% Solutions" of $Me_2NNHMe.BX_3$

Me_2NNHMe # m.moles	BMe_3 # m.moles	BF_3 # m.moles	BCl_3 # m.moles	CH_2Cl_2 grams	% Adduct in Solvent
1.715				1.1602	(9.9%)
1.103	1.105			1.2328	10.4%
1.022		1.022		1.4121	9.3%
0.718			0.720	1.2036	10.3%

Table II.3 Chemical Shifts (τ Values) [a] for $Me_2NNHR.BX_3$

Compound	Solvent	Temp. °C	MeN	Me_2N	N-H	Other Nucleus	Shift
Me_2NNH_2	CH_2Cl_2	-45		7.58	6.76		
$Me_2NNH_2.BMe_3$	CH_2Cl_2	-45		7.39	6.19	H^1_{CB}	10.33
$Me_2NNH_2.BF_3$	CH_2Cl_2	-45		7.18	5.89	F^{19}_{BF}(b)(c)	166.9 p.p.m.
$Me_2NNH_2.BCl_3$	DMSO-d^6	+35		6.97	5.05		
Me_2NNHMe	CH_2Cl_2	+10	7.45	7.58			
$Me_2NNHMe.BMe_3$	CH_2Cl_2	+10	7.50	7.50	6.22	H^1_{CB}	10.30
$Me_2NNHMe.BF_3$	CH_2Cl_2	+10	7.42	7.30	5.97	F^{19}_{BF}(b)(c)	162.7 p.p.m.
$Me_2NNHMe.BCl_3$	CH_2Cl_2	+10	7.16	6.99			

(a) H^1 Chemical shifts were measured relative to tetramethylsilane $\tau = 10.0$

(b) F^{19} chemical shifts were measured relative to $CFCl_3$

(c) B-F coupling constants in c.p.s. as follows: $Me_2NNH_2.BF_3$, J_{BF}, 13.5; $Me_2NNHMe.BF_3$, J_{BF}, 14.2

Table II.4 NMR Data for $MeNHNH_2.BX_3$ and $Me_2NNMe_2.BX_3$ Systems[a]

Compound	Solvent	Temp°C	MeN	N-H	Me_2N	Other Nucleus	Other Shift
$MeNHNH_2$	$CDCl_3$[a1]	39	7.45	6.7			
$MeNHNH_2.BMe_3$[b]	CH_2Cl_2[a2]	17	7.41	6.02		H^1CB	10.35
$MeNHNH_2.BF_3$	DMSO-d^6[a4]	39	7.33 7.23[c]	6.70 2.62[d] 1.85		$F^{19}B$[a3]	159.2 ppm[e] 151.6 ppm 149.3 ppm
Me_2NNMe_2	$CDCl_3$[a1]	39			7.79		
$Me_2NNMe_2.BF_3$	DMSO-d^6[a2]	39			7.62	$F^{19}B$[a3]	151.1 ppm[f] 149.2 ppm 147.3 ppm
$Me_2NNMe_2BCl_3$	DMSO-d^6[a2]	39			7.18		

(a) H^1 chemical shifts measured relative to tetramethylsilane τ=10; 1. as internal reference; 2. as external reference; 3. F^{19} chemical shifts in ppm relative to external $CFCl_3$.

(b) H^1 spectrum temperature dependent; see discussion.

(c) NMe peaks assigned $F_3B.NH(Me)NH_2$, 7.33τ; $MeNHNH_2.BF_3$, 7.23τ; see discussion.

(d) NH peaks assigned $F_3B.NH(Me)NH_2$, (NH_2) 6.70τ (NH) 1.85τ; $MeNHNH_2.BF_3$ (exchanging N-H), 2.62τ; see discussion.

(e) F^{19} peaks assigned $F_3B.NH(Me)NH_2$, 159.2 ppm, J_{BF} 15.5 cps; $MeNHNH_2.BF_3$, 151.6 ppm, J_{BF} 17.0 cps; $BF_4^{\ominus}$, 149.3 ppm, J_{BF} 1.0 cps, see discussion.

(f) F^{19} peaks assigned $Me_2NNMe_2.BF_3$, 151.1 ppm, J_{BF}, 15.8 cps; $BF_4^{\ominus}$, 149.2 ppm, J_{BF}, 1.2 cps; $RNBF_2$, 147.3 ppm; see discussion.

Table II.5. Reaction Quantities for R_2NNR_2 + BX_3 {For Infrared Measurements}

Hydrazine	Weight in Grams	BMe_3		BF_3		BCl_3	
		# m.moles	# m/moles	# m.moles		# m.moles	
$MeNHNH_2$	0.0258	0.561	0.552				
$MeNHNH_2$	0.0157	0.341		0.402			
$MeNHNH_2$	0.1495	3.250				3.164	
Me_2NNH_2	0.0374	0.623	0.615				
Me_2NNH_2	0.0437	0.728		0.733			
Me_2NNH_2	0.1800	3.000				2.810	
Me_2NNHMe	0.0331	0.447	0.460				
Me_2NNHMe	0.0330	0.446		0.450			
Me_2NNHMe	0.0429	0.580				0.577	

Table II.6

$MeNHNH_2$: Infrared Spectrum[a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
755	84	975	49	1478	28
768	85	1005(sh)	44	1580(broad)	14
775	83	1120	49	2797	61
871	86	1279	23	2845	66
884	100	1296	25	2885(sh)	59
898	90	1305(sh)	18	2950	74
946	45	1448	35	3250(broad)	28
962	59	1462	28		

(a) Spectrum measured on gas phase; 10 cm cell, NaCl windows; using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 884 cm^{-1} = 100 units

Table II.7

$MeNHNH_2.BMe_3$; Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
671	43	1287	93	2945(sh)	54
815	17	1408	28	3002	30
841	37	1455	48	3155	39
869	26	1601	55	3225	36
989	84	2817	78	3257	43
1028	59	2846(sh)	68	3270(sh)	35
1088	70	2885(sh)	91	3345	36
1152	41	2912	100		

(a) Spectrum measured on liquid pressed between NaCl plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 2912 cm^{-1} = 100 units.

Table II.8

$MeNHNH_2.BF_3$: Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
709	61	1399	80	3195	89
755	34	1460	86	3303	90
796	61	1620	84	3353	95
899	94	2475(sh)	49	3585(broad)	56
930(broad)	87	2560(sh)	52		
1060(broad)	100	2675(sh)	76		
1220(broad)	85	2755(broad)	86		
1280	78	3045(broad)	91		

(a) Spectrum measured on liquid pressed between NaCl plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1060 cm^{-1} = 100 units.

Table II.9

" $MeNHNH_2.BCl_3$ " : Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
421	22	1146(sh)	44	1590	56
509	24	1242	51	2485	71
887	49	1330	60	2750(broad)	91
924	64	1400	53	2870	91
1001	62	1455	58	2940(broad)	98
1108	87	1480	58	3120	100
				3200	98
				3400(broad)	82

(a) Spectrum measured on KBr disk using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 3120 cm^{-1} = 100 units.

Table II. 10

Me_2NNH_2 ; Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
795	73	1141	62	2765	99
803	79	1153	22	2785(sh)	92
815(sh)	62	1213	25	2815	97
895	93	1300	44	2828	85
905	100	1310	33	2845(sh)	83
915(sh)	92	1437(sh)	61	2865(sh)	72
1030	63	1448	67	2958	94
1045(sh)	62	1457	72	3185	43
1055(sh)	57	1475(sh)	46		
1115	22	1586	46		

(a) Spectrum measured on gas phase; 10 cm cell; NaCl windows; using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 905 cm^{-1} = 100 units.

Table II.11

$Me_2NNH_2.BMe_3$; Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
675	51	1104	93	1462(sh)	72
807	67	1155(sh)	34	1475(sh)	64
820(sh)	63	1235	31	1592	70
850	37	1298	100	2835 (br.sh)	81
929	87	1353	27	2910(broad)	87
989	85	1396(sh)	31	3000(sh)	51
1048(sh)	78	1425(sh)	70	3270(sh)	39
1078	93	1445	75	3338	43

(a) Spectrum measured on gas phase, 10 cm cell: NaCl windows using Perkin-Elmer 457 spectrophotometer. Spectra on solid sample showed equivalent peaks although not as highly resolved.

(b) Intensities relative to band at 1298 cm^{-1} = 100 units.

Table II.12

$Me_2NNH_2.BF_3$: Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
687	63	1390(sh)	28	3025	23
760	10	1436(sh)	48	3205	40
837	61	1468	75	3304	42
915	98	1615	59	3360	60
1110 (very broad)	100	2715	22		
1282	22	2967	27		

(a) Spectrum measured on liquid pressed between NaCl plates using a Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1110 cm^{-1} = 100 units

Table II.13

$Me_2NNH_2.BCl_3$: Infrared Spectrum [a][c]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
665	29	990(sh)	62	1280(sh)	85
812	31	1020	69	1330	98
867	40	1063	58	1420(broad)	90
892	29	1103	73	2500(broad)	100
946	44	1245(sh)	73	3000(broad)	92

(a) Spectrum measured on solid pressed between NaCl plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 2500 cm^{-1} = 100 units.

(c) Spectrum poorly resolved.

Table II.14

Me_2NNHMe : Infrared Spectrum (a)

cm^{-1}	Intensity(b)	cm^{-1}	Intensity	cm^{-1}	Intensity
738	67	1096	58	2775	98
750(sh)	63	1101(sh)	54	2825	95
876	89	1130	49	2880(sh)	86
963(sh)	46	1201	43	2960	100
970	58	1213(sh)	41	2995(sh)	87
979	45	1466	77	3210	57
1015)doublet	53	1483(sh)	71		
1026	53	1580(broad)	12		

(a) Spectrum measured on gas phase; 10 cm cell; NaCl windows using Perkin-Elmer 457 spectrophotometer

(b) Intensities relative to band at 2960 cm^{-1} = 100 units.

Table II.15

$Me_2NNHMe.BMe_3$; Infrared Spectrum (a)

cm^{-1}	Intensity(b)	cm^{-1}	Intensity	cm^{-1}	Intensity
669	43	1098	63	1488	50
723	72	1108	56	2808	74
811	24	1147	50	2919	100
849	23	1236	20	2963	71
941	59	1290	93	3015	39
980	71	1304	70	3270	13
1051(sh)	55	1393	17	3357	37
1068	72	1405(sh)	16		
1080	71	1469	65		

(a) Spectrum measured on liquid pressed between NaCl plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 2919 cm^{-1} = 100 units.

Table II.16

$Me_2NNHMe.BF_3$: Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
590	75	1055	65	1510	40
614	52	1095(sh)	77	1625(broad)	11
672	58	1160	100	2807(sh)	11
682	49	1202(sh)	81	2905(sh)	23
769	67	1258	49	2980	35
865(sh)	47	1335	20	3026	21
905	99	1390	23	3260	19
988	37	1440(sh)	44	3350	32
1001	37	1476	70		

(a) Spectrum measured on liquid pressed between NaCl plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1160 cm^{-1} = 100 units.

Table II.17

$Me_2NNHMe.BCl_3$: Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
660(broad shoulder)	89	1030(sh)	56	1460(broad)	96
685(broad)	93	1052	71	1585	59
766	74	1116	83	2035	17
801(sh)	38	1130(sh)	79	2445(broad)	98
888	50	1203(broad)	79	2625(very broad)	100
925	38	1240(broad)	70	2865(broad shoulder)	87
949	47	1328	63	2930(broad)	90
964	50	1400(broad)	93	3195	63

(a) Spectrum measured on liquid pressed between NaCl plates using a Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 2625 cm^{-1} = 100 units.

D. Reactions of Methylhydrazine and 1,1-dimethylhydrazine with Polyhalomethanes

1. Reactions with CCl_4

(a) Reaction of $MeNHNH_2$ with CCl_4 in Triethylamine for seven days

$MeNHNH_2$ (29.440 m.moles), CCl_4 (32.556 m.moles) and Et_3N (5.5494 g) were condensed into a one-litre round bottom flask, fitted with a Springham greaseless high vacuum stopcock, and into which a quantity of ground glass had previously been added. The tap was closed and the system allowed to come to room temperature. No reaction was observed for one half hour on the undisturbed mixture, but once the flask was swirled bubbles quickly formed. Bubbling continued at a slackening pace for four days before ceasing. The product mixture was allowed to stand, with intermittent agitation for three more days before determination of products. A non-condensable gas was removed and measured by means of a Sprengel pump. Liquid products, rewarmed to room temperature, evolved more non-condensable gas, which was removed in the same manner (total, 13.05 m.moles). The gas gave the infrared spectrum for CH_4(2) and a mass spectrum, indicating the gas to be a mixture of CH_4 (m/e = 16), and N_2 (m/e = 28). The ratio of CH_4 to N_2

was calculated from the observed mean molecular weight (Mobs = 23.5) to be $CH_4:N_2$ = 3:5, indicating their quantities to be 4.894 m.moles CH_4 and8.156 m.moles N_2. The -120° fraction showed the infrared spectrum (13) and mass spectrum (m/e = 17) for ammonia (3.156 m.moles). Fractions at -96°, -63°, and -45°, analysed by mass, infrared and NMR spectroscopy, consisted of varying concentrations of $CHCl_3$, CCl_4 and Et_3N, plus some unidentified materials (total, 10.5553 g). An NMR spectrum of a homogeneous mixture of all three fractions indicated $CHCl_3$ to be present as a .156 mole fraction of Et_3N (Et_3N; CH_3(triplet) 9.03τ, J(CH_3CH_2)7.2 cps; CH_2(quartet) 7.57τ, J(CH_2CH_3) 7.2 cps; $CHCl_3$; 2.7τ). A non volatile pale yellow solid remained in the reaction flask (1.0030 g., by difference) which gave an NMR spectrum in D_2O, analysed as an equimolar mixture of $MeNHNH_2.2HCl$ and $Et_3N.HCl$ (Et_3N; CH_3(triplet) 8.72τ, J(CH_3CH_2)7.2 cps, CH_2 (quartet) 6.78τ, J(CH_2CH_3) 7.2 cps; $MeNHNH_2$; $N.CH_3$ 7.12τ; HDO; 5.28τ, TMS external). Aqueous solutions gave a positive test for Cl^- with $AgNO_3$; Ag° was precipitated on longer standing indicating the presence of a free hydrazine. Quantities of reactants and products are listed in Table II.18.

Table II.18 Reactants and Products from $MeNHNH_2$ + CCl_4

Reactants	# m.moles	Products	# m.moles
$MeNHNH_2$	29.439	N_2	8.156
CCl_4	32.608	CH_4	4.894
Et_3N	54.945	NH_3	3.156
		Et_3N	51.0 (a)
		$CHCl_3$	8.0 (b)
		$MeNHNH_2.2HCl$	3.9 (c)
		$Et_3N.HCl$	3.9 (c)
		CCl_4	?

(a) Calculated from $Et_3N.HCl$ found

(b) Calculated as 15.6% moles Et_3N

(c) Calculated from the weight and composition of solids.

(b) Reaction of $MeNHNH_2$ with CCl_4 in Triethylamine for Two Days

$MeNHNH_2$ (55.788 m.moles), CCl_4 (65.995 m.moles and Et_3N (11.4610 g.) were condensed into a one litre flask as before, and allowed to react for two days before determination of products. A non-condensable gas, removed and measured by means of a sprengel pump, was shown by infrared and mass spectroscopy to be a mixture of CH_4 and N_2 in a molar ratio of 1:3 (mean molecular weight 25.05; n calc. CH_4, 2.4 moles, n calc. N_2, 6.4 moles). Fractionation of the remaining liquid, which liberated more non-condensables at room temperature, was accomplished across a five trap system

at -45^{o}, -63^{o}, -96^{o}, -120^{o} and -196^{o}. The -196^{o} fraction showed the infrared and mass spectra for NH_3. The -120^{o} fraction showed the mass spectrum expected for a mixture of NH_3 (m/e = 17), Et_3N (m/e = 101) and possibly $MeNH_2$ (m/e = 31). The gas phase infrared spectrum showed strong bands due to NH_3, weak bands attributable to Et_3N, and a strong characteristic PQR structured band at 1050 cm^{-1} due to $MeNH_2$(2) The -96^{o} fraction analysed by infrared and mass spectroscopy as a mixture of $MeNH_2$, Et_3N, and CH_2Cl_2. The -63^{o} and -45^{o} fractions, analysed by infrared, mass and NMR spectroscopy indicated the presence of Et_3N, $CHCl_3$ and CH_2Cl_2 and unreacted $MeNHNH_2$ and CCl_4. D_2O solutions of a non volatile solid remaining in the flask showed the NMR spectrum expected for an equimolar mixture of $MeNHNH_2.2HCl$ and $Et_3N.HCl$, gave a postive test with $AgNO_3$ for $Cl^{\ominus}$ and quickly reduced Ag^{1} to Ag^{o}. No CH_3Cl was detected in the infrared, NMR or mass spectra. A summary of reactants and products is given in Table II.19.

Table II.19. Reactants and Products from $MeNHNH_2$ + CCl_4

Reactants	Products	
$MeNHNH_2$	N_2	$CHCl_3$
CCl_4	CH_4	CH_2Cl_2
Et_3N	NH_3	$MeNHNH_2.2HCl$
	$MeNH_2$	$Et_3N.HCl$

2. Reactions with CH_2Cl_2

(a) Reaction of $MeNHNH_2$ with CH_2Cl_2 in Triethylamine for Eighteen Days

$MeNHNH_2$ (24.548 m.moles), CH_2Cl_2 (25.053 m.moles) and Et_3N (10.8640 g.) were condensed into a reaction flask fitted with an in situ filtration apparatus, sealed and allowed to warm to room temperature. A reaction was not immediately apparent, but after twenty hours, two immiscible layers were observed, the bottom layer a clear colorless oil. The quantity of the bottom layer gradually increased over one week, at which time colorless crystals appeared in the top layer. Eighteen days following the mixing of reactants, products were fractionated, yielding CH_2Cl_2 (17.87 m.moles), Et_3N (10.5806 g.), a mixture of $Et_3N.HCl$ and $MeNHNH_2.HCl$, and a white volatile solid $(-N(Me)NHCH_2-)_2$ (compound I, 2.01 m.moles, 49%; m.p. 118-120°C). Compound I was purified by repeated vacuum fractionation. Infrared (Table II.20), NMR (Table II.25) and mass spectroscopy (Table II.21) were used to confirm the proposed formula.

Table II.20

$(-N(Me)NHCH_2-)_2$ (Compound I): Infrared Spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
309	44	1415	50	2190	9
336	67	1442	86	2234	13
444	46	1447(sh)	84	2265	12
675	56	1461	83	2685	59
818	97	1486	83	2793	97
845	44	1605(broad)	36	2829	100
908	95	1879	31	2868	98
990	97	1904(sh)	12	2935	99
1079	93	1945(sh)	20	2950	99
1124	83	1956	22	2975	92
1168	85	2026(sh)	12	2990	92
1217	90	2050(sh)	13	3122	93
1288	83	2090	23	3218	55
1357	80	2143	12		

(a) Spectrum measured on KBr disk using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 2829 cm^{-1} = 100 units.

Table II.21

$(-N(Me)NHCH_2-)_2$ Compound I ; Mass Spectrum

m/e	Intensity[a]	m/e	Intensity	m/e	Intensity
12	2	32	18	56	7
13	3	38	3	57	116
14	17	39	6	58	110
15	97	40	8	59	332
16	31	41	27	60	12
26	9	42	582	71	1000
27	70	43	204	72	55
28	194	44	75	116	113
29	58	45	48	117	8
30	245	46	33		
31	22	55	7		

(a) Intensities relative to peak at m/e = 71 = 1000 units

(b) Reaction of $MeNHNH_2$ with CH_2Cl_2 for one day

$MeNHNH_2$ (79.89 m.moles) and CH_2Cl_2 (135.99 m.moles) were condensed into a reaction flask fitted with an in situ filtration apparatus; the flask was sealed, and reaction was allowed to take place at room temperature, for one day. fractionation of products yielded $MeNHNH_2$ (43.55 m.moles), CH_2Cl_2 (116.37 m.moles), and $MeNHN{=}CH_2$ (compound II) (5.17 m.moles). Compound II was identified by its infrared (Table II.22) NMR (Table II.25) and mass spectra, (Table II. 23).

Table II.22

$MeNHN{=}CH_2$ compound II: Infrared spectrum [a]

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity
770	43	1240	32	1605	62
804	35	1420	28	2900	100
908	83	1460(sh)	48	3080	51
922	81	1480	59	3445	48
1132	96	1495	61		

(a) Spectrum measured on gas phase; 10 cm. cell; NaCl windows using Perkin Elmer 457 Spectrophotometer. Frequency assignments ±5 cm^{-1}

(b) Intensities relative to band at 2900 cm^{-1} = 100 units.

Table II.23

$MeNHN=CH_2$ (compound II); Mass spectrum

m/e	Intensity[a]	m/e	Intensity	m/e	Intensity
12	1	28	1000	43	86
13	3	29	200	45	32
14	33	30	126	46	14
15	104	31	105	56	3
16	2	32	265	57	15
24	2	39	6	58	314
25	9	40	12	59	18
26	81	41	16		
27	187	42	35		

(a) Intensities relative to peak at m/e = 28 = 1000 units.

(c) Reaction of Me_2NNH_2 with CH_2Cl_2

Me_2NNH_2 (10 mls) was added to CH_2Cl_2 (100 mls) in a 250 ml erlenmeyer flask and stoppered. After one day, two immiscible layers were observed, the top layer diminished in volume during one week while white crystals formed in the flask. The crystals were filtered off, washed three times in Et_2O and remaining traces of solvent were pumped off under vacuum for 20 hours. The infrared (Table II.24) and NMR spectra (Table II.25) are consistent with the formulation

$[Me_2N(CH_2Cl)NH_2]^+ Cl^-$ (III). Compound III was insoluble in $CHCl_3$ and CH_2Cl_2, but aqueous solutions gave a posative test for Cl^- with $AgNO_3$. The melting point was observed as 120-121°C. The product, recrystallized from an ethyl acetate-methanol mixture showed the same melting point, infrared and NMR spectra.

Table II.24

$[Me_2N(CH_2Cl)NH_2]^+ Cl^-$ (Compound III); Infrared spectrum[a]

cm^{-1}	I[b]	cm^{-1}	I	cm^{-1}	I
368	52	1008	51	1472	82
376(sh)	30	1099	82	1628	73
438	36	1119	65	2130(br)	28
470	59	1149	52	2860(sh)	85
507	72	1242	72	2950(sh)	98
735	20	1307	41	3000(br)	100
801	97	1353	69	3070(sh)	98
888	94	1402	62	3150	97
920	72	1431	67		
977	57	1452(sh)	77		

(a) Spectrum measured on sample as a KBr disk using a Perkin-Elmer 457 spectrometer.

(b) Intensities relative to peak at 3000 cm^{-1} = 100 units.

Table II.25

NMR spectra for products from alkylhydrazine-polyhalomethane reactions.

Compound	Solvent	Pattern splitting	Chem. shift (a)	Assignment.
$(-N(Me)NHCH_2-)_2$	$CDCl_3$	singlet	7.63	N-Me
		singlet	6.40	$\begin{matrix}N\\N\end{matrix}>CH$
		singlet	6.96	N-H
$MeNHN=CH_2$	CH_2Cl_2	singlet	7.25	NMe
		AB quartet	A 3.67	= CH_2
		J_{AB}, 11.5 cps	B 4.07	
$[MeNH(CH_2Cl)NH_2]^+Cl^-$	D_2O	singlet	6.46	NMe_2
		singlet	4.60	$N-CH_2Cl$
		singlet	5.43	HDO

(a) Chemical shift measured relative to tetramethylsilane = 10.0 τ.

E. Preparation and Characterization of (Trifluoromethylphosphino)hydrazines

1. Experimental Procedure

All preparative, separation and purification procedures were carried out using a vacuum system. After experimentation with various reaction vessels, the most convenient apparatus consisted of a 22 mm. pyrex tube sealed at both ends, and separated into two chambers by a sintered glass filter (Figure II.1). Side arms from each chamber allowed access for introduction of reactants and removal of products. Typically, reactions were executed according to the following procedure:

a) reactant 1 was condenced into chamber A under vacuum, the reaction vessel being cooled with liquid nitrogen;

b) a solvent was condenced into chamber A under the same conditions;

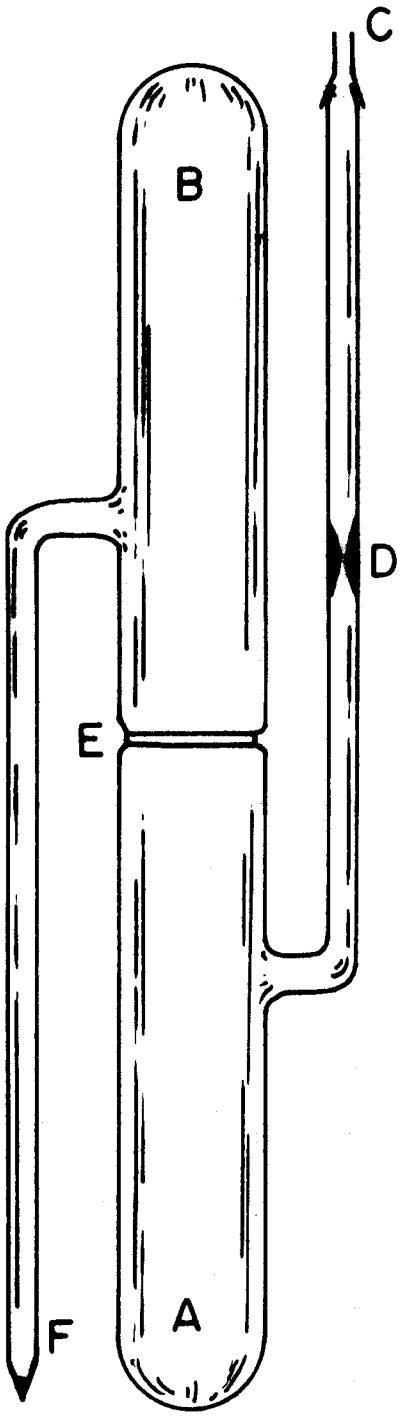
c) the reaction vessel was allowed to warm to room temperature to effect mixing of the reactant and solvent;

d) the reaction vessel was cooled once more in liquid nitrogen and reactant 2 was condenced into chamber A;

e) the side arm to chamber A was sealed and the reaction vessel allowed to warm to room temperature to effect the reaction;

f) after a length of time (usually 24 hours) the solution was filtered by inverting the vessel and allowing liquid

Reaction Flask for the Preparation of (trifluoromethyl)phosphinohydrazines



A Reaction chamber
B Chamber for receiving liquid products
C B-14 cone to vacuum system
D Capillary constriction
E Scintered glass filter
F Sealed side arm to be opened for removal of liquid products via vacuum system

Figure II.1

products to pass into chamber B;

g) the side arm to chamber B was then opened to the vacuum system permitting the removal of solvent and products.

Vacuum fractionation of the solvent and condensable products followed standard procedures across a five trap fractionation system. Composition of materials in the various traps was monitored by gas phase infrared and vapour phase molecular weight measurements. Choice of solvent for reactions depended on solubility considerations, and on the need for a suitable vapour pressure differential between solvent and products.

2. Preliminary Reactions in the absence of solvent

(a) Reaction of $(CF_3)_3P$ with H_2NNH_2* (14)

Mixtures of $(CF_3)_3P$ and H_2NNH_2 in the absence of solvent showed no observable reaction at room temperature, and heating to 100°C for 36 hours yielded only trace amounts of CF_3H. The addition of trimethylamine increased fluoroform production, and a variety of volatile products were obtained which subsequently condensed within the fractionation line, producing more fluoroform and nonvolatile waxy deposits.

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* Reactions involving hydrazine were investigated by Dr. L.K. Peterson, and are included for comparison and completeness.

(b) Reaction of $(CF_3)_2PX$ (X = I, Cl) with H_2NNH_2

These reactions resembled that of $(CF_3)_3P$ with H_2NNH_2 in that trimethylamine was required to initiate reaction. Products obtained also condensed during handling to give nonvolatile waxes with concurrent evolution of fluoroform.

(c) Reaction of $(CF_3)_3P$ with $(CH_3)_2NNH_2$

$(CF_3)_3P$ (2.267 m.mole) was condensed into a reaction vessel, followed by $(CH_3)_2NNH_2$ (1.711 m.mole). A reaction occurred at the melting point of the system; with the formation of a yellow oil and a white solid. After one day at room temperature, fractions recovered indicated CF_3H, $(CF_3)_3P$ and unreacted $(CH_3)_2NNH_2$ along with a small amount ($\approx$0.15 m.mole, 8.7% yield) of a white crystalline substance later found to be $(CF_3)_2PNHN(CH_3)_2$ (Compound IV).

(d) Reaction of $(CF_3)_2PI$ with $(CH_3)_2NNH_2$

$(CF_3)_2PI$ and $(CH_3)_2NNH_2$ reacted in the absence of solvent to give a white precipitate in a pink solution. After several days, fractionation yielded most of the $(CF_3)_2PI$, together with products which condensed within the fractionation line to white waxy deposits. A small fraction in barely sufficient quantity for a gas phase infrared spectrum, showed infrared bands equivalent to those for the compound later found to be $(CF_3)_2PNHN(CH_3)_2$ (Compound IV).

3. Reactions in the presence of solvent

(a) (i) Reaction of $(CF_3)_2PX$ with Me_2NNH_2 in diethyl ether

$(CF_3)_2PI$ (6.368 m.moles) and diethyl ether (3.8672 g.) were condensed into a reaction vessel and allowed to mix at room temperature. Following the recooling of the $(CF_3)_2PI$ - ether solution in liquid nitrogen, Me_2NNH_2 (16.105 m.moles) was condensed into the vessel; the vessel was sealed, and allowed to warm to room temperature. A reaction occurred on melting to form a white precipitate. After 60 hours, fractionation yielded ether (3.8600 g.), unreacted Me_2NNH_2 (4.830 m.moles), $Me_2NNH_2.HI$ (6.313 m.moles), and $(CF_3)_2PNHNMe_2$, (compound IV), (6.000 m.moles; 94% yield. Reactions using $(CF_3)_2PCl$ similarly gave compound IV in high yields (95%). Compound IV was identified by vapour phase molecular weight (M_{obs} 231, M_{calc} 228), mass spectroscopy (Table II.28) (P_{obs} 228, P_{calc} 228), infrared (Table II.27) and nuclear magnetic resonance (NMR) spectroscopy, (Tables II.46 and II.47). The infrared spectrum, for the compound from the reaction of $(CF_3)_3P$ with $(CH_3)_2NNH_2$ in the absence of solvent, was identical to that obtained for compound IV from solution reactions of $(CF_3)_2PX$ and $(CH_3)_2NNH_2$.

(ii) Reaction of $(CF_3)_2PNHN(CH_3)_2$ with anhydrous HCl

Reaction between $(CF_3)_2PNHN(CH_3)_2$ (0.778 m.moles) and an excess of HCl (2.323 m.moles) in a sealed pyrex reaction tube yielded $(CH_3)_2NNH.HCl$ (obs. 0.843 m.moles; calc. 0.778 m.moles) HCl gas (obs. 0.667 m.moles; calc. 0.767 m.moles) and $(CF_3)_2PCl$ (obs. 0.757 m.moles ; calc. 0.778 m.moles) calculated on the basis of equation (2-8).

$$(CF_3)_2PNHN(CH_3)_2 + 2HCl \rightarrow (CH_3)_2NNH_2.HCl + (CF_3)_2PCl \quad (2\text{-}8).$$

The yield of $(CF_3)_2PCl$ was essentially quantitative; the minor discrepancies in the quantities of HCl and $(CH_3)_2NNH_2$. HCl were probably due to the formation of some $(CH_3)_2NNH_2$. 2HCl . Infrared spectra of the dimethylhydrazine hydrochloride salt from the reaction, and that prepared independently by reaction between the alkyl hydrazine and HCl gas, were identical.

(iii) Reaction of Me_2NNH_2 with an excess of $(CF_3)_2PCl$

$(CF_3)_2PCl$ (12.707 m.moles) was allowed to react with Me_2NNH_2 (16.795 m.moles) in diethyl ether (4.9980 g.) as previously noted. The mixture was kept at room temperature for one week. The reaction stoichiometry found is noted in equation (2-9).

$$(CF_3)_2PCl + 2Me_2NNH_2 \rightarrow (CF_3)_2PNHNMe_2 + Me_2NNH_2.HCl \quad (2\text{-}9)$$

There was no evidence of the bis(phosphino) derivative $[(CF_3)_2P]_2NNMe_2$.

Products found were $(CH_3)_2NNH_2.HCl$ (obs = 8.321 m.moles; calc. = 8.398 m.moles), $(CF_3)_2PNHN(CH_3)_2$ (obs = 8.300 m.moles; calc. = 8.398 m.moles), and an "ether fraction (diethyl ether plus unreacted $(CF_3)_2PCl$; obs = 5.8846 g.; calc. = 5.8996 g.)(calculated values based on eqn. (2-9)). The presence of $(CF_3)_2PCl$ in the ether fraction was confirmed by infrared measurements, and the existence of $(CF_3)_2PNHN(CH_3)_2$ as sole phosphinohydrazine product was noted from infrared, NMR, and mass spectral measurements.

(iv) Physical data for $(CF_3)_2PNHNMe_2$

$(CF_3)_2PNHNMe_2$ was observed as a clear white solid melting at $40.15 \pm 0.15^{\circ}C$ as determined on samples sealed in glass capillaries under vacuum. Saturated vapour pressures of solid-vapour and liquid-vapour equilibria were measured with a mercury tensimeter. Compound IV was stable to at least $120^{\circ}C$ as shown by reproducible vapour pressures. Representative vapour pressure data are shown in Table II.26. The boiling point, extrapolated from the liquid-vapour equilibrium curve, is $112^{\circ}C$. The latent heat of vaporization at the boiling point is 8570 cal. $mole^{-1}$. The latent heat of fusion at the melting point is 5940 cal. $mole^{-1}$ and the latent heat of sublimation at the melting point is 15,500 cal. $mole^{-1}$. The Trouton constant was found to be 22.2 cal. deg^{-1}.

Table II.26

Saturated vapour pressure data for $(CF_3)_2PNHN(CH_3)_2$

(a) Solid

T°C	Pmm obs.	Pmm calc.	T°C	Pmm obs.	Pmm calc.
20.6	9.90	9.51	31.6	24.1	24.8
22.6	11.8	11.4	34.2	30.2	30.8
25.8	15.4	15.1	36.2	36.3	36.3
29.1	20.2	20.1	39.4	46.8	47.0

Log Pmm = 12.51 - 3388/T

(b) Liquid

T°C	Pmm obs.	Pmm calc.	T°C	Pmm obs.	Pmm calc.
41.1	52.1	52.0	79.8	267	266
50.6	81.5	81.1	89.6	377	376
60.6	125.7	125.5	100.1	536	531
73.4	208.6	209.7	111.9	749	755

Log Pmm = 6.6638 - 0.005465T + 1.75T - 2389/T

Table II.27

$(CF_3)_2PNHN(CH_3)_2$; Infrared spectrum[a] compound IV

cm^{-1}	Intensity[b]	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
423	26	902	24	1285	9	2790	33
447	21	1019	12	1386	12	2835	30
476	sh	1069	sh.	1455	19	2865	20
491	21	1109	80	1460	20	2912	11
541	11	1151	sh. 99	1470	22	2939	8
562	18	1155	100	2250	4	2975	32
739	2	1160	sh 98	2272	4	3008	27
744	2	1167	98	2295	3	3300	15
798	2	1206	93	2310	2	3422	5

(a) Measured in the gas phase (10 cm. cell, KBr windows) using a Beckmann I.R.12 spectrophotometer.

(b) Intensities reported relative to the band at 1155 cm^{-1} = 100 units. sh = shoulder.

Table II.28

$(CF_3)_2PNHNMe_2$; Mass spectrum[a]

m/e	I[b]	m/e	I	m/e	I
14	17	43	100	69	100
15	113	44	200	81	7
16	30	45	9	84	8
18	40	46	80	89	40
28	45	50	16	94	6
29	35	51	9	100	10
30	112	56	9	107	6
31	24	57	8	109	12
32	6	58	7	159	45
40	9	59	1000	228	60
41	18	60	45	229	6
42	120	66	12		

(a) Peaks with relative intensities less than 5 are not included.

(b) I = Relative intensity.

(b) (i) Reaction of $(CF_3)_2PI$ with Me_2NNHMe in diethyl ether

Me_2NNHMe (12.404 m.moles), and diethyl ether (1.4100 g.) were condensed into a reaction vessel, and allowed to mix at room temperature. Following the recooling of the hydrazine-ether solution, $(CF_3)_2PI$, (4.077 m.moles) was condensed into the vessel; the vessel was sealed and allowed to warm to room temperature. A reaction occurred on melting to form a white precipitate. After twelve hours, fractionation yielded an "ether fraction" (diethyl ether plus unreacted Me_2NNHMe, 1.5671 g.), excess Me_2NNHMe (3.013 m.moles), $Me_2NNHMe.HI$ (3.983 m.moles) and $(CF_3)_2PNMeNMe$ (compound V; 3.414 m.moles,(83%). In addition, $(CF_3)_2PNHNMe_2$ (compound IV; $\simeq$ 0.45 m.moles 11%) was observed as a minor product. Compound V was identified by its vapour phase molecular weight (M_{obs} 240.8, M_{calc} 242) mass spectrum (P_{obs} 242, P_{calc} 242; Table II.31) infrared (Table II.30), and NMR (Table II.46 and II.47) spectra.

(ii) Reaction of $(CF_3)_2PN(CH_3)N(CH_3)_2$ with anhydrous HCl

A mixture of $(CF_3)_2PN(CH_3)N(CH_3)_2$ (0.28 m.moles) and HCl (1.02 m.moles) in chlorobenzene reacted yielding $(CF_3)_2PCl$ (0.27 m.moles) (M_{obs} = 202; M_{calc} = 204.5) and $(CH_3)_2NNH(CH_3).2HCl$ (0.28 m.moles), according to equation (2-10).

$$(CF_3)_2PN(CH_3)N(CH_3)_2 + 3HCl \rightarrow (CF_3)_2PCl + (CH_3)_2NNH(CH_3).2HCl \qquad (2\text{-}10)$$

(iii) Physical data for $(CF_3)_2PN(CH_3)N(CH_3)_2$

Compound V was observed as a clear white liquid at room temperature, melting at -47.00 ± 0.20°C, as determined on samples sealed in glass capillary tubes. Saturated vapour pressures for the liquid-vapour equilibrium were measured with a mercury tensimeter. The extrapolated boiling point, obtained using the equilibrium vapour pressure curve, is 130.5°C. The latent heat of vaporization at the boiling point is 8200 cal. $mole^{-1}$. Representative vapour pressure data are shown in Table II.29. The Trouton constant was found to be 20.3 cal deg^{-1}.

(c) (i) Reaction of $(CF_3)_2PI$ with $MeNHNH_2$ in diethyl ether

$(CF_3)_2PI$ (4.040 m.moles), $MeNHNH_2$ (9.891 m.moles), and diethyl ether (5.1805 g.) were condensed into a reaction vessel as previously described. A reaction occurred on melting forming a white precipitate. After one hour at room temperature, fractionation yielded an "ether fraction" (diethyl ether plus unreacted $MeNHNH_2$, 5.2396 g.), $MeNHNH_2$.HI (4.480 m.moles) and a mixture of two isomers, $(CF_3)_2PNMeNH_2$ (compound VI), and $(CF_3)_2PNHNHMe$ (compound VII), (Total 3.677 m.moles, 91%). The isomers were

Table II.29

Saturated vapour pressure data for liquid $(CF_3)_2PN(CH_3)N(CH_3)_2$

T^oC	Pmm obs	Pmm calc	T^oC	Pmm obs	Pmm Calc
26.6	15.4	14.8	63.0	83.7	83.8
29.7	17.8	17.4	69.2	108	108
38.8	27.9	27.9	76.5	144	143
47.0	41.6	41.4	81.2	170	170
54.5	58.3	58.3	91.4	247	242

Log Pmm = 6.7566 - 0.005896 T + 1.75 log T - 2245/T

Table II.30

$(CF_3)_2PN(CH_3)N(CH_3)_2$; Infrared Spectrum [a]

cm^{-1}	Intensity [b]	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
422	8	658	7	1153	100	2788	14
449	13	738	2	1198	70	2825	15
473	23	848	20	1222	sh	2853	13
475	23	868	8	1280	sh	2875	Shr.
540	4	1000	7	1456	12	2912	11
560	8	1020	7	2244	4	2960	25
563	8	1109	68	2300	2	2995	16

(a) Spectrum measured on the gas phase (10 cm.cell, KBr windows), using a Beckman I.R. 12 infrared spectrophotometer.

(b) Intensities measured relative to peak at 1153 cm^{-1} = 100 units.

Table II.31

$(CF_3)_2PNMeNMe_2$; Mass spectrum

m/e	I	m/e	I	m/e	I
14	18	45	25	78	30
15	228	46	100	80	42
16	12	47	23	81	9
17	6	49	15	82	5
18	65	50	19	84	78
20	5	51	16	86	50
27	18	57	20	88	10
28	135	58	30	89	20
29	14	59	250	94	40
30	105	60	190	100	15
31	40	61	11	107	5
32	70	62	5	108	5
33	15	65	5	119	15
35	6	66	5	123	18
40	9	69	132	130	20
41	17	71	23	159	9
42	265	72	23	173	25
43	265	73	1000	228	9
44	300	74	45	242	25

subsequently separated by repeated vacuum fractionation into roughly equivalent molar proportions (compound VI: compound VII = 1.09) and identified by their vapour phase molecular weights (M_{obs} 215-219, M_{calc} 214) mass spectra (P_{obs} 214, P_{calc} 214; Table II.34 and II.35) and infrared (Table II.32 and II.33) and NMR spectra (Table II.46 and II.47). The infrared and NMR measurements facilitated discrimination between the two isomers. Whereas compound VII could be obtained in pure form, compound VI could not be freed of all traces of its isomer.

(ii) Physical data for $(CF_3)_2PNMeNH_2$ and $(CF_3)_2PNHNHMe$

Table II.32

$(CF_3)_2PNMeNH_2$: Infrared Spectrum (a)

cm^{-1}	Intensity (b)	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
687	24	1111	82	1470	4	2921	13
835	21	1148	100	1480	4	2948(sh)	
852	23	1195	86	1605	4	2995(sh)	
868	24	1280	7	2250	2	3410	2
1010	29	1425		2825	7		
1035		1442	5	2880(sh)			

(a) Spectrum measured on gas phase; 10 cm.cell, NaCl windows, using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1148 cm^{-1} = 100 units

Table II.33

$(CF_3)_2PNHNHMe$: Infrared Spectrum (a)

cm^{-1}	I(b)	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I
740	9	1204	84	1485(sh)	3	2924(sh)	10
810	17	1270(sh)	3	2250	1	2970	13
978	11	1375	3	2810	8	3008(sh)	9
1110	71	1440(sh)	2	2865	13	3340	5
1158	100	1450	7	2880(sh)	10	3428	4

(a) Spectrum measured on gas phase; 10 cm cell, NaCl windows, using Perkin-Elmer 457 spectrophotometer.

(b) I = Intensity; measured relative to band at 1158 cm^{-1} = 100 units.

Table II.34

$(CF_3)_2PNMeNH_2$: Mass Spectrum

m/e	I	m/e	I	m/e	I	m/e	I
18	10	59	10	83	5	119	25
27	5	60	25	84	8	124	10
28	90	62	10	85	5	125	20
29	40	65	5	86	5	126	5
30	150	66	180	88	5	142	5
31	20	68	5	93	55	143	25
32	5	69	530	94	10	145	365
41	5	70	5	95	470	146	10
42	10	71	5	96	25	163	10
43	80	73	8	97	8	168	5
44	35	75	135	100	60	169	5
45	1000	76	10	101	5	170	10
46	260	78	20	104	5	171	5
47	15	79	5	113	50	184	5
48	5	80	35	114	10	213	10
50	40	81	35	115	5	214	180
51	20	82	10	116	30	215	8

Table II.35

$(CF_3)_2PNHNHMe$; Mass spectrum

m/e	I	m/e	I	m/e	I
14	12	46	60	78	30
15	67	47	12	79	5
16	32	48	7	80	11
17	18	50	32	81	19
18	63	51	19	82	5
19	5	55	12	83	11
20	7	56	9	84	19
26	8	57	9	93	5
27	42	58	7	95	232
28	20	59	61	96	7
29	128	60	118	98	5
30	226	61	26	100	19
31	200	62	9	101	28
32	12	65	5	103	18
33	14	66	179	145	153
35	5	69	205	146	5
39	8	70	5	168	7
41	21	71	5	169	5
42	29	73	58	213	5
43	111	74	34	214	84
44	58	75	18	215	5
45	1000	76	9		

(d)(i) Reaction of CF_3PI_2 with Me_2NNH_2 in Chlorobenzene

In ether, cyclohexane, or tetrachloroethylene, CF_3PI_2 reacted with Me_2NNH_2 to form unidentifiable products, ranging from white waxes to highly colored oils and solids. However, a reaction between CF_3PI_2 (1.592 m.moles) and Me_2NNH_2 (16.135 m.moles) in chlorobenzene (2.8921 g) yielded a white precipitate and a pale yellow solution, which became colorless after twelve hours. Fractionation gave a "chlorobenzene fraction" (C_6H_5Cl plus unreacted Me_2NNH_2, (3.3730 g), $CF_3P(NHNMe_2)_2$ (compound VIII), and a non volatile solid (0.7973 g) ($Me_2NNH_2.HI$ plus polymeric materials). Compound VIII was identified by its mass spectrum (P_{obs} 218, P_{calc} 218, Table II.38), infrared (Table II.37), and NMR spectra (Tables II.46 and II.47).

(ii) Physical Data for $CF_3P(NHNMe_2)_2$

Compound VIII was isolated as a clear white solid melting at 49.20 ±0.20°C as determined on samples sealed into capillary tubes. Vapour pressure measurements, assessed with a mercury tensimeter, indicated decomposition at temperatures over 100°C, requiring these measurements to be taken on fresh samples in the minimum time to reach equilibrium. Vapour pressure data are shown in Table II.36. The extrapolated boiling point is 184°C and the latent heat of vapourization at the boiling point is 12700 cal $mole^{-1}$.

Table II.36

Saturated Vapour Pressure Data for liquid $CF_3P(NHN(CH_3)_2)_2$

T^oC	Pmm.obs	Pmm.calc	T^oC	Pmm.obs	Pmm.calc
49.4	1.70	1.75	93.2	21.4	21.4
63.1	4.10	4.13	115.0	56.4	59.2
72.5	7.00	7.11	134.0	128	130
86.6	15.3	15.3	151.0	248	249

Log Pmm. = 5.9707-0.002678 T + 1.75 log T -2985/T

Table II. 37

$CF_3P(NHNMe_2)_2$: Infrared Spectrum (a)

cm^{-1}	Intensity(b)	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
412	54	1106	88	1380 b.	14	2965	62
504	36	1115	87	1455	51	2997	42
					51	3196	12
560	50	1159	87	1467			
889	77	1174(sh)	90	2781	62	3296	14
973	77	1185	100	2826	56		
1013	50	1218	28	2863	50		
1051	35	1231	31	2902	35		

(a) Spectrum measured on mulls in nujol and halo oil, and on the pure solid between KBr plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1185 cm^{-1} = 100 units, sh = shoulder, b. = broad.

Table II.38

$CF_3P(NHNMe_2)_2$; Mass spectrum

m/e	I	m/e	I	m/e	I
13	6	39	7	64	5
14	27	40	16	66	12
15	90	41	65	69	47
16	24	42	290	71	60
17	50	43	280	72	100
18	200	44	480	73	300
19	14	45	310	74	175
20	5	46	55	75	65
26	16	47	6	77	9
27	44	50	9	78	10
28	115	51	10	80	7
29	160	57	36	89	50
30	200	58	185	91	16
31	560	59	1000	94	16
32	43	60	255	100	5
36	9	61	17	104	50
38	5	63	22	105	38

m/e	I	m/e	I	m/e	I
106	18	123	7	175	23
107	20	149	10	176	10
109	16	157	6	190	7
112	11	158	5	218	40
114	5	159	15	219	5
119	5	173	45		
122	5	174	220		

(e)(i) Reaction of CF_3PI_2 with Me_2NNHMe in diethyl ether

Reactions between CF_3PI_2 and Me_2NNHMe in chlorobenzene gave quantitative yields of $Me_2NNHMe.HI$ but no other products could be identified. In diethyl ether (6.5410 g.) however, CF_3PI_2 (2.18 m.moles) reacted with Me_2NNHMe (10.97 m.moles) yielding an "ether fraction" (6.5410 g.), $Me_2NNHMe.HI$ (4.61 m.moles), and $CF_3P(NMeNMe_2)_2$ (compound IX) in good yield. Compound IX was identified by its mass spectrum (P_{obs} 246, P_{calc} 246, Table II.40), infrared (Table II.39), and NMR (Tables II.46 and II.47) spectra.

Due to the presence of Me_2NNH_2 as a contaminant in the $Me_2NNH(Me)$ some compound VIII was produced in the reaction as well. This impurity was easily identified in the NMR and showed peaks in the mass spectrum. A small pure sampe of compound IX was obtained in quantities enough for infrared measurements.

(ii) Physical data for $CF_3P(NMeNMe_2)_2$

Table II.39

$CF_3P(NMeNMe_2)_2$: Infrared spectrum (a)

cm^{-1}	Intensity (b)	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
479	50	887	36	1278	sh.	2820	58
504	53	987	33	1387	sh.	2838	57
556	34	1019	41	1408	sh.	2864	66
637	12	1097	100	1445	sh.	2892	59
667	22	1154	57	1456	59	2949	78
848	63	1177	98	1471	sh.	2982	53
861	83	1235	45	2780	55		

(a) Spectrum measured on liquid pressed between KBr plates using a Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1097 cm^{-1} = 100 units

Table II.40

$CF_3P(NMeNMe_2)_2$; Mass spectrum

m/e	I	m/e	I	m/e	I
14	19	50	7	87	7
15	49	51	8	89	18
16	9	57	32	94	39
18	27	58	25	105	15
27	21	59	741	107	5
28	1000	60	71	108	6
29	50	61	5	109	7
30	188	62	5	112	23
31	87	69	38	114	6
32	411	71	27	118	6
36	7	72	26	123	33
40	26	73	1000	134	6
41	17	74	491	159	11
42	241	75	21	177	5
43	170	76	7	192	10
44	242	77	12	220	8
45	56	78	13	232	19
46	62	80	21	246	20

(f)(i) Reaction of CF_3PI_2 with $MeNHNH_2$ in diethyl ether

A reaction between CF_3PI_2 and $MeNHNH_2$ in chlorobenzene occurred near room temperature to yield a very small quantity of a white crystalline compound, the mass spectrum of which showed a peak at m/e = 288. With diethyl ether as solvent, the reaction proceeded at a temperature lower than that using chlorobenzene, but higher than all previous trifluoroalkyl-alkylhydrazine reactions. A further deviation from this family of reactions was noted as the formation of small amounts of nitrogen gas as a product. Reactions between CF_3PCl_2 and $MeNHNH_2$ in diethyl ether gave no noncondensable products.

A typical reaction was as follows: CF_3PI_2 (2.49 m.moles) was condensed into a $MeNHNH_2$ (14.89 m.moles)-diethyl ether (5.2446 g.) mixture. On warming, reaction was observed to give a white solid in a pale yellow solution. After one hour at room temperature, fractionation indicated the presence of a noncondensable gas, shown to be N_2 by its gas phase molecular weight (M_{obs} 27.8, M_{calc} 28). Subsequent calibration of the fractionation line, including attached reaction flask, indicated the

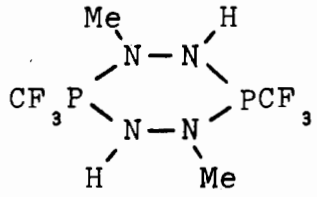
quantity of molecular nitrogen to be 1.92 ± .15 m.moles. Condensable products yielded an "ether fraction" (5.3723 g.), a "volatile product mixture" fraction (0.1064 g.), and a "nonvolatile product mixture" fraction (1.2321 g.) which remained in the reaction flask. Infrared spectra indicated the first fraction to be diethyl ether with unreacted $MeNHNH_2$. By repeated fractionation, the "volatile product mixture" fraction was separated into two components, one solid and one liquid at room temperature. The mass spectra of the two components were very similar, with identical parent ions (P_{obs} 288, Tables II.43 and II.44); two isomeric structures of $CF_3P(NMeNH)_2PCF_3$, compounds X and XI, are proposed. The yield of the combined products was 0.37 m.moles (30%). Total separation of the two isomers was not achieved, but NMR measurements (Tables II.46 and II.47) on nearly pure solid compound X and on a mixture of compounds X and XI, permitted discrimination between the two isomers. Infrared spectra (Tables II.41 and II.42) of small quantities of the pure isomers lend support to these formulations.

The third, "nonvolatile product" fraction,

originally consisted of a white solid and a pale yellow oil, the solid, over a period of a few days, melting and mixing with the yellow oil. Separation was effected by their differential solubility in $CDCl_3$, the yellow oil dissolving readily. NMR spectra suggested the white solid (later liquid) to be $MeNHNH_2.HI$, while the yellow oil in $CDCl_3$ showed complicated H^1 and F^{19} spectra, the latter consisting of twenty-two lines, some single and sharp, and some broad with unresolved fine structure. This data, coupled with mass spectral evidence (m/e = 506, Table II.45), suggests a mixture of higher polymers, resulting from the reaction between the bifunctional phosphine and the potentially trifunctional hydrazine. No attempt was made to separate this mixture.

(ii) Physical data for $CF_3P(NRNR^1)_2PCF_3$ isomers and (trifluoromethyl)phosphinohydrazine polymers

Table II.41



Infrared Spectrum (a)

cm^{-1}	Intensity(b)	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
401	62	813	28	1229	61	2808	13
457	53	1000	61	1392	40	2913	34
521	55	1100	100	1425	32	2954	30
543	60	1118	90	1441	31	2972	32
582	52	1145	70	1478	36	2995	20
721	72	1179	90	2760	10	3311	52

(a) Spectrum measured on mulls in nujol and halo oil and on the pure solid between KRr plates, using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1100 cm^{-1} = 100 units.

Table II.42

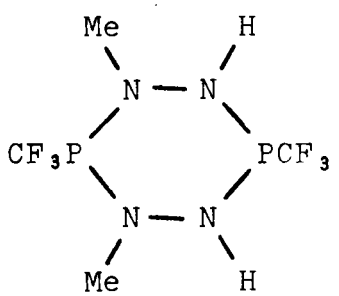
$CF_3P(NMeNH)_2PCF_3$: Infrared spectrum (a)

cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity	cm^{-1}	Intensity
449	65	809	35	1397	24	2906	46
480	sh.	997	68	1437	34	2949	42
524	57	1099	100	1479	40	2988	sh
538	sh.	1159	sh	1600 bd	8	3150	sh
706	55	1177	94	2798	20	3350 bd	35
730	23	1226	60	2860	sh		

(a) Spectrum measured on liquid between KBr plates using Perkin-Elmer 457 spectrophotometer.

(b) Intensities relative to band at 1099 cm^{-1} = 100 units.

Table II.43



Mass spectrum

m/e	I	m/e	I	m/e	I
14	7	61	14	93	9
15	5	62	14	94	5
16	5	63	6	95	14
28	13	66	9	97	10
32	5	69	28	104	16
37	9	72	5	106	28
38	9	73	26	107	7
39	6	74	57	110	9
43	20	75	63	111	18
45	19	76	38	112	1000
46	49	77	333	113	79
47	9	78	34	114	346
49	17	80	31	115	23
50	69	81	5	120	17
51	79	84	69	121	6
52	6	86	44	125	79
59	9	88	9	126	21
60	231	90	10	134	5

m/e	I	m/e	I	m/e	I
140	21	218	6	288	159
143	12	219	1000	289	11
145	5	220	47		

Table II.44

$CF_3P(NMeNH)_2PCF_3$: Mass Spectrum

m/e	I	m/e	I	m/e	I
13	5	32	34	51	8
14	7	33	7	55	5
15	16	40	5	56	5
16	10	41	10	57	27
17	11	42	26	58	33
18	33	43	84	59	20
27	22	44	55	60	469
28	206	45	367	61	14
29	78	46	469	62	12
30	80	47	17	66	15
31	151	50	7	69	37

m/e	I	m/e	I	m/e	I
71	7	96	6	126	27
73	5	97	11	127	6
74	6	98	6	130	7
75	49	100	6	132	5
76	12	104	37	134	9
77	14	105	9	140	37
78	36	106	49	141	5
79	10	107	33	142	16
80	67	109	5	143	15
81	10	110	12	145	13
82	5	111	16	148	7
83	10	112	5	149	21
84	15	113	15	150	5
85	12	114	10	168	6
86	7	116	5	169	259
90	22	119	5	170	12
91	12	120	18	175	19
92	14	121	14	219	1000
93	21	122	7	220	50
94	9	124	14	233	14
95	28	125	139	288	34

Table II.45

Mixture of Polymers from the Reaction of CF_3PI_2 with $MeNHNH_2$: Mass Spectrum

m/e	I	m/e	I	m/e	I
14	5	45	1000	66	167
15	22	46	657	69	196
16	28	47	41	70	6
17	40	48	15	71	10
18	91	50	28	73	12
26	5	51	32	74	13
28	557	55	10	75	119
29	166	56	9	76	18
30	343	57	32	77	33
31	240	58	40	78	42
32	62	59	29	79	14
33	14	60	600	80	129
39	5	60.5	5	81	17
40	6	61	35	82	8
41	22	62	23	83	13
42	60	63	10	84	7
43	343	64	6	85	23
44	87	65	19	86	5

m/e	I	m/e	I	m/e	I
87	5	110	9	140	55
88	7	111	11	141	9
90	21	113	15	142	6
91	7	114	15	144	11
92	32	115	7	145	49
93	45	116	8	146	12
94	16	118	6	147	26
95	386	119	16	148	5
96	18	120	23	149	12
97	12	121	56	152	5
98	5	122	7	154	17
99	5	124	6	160	9
100	57	125	147	161	7
101	16	126	20	162	36
102	8	127	6	163	14
103	5	128	8	164	58
104	21	129	15	165	5
105	7	130	15	169	116
106	44	131	7	170	7
107	8	132	5	175	39
109	5	134	7	185	7

m/e	I	m/e	I	m/e	I
186	5	214	12	289	21
188	9	219	500	319	19
189	9	220	26	363	5
190	43	235	6	388	5
201	10	239	9	432	2
204	10	287	8	469	1
205	6	288	41	506	2

Table II.46 (Trifluoromethyl)phosphinohydrazines: H^1 NMR Spectra (a)(b)

	IV	V	VI	VII	VIII(c)	IX	X	XI
$-N(H)H$			6.15					
$-N(Me)Me$	7.50	7.50			7.59	7.50		
$-N(H)Me$				6.39				
$-N(H)Me$				7.37				
$-N(H)P$	5.95			5.70	5.92		5.15	5.54
$-N(Me)P$		7.13	6.93			7.15	7.04	7.03

(g) NMR data for (trifluoromethyl)Phosphinohydrazines

Table II.46 continued...

(a) Chemical shifts reported in τ, relative to TMS as internal standard.

(b) Compounds run at 39°C as $CDCl_3$ solutions, unless otherwise noted.

(c) Spectrum measured on chlorobenzene solution.

IV $(CF_3)_2PNHNMe_2$

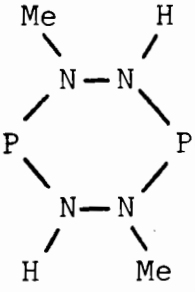
V $(CF_3)_2PNMeNMe_2$; J_{PNCH}, 3.6 cps, J_{FCPNCH}, 0.7 cps.

VI $(CF_3)_2PNMeNH_2$; J_{PNCH}, 8.5 cps.

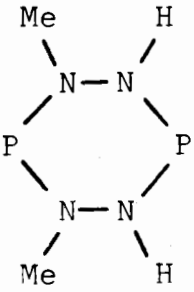
VII $(CF_3)_2PNHNHMe$

VIII $CF_3P(NHNMe_2)_2$, J_{PNH}, 20 cps.

IX $CF_3P(NMeNMe_2)_2$, J_{PNCH}, 7.0 cps, J_{FCPNCH}, 0.7 cps.

X 

J_{PNCH}, 13.0 cps, J_{PNH}, 40.0 cps.

XI 

J_{PNCH}, 14.0 cps, J_{PNH}, 43.0 cps.

Table II.47

(Trifluoromethyl)phosphinohydrazines: F^{19} NMR Spectra[a]

Compound	Chemical Shift. p.p.m. $-P(CF_3)_2$	PCF_3
IV	65.0	
	J_{PCF} 84 cps	
V	61.5	
	J_{PCF} 82 cps	
VI	60.6	
	J_{PCF} 84 cps	
VII	63.8	
	J_{PCF} 80 cps	
VIII		65.4
		J_{PCF} 83 cps
IX		62.7
		J_{PCF} 92 cps
X		64.8
		J_{PCF} 99.5 cps
XI	$P(NMe)_2$ 66.0 ppm	$P(NH)_2$ 64.2 ppm
	J_{PCF} 94 cps	J_{PCF} 85 cps

(a) Chemical shifts reported in ppm relative to $CFCl_3$ as internal standard.

F. Borane Adducts of (trifluoromethyl)-phosphinohydrazines.

1. Experimental Procedure

Reactions between various phosphinohydrazines and BX_3 (X = Me, F, Cl) were performed, both in the presence and in the absence of a solvent. The procedure for reactions using a solvent was similar to that for the preparation of the phosphinohydrazines, except that the reaction vessel consisted of a sealed glass tube. A solvent and the phosphinohydrazine were condensed into a reaction vessel, allowed to mix at room temperature and recooled in liquid nitrogen before the addition of borane. Solutions were allowed to react at room temperature for at least one hour before the separation of solvent and products was effected by fractionation. In early experiments, products were transferred to NMR tubes which were then sealed under vacuum. Later, modified NMR tubes, fitted with B-7 cones, were used to receive products; filled with dry nitrogen and capped, spectra measured on samples prepared in this fashion gave satisfactory results.

Reactions between phosphinohydrazines and BX_3 in the absence of solvent were performed at $-33^{\circ}C$ for one hour, in the manner of the R_2NNR_2 plus BX_3 reactions. Unreacted species were removed before vacuum transfer of products to either vacuum sealed or modified NMR tubes.

2. The Formation of Adducts

(a) Reaction of $(CF_3)_2PNHNMe_2$ with BMe_3 in cyclohexane.

$(CF_3)_2PNHNMe_2$ (0.725 m.moles) was condensed into a reaction vessel with cyclohexane (1.2622 g), warmed to room temperature to allow mixing of the components, and recooled in liquid N_2 before the addition of BMe_3 (1.421 m.moles). After two hours at room temperature, products were fractionated yielding cyclohexane (1.2627 g.) and BMe_3 (0.717 m.moles), determining the stoichiometry as in equation (2-11) .

$$(CF_3)_2PNHNMe_2 + BMe_3 \rightarrow (CF_3)_2PNHNMe_2.BMe_3 \qquad (2\text{-}11)$$

The adduct, $(CF_3)_2PNHNMe_2.BMe_3$ (compound XI) was observed as a volatile white solid easily transferred to an NMR tube. The NMR data is reported in Tables III.6 and III.7.

(b) Reaction of $(CF_3)_2PNHNMe_2$ with BF_3 in cyclohexane

$(CF_3)_2PNHNMe_2$ (2.019 m.moles) was condensed into a reaction tube followed by 2.2926 g. of cyclohexane. The system was warmed to room temperature allowing components to mix, and then recooled in liquid N_2. BF_3 (7.043 m.moles) was condensed into the tube and the system allowed to react at room temperature for one hour. Fractionation yielded cyclohexane (2.2915 g),

BF_3 (5.021 m.moles), and a white crystalline solid (m.p. $42^{\circ}\pm2^{\circ}C$), $(CF_3)_2PNHNMe_2.BF_3$ (1.947 m.moles) (compound XII) indicating the stoichiometry as in equation (2-12).

$$(CF_3)_2PNHNMe_2 + BF_3 \rightarrow (CF_3)_2PNHNMe_2.BF_3 \qquad (2\text{-}12)$$

The volatility of the adduct permitted its vacuum transfer to an NMR tube; for NMR data see Tables III.6 and III.7.

(c) Reaction of $(CF_3)_2PNHNMe_2$ with BCl_3 in chlorobenzene

$(CF_3)_2PNHNMe_2$ (0.623 m.moles) was allowed to react with BCl_3 (1.220 m.moles) in 1.3494 g. of chlorobenzene in the previously described manner. Fractionation yielded chlorobenzene (1.3268 g), BCl_3 (0.593 m.moles) and a volatile white solid. Reaction stoichiometry is consistent with simple adduct formation (equation 2-13)

$$(CF_3)_2PNHNMe_2 + BCl_3 \rightarrow (CF_3)_2PNHNMe_2.BCl_3 \qquad (2\text{-}13).$$

After one week at room temperature, sealed samples of $CDCl_3$ solutions of the adduct (compound XIII) became dark brown, and a white solid precipitated. NMR data of the adduct are found in Tables III.6 and III.7.

(d) Reaction of $CF_3P(NHNMe_2)_2$ with BF_3 in chlorobenzene

$CF_3P(NHNMe_2)_2$ (0.369 m.moles) was allowed to react with BF_3 (1.228 m.moles) in 1.0867 g. of chlorobenzene in the previously described manner. Fractionation yielded chlorobenzene (1.0805 g) and BF_3 (0.445 m.moles) determining the stoichiometry as in equation (2-14).

$$CF_3P(NHNMe_2)_2 + 2BF_3 \rightarrow CF_3P(NHNMe_2)_2.2BF_3 \quad (2\text{-}14)$$

The adduct, $CF_3P(NHNMe_2)_2.2BF_3$ (compound XXI) possessed a very low vapour pressure; at least forty-eight hours were required for the transfer of sufficient material to an NMR tube for spectroscopic analysis. For NMR data see Tables III.6 and III.7.

(e) Reaction of $(CF_3)_2PNMeNMe_2$ with BMe_3

$(CF_3)_2PNMeNMe_2$ (0.587 m.moles), followed by BMe_3 (0.453 m.moles), were condensed into a reaction tube, and the system allowed to equilibrate at $-33^{\circ}C$ for one hour. Products were then allowed to warm to room temperature and condensed into an NMR tube containing TMS and $CFCl_3$ The H^1 and F^{19} NMR spectra (see Tables III.6 and III.7) indicated that a 1:1 adduct $(CF_3)_2PNMeNMe_2.BMe_3$ (compound XIV) had been formed. Peaks arising from uncomplexed $(CF_3)_2PNMeNMe_2$ were also present in the spectrum, consistent with the excess (trifluoromethyl)phosphinohydrazine used in the reaction.

(f) Reaction of $(CF_3)_2PNMeNMe_2$ with BF_3 in toluene

$(CF_3)_2PNMeNMe_2$ (0.40 m.moles) and toluene (1.4453 g), were condensed into a reaction tube, and the system warmed to allow mixing. Following re-cooling in liquid N_2, BF_3 (1.50 m.moles), was added, and the reaction allowed to proceed at room temperature for one hour. Fractionation yielded BF_3 (1.03 m.moles) and toluene (1.4337 g). Quantities of reactants used suggests the formation of the 1:1 adduct (compound XV) as in equation (2-15). A sample was condensed into

$$(CF_3)_2PNMeNMe_2 + BF_3 \rightarrow (CF_3)_2PNMeNMe_2.BF_3 \qquad (2\text{-}15)$$

an NMR tube and sealed. The NMR spectra (Tables III.6 and III.7) were consistent with the given formulation of the adduct.

(g) Reaction of $(CF_3)_2PNMeNMe_2$ with BCl_3

Reactions between $(CF_3)_2PNMeNMe_2$ and BCl_3 gave nonvolatile products, which could not be transferred under vacuum. To avoid exposure of the products to moisture, reactions were carried out in thin walled NMR tubes. In this variation of the reaction procedure, BCl_3 (0.68 m.moles) was condensed into the bottom of an NMR tube. $(CF_3)_2PNMeNMe_2$ (0.47 m.moles) was then condensed into a distinct layer above the BCl_3 and the system

allowed to warm slowly to room temperature. At the melting point of $(CF_3)_2PNMeNMe_2$ (-47.0± 2.0°C), BCl_3 (v.p, -47.8 = 40 mm. (15)) was observed to bubble into and through the phosphinohydrazine. Volatile materials were allowed access to a 200 ml. ballast bulb to prevent a pressure greater than one atmosphere from developing within the system. Gaseous BCl_3 was repeatedly re-condensed into the NMR tube until only solid products remained. Excess BCl_3 was removed, $CFCl_3$ and TMS were added, and the NMR tube sealed. NMR spectra (Tables III.6 and III.7) suggested that $(CF_3)_2PNMeNMe_2.BCl_3$ (compound XVI)had been formed. After three weeks products were observed as a dark brown liquid, immiscible in $CFCl_3$.

(h) Reaction of $(CF_3)_2PNMeNH_2$ with BMe_3

$(CF_3)_2PNMeNH_2$ (0.485 m.moles) followed by BMe_3 (0.494 m.moles) were condensed into a reaction tube and the system held at -33°C for one hour. The product, a volatile colorless liquid at room temperature, was condensed into an NMR tube along with $CDCl_3$, TMS and $CFCl_3$. H^1 and F^{19} spectra (Tables III.6 and III.7) suggested the product to be $(CF_3)_2PNMeNH_2.BMe_3$ (compound XVII). NMR spectra showed the presence of $(CF_3)_2PNHNHMe.BMe_3$ as an impurity (13%).

(i) Reaction of $(CF_3)_2PNMeNH_2$ with BF_3

$(CF_3)_2PNMeNH_2$ (0.573 m.moles) and BF_3 (0.571 m.moles) were allowed to react at -33°C for one hour. Initially a colorless liquid, the product crystallized to a white solid (m.p. ≃ 40°C). H^1 and F^{19} NMR spectra (Tables III.6 and III.7) suggested the product to be $(CF_3)_2$ - $PNMeNH_2.BF_3$ (compound XVIII). F^{19} spectra indicated the presence of $(CF_3)_2PNHNHMe.BF_3$ (17%).

(j) Reaction of $(CF_3)_2PNHNHMe$ with BMe_3

$(CF_3)_2PNHNHMe$ (0.535 m.moles), and BMe_3 (0.529 m.moles) were allowed to react at -33°C for one hour. The product, a colorless solid at room temperature was condensed into an NMR tube along with $CDCl_3$, TMS, and $CFCl_3$. H^1 and F^{19} spectra (Tables III.6 and III.7) suggested the product to be $(CF_3)_2PNHNHMe.BMe_3$. (compound XIX).

(k) Reaction of $(CF_3)_2PNHNHMe$ with BF_3

$(CF_3)_2PNHNHMe$ (1.276 m.moles) was allowed to react with BF_3 (1.270 m.moles) at -33°C for one hour. The colorless crystalline product was transferred in vacuo to an NMR tube along with $CDCl_3$, TMS, and $CFCl_3$. H^1 and F^{19} NMR spectra (Tables III.6 and III.7) suggested the product to be $(CF_3)_2PNHNHMe.BF_3$. (compound XX). Temperature variation of both H^1 and F^{19} spectra was observed.

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CHAPTER III

Results and Discussion

A. Borane Adducts of Methylhydrazines

1. Introduction

In the course of studies of the basicities of a series of alkyl(trifluoromethyl)phosphinohydrazines towards the Lewis acids BX_3 (X = Me, F, Cl) (Section III.D), we were led to investigate the basicities of some alkylhydrazines towards the same Lewis acids. It was observed that the H^1 NMR chemical shifts of the phosphinohydrazines were influenced by adduct formation; the effect of adduct formation is to deshield the protons on the substituted hydrazine. If the deshielding is caused primarily via an inductive withdrawal of electrons, the effect should be strongest for protons nearest the site of adduct formation; hence the site of adduct formation may be inferred by observing the changes in the chemical shifts of a series of adducts in which the Lewis acidity of BX_3 varies. As a test of this hypothesis, to determine the approximate magnitude of this effect, and to locate the site of borane addition to unsymmetrically substituted methylhydrazines, H^1 and F^{19} NMR spectra were measured on series of methylhydrazine.BX_3 adducts.

The use of NMR spectroscopy in the study of adduct formation is well established (1 - 10). The variation

of the proton chemical shifts of a series of adducts HD→A (D = donor, A = acceptor) where A varies, will depend mainly on the variation of the electron density distribution around the proton H, as long as the stereochemistry of the adducts remains constant over the series. The electron density distribution in turn is influenced by the acceptor power of A. In this way, the proton chemical shift data for a series of adducts, $HD \rightarrow BX_3$, where D is a common Lewis base, have been used as an indication of relative Lewis acid strengths for a series of BX_3 species; thus $BI_3 > BBr_3 > BCl_3 > BF_3 \sim BH_3 > BMe_3$ (1 - 8). Results for relative base strengths have been determined in D→AH systems, where D varies and A is a common Lewis acid. In this case, an increase in the basicity of D causes an increase in the shielding at the proton on A (1). F^{19} chemical shifts of BF_3 adducts have similarly been correlated with the base strengths of various donor molecules (1). Systems of the type HDr + HDx/A (HDr = reference base, HDx = series of unknown bases, A = common acceptor molecule), have been used to determine relative Lewis basicity. In the absence of exchange, the possible species HDr, HDx, HDr→A, and HDx→A are distinguishable in the H^1 NMR spectra. The relative base strengths are readily established from the relative concentrations of the complexed species, as determined by integration over the respective H^1 NMR signals (9, 10).

The problems encountered in determining the site of adduct formation in the alkylhydrazine.BX_3 systems by similar methods include, (a) the detection by H^1 NMR of the appropriate species (ie: the 1:1 addition compound $RR^1NNR^{11}R^{111}.BX_3$ rather than a 1:2 adduct, or other products of reaction), and (b) the measurement of consistent values for the H^1 NMR chemical shifts.

The hydrazines have potential dibasic character, as is shown towards sterically small reference acids H^+ (11), "BH_3" (12), and BF_3 (13). Under certain conditions the 1:1 adduct $H_2NNH_2.BF_3$ can be isolated (13). In the case of unsymmetrically substituted methylhydrazines, the two nitrogens are expected to show differing basicities, with the more highly substituted nitrogen being the more basic due to the inductive effect of the methyl groups (14). Thus, quaternization of alkylhydrazines, in the absence of large steric effects, occurs at the more highly substituted nitrogen atom (14). The reaction between diphenylphosphoric acid and 1,1-dimethylhydrazine, yields $Me_2\overset{+}{N}NH_3$ $\overset{-}{O}(O)P(OC_6H_5)_2$, the mode of quaternization reflecting the steric influence of the bulky anion (15). Infrared data for 1,1-dimethylhydrazine hydrochloride, however, are consistent with the formulation, $Me_2\overset{+}{N}HNH_2$ Cl^- (16), and empirical calculations of the pKa values for the alkylhydrazines in aqueous solution are consistent with

protonation at the more highly substituted nitrogen (17).

The preparation of hydrazineborane addition compounds have generally been undertaken only as a possible route to hydrazinoboranes; the pyrolysis of $H_2NNH_2.BH_3$ (p.166 of ref. 18) and $H_3B.Me_2NNH_2.BH_3$ (19), give $H_2BNHNHBH_2$ and $H_3B.Me_2NNHBH_2$ respectively. Similarly, trialkylborane adducts of methylhydrazine, 1,1-dimethylhydrazine, and phenylhydrazine are pyrolysed at 150-200°C to give hydrazinoalkylboranes, hydrogen and alkanes (20). The 1:1 adduct, $Me_2NNH_2.BH_3$ has been studied however; the site of addition has been inferred from B^{11} NMR data to be at the more highly alkylated nitrogen (p.217 of ref.21). The interaction of BX_3 with R_2NNRH may either take the form of an elimination reaction (equation 3-1), or adduct formation (equation 3-2). At room temperature,

$$BX_3 + 2R_2NNRH \rightarrow R_2NNRBX_2 + R_2NNRH.HX \qquad (3\text{-}1)$$

$$BX_3 + R_2NNRH \rightarrow R_2NNRH.BX_3 \qquad (3\text{-}2)$$

reaction 3-2 may be favored for the Lewis acids BMe_3 and BF_3: the aminolysis of the B-F bond does not readily occur at room temperature, and only under special conditions can B-fluoroaminoboranes be prepared directly (22). The alkylboranes react with hydrazine to give hydrazinoalkylboranes only at elevated temperatures (20). On the other hand, BCl_3 reacts readily with H_2NNH_2 (40), and the hydrazinolysis of the B-Cl bond has been found

effective in the preparation of some hydrazinoboranes (equation 3-3) (p.167 of ref.18).

$$R_2BCl + 2Me_2NNH_2 \rightarrow R_2BNHNMe_2 + Me_2NNH_2.HCl \qquad (3\text{-}3)$$

2. Infrared Data

As a check on the formulation of the species under observation, infrared measurements were made on $MeNHNH_2$, Me_2NNH_2, Me_2NNHMe and their BX_3 (X = Me, F, Cl) adducts (Tables II.6 to II.17).

The B-N dative bond stretching frequency has been reported to appear in the 650-800 cm^{-1} region. Typical assigned values for $\nu(N\rightarrow B)$ are $H_3N.BH_3$, 787 cm^{-1}; $Me_3N.BH_3$, 667 cm^{-1}; $Me_3N.BF_3$, 697 cm^{-1}; $Me_3N.BCl_3$, 748 cm^{-1} (p.59 of ref.23). B-N stretching frequencies for the aminoboranes are reported to appear in the 1350-1530 cm^{-1} region, with typical assigned values for Me_2BNMe_2 and Cl_2BNMe_2 at 1525 cm^{-1} and 1528 cm^{-1} respectively (p.71 of ref.24). Associated with reaction 3-1 is the production of HX which could be trapped either as a hydrazine hydrohalide, or a hydrazinoborane hydrohalide (18). The infrared spectra of hydrazinium salts show bands in the 2500 cm^{-1} region, which have been assigned, by comparison with amine salts, as $R_3\overset{+}{N}H$ or $R_2\overset{+}{N}H_2$ amino proton stretching frequencies (16, 25). Table III.1 lists those bands found in these three regions for the hydrazineborane systems investigated in this study.

Table III.1 Selected Infrared Stretching Frequency Ranges for the Hydrazineborane Systems

Compound	ν N→B 650∿800 cm^{-1}	ν N-B 1350∿1530 cm^{-1}	ν R $\overset{+}{N}$-H 2100∿2700cm^{-1}
$MeNHNH_2$	755, 768, 775	1448,1462,1478	-
$MeNHNH_2.BMe_3$	671	1408,1455	-
$MeNHNH_2.BF_3$	709,755,796	1460	2475,2560,2675
"$MeNHNH_2.BCl_3$"	-	1400,1455,1480	2485
Me_2NNH_2	795,803	1437,1448,1457 1475	-
$Me_2NNH_2.BMe_3$	675,807	1353,1396,1425 1445,1462,1475	-
$Me_2NNH_2.BF_3$	678,760	1390,1436,1468	-
$Me_2NNH_2.BCl_3$	665	1420	2500
Me_2NNHMe	738,750	1466,1483	-
$Me_2NNHMe.BMe_3$	669,723	1393,1405,1469 1488	-
$Me_2NNHMe.BF_3$	614,672,682 769	1390,1440,1476 1510	-
$Me_2NNHMe.BCl_3$	660,685,755, 801	1400,1460	2445,2625

All the compounds listed have bands in the B-N dative bond stretching frequency range, except for the "$MeNHNH_2.BCl_3$" system. Bands in the B-N σ bond stretching frequency range are found in the free hydrazine as well as in the complexed species; the assignment of these bands for the complexed species have not been attempted since it is difficult to discriminate between bands arising from a shift in the frequency of a normal mode of the hydrazine moiety, and bands arising from a B-N dative or σ bond. On the other hand, bands appearing in the 2500 cm^{-1} range may correspond to the $>\overset{+}{N}-H$ stretching frequency of a hydrazinium salt. The complexes showing such bands include all of the BCl_3 complexes, as well as $MeNHNH_2.BF_3$. Thus, hydrazinolysis of the B-Cl bond may occur, at least to some extent, with Me_2NNH_2 and Me_2NNHMe; the infrared spectrum of products from the reaction of $MeNHNH_2$ with BCl_3 suggests that the reaction to give (methyl)hydrazinoboranes takes precedence over adduct formation. Thus, for the study by NMR on the site of borane addition to methylhydrazines, only the $Me_2NNH_2.BX_3$ and $Me_2NNHMe.BX_3$ systems were used.

3. NMR Correlations and the Site of Borane Addition to Me_2NNH_2 and Me_2NNHMe

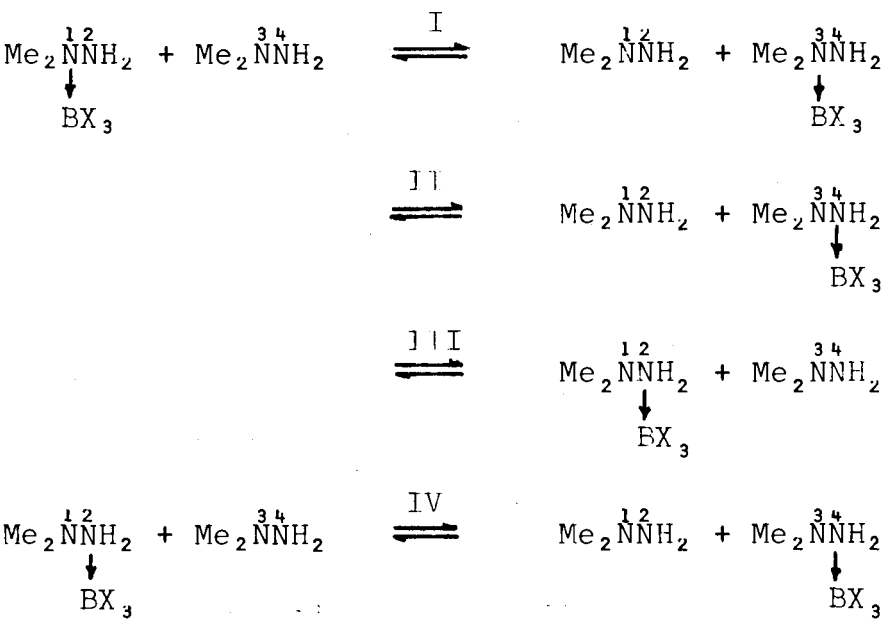
The proton chemical shift depends on a number of factors; (a) bulk diamagnetic susceptibility effects, (b) neighbour anisotropic shielding, (c) intramolecular electric field effects, (d) intermolecular interactions,

and (e) the diamagnetic shielding caused by the electron cloud about the nucleus (p.666 of ref.31). Tetramethylsilane and $CFCl_3$ were used as internal reference compounds to avoid the necessity for bulk diamagnetic susceptibility corrections. Neighbour anisotropic shielding, which may arise from neighbouring double bonds, and intramolecular electric field effects, which arise if the molecule under observation has a permanent dipole moment, have been assumed to be constant within each series of adducts studied.

The major intermolecular interactions, other than chemical reaction, which may influence the chemical shift are solvent-solute, and solute-solute interactions. Both give rise to solvent, concentration and temperature effects. Chemical exchange effects also influence the chemical shift; if exchange is very fast, the observed chemical shift will be at a weighted average of the chemical shifts for the complexed and uncomplexed species.

Differential effects on the chemical shifts from solvent, concentration, and temperature effects were minimized, by observing the spectra of each series of adducts, in the same solvent, at the same concentration, and at a temperature at which no exchange was observed to occur. The possible modes of chemical exchange in the hydrazine-borane systems are represented in Figure III.1, using $Me_2NNH_2.BX_3$ as an example.

Figure III.1 Chemical Exchange in Hydrazineborane Systems



To observe whether or not chemical exchange was occurring in the $Me_2NNH_2.BX_3$ and $Me_2NNHMe.BX_3$ systems, spectra were measured on the adducts dissolved in a solution of solvent and excess alkylhydrazine. For the {$Me_2NNHMe.BX_3$ plus Me_2NNHMe}system at +10°C, the spectra for X=Me, F, and Cl, showed peaks corresponding to both complexed and uncomplexed species. For the {$Me_2NNH_2.BX_3$ plus Me_2NNH_2} system at +10°C (X = Me), one peak was observed for NMe_2 and one for NH_2 indicating rapid exchange. At -45°C however, two NMe_2 signals were observed corresponding to the complexed and uncomplexed species. The coalescence temperature was observed to be -25°C indicating an exchange rate (26) faster than 25 sec^{-1} at room temp-

erature. The $BF_3$and BCl_3 complexes of Me_2NNH_2 showed no exchange at +35°C. For comparison of chemical shifts, spectra were run at -45°C, except for $Me_2NNH_2.BCl_3$ which, being insoluble in either $CDCl_3$ or CH_2Cl_2, was run in DMSO (d^6) at +35°C.

All other factors influencing the chemical shifts being small, or at least fairly constant within each hydrazineborane system, the chemical shift changes within each series can be said to be a qualitative measure of the changes in the electron cloud density at the protons on the hydrazine, as influenced by the changes in the relative acceptor powers of the BX_3 molecules. The relative acceptor powers of BX_3 may be assumed to be in the same ratio as the standard heats of formation of their adducts; thus ΔHf ($py.BMe_3$) = -21.4 Kcal/mole; ΔHf ($py.BF_3$) = -32.9 Kcal/mole; and ΔHf ($py.BCl_3$) = -46.0 Kcal/mole; py = pyridine (27, p.110). Hence relative acid strengths are in the ratio $BMe_3:BF_3:BCl_3$ = 1:1.54:2.15. A plot of the NMe and NH chemical shifts against relative acid strengths of BX_3 should give a straight line. Miller and Onyszchuck found a direct correlation between the heats of formation of $MeCN.BX_3$ (X=F, Cl, Br), and the MeCN H^1 chemical shifts (7). The chemical shift trends of the NMe and NH protons for the BX_3 adducts of Me_2NNH_2 and MeNNHMe, given in Table II.3 , are shown graphically in Figures III.2 and III.3. Chemical shift data for the amine series

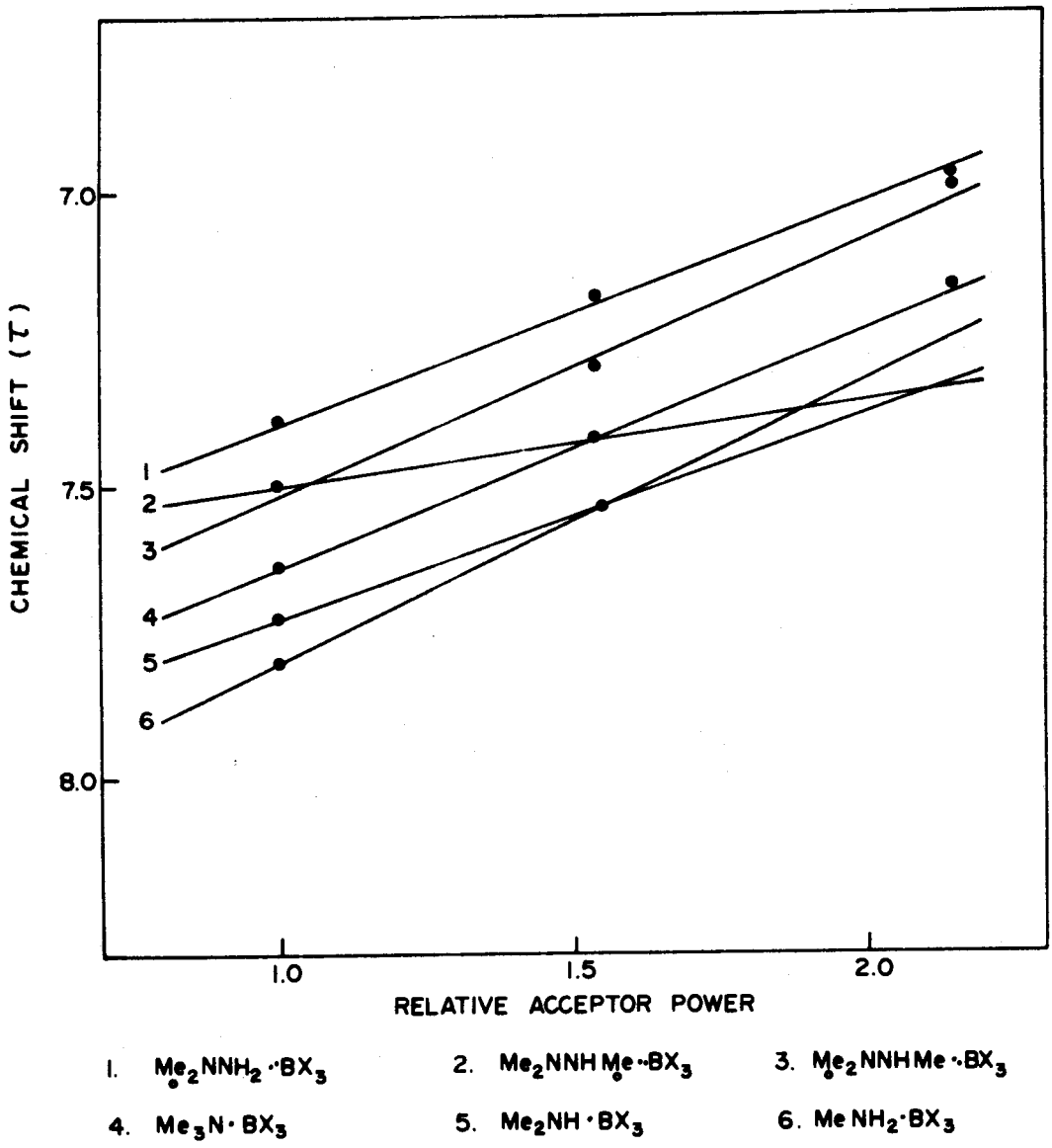


Figure III.2 NMe Chemical Shift Trends for $Me_2NNHR.BX_3$ Systems

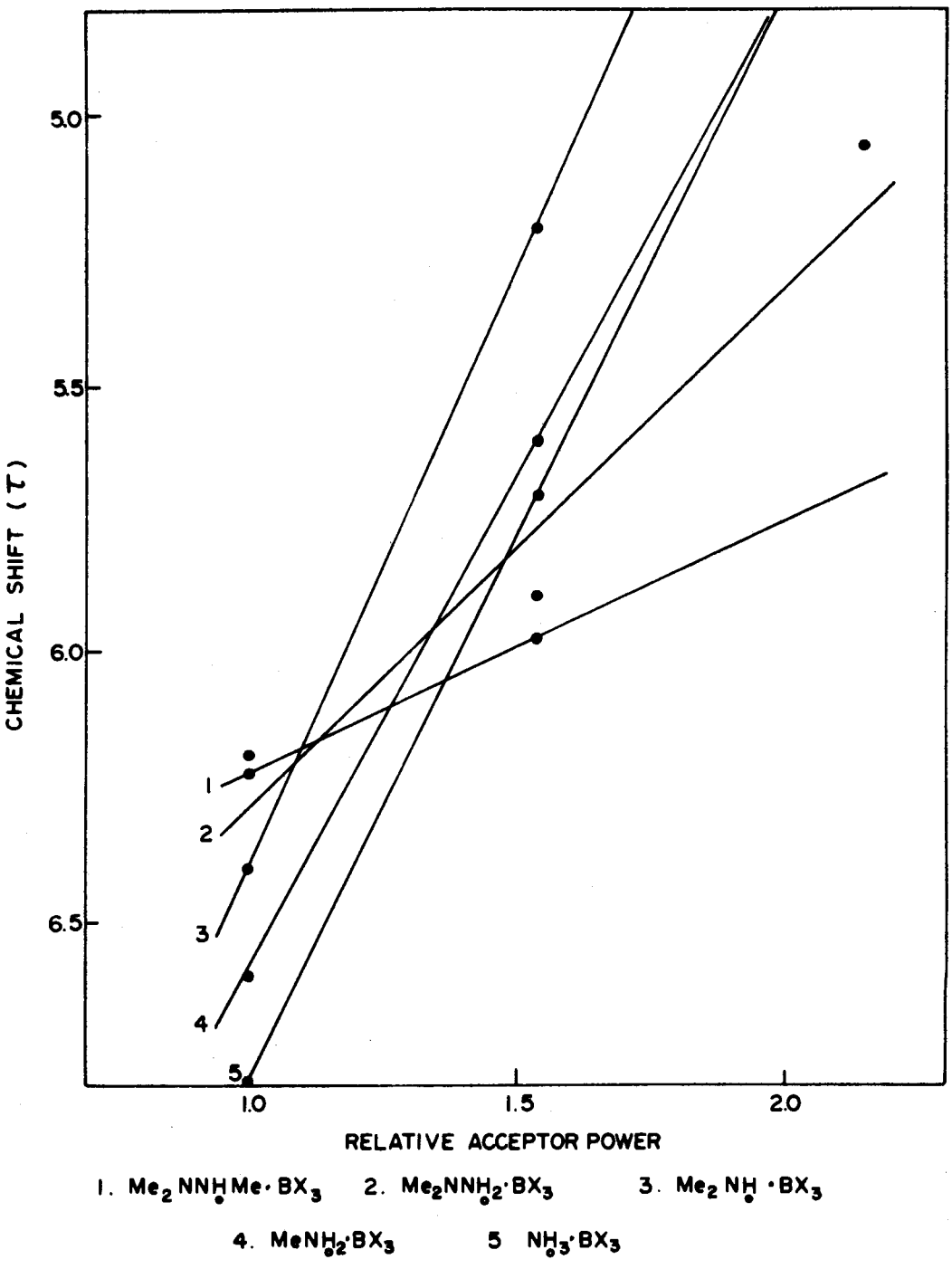


Figure III.3 NH Chemical Shift Trends for $Me_2NNHR.BX_3$ Systems

$Me_nNH_{(3-n)}.BX_3$ (n=0-3; x=Me, F, Cl) were obtained from the literature (1) (Table III.3), and are included on Figures III.2 and III.3 for comparison.

To distinguish the more basic of the two nitrogen atoms, the expected sensitivity order is, adjacent protons > protons remote by one bond > protons remote by two bonds. The slopes for the curves, being qualitative measures of sensitivity toward deshielding effects, are collected in Table III.2. The slope value (arbitrary units, τ/relative acid strength x 10^2) for adjacent N-H protons in N-H, is in the range 185-225; for H-C-N, the range is 35-45; for H-C-N-N, the much smaller value, 15 is indicated. Comparison of N-C-H and N-N-H systems indicate that the deshielding effect is about the same in each case. Thus, for trimethylhydrazine, and for 1,1-dimethylhydrazine, adduct formation occurs at the more substituted nitrogen atom, as shown in Figure III.4.

Figure III.4

Site of adduct formation in $Me_2NNH_2.BX_3$(a) and $Me_2NNHMe.BX_3$(b)

Me_2NNH_2
↓
BX_3

(a)

Me_2NNHMe
↓
BX_3

(b)

Table III - 2

Slope values (arbitrary units, τ/relative acid strength, x 10^2, from Figures III-2 and III-3

	Me_2N-	MeN	N-H
Me_2NNHMe	43	15	46
Me_2NNH_2	38	-	97
Me_3N	41	-	-
Me_2NH	35	-	224
$MeNH_2$	-	48	186
NH_3	-	-	205

Table III - 3

Chemical shift data[(a)] for $Me_nNH_{(3-n)}.BX_3$ adducts

	NMe	NH
$Me_3N.BMe_3$	7.64	-
$Me_3N.BF_3$	7.42	-
$Me_2NH.BMe_3$	7.73	6.4
$Me_2NH.BF_3$	7.54	5.2
$MeNH_2.BMe_3$	7.8	6.6
$MeNH_2.BF_3$	7.54	5.6
$NH_3.BMe_3$	-	6.8
$NH_3.BF_3$	-	5.7

(a) Compiled, relative to tetramethylsilane with τ = 10.0, from the report of C.W. Heitsch (1).

4. Reactions of $MeNHNH_2$ and Me_2NNMe_2 with BX_3

The data for compounds obtained from reactions of $MeNHNH_2$ and Me_2NNMe_2 with BX_3, are not consistent with simple adduct formation throughout the series X = Me, F, Cl. Me_2NNMe_2 does not form an adduct with BMe_3 at room temperature. Equimolar amounts of BMe_3 and Me_2NNMe_2 were allowed to react at -33°C for one hour, after which time fractionation at room temperature yielded the starting materials. Whereas Me_2NNMe_2 reacts with B_2H_6 to give $Me_2NNMe_2.2BH_3$, and with MeI to give $Me_2\overset{+}{N}\overset{+}{N}Me_3\ I^-$ at -16°C, $Me_2NNMe_2.BMe_3$ is completely dissociated (28); molecular models of the adduct indicate large steric interactions to be present. With BCl_3 the reaction is quite exothermic, giving a yellow, highly viscous oil, showing a single H^1 NMR absorption band (7.18 τ). With BF_3, an unstable adduct, a colorless liquid at room temperature, is formed. The H^1 NMR spectrum consists of a single band, (7.62 τ), while the F^{19} NMR spectrum is a 1:1:1:1 quartet (δ midpoint 151.1 ppm; J_{BF}, 15.8 cps). Absorption bands due to decomposition products appear rapidly however; a 1:1:1:1 quartet (149.2 ppm; J_{BF}, 1.2 cps) is indicative of BF_4^- (δ midpoint 149.8 ppm; J_{BF}, 1.10 cps) (29). A third broad and unresolved peak (147.3 ppm) may correspond to a R_2NBF_2 system. When equimolar amounts of $MeNHNH_2$ and BMe_3 are allowed to react, the 1:1 adduct

$MeNHNH_2.BMe_3$ is obtained. The infrared spectrum (Table II.7) and the H^1 NMR spectrum (Figure III.5, spectra (b) and (d); NH, 6.03 τ; NMe, 7.41 τ; BMe_3, 10.35 τ)are consistent with adduct formation (cf. uncomplexed BMe_3, 9.23 τ (100)). At -40°C (Spectrum (c), Figure III.5), the NMe and NH peaks are split into doublets; the ratio of NMe:NH = 3:2 (coalescence temperature ∿ -35°C). Splitting of this nature may arise from conformational isomers, arising from restricted rotation about the N-N bond, or from separate signals resulting from an equimolar mixture of two isomers (a) and (b). The integrated ratios of the

(a) $MeNHNH_2 \rightarrow BMe_3$ (b) $MeNHNH_2 \rightarrow BMe_3$

NMe and NH signals, however, suggest that in this case, the splitting may arise from spin-spin coupling to the MeN-H amino proton (J_{HNNH}, 4.5 cps; J_{HCNH}, 5.8 cps). The general case of monosubstituted hydrazines give H^1 NMR spectra, in which the NH_2 and RNH amino protons appear as a single sharp line (30), indicating that rapid exchange is occurring. If exchange becomes slow, spin-spin coupling may be observed (p.544 of ref. 31). The MeNH amino proton was not observed, presumably because the theoretical 12 line spectrum (Figure III.6) is lost in the background

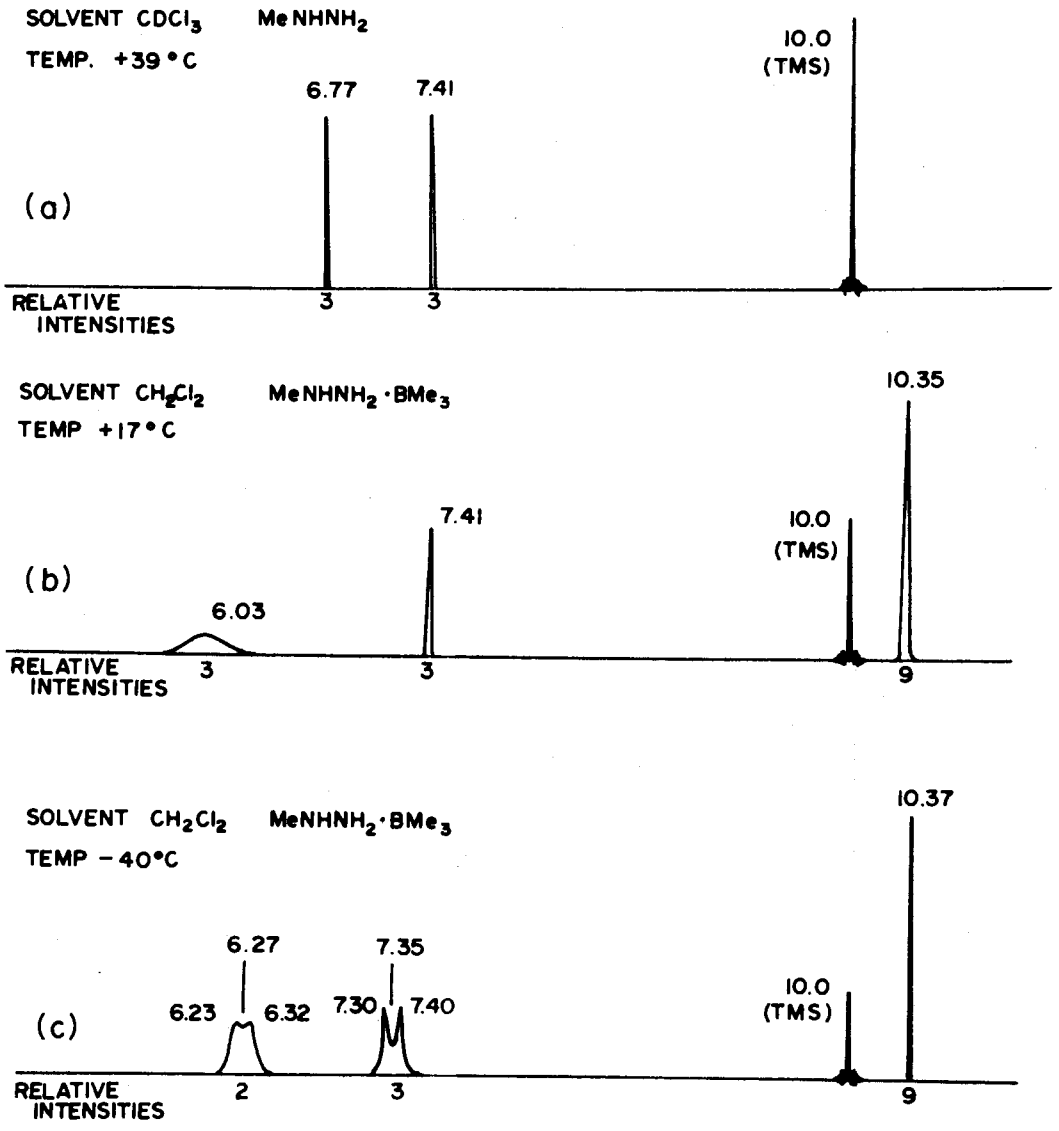


Figure III.5 H^1 NMR Spectra for $MeNHNH_2.BMe_3$

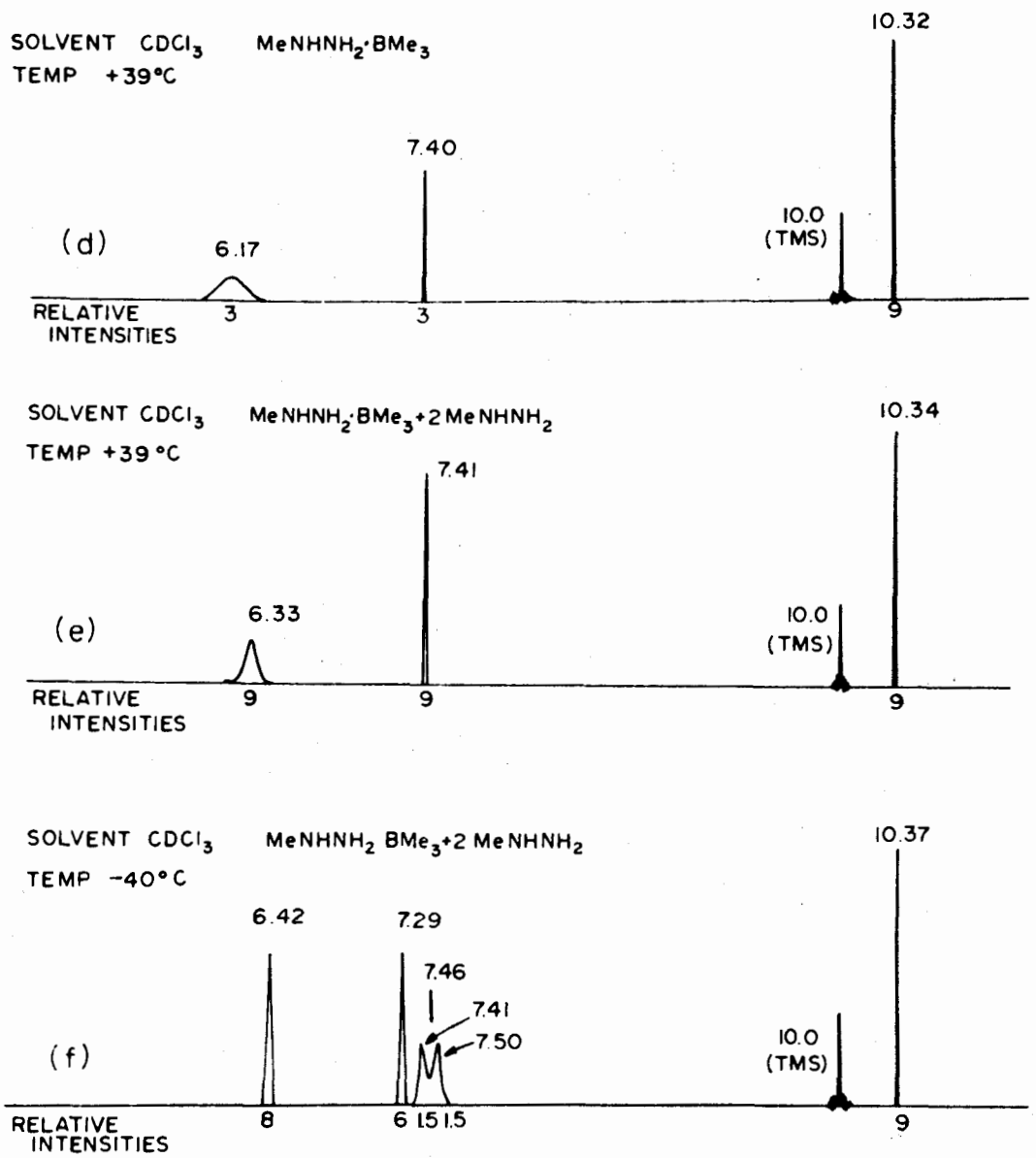
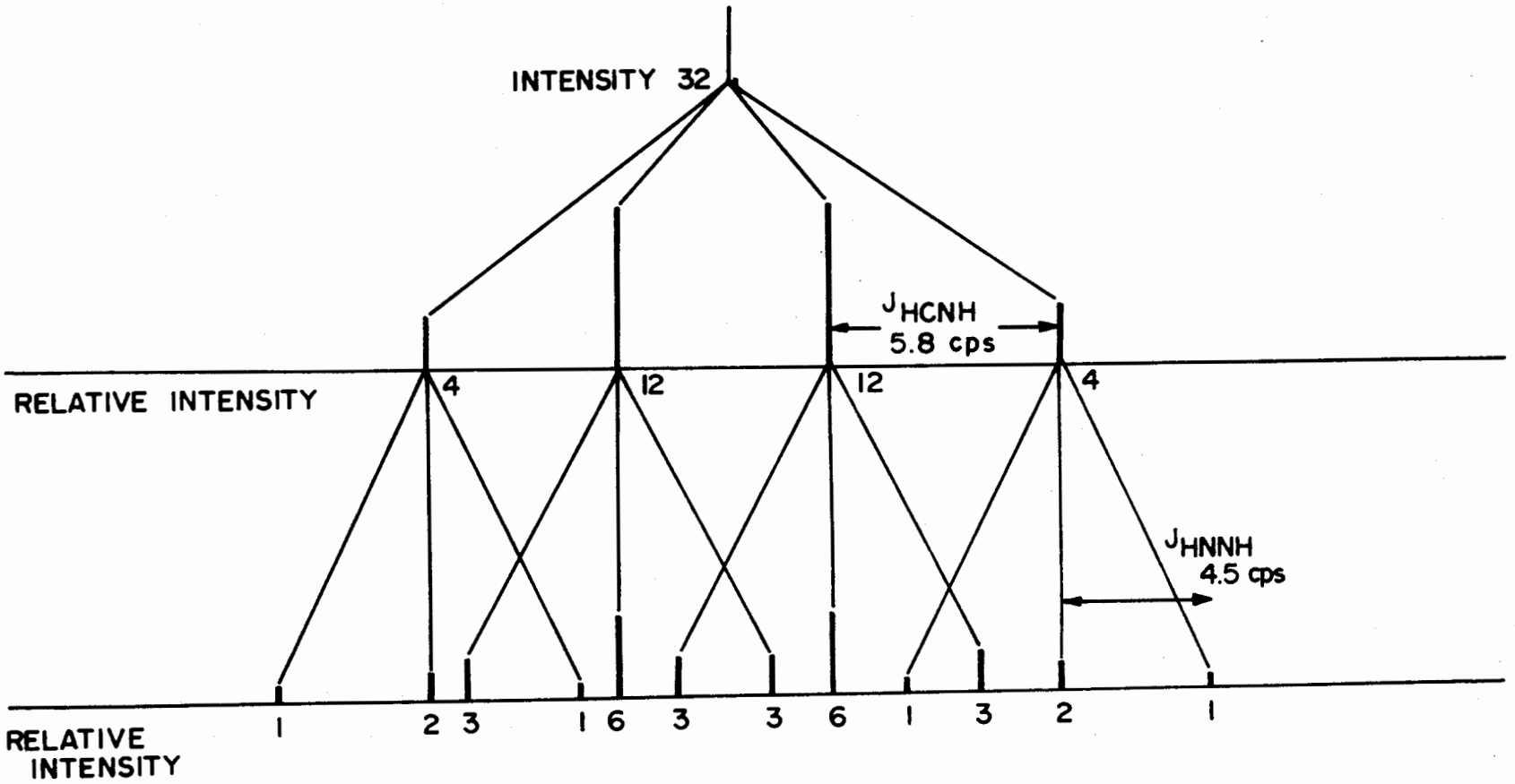

SOLVENT CDCl3
MeNHNH2·BMe3
TEMP +39°C
10.32
7.40
(d)
6.17
10.0
(TMS)
RELATIVE INTENSITIES
3
3
9
SOLVENT CDCl3
MeNHNH2·BMe3+2 MeNHNH2
TEMP +39 °C
10.34
7.41
(e)
6.33
10.0
(TMS)
RELATIVE INTENSITIES
9
9
9
SOLVENT CDCl3
MeNHNH2 BMe3+2 MeNHNH2
TEMP −40°C
10.37
6.42
7.29
7.46
7.41
7.50
(f)
10.0
(TMS)
RELATIVE INTENSITIES
8
6 1.5 1.5
9

Figure III.5



THEORETICAL SPECTRUM FOR THE MeNH AMINO PROTON IN $MeNHNH_2 \cdot BMe_3$

Figure III.6

due to quadripolar relaxation of the nitrogen to which the proton is attached.

When excess $MeNHNH_2$ is added to a solution of $MeNHNH_2.BMe_3$, the H^1 NMR signals for the complexed and uncomplexed species are indistinguishable (spectrum (e), Figure III.5). Thus, rapid intermolecular exchange of BMe_3 is indicated. At -40^oC (spectrum (f), Figure III.5) the signals corresponding to NMe (complexed) and NMe (uncomplexed) are resolved, while the signal corresponding to the amino protons is present as a single line. Intermolecular exchange between the NH_2 protons of $Me_3B.MeNHNH_2$, and all three amino protons of $MeNHNH_2$ is indicated. This tends to support the conclusion that the splitting arises from spin-spin coupling, rather than from the presence of equimolar quantities of isomers (a) and (b); if the NH_2 protons of isomer (b) are exchangeable, then the MeNH amino proton of isomer (a) should also be exchangeable. The integrated ratios of the signals in spectrum (f)(Table III.5) suggests that the latter exchange does not occur.

An interesting observation is that the NMe (complexed) signal appears upfield from the NMe (uncomplexed) signal, suggesting that for $MeNHNH_2.BMe_3$, adduct formation causes shielding rather than deshielding of the NMe protons.

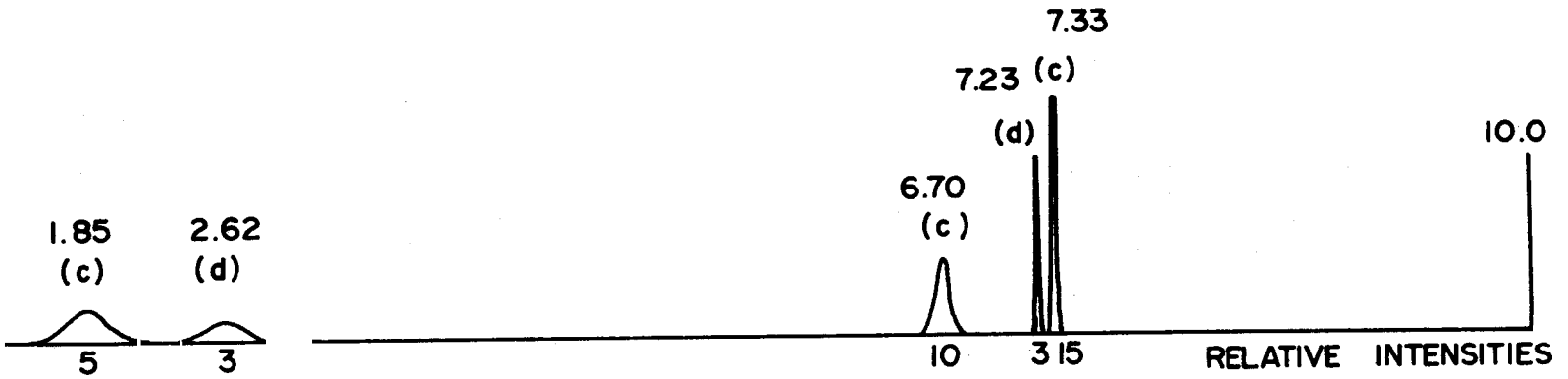
The interaction of BF_3 with $MeNHNH_2$ gives a white crystalline solid which is insoluble in $CDCl_3$ and CH_2Cl_2. The infrared spectrum (Table II.8) of the product mixture

contains bands in the 2500 cm^{-1} range, suggesting a hydrazinium salt to be present. H^1 and F^{19} NMR spectra, measured on the volatile products, dissolved in DMSO-d^6, indicate that two isomers are formed (Figure III.7)

(c) $MeNHNH_2 \downarrow BF_3$ (d) $MeNHNH_2 \downarrow BF_3$

Figure III.7 Isomeric Products from the Reaction of $MeNHNH_2$ with BF_3

The F^{19} spectrum consists of three absorptions. A 1:1:1:1 quartet (149.3 ppm, J_{BF}, 1.0 cps), present in a small amount, is indicative of BF_4^-. The other two are assigned as arising from the isomers (c) and (d) ($F_3B.MeNHNH_2$; 150.2 ppm, J_{BF}, 15.5 cps: $MeNHNH_2.BF_3$; 149.3 ppm, J_{BF}, 17.0 cps). The higher field F^{19} shift for isomer (c) is in accord with a more basic NMe nitrogen. The larger J_{BF} coupling constant for isomer (d) may reflect steric factors imposed by the symmetry at the nitrogen to which the boron is coordinated (cf. $Me_3N.BF_3$; J_{BF}, 13.8 cps: $H_3N.BF_3$; J_{BF}, 13.8 cps: $Me_2NH.BF_3$; J_{BF}, 15.5 cps: $MeNH_2.BF_3$; J_{BF}, 15.7 cps (1)). The relative concentrations of (c) to (d) is approximately 5:1, as suggested by integration over the respective signals. The H^1 NMR spectrum is consistent with the presence of two isomers (Figure III.8). Two signals at 7.33 τ and 7.23 τ, in a



H^1 NMR SPECTRUM OF $F_3BNH(Me)\overset{(c)}{NH_2}$ + $MeNHNH_2 \cdot \overset{(d)}{BF_3}$

Figure III.8

5:1 integrated ratio, correspond to the NMe signals for isomers (c) and (d) respectively. The signal for the NMe protons of isomer (c) is observed as a poorly resolved 1:1:1:1 quartet, indicating coupling to the spin 3/2 B^{11} nucleus (J_{BNCH}, ~1.5 cps) (cf. $Me_3N.BF_3$; J_{BNCH}, 1.54 cps: $Me_2NH.BF_3$; J_{BNCH}, 1.79 cps: $MeNH_2.BF_3$; J_{BNCH}, 2.05 cps (1)). The three broad NH signals are assigned on the basis of their integrated intensities ($F_3BNHMeNH_2$; (NH_2), 6.70 τ, (NH), 1.85 τ; $MeNHNH_2.BF_3$; (exchanging NH), 2.62 τ). Addition of excess $MeNHNH_2$ caused the coalescence of the NMe signals (7.43 τ) and the NH signals (4.88 τ) indicating intermolecular exchange at +39°C to be fast. Low temperature studies were restricted by the nature of the solvent (DMSO, m.p., 18.45°C (32)).

The reaction between $MeNHNH_2$ and BCl_3 was observed to occur quite violently below -45°C, leading to the production of a white glassy solid, and HCl. The quantity of BCl_3 recovered suggests the reaction stoichiometry as in equation 3-4. The infrared spectrum of the solid showed

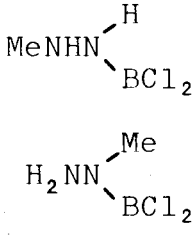
$$2MeNHNH_2 + BCl_3 \rightarrow MeNHNHBCl_2 + MeNHNH_2.HCl \qquad (3\text{-}4)$$

bands in the 2500 cm^{-1} region, indicative of a hydrazinium salt, and the absence of bands in the N→B dative bond region, suggests that if an adduct is formed, its lifetime is short. The presence of excess HCl suggests reaction

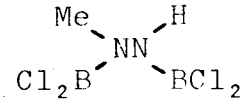
3-4 to be only one of several possible reactions. Boron trichloride, reacting at both nitrogens, could give rise to a large number of isomers, some possibilities of which are shown in Figure III.9, as well as polymeric materials.

Figure III.9 Possible Products from $MeNHNH_2 + BCl_3$

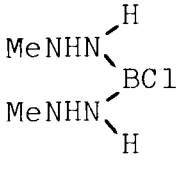
(a) monohydrazinoboranes



(b) bis(dichloroboron)-hydrazines



(c) (bis)hydrazinoboranes



(d) (tris)hydrazino-boranes

$(MeNHNH)_3B$ etc.

Interpreting the $BR^1NNR^{11}R^{111}.BMe_3$ system as a D→AH system, the relative order of base strengths is seen to be, $MeNHNH_2 > Me_2NNH_2 > Me_2NNHMe >> Me_2NNMe_2$, in agreement with Hinman's series (33). If the F^{19} chemical shifts for the BF_3 adducts are interpreted in a similar fashion, the base sequence suggested, is $Me_2NNH_2 > Me_2NNHMe$

> $MeNHNH_2$ > Me_2NNMe_2. $MeNHNH_2$ has changed position in the sequence. The $MeNHNH_2.BF_3$ system however is anomalous, since it forms two types of adducts, and since the correlation between changes in chemical shifts, and Lewis acidity should depend on the maintenence of one general stereochemistry throughout the series, D→AF, the $MeNHNH_2.BF_3$ system may be expected to show deviations from Hinman's series.

B. Reactions of $MeNHNH_2$ and Me_2NNH_2 with Polyhalomethanes

1. Reaction of $MeNHNH_2$ with CCl_4

The oxidation of hydrazine by a large variety of oxidizing agents has received considerable attention (34), while the oxidation of the methylhydrazines has been studied less extensively (35, 36). Carbon tetrachloride is not commonly regarded as being a good oxidizing agent, but is observed to oxidize hydrazine (37, 38) to give N_2, NH_3, $CHCl_3$ and traces of CH_2Cl_2. Diimide (HN=NH) has been postulated as the intermediate in a free radical reaction leading to the production of N_2 (38) (Equations 3-5 to 3-8). Huyser and Wang (39) suggest that the oxidation of phenylhydrazine by carbon tetrachloride occurs by a similar

$$\cdot CCl_3 + H_2NNH_2 \rightarrow CHCl_3 + H_2\dot{N}NH \qquad (3\text{-}5)$$

$$H_2\dot{N}NH + CCl_4 \rightarrow \cdot CCl_3 + H_2NNHCl \qquad (3\text{-}6)$$

$$H_2NNHCl + H_2NNH_2 \rightarrow H_2NNH_2.HCl + HN{=}NH \qquad (3\text{-}7)$$

$$2HN{=}NH \rightarrow N_2 + H_2NNH_2 \qquad (3\text{-}8)$$

mechanism to give C_6H_6, C_6H_5Cl, N_2, and $C_6H_5NNH_2.HCl$ according to equations 3-9 to 3-12. Our studies of

reactions between $MeNHNH_2$ and CCl_4 indicate that a similar reaction scheme is followed, giving rise to CH_4, N_2, NH_2, $MeNH_2$ $CHCl_2$, CH_2Cl_2 and $MeNHNH_2.HCl$.

$$\cdot CCl_3 + C_6H_5NHNH_2 \rightarrow CHCl_3 + C_6H_5\dot{N}NH_2 \qquad (3\text{-}9)$$

$$C_6H_5\dot{N}NH_2 + CCl_4 \rightarrow HCl + C_6H_5N{=}NH + .CCl_3 \qquad (3\text{-}10)$$

$$HCl \xrightarrow{C_6H_5NHNH_2} C_6H_5NHNH_2.HCl$$

$$C_6H_5N{=}NH + CCl_4 \rightarrow C_6H_5Cl + CHCl_3 + N_2 \qquad (3\text{-}11)$$

$$C_6H_5N{=}NH \rightarrow C_6H_6 + N_2 \qquad (3\text{-}12)$$

In various experiments, CCl_4 and $MeNHNH_2$ were mixed to determine the reaction products; although Et_3N was used as the hydrogen halide acceptor, NMR spectra of the salts produced suggested them to be an equimolar mixture of $Et_3N.HCl$ and $MeNHNH_2.2HCl$. This is surprising in view of the difference in the pK values of the free bases in aqueous solution: pKa Et_3N, 11.01 (32, p.D117), pKa $MeNHNH_2$, 7.87 (33). The reaction between CCl_4 and $MeNHNH_2$ was observed to be surface dependent; mixtures of $MeNHNH_2$ and CCl_4 in clean flasks showed evolution of gas only at points of imperfection in the glass surface, and the addition of crushed pyrex glass to the reaction mixture dramatically increased gas evolution.

In a preliminary experiment, CCl_4 (32.57 m.moles) and $MeNHNH_2$ (29.44 m.moles) in Et_3N (54.95 m.moles) were allowed to react in a closed system for one week. The products found were CH_4 (4.89 m.moles), N_2 (8.16 m.moles), NH_3 (3.16 m.moles), $CHCl_3$ (8.0 m.moles), $Et_3N.HCl$ (3.9 m.moles) and $MeNHNH_2.2HCl$ (3.9 m.moles). CH_4 and N_2 were removed and measured by means of a Sprengel pump; the molar ratio of CH_4 to N_2 was calculated from the observed mean molecular weight of the gas (M_{obs}, 23.5) to be 3:5. This ratio varied for different reactions, but the quantity of N_2 always exceeded that of CH_4. Mass spectra of the gas mixture gave peaks at m/e = 16 (m/e_{calc}= 16) and m/e = 28 (m/e_{calc} = 28). NH_3 was isolated by vacuum fractionation and identified by its characteristic infrared spectrum (41) and its mass spectrum (m/e = 17).

Liquid products, isolated from the reaction gave an NMR spectrum which indicated the presence of $CHCl_3$ (2.6 τ) and Et_3N (CH_3 (triplet), 9.03 τ, CH_2 (quartet), 7.57 τ, $J_{CH_3CH_2}$, 7.2 cps). Gas phase infrared spectra of this mixture showed bands attributable to both Et_3N and $CHCl_3$.

The products of the reaction are consistent with the mechanism proposed for the oxidation of $C_6H_5NHNH_2$ by CCl_4 (equations 3-9 to 3-12), with two exceptions. An identical mechanism would predict MeCl as a product, while NH_3

would not be expected. The absence of detectable amounts of MeCl might be rationalized in terms of the stability of the intermediate, methyldiimide (MeN=NH), which may yield CH_4 and N_2 almost immediately after its formation. Alternatively, MeCl may be trapped in the solid phase as $MeNHNH_2.MeCl$. A scheme representing this sequence of reactions is presented in equations 3-13 to 3-16.

$$MeNHNH_2 + \cdot CCl_3 \rightarrow Me\dot{N}NH_2 + CHCl_3 \qquad (3\text{-}13)$$

$$Me\dot{N}NH_2 + CCl_4 \rightarrow MeN{=}NH + HCl + \cdot CCl_3 \qquad (3\text{-}14)$$

$$HCl \xrightarrow{MeNHNH_2} MeNHNH_2.HCl$$

$$MeN{=}NH \xrightarrow{\text{very fast}} CH_4 + N_2 \qquad (3\text{-}15)$$

$$MeN{=}NH + CCl_4 \not\rightarrow CH_3Cl + CHCl_3 + N_2 \qquad (3\text{-}16)$$

In this reaction sequence, if reaction 3-15 is very fast, the step represented by reaction 3-16 may be insignificant. This sequence however, predicts the equimolar production of CH_4 and N_2, contrary to observation.

If the reaction is allowed to proceed for a shorter period of time, additional intermediates are found. Products noted from a reaction between $MeNHNH_2$ and CCl_4 in Et_3N after two days, were N_2, CH_4, NH_3, $MeNH_2$, $CHCl_3$,

CH_2Cl_2, $MeNHNH_2.2HCl$, and $Et_3N.HCl$. N_2, CH_4, NH_3, and $MeNH_2$ gave mass spectral peaks at m/e = 28, m/e = 16, m/e = 17, and m/e = 31 respectively. CH_4, NH_3, $MeNH_2$, $CHCl_3$ and CH_2Cl_2 also showed their characteristic infrared spectra. Both $CHCl_3$ and CH_2Cl_2 appeared in the NMR spectra of the liquid products ($CHCl_3$, 2.09 τ; CH_2Cl_2, 4.77 τ), and the NMR spectrum of a D_2O solution of the solid products, analysed as an equimolar mixture of $Et_3N.HCl$ and $MeNHNH_2.2HCl$. From the observation of the additional intermediates, a scheme for the reaction of CCl_4 with $MeNHNH_2$ can be proposed, including reactions 3-13 to 3-15, and the additional reactions 3-17 to 3-24.

$$MeNHNH_2 + \cdot CCl_3 \rightarrow H_2\dot{C}NHNH_2 + CHCl_3 \qquad (3\text{-}17)$$

$$H_2\dot{C}NHNH_2 + CCl_4 \rightarrow HCl + H_2C{=}NNH_2 + \cdot CCl_3 \qquad (3\text{-}18)$$

$$\xrightarrow{MeNHNH_2} MeNHNH_2.HCl$$

$$H_2C{=}NNH_2 + 2CCl_4 \rightarrow H_2CCl_2 + N_2 + 2CHCl_3 \qquad (3\text{-}19)$$

$$2H_2C{=}NNH_2 \rightleftharpoons H_2C{=}NN{=}CH_2 + H_2NNH_2 \quad (35) \qquad (3\text{-}20)$$

$$H_2C{=}NN{=}CH_2 + MeNHNH_2 \rightleftharpoons H_2C{=}NNH_2 + MeNHN{=}CH_2 \qquad (3\text{-}21)$$

$$H_2NNH_2 + \cdot CCl_3 \rightarrow \dot{H}NNH_2 + CHCl_3 \qquad (3\text{-}22)$$

$$\dot{H}NNH_2 \rightarrow \text{Wolinsky and Schultz mechanism to } N_2 \quad (38) \qquad (3\text{-}23)$$

$$2HNNH_2 \rightarrow H_2NNHNHNH_2 \rightarrow N_2 + NH_3 \quad (34) \qquad (3\text{-}24)$$

The operation of reactions 3-15 and 3-19 alone are enough to explain the higher yield of N_2 with respect to CH_4, reaction 3-19 giving CH_2Cl_2. NH_3 may arise from the oxidation of H_2NNH_2 as in reaction 3-24, hydrazine arising from the disproportionation of formaldehydehydrazone as in reaction 3-20. These reactions depend on the formation of formaldehydehydrazone as an intermediate, which could arise from hydrogen abstraction at the methyl group as in equation (3-17),or by a diazene-hydrazone type of rearrangement of $CH_3N=NH$,as has been found to occur with diazomethane (42). Methylamine may arise by a reaction similar to that producing NH_3 (equation (3-24)) through the decomposition of 1,4-dimethyltetrazane as in equation (3-25).

$$2MeNHNH \rightarrow MeNHNHNHNHMe \rightarrow 2MeNH_2 + N_2 \qquad (3\text{-}25)$$

The observed disappearance of CH_2Cl_2during the reaction is caused by a secondary reaction in which $MeNHN=CH_2$is produced, according to equation 3-26, as was observed by ourselves in separate reactions between $MeNHNH_2$ and CH_2Cl_2

$$3\ MeNHNH_2 + CH_2Cl_2 \rightarrow MeNHNH=CH_2 + 2MeNHNH_2.HCl \qquad (3\text{-}26)$$

$MeNH_2$ produced would lead to the production of $MeNH_2.HCl$, since it has a basicity close to that of Et_3N (pKa $MeNH_2$, 10.62 (43); pKa Et_3N, 11.01 (32, p. D117)), and the salts produced in the reaction may in fact be a mixture of

$MeNH_2.HCl$ and $Et_3N.HCl$.

2. Reaction of $MeNHNH_2$ with CH_2Cl_2

Reactions between hydrazine and ethylenedichloride, give ethylene hydrazine polymers (44). The mechanism has been interpreted as a stepwise condensation polymerization with the elimination of HCl, which is trapped as hydrazine hydrochloride. Solvolysis of the carbon chlorine bond has similarly been used to prepare hydrazones (45) (equation 3-27). Formaldehyde methylhydrazone, ($MeNHN=CH_2$), has

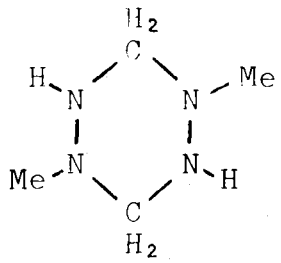
$$R_2CCl_2 + 3R^1_2NNH_2 \xrightarrow{\Delta} R_2C=NNR^1_2 + 2R^1_2NNH_2.HCl \qquad (3\text{-}27)$$

been prepared by the pyrolysis of the sodium salt of 1,1-dimethyl-2-benzenesulphonylhydrazine in ethylene glycol (42) (equation 3-28), and the base catalysed isomerization of azomethane (45) (equation 3-29). Miller and

$$Me_2NNSO_2C_6H_5^- \; Na^+ \xrightarrow[\Delta]{D.E.G.} MeNHN=CH_2 \qquad (3\text{-}28)$$

$$MeN=NMe \xrightarrow{base} MeNHN=CH_2 \qquad (3\text{-}29)$$

Rundle (46), reported a dimeric form of formaldehyde methylhydrazone from the reaction of formaldehyde with methylhydrazine, and the reaction between CH_2Cl_2 has been reported to yield the compound formulated as I (47).



I = 1,4-dimethylhexahydro-s-tetrazine (48, P.147)

Our studies of reactions between CH_2Cl_2 and $MeNHNH_2$ confirm these conclusions and suggest that the production of 1,4-dimethylhexahydro-s-tetrazine is stepwise, involving the consecutive elimination of HCl to form formaldehyde methylhydrazone, which then dimerizes to give 1,4-dimethylhexahydro-s-tetrazine (Equations 3-30 to 3-32).

$$2MeNHNH_2 + CH_2Cl_2 \rightarrow MeNHN\begin{matrix}CH_2Cl\\ \diagup\\ \diagdown\\ H\end{matrix} + MeNHNH_2.HCl \qquad (3\text{-}30)$$

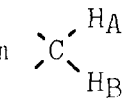
$$MeNHN\begin{matrix}CH_2Cl\\ \diagup\\ \diagdown\\ H\end{matrix} + MeNHNH_2 \rightarrow MeNHN{=}CH_2 + MeNHNH_2.HCl \qquad (3\text{-}31)$$

$$2MeNHN{=}CH_2 \rightarrow (-N(Me)NH\text{-}CH_2\text{-})_2 \qquad (3\text{-}32)$$

Reactions between CH_2Cl_2 and $MeNHNH_2$ in Et_3N, allowed to proceed for eighteen days, gave a 49% yield of $(-N(Me)NH\text{-}CH_2\text{-})_2$ (compound I). Compound I was isolated as a white crystalline solid, easily sublimed in vacuo at 58°C, and having a melting point of 118° - 120°C (lit. = 121° - 123°C (46)). The mass spectrum showed a parent peak at P=116 (P_{calc} = 116) with the most intense peak appearing at m/e=71, corresponding to a $H_2C\text{-}\overset{Me}{N}\text{-}N\text{-}CH_2$

ion fragment (m/e_{calc} = 71). This fragment would be expected to be quite stable as $(H_2C{=}N(Me)N{=}CH_2)^+$. Other intense peaks appeared at m/e = 59, 43, 42, 30, and 28, having possible assignments of $(H_2N(Me)N{=}CH_2)^+$, or $(MeNH{=}NMe)^+$ (m/e = 59), $(H_2C{=}N{=}NH)^+$ (m/e = 43), $(H_2C{=}N{=}CH_2)^+$ (m/e = 42), $(H_2C{=}NH_2)^+$ (m/e = 30), and N_2^+ (m/e = 28) (Table II.21).

The infrared spectrum of compound I (Table II.20) consisted of sharp, well defined bands; two bands at 3122 and 3218 cm^{-1} correspond to N-H stretching modes. These bands could arise from nonequivalent axial and equatorial hydrogens in a cyclohexane like structure, or from hydrogen bonded and free species. Eight bands in the C-H stretching region correspond to the six methyl, and four methylene protons.

The H^1 NMR spectrum of compound I (Table II.25) in $CDCl_3$ consisted of three resonance absorptions in a 3:2:1 integrated ratio, corresponding to NMe (7.63 τ), CH_2 (6.40 τ), and NH (6.96 τ). The methylene signal was not split but was significantly broadened (peak width at ½ height, 5 cps) as compared to the NMe peak (peak width at ½ height, 1.3 cps). The broadening may arise from  geminal coupling in a locked system, or from long range coupling to the NH protons. A study of proton-deuterium exchange, using D_2O and a solution of compound I

in CH_3CN, showed that the NH protons (6.96_τ) are indeed exchangeable, at a fast rate on the NMR time scale, since the NH peak disappears when D_2O is present.

If products from the reaction between CH_2Cl_2 and $MeNHNH_2$ are analysed, allowing a shorter reaction period, $MeNHN=CH_2$ (compound II) can be isolated. A colorless oil, infrared spectra (Table II.22) of compound II show a strong band at 1605 cm^{-1}, in the C=N stretching frequency range (49). This band could also correspond to an N-H bending mode. Dimerization of compound II causes a broadening and weakening of this band. The mass spectrum of compound II shows a peak at P=58 corresponding to the parent ion fragment (P_{calc}, 58). The most intense peak occurred at m/e=28 corresponding either to N_2^+ or $H_2C=N^+$ (m/e calc=28). Other intense peaks appeared at m/e=32,31 30,29,27 and 15. (See Table II.23).

The NMR spectrum (Table II.25) of $MeNHN=CH_2$ in CH_2Cl_2 showed an AB quartet (τ_A, 3.67, τ_B, 4.07, J_{AB}, 11.5 cps) arising from the methylene group, and a singlet (7.25_τ) arising from the N-Me group. The N-H proton was not observed (Literature: (41) AB quartet τ_A, 3.67, τ_B, 4.09; J_{AB}, 11.5 cps; NMe, 7.28_τ, J_{HCNH}, 4 cps; when traces of water are present the NMe peak appears as a singlet). After standing for a few days, compound II became crystalline, giving the infrared, NMR, and mass spectrum for compound I.

The ratio of the quantities of CH_2Cl_2 and $MeNHNH_2$ used in the partially completed reaction were found to be $MeNHNH_2:CH_2Cl_2$ = 2:1; if the reaction was allowed to proceed for a longer period of time, the ratio $MeNHNH_2$: CH_2Cl_2 = 3:1 was observed. This suggests that the reactions are sequential, with the initial production of $MeNHNH(CH_2Cl)$, which in turn reacts with another mole of $MeNHNH_2$, eliminating HCl, to give compound II.

A reaction scheme accounting for the observed results is presented in Figure III.10.

$$2MeNHNH_2 + CH_2Cl_2 \rightarrow MeNHNH(CH_2Cl) + MeNHNH_2.HCl$$

$$MeNHNH(CH_2Cl) + MeNHNH_2 \rightarrow MeNHN{=}CH_2 + MeNHNH_2.HCl$$

$$MeNHN{=}CH_2 + MeNHN{=}CH_2 \rightarrow$$

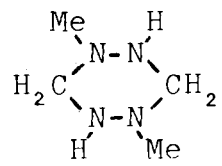


Figure III.10 Reaction Scheme for $MeNHNH_2 + CH_2Cl_2$

3. Reaction of CH_2Cl_2 with Me_2NNH_2

While reactions between CH_2Cl_2 and $MeNHNH_2$ suggest that CH_2Cl_2 reacts at both nitrogens, reactions of CH_2Cl_2 with Me_2NNH_2 give the quaternized 1,1-dimethyl-1-chloromethyl-hydrazinium chloride (Compound III), $[Me_2N(CH_2Cl)NH_2]^+ Cl^-$. This observation agrees with results found by Evans et.al. (25); it was found that reactions between poly-

methylene dihalides and 1,1-dimethylhydrazine yielded polymethylenebis-(1,1-dimethylhydrazine) dihalides,

$$Me_2\overset{+}{N}(H_2N)-(CH_2)_n-\overset{+}{N}Me_2(NH_2).2HX$$

rather than polymeric materials. A second possible formulation for the product, III a, was rejected on the basis of infrared and NMR spectral results.

$$\left[\begin{matrix} Me_2NNH_2 \\ | \\ CH_2 \\ | \\ Me_2NNH_2 \end{matrix}\right]^{+2} \qquad 2Cl^-$$

III a

Compound III was isolated from the reaction of an excess of CH_2Cl_2 with Me_2NNH_2 as a white crystalline solid (m.p. = 120-121 decomp.) insoluble in either $CHCl_3$ or CH_2Cl_2. Aqueous solutions gave a positive test for Cl^-. NMR spectra (Table II.25) of D_2O solutions of compound III showed three singlet resonance absorptions, (NMe_2) 6.46τ; N-CH_2Cl , 4.60τ ; exchangeable protons, 5.43τ (TMS external) in a 3:1:1 integrated ratio. A formulation of III a for the compound would be expected to result in an intensity ratio of 6:1:2 for the NMe_2: CH_2 : NH_2 protons.

An infrared spectrum of compound III in KBr showed poorly resolved bands in the N-H and C-H stretching frequency range, but showed a strong band at 1628 cm^{-1} suggesting a free -NH_2 group (25). This indicates that

quaternization occurs at the most highly substituted nitrogen atom. A strong band at 801 cm^{-1} suggests the presence of C-Cl (49) (Table II.24). Satisfactory mass spectral data were not obtained. Samples in the solid sample receiver decomposed quite violently, causing rapid fluctuations in the pressure within the ionization chamber. The highest m/e peak was observed at m/e=86, (m/e, $Me_2\overset{+}{N}(CH_2Cl)NH_2$ = 109, 111). Peaks at m/e=36 and m/e=38 in a 3:1 intensity ratio, correspond to HCl, while the highest m/e fragment containing chlorine, appears at m/e = 50, 52, corresponding to $\overset{+}{C}H_3Cl$ or $H\text{-}\overset{+}{N}\text{-}Cl$.

C. (Trifluoromethyl)phosphinohydrazines

1. Introduction

Trifluoromethylhalophosphines, $(CF_3)_nPX_{3-n}$, (n=1 or 2) react with 1,1-dimethylhydrazine, and trimethylhydrazine to give the corresponding (trifluoromethyl)phosphino-hydrazines (equations 3-33 and 3-34). Monomethylhydrazine

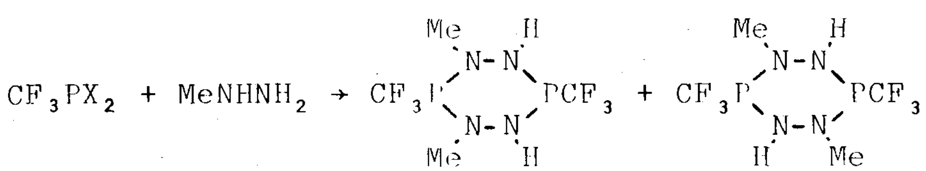
$$(CF_3)_2PX + 2HNRNMe_2 \rightarrow (CF_3)_2PNRNMe_2 + Me_2NNHR.HX \quad (3\text{-}33)$$

$$CF_3PX_2 + 4HNRNMe_2 \rightarrow CF_3P(NRNMe_2)_2 + 2Me_2NNHR.HX \quad (3\text{-}34)$$

(R = H, Me) (X = I, Cl)

reacts with bis(trifluoromethyl)halophosphine, giving a mixture of isomers of bis(trifluoromethyl)phosphinomethyl-hydrazine (equation 3-35), and with trifluoromethyldihalo-phosphine, giving a mixture of isomers of cyclodimethyl-(1,4-bistrifluoromethyl)bishydrazino-1,4-diphosphine (equation 3-36), plus polymeric materials. In suitable solvents, reactions 3-33 to 3-35 are nearly quantitative, while a competing condensation polymerization restricts the yield of products in 3-36.

$$2(CF_3)_2PX + 4MeNHNH_2 \rightarrow (CF_3)_2PNMeNH_2 + (CF_3)_2PNHNHMe \quad (3\text{-}35)$$
$$+ 2MeNHNH_2.HX$$

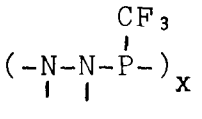


(3-36)

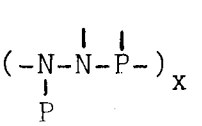
$$+ MeNHNH_2.HX + polymer$$

The reactions between $(CF_3)_nPX_{3-n}$ and $HR^1NNR^{11}R^{111}$ appear to be solvent dependent; chlorobenzene, as solvent, is required in the reaction of CF_3PI_2 with Me_2NNH_2, to give $CF_3P(NHNMe_2)_2$ (equation 3-34). Reactions in the absence of solvent give very low yields of the phosphinohydrazines as products. Thus, in the absence of a solvent, the reaction between $(CF_3)_2PI$ and Me_2NNH_2 gave very low yields of $(CF_3)_2$-$PNHNMe_2$. The cleavage of fluoroform from $(CF_3)_3P$ with Me_2NNH_2 to give $(CF_3)_2PNHNMe_2$ occurred only to a minor extent, in contrast to the ammonolysis of $(CF_3)_3P$ with ammonia, which gives $(CF_3)_2PNH_2$ and CF_3H (50). The lower basicity of Me_2-NNH_2 relative to NH_3 (pKa($MeNNH_2$), 7.21 (17); pKa (NH_3), 9.25 (32, p.D-117)) is a possible explanation for the observations.

Hydrazine failed to react with $(CF_3)_2PI$ in the absence of a solvent: only traces of CF_3H were found when mixtures of H_2NNH_2 with $(CF_3)_3P$ were heated to 100°C for 36 hours. Reactions of hydrazine with $(CF_3)_3P$ or $(CF_3)_2PI$ in trimethylamine however, gave products which condensed during handling, yielding fluoroform and involatile residues, for which a variety of polymeric and cross linked structures are possible (51).



(a)



(b)

Thus, it appears that hydrazine, which is slightly more basic than 1,1-dimethylhydrazine (33) does not possess the necessary nucleophilic character to cleave CF_3H from $(CF_3)_3P$, or HI from $(CF_3)_2PI$.

2. $(CF_3)_2PNHNMe_2$: Compound IV

The first solution reaction attempted was that between $(CF_3)_2PI$ and Me_2NNH_2 in diethyl ether, which gives a nearly quantitative yield of 1,1-dimethyl, 2-bis(trifluoromethyl)-phosphinohydrazine, $(CF_3)_2PNHNMe_2$ (compound IV),according to equation 3-33. The formation of the bis(phosphino)hydrazine, $((CF_3)_2P)_2NNMe_2$, was not observed; reactions carried out using an excess of $(CF_3)_2PX$ with Me_2NNH_2 gave compound IV as sole product. Steric factors, and $N(p\pi)$-$P(d\pi)$ bonding may account for the absence of $((CF_3)_2P)_2NNMe_2$. If the auxiliary bonding is strong, the nitrogen atom may be deactivated as a base (52); then reaction with a second phosphine through nucleophilic attack by nitrogen, would not readily occur.

Compound IV was characterized by vapour phase molecular weight measurements. (M_{obs}, 231: M_{calc} 228), by mass spectroscopy(P_{obs} 228; P_{calc} 228), and by quantitative cleavage of the P-N bond with HCl, according to equation 3-37.

$$(CF_3)_2PNHNMe_2 + 2HCl \longrightarrow Me_2NNH_2.HCl + (CF_3)_2PCl \quad (3\text{-}37)$$

Significant features of the mass spectrum (Table II.28) include the parent peak (P=228), and peaks corresponding to fragments $(CF_3)PNHNMe_2$ (m/e = 150), CF_3(m/e = 69), Me_2NNH (m/e = 59), and Me_2N (m/e = 44). High resolution work

would be necessary to verify these assignments. The most intense peak occurred at m/e = 59, corresponding to the hydrazine fragment, Me_2NNH^+, resulting from the cleavage of the P-N bond, this being a salient feature of the mass spectral data for nearly all of the phosphino-hydrazine compounds synthesized.

The H^1 NMR spectrum showed a broadened peak and a sharp peak at 5.95 τ and 7.50 τ respectively, in a 1:6 integrated ratio, consistent with one amino proton, and two equivalent methyl groups attached to nitrogen. The F^{19} spectrum showed a doublet at 65.0 ppm above $CFCl_3$ corresponding to two equivalent CF_3 groups attached to phosphorus, the splitting arising from coupling with spin 1/2 P^{31} nucleus (J_{FCP}, 84 cps). Invariance of the spectra from -50°C to +60°C suggests free rotation about the P-N bond over this temperature range. A complete list of the NMR spectral data for all of the phosphino-hydrazines is presented in Tables II.46 and II.47.

The infrared spectrum (Table II.27) is consistent with the proposed formulation, showing bands corresponding to NH (3300 and 3422 cm^{-1}), CH_3 (2790-3308 cm^{-1}) and CF_3 (1069-1167 cm^{-1}) stretching modes. The two bands assigned to NH deformations could arise from associated and free species, or as has been suggseted (51), the second band at 3422 cm^{-1} may be a Fermi resonance enhanced overtone of an

NH bending mode. Seven bands appear in the C-H stretching region, only six of which can be attributed to two methyl groups attached to a molecule lacking in symmetry features. The seventh would exist as an overtone or combination band.

Although other formulations are possible for compound IV, with a molecular weight of 228, none would give the combined chemical, infrared, NMR, and mass spectral results found; thus, a possible Arbuzov type of rearrangement to yield a pentavalent, four-coordinate phosphorus compound is precluded on the basis of the F^{19} data, J_{FCP} coupling constants being larger for these molecules ($(CF_3)_2P{=}O$; J_{FCP}, 113.4 cps (53)). Similarly, a dimethylamino group attached to phosphorus would appear in the H^1 spectrum as a doublet, arising from P-N-C-H spin-spin coupling.

3. $(CF_3)_2PNMeNMe_2$: Compound V

1,1,2-trimethyl,2-bis(trifluoromethyl)phosphinohydrazine, $(CF_3)_2PNMeNMe_2$, (Compound V), was prepared by the reaction of $(CF_3)_2PX$ with Me_2NNHMe in diethyl ether according to equation 3-33. Compound V was isolated in 83% yield from the reaction, together with compound IV (11%) resulting from a Me_2NNH impurity in the trimethylhydrazine. With pure starting materials, even higher yields of compound V would be expected.

Compound V showed a vapour phase molecular weight of 241 (M_{calc} = 242) suggesting absence of association in the vapour phase. The mass spectrum (Table II.31) showed a parent peak at P = 242 (P_{calc} = 242) with prominent peaks corresponding to the fragments $CF_3PNMeNMe_2$ (m/e = 173), $NMeNMe_2$ (m/e = 73), CF_3 (m/e = 69) and Me_2N (m/e = 44). The most intense peak appeared at m/e = 73. High resolution mass spectroscopy would be required to verify these assignments.

Reaction of compound V with HCl resulted in cleavage of the P-N bond with the formation of $(CF_3)_2PCl$ and $Me_2NNHMe.HCl$ according to equation 3-38.

$$(CF_3)_2PNMeNMe_2 + 3HCl \rightarrow (CF_3)_2PCl + Me_2NNHMe.HCl \quad (3\text{-}38)$$

The H^1 NMR spectrum of compound V consisted of two resonance absorptions in a 2:1 integrated ratio, corresponding to 6 methyl protons (7.50 τ), and 3 methyl protons (7.13 τ). The latter signal, corresponding to the P-N-Me protons, was a doublet, consistent with spin-spin coupling to spin 1/2 P^{31} nucleus (J_{PNCH}, 3.6 cps). Fine structure on this doublet revealed long range F-C-P-N-C-H coupling (J_{FCPNCH}, ≈0.7 cps), recognizable as two overlapping septets arising from coupling to two equivalent CF_3 groups. The F^{19} resonance consisted of the familiar doublet arising from F^{19}-P^{31} spin-spin coupling (δ midpoint, 61.5 ppm; J_{FCP}, 82 cps).

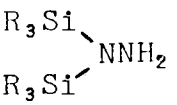
The infrared spectrum (Table II.30) is consistent with the formulation given for compound V, with bands corresponding to CH_3 and CF_3 stretching modes.

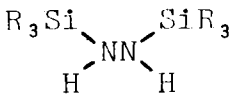
4. $(CF_3)_2PNMeNH_2$ and $(CF_3)_2PNHNHMe$

Compounds VI and VII

Reactions between $(CF_3)PI$ and $MeNHNH_2$ in diethyl ether give the isomeric products, 1-methyl,1-bis(trifluoromethyl)phosphinohydrazine, $(CF_3)_2PNMeNH_2$, Compound VI, and 1-methyl,2-bis(trifluoromethyl)phosphinohydrazine, $(CF_3)_2PNHNHMe$, Compound VII, in a combined yield of 91%, according to equation 3-35.

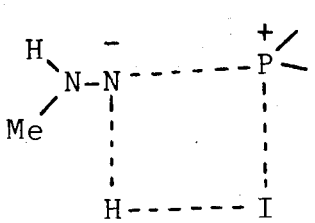
Whereas substitution might be expected to occur primarily at the methyl nitrogen, similar to the alkylation of $MeNHNH_2$ (14), it was found that $(CF_3)_2PI$ reacted with near equal preference at both nitrogens, leading to the isomeric products found. The analogous reaction with bis(trifluoromethyl)chloroarsine, $(CF_3)_2AsCl$, leads to one isomer only, formed by substitution at the least alkylated site (54). Reactions of trialkylsilylhydrazine with chlorosilanes give mixtures of 1,1-bis (trialkylsilyl)hydrazine and 1,2-bis(trialkylsilyl)-hydrazine, (a) and (b) (55). Jensen (56) reports the

(a) 

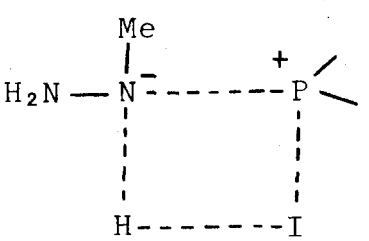
(b) 

reaction between trimethylchlorosilane, Me_3SiCl, and $MeNHNH_2$ to give 1-methyl,1-(trimethylsilyl)hydrazine, $Me_3SiN(Me)NH_2$, as the only mono-silylated products. Lithium methylhydrazide and trimethylbromogermane are believed to react to give an unstable monosubstituted derivative, of unknown structure, which gives rise to methylhydrazine and the isomers of bis(trimethylgermyl) methylhydrazine, $(Me_3Ge)_2NNHMe$ and $Me_3GeNMeNHGeMe_3$ (57). A report in the literature (58) of the reaction between diphenylchlorophosphine, $(C_6H_5)_2PCl$, and $MeNHNH_2$ indicates that a mixture of (mono-phosphino)hydrazine isomers was found, but their separation was not achieved.

The isolation of compounds VI and VII suggest, either that steric interactions compensate the enhanced basicity of the methyl nitrogen or, that the difference in the basicities of the two nitrogens is not sufficiently great to cause preferential nucleophilic attack towards the phosphine: thus, the activation energies for the two intermediate four-centre complexes may be quite similar (a and b).



(a)

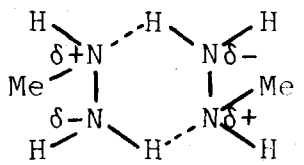


(b)

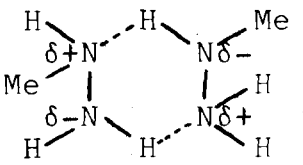
NMR spectra of $MeNHNH_2$ show two resonance absorptions only, one arising from the NMe group (≃ 7.45 τ) and one arising from exchanging MeNH and NNH_2 amino protons (≃ 6.7 τ). Attempts to resolve the MeNH and NH_2 amino protons failed; a single NH resonance absorption was observed with pure $MeNHNH_2$ at temperatures down to -50°C, and to -120°C (est.) with diethyl ether solutions of $MeNHNH_2$. Similarly, addition of HCl did not reveal the presence of the two NH environments (cf. protonation of $MeNH_2$ (p.494 of ref. 31)). Thus, exchange between the amino protons must be rapid, and might occur through self protonation, which can be represented:

$$MeNHNH_2 \rightleftharpoons Me\overset{+}{N}H_2\overset{-}{N}H$$

The mechanism for this exchange may be through the formation of solution dimers (a) and (b), as has been suggested to occur with Me_2NNH_2 and Me_2NNHMe (59). In reactions with

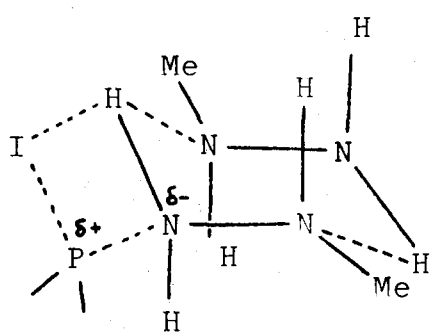


(a)



(b)

$(CF_3)_2PI$, mode (a) would promote substitution at the least alkylated site, while mode (b) could give rise to a mixture of isomers. The importance of the dimeric $MeNHNH_2$ structure, and of forms (a) and (b), would determine the mole ratio of isomeric products. Reactions of modes (a) or (b) with $(CF_3)_2PI$ would facilitate fast reactions since the base, accepting HI, would be present in the intermediate (c).



(c)

$(CF_3)_2PNMeNH_2$ (VI) and $(CF_3)_2PNHNHMe$ (VII), on fractionation were observed as visibly distinct colorless crystals in a colorless liquid. Repeated fractionations ultimately yielded a sample of pure solid $(CF_3)_2PNHNHMe$ having a melting point of $35.5\pm0.1^{\circ}C$, while $(CF_3)_2N(Me)NH_2$ still retained traces of its isomer.

Gas phase molecular weights for both compounds ranged from M=215-219 (M_{calc} = 214), while mass spectral data

gave parent peaks at P = 214 (P_{calc} = 214) (Tables II.34 and II.35). Significant peaks for both compounds appeared for fragments $CF_3PNMeNH_2$ and $CF_3PNHNHMe$ (m/e = 145), CF_3 (m/e = 69) and MeNHNH (m/e = 45), the last peak being most intense in both spectra.

The H^1 NMR spectra for the isomers were quite different. The spectrum for $(CF_3)_2PNMeNH_2$ consisted of two resonance absorptions in a 2:3 integrated ratio, the first a broad band, corresponding to the NH_2 protons (6.15 τ), and the second to the NMe protons (6.93 τ). The latter peak was split into a doublet, consistent with coupling to the P^{31} nucleus (J_{PNCH}, 8.5 cps). $(CF_3)_2PNHNHMe$ showed resonance absorptions corresponding to NMe (7.37 τ), MeN-H (6.39 τ), and PN-H (5.70 τ) protons in an integrated ratio of 3:1:1. The assignments given the N-H signals were based on comparison with N-H chemical shifts of analogous compounds containing protons in similar environments (Table II.46), and on the basis that the least shielded proton will likely be closest to the electronegative $(CF_3)_2P$ group. The F^{19} absorptions were the familiar doublets arising through nuclear P^{31} spin-spin coupling, {$(CF_3)_2PNMeNH_2$: δ midpoint, 60.6 ppm, J_{FCP}, 84 cps; for $(CF_3)_2PNHNHMe$: δ midpoint, 63.8 ppm, J_{FCP}, 80 cps}

The main features of the infrared spectra for compounds VI and VII correspond to bands due to CF_3, CH_3, and N-H

or NH_2 vibrations (Tables II.32 and II.33). Compound VII shows two NH stretching frequencies at 3340 and 3428 cm^{-1} arising from the distinct PN-H and MeN-H groupings, while compound VI has only one band in this region at 3410 cm^{-1} corresponding to the NH_2 stretching mode. A band at 1605 cm^{-1} is consistent with the presence of a primary amino group (25). The infrared spectrum of compound VII includes a medium band at 2810 cm^{-1} consistent with the C-H symmetric vibration of a terminal NMe group (60).

5. $CF_3P(NHNMe_2)_2$: Compound VIII

Reactions between CF_3PI_2 and Me_2NNH_2 in chlorobenzene give good yields of bis(1,1-dimethylhydrazino)trifluoromethylphosphine, $CF_3P(NHNMe_2)_2$, Compound VIII, according to equation 3-34. Compound VIII, having a very low vapour pressure at room temperature, was difficult to handle in the vacuum line, 48 hours minimum time being required to condense enough product into an NMR tube for good spectra. Vapour phase molecular weight determinations were impractical, but mass spectral data indicated a parent peak at P = 218, (P_{calc} = 218) (Table II.38). A low intensity peak at m/e = 149 suggests a low probability of losing a $-CF_3$ group from the parent compound, as compared to the bis(trifluoromethyl)phosphinohydrazines (Compounds IV to VII), where such fragmentation

occurs readily. The most intense high molecular weight fragment on the other hand, corresponds to the breaking of an N-N bond with the loss of a Me_2N group, assigned as $CF_3P(NHNMe_2)(NH)$ (m/e = 174). This is the only significant high molecular weight fragment, suggesting a high degree of molecular cleavage in the ionization chamber. The most intense peak occurs at m/e=59 corresponding to the Me_2NNH^+ fragment.

The H^1 NMR spectrum of compound VIII is in agreement with the postulated structure, indicating twelve N-Me protons at 7.59τ and two N-H protons, present as a doublet, at δ midpoint, 5.92 τ . The N-H doublet may arise from non-equivalence of rotational isomers, or through coupling with the spin 1/2 P^{31} nucleus. NMR measurements at temperatures up to 104°C gave identical spectra, thus precluding the former possibility, while the coupling constant value (J_{PNH}, 20 cps) is consistent for the latter alternative. (58). The F^{19} spectrum showed the familiar doublet at δ midpoint, 65.4 ppm (J_{PCF}, 83 cps).

Due to the low volatility of compound VIII, gas phase infrared spectra showed only a few extremely weak bands. Satisfactory results were obtained, however, by taking spectra of the compound in nujol and halo oil mulls, and on the pure solid, between KBr plates (Table II.37.).

Samples were prepared under a dry N_2 atmosphere and run immediately to avoid the possibility of decomposition or reaction. Bands were assigned to compound VIII by noting only those in the "transparent" areas of the mulls. While bands underwent solvent shifts (up to 5 cm^{-1}), tablulated values are in spectral agreement in at least two of the three different sample spectra.

A characteristic feature of those compounds having only one CF_3 group rather than two or three such groups is the relatively lessened intensity of the CF_3 stretching modes. As well, it is expected that only two major bands will be observed, rather than the three very intense major bands usually found for the $(CF_3)_2P$ grouping (61). Both of these effects introduces some confusion as to the assignment of the C-F stretching frequencies, since skeletal modes, superimposed upon the C-F stretching modes in the $(CF_3)_2P$ compounds, may now be prominent. The C-F bands however would be expected to appear in the 1100 - 1200 cm^{-1} region, and would have reasonable intensity; the infrared spectrum for compound VIII shows intense bands in this region. Six bands from 2781 - 2797 cm^{-1} correspond to C-H stretching modes, and two bands at 3196 and 3296 cm^{-1} correspond to N-H stretching modes.

6. $CF_3P(NMeNMe_2)_2$: Compound IX

Initial attempts to prepare compound IX in chlorobenzene failed, while the reaction of CF_3PI_2 with Me_2NNHMe in diethyl ether gave good yields of bis(trimethylhydrazine)trifluoromethylphosphine, $CF_3P(NMeNMe_2)_2$ compound IX, according to equation 3-34. While compound IX is a liquid at room temperature, the problem of low volatility with respect to difficulty of handling parallelled that of compound VIII.

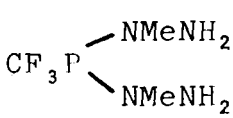
Vapour phase molecular weight determinations were impractical, but the mass spectrum showed a parent peak at P = 246 (P_{calc} = 246). (Table II.40). Again, the peak corresponding to loss of a CF_3 group was low, and the only peak assigned with some confidence is that due to Me_2NNMe^+ (m/e = 73). Contamination of the trimethylhydrazine with 1,1-dimethylhydrazine led to formation of some of compound VIII in the product which was difficult to remove. A reasonably intense peak at m/e = 59 corresponding to the Me_2NNH^+ fragment is in evidence in the mass spectrum. Compound VIII showed in the NMR spectra as well, and was readily recognized as such. A small amount of compound IX, showing absence of N-H stretching modes in the infrared, was isolated, such that infrared absorption bands could be assigned to compound IX with confidence.

The H^1 NMR spectrum consisted of two signals corresponding to 12 NMe protons at 7.50 τ and 6 NMe protons at 7.15 τ, in a 2:1 integrated ratio. The latter signal was split due to spin 1/2 P^{31} coupling (J_{PNCH}, 7.0 cps) while fine structure analysis of high resolution spectra showed the doublet to be a doublet of quartets, indicating long range coupling to CF_3 (J_{FCPNCH}, 0.7 cps). The F^{19} spectrum was a doublet (δ midpoint, 62.7 ppm, J_{PCF}, 92 cps). Integration over the F^{19} signals indicated a 15% impurity of compound VIII.

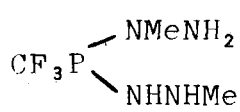
The infrared spectrum of compound IX (Table II.39) was obtained on the liquid held between KBr plates. Two bands at 1097 and 1177 cm^{-1} may be assigned to C-F stretching modes. Seven bands in the C-H stretching region, between 2780 and 2982 cm^{-1} are also observed.

7. Two Isomers of $CF_3P(NHNMe)_2PCF_3$: Compounds X, XI

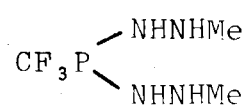
The reaction between CF_3PI_2 and $MeNHNH_2$ might be expected to give three isomeric products, (a), (b) and (c). However, none of these products were isolated or detected.



(a)



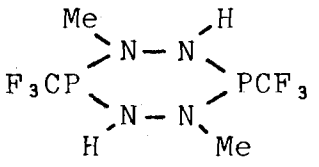
(b)



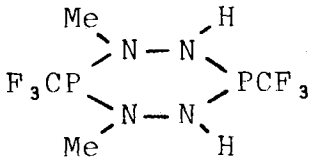
(c)

Instead, two isomeric ring compounds were found, cyclo-2,5-dimethyl(1,4-bistrifluoromethyl)bishydrazino,1,4-diphosphine,

compound X, and cyclo-2,6-dimethyl(1,4-bistrifluoromethyl) bishydrazino,1,4-diphosphine, compound XI. Compounds X



X



XI

and XI, obtained from the reaction of CF_3PI_2 with $MeNHNH_2$ in diethyl ether according to equation 3-36, were isolated in relatively low yield (30% combined). Other products indicated that the mechanism of formation of the cyclic compounds is a termination reaction (ring closure) of a stepwise condensation polymerization leading to long chain and closed ring $(-P\text{-hydrazine-})_n$ systems.

A few polycyclic, or cage phosphorus-nitrogen compounds have been reported. $P_4(NMe)_6$ (62) along with the arsenic analogue (63), and $P_4(NNMe_2)_6$ (64), have the cage structure in Figure III.11. Reactions between phosphorus or arsenic, and hexafluoro-2-butyne have led to interesting cage compounds (65) (Figure III.12) and their skeletal analogues based on 1,2-dimethylhydrazine have been prepared (66, 67) (Figure III.13). The polycyclic compound $P(NMeNMe)_3P$ undergoes reaction with PCl_3 giving a quantitative yield of $ClP(NMeNMe)_2PCl$ (Figure III.14) in which it is suggested that the ring structure is puckered (66).

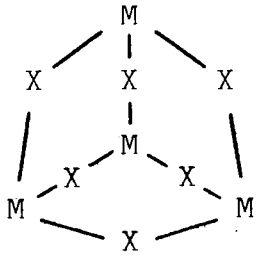


Figure III.11

Structures of M_4X_6

(M = P, X = NMe, NNMe)(62, 64)

(M = As, X = NMe)(63)

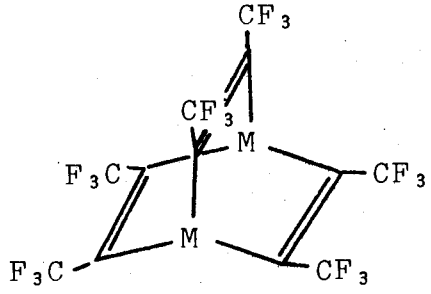


Figure III.12

M = P, As (65)

diarsina- and diphospha-bicyclooctatrienes

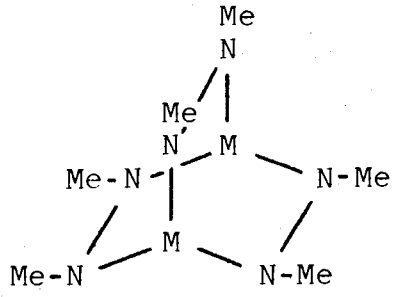


Figure III.13

M = P (66)

M = As (67)

Bicyclophospha- and arsena-hydrazines

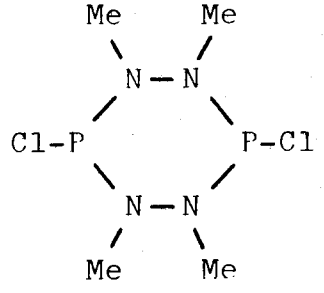


Figure III.14

A cyclic diphosphinohydrazine (66)

The mass spectrum for the ring compounds X and XI (see Tables II.43 and II.44), show parent peaks at P = 288 (P_{calc} = 288), and similar to the bis(trifluoromethyl)phosphinohydrazine (compounds IV to VII) spectra, show intense peaks, at m/e = 219, corresponding to the loss of a CF_3 group. However, unlike the spectra for compounds IV through VII, the m/e = 219 peak, assigned as $CF_3P(NMeNH)_2P^+$ is the most intense, suggesting this ion to be quite stable. The corresponding peak appears only weakly in the spectra of compounds VIII and IX; the greater stability of $CF_3P(NMeNH)_2P^+$ from X or XI, may result from electron delocalization via (p-d)π bonding with the ring system.

The H^1 NMR spectrum of compound X showed two doublets, consistent with both N-H and NMe coupling to the spin 1/2 P^{31} nucleus, the N-H protons at δ midpoint, 5.15 τ (J_{P-N-H}, 40.0 cps), and the NMe protons at δ midpoint 7.04 τ($J_{P-N-C-H}$, 13.0 cps) in a 1:3 integrated ratio. The F^{19} spectrum was a doublet at δ midpoint, 64.8 ppm. (J_{P-C-F}, 88.5 cps).

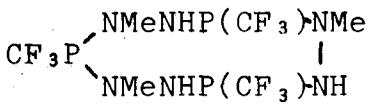
Compound XI showed an H^1 NMR spectrum identical in appearance with that of compound X but with different chemical shifts and coupling constants; N-H, δ midpoint, 5.54 τ (J_{P-N-H}, 43 cps); NMe, δ midpoint, 7.03 τ ($J_{P-N-C-H}$, 14.0 cps). A mixture of compounds X and XI showed all peaks belonging to both compounds as distinct

and separate resonance frequencies. The F^{19} NMR spectrum of compound XI showed two doublets, consistent with the two nonequivalent CF_3 groups on the ring, at $(MeN)_2PCF_3$ δ midpoint, 66.0 ppm (J_{P-C-F}, 94 cps) and $(HN)_2PCF_3$ δ midpoint, 64.2 ppm (J_{P-C-F}, 85 cps). Assignments of the two $P-CF_3$ resonance absorption positions were made by comparison with $CF_3P(NMeNMe_2)_2$ (J_{P-C-F}, 92 cps), and $CF_3P(NHNMe_2)_2$ (J_{P-C-F}, 83 cps).

The infrared spectra of compounds X and XI are presented in Tables II.41 and II.42. Pure solid, nujol and halo oil mull spectra, were obtained on the crystalline compound X while spectra of compound XI were measured on the liquid held between KBr plates. Both showed reasonably strong bands in the CF_3 absorption frequency range (1100 - 1200 cm^{-1}), and bands corresponding to methyl C-H stretching modes. Compound X showed one sharp band for the N-H stretching mode at 3311 cm^{-1}, while compound XI showed a broad band centered at 3350 cm^{-1} accompanied by a broad shoulder centered at 3150 cm^{-1}.

A nonvolatile yellow oil was eventually isolated from the intractable, polymeric residue of reactions leading to compounds X and XI. The mass spectrum of the oil showed peaks to m/e = 506 (See Table II.45). While it is difficult to assign structures unambiguously for ion fragment molecular weights, if the reaction between

CF_3PI_2 and $MeNHNH_2$ proceeds as a stepwise condensation polymerization, the compounds $MeNHNHP(CF_3)NMeNHP(CF_3)NMeNH_2$ (and isomers) (m/e - 334) and the closed ring,



(and isomers) (m/e = 432)

might be expected. Peaks corresponding to these ions are indeed found. Evidence for a complicated mixture of products in this non-volatile fraction also comes from the F^{19} NMR spectra, in which 22 lines appear; if CF_3 is not cleaved from phosphorus during the reaction, this represents eleven possible products. The presence of 22 lines may be interpreted in another fashion. If the fraction consisted of a mixture of the two compounds noted (with m/e = 334, and m/e = 432), the 22 lines can be accounted for as follows: the m/e = 334 compound has four unique isomers; three isomers have two different phosphorus environments, one isomer has two equivalent phosphorus environments. A mixture of the four isomers would give rise to 14 lines. The ring compound (m/e = 432) has two unique isomers; one isomer has three non equivalent phosphorus environments, the other has all equivalent phosphorus environments. A mixture of these isomers would give rise to 8 spectral lines. A mixture of these two compounds in their various isomeric forms therefore, would give rise to the 22 lines observed. Mass spectral evidence, however, suggests that there are

more than two products, but of the 22 lines in the F^{19} spectrum, some could represent two or more superimposed lines.

8. General Correlations

(a) H^1 NMR Data

(i) Chemical Shifts

The hydrogen chemical shift depends on a number of factors, (a) bulk diamagnetic susceptibility effects, (b) intermolecular association, (c) neighbour anistropic shielding, (d) intramolecular electric field effects and (e) the diamagnetic shielding caused by the electron cloud about the nucleus (31, p.666). If the effects caused by (a) to (d) are small, or at least fairly constant over a range of similar compounds, the chemical shift may be said to be a measure of the electron density about the nucleus under observation. Thus, the chemical shifts of the methyl protons in CH_3X have been correlated with the electronegativity of X (31, p.996); a larger amount of deshielding is observed as X becomes more electronegative.

Listed in Table III.4 are the H^1 NMR data obtained for Me_2NNH_2, Me_2NNHMe, and $MeNHNH_2$, and their trifluoromethylphosphine derivatives. In all cases, replacement of an amino hydrogen by $(CF_3)_2P-$ or CF_3P- causes the NMe and NH proton signals to move downfield relative to the "free hydrazine" signals. The deshielding is strongest

Table III.4 NMR Data for some Methyl- and Trifluoromethylphosphino-hydrazines

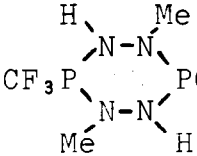
Compound	NH	NH_2	NMe	NMe_2	F^{19}: CF_3
Me_2NNH_2		6.93		7.58	
Me_2NNHMe			7.45	7.58	
$MeNHNH_2$	6.7		7.45		
$(CF_3)_2PNHNMe_2$ IV	5.95			7.50	65.0 J(PCF) 84
$(CF_3)_2PNMeNMe_2$ V			7.13 J(FCPNCH)0.7 J(PNCH) 3.6	7.50	61.5 J(PCF) 82
$(CF_3)_2PNMeNH_2$ VI		6.15	6.93 J(PNCH) 8.5		60.6 J(PCF) 84
$(CF_3)_2PNHNHMe$ VII	NNH 6.39 PNH 5.70		7.37		63.8 J(PCF) 80
$CF_3P(NHNMe_2)_2$ VIII	5.92 J(PNH) 20			7.59	65.4 J(PCF) 83
$CF_3P(NMeNMe_2)_2$ IX			7.15 J(FCPNCH)0.7 J(PNH) 7.0	7.50	62.7 J(PCF) 92
$CF_3P(NHNMe)_2PCF_3X$	5.15 J(PNH) 40		7.04 J(PNCH) 13		64.8 J(PCF) 88.5
$CF_3P(NHNMe)_2PCF_3XI$	5.54 J(PNH) 43		7.03 J(PNCH) 14	$(MeN)_2PCF_3$ 66.0, J(PCF) 94 $(HN)_2PCF_3$ 64.2, J(PCF) 85	

for protons nearest the phosphine moiety, as would be expected, since the trifluoromethylphosphine group is electron withdrawing. The magnitude of deshielding can be represented by $\Delta\delta H$ ($\Delta\delta H$ = δ alkylhydrazine - δ (trifluoromethyl)phosphinoalkylhydrazine, where δ = the chemical shift in ppm); these values are collected in Table III.5. The deshielding effect of the trifluoromethylphosphine group, across two bonds, is to cause the proton signal to move approximately 1 ppm downfield relative to the position of the corresponding signal in the free hydrazine. Across three bonds, $\Delta\delta H \simeq 0.31$ ppm, and across four bonds, $\Delta\delta H \simeq 0.08$ ppm. $(CF_3)_2PNMeNH_2$ presents a case where $\Delta\delta H = 0.53$ ppm across three bonds; in this instance, intermolecular association may introduce an important contribution to the deshielding. The ring compounds, X and XI, present a situation where the NMe and NH protons feel the deshielding effect of two phosphine groups. If the deshielding is additive, $\Delta\delta H$ can be calculated for these signals ($\Delta\delta NMe_{calc} = 0.39$, $\Delta\delta NH_{calc} = 1.31$). The observed values are; compound X, $\Delta\delta NMe = 0.41$, $\Delta\delta NH = 1.55$: compound XI, $\Delta\delta NMe = 0.42$, $\Delta\delta NH = 1.16$. The calculated $\Delta\delta NMe$ values are close to those observed, but the $\Delta\delta NH$ calculated value is low compared to the observed value for compound X, and high compared to that observed for compound XI. Neighbour anisotropic shielding

Table III.5 Effect of Substitution by $(CF_3)_2P$ and $CF_3P<$ on the H^1 Chemical Shifts of $HNRNR^1R^{11}$

Hydrazine	Substituted Hydrazine[b]	$\Delta\delta H$[a] across 2 bonds		across 3 bonds		across 4 bonds	
H_2NNMe_2	$(CF_3)_2PNHNMe_2$	N-H	0.98			NMe_2	0.08
$HNMeNMe_2$	$(CF_3)_2PNMeNMe_2$			NMe	0.32	NMe_2	0.08
H_2NNHMe	$(CF_3)_2PNMeNH_2$			NMe N-H	0.52 0.55		
H_2NNHMe	$(CF_3)_2PNHNHMe$	N-H	1.00	N-H	0.31	NMe	0.08
H_2NNMe_2	$CF_3P(NHNMe_2)_2$	N-H	1.01			NMe_2	0.0
$HNMeNMe_2$	$CF_3P(NMeNMe_2)_2$			NMe	0.30	NMe_2	0.08

(a) $\Delta\delta H$ = δ alkylhydrazine -δ(trifluoromethyl)phosphinohydrazine, in ppm.

(b) For  , $\Delta\delta NMe=0.41$, $\Delta\delta NH=1.55$: for $CF_3P(NHNMe)_2PCF_3$, $\Delta\delta NMe=0.42$, $\Delta\delta NH=1.16$

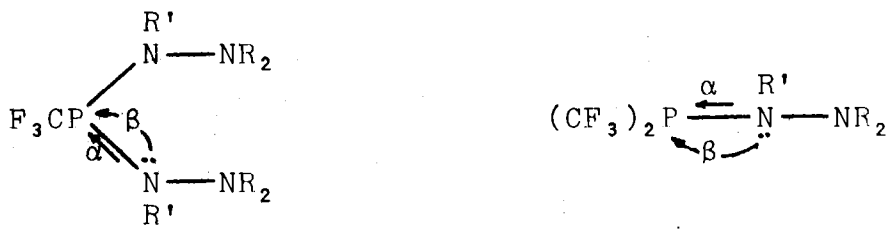
arising from ring currents, introduced via (p-d)π bonding would be expected to influence the amino proton signals more than the NMe signals.

An interesting observation arises from the comparison of the deshielding caused by the $(CF_3)_2P$- group as compared to the $CF_3P<$ group. Deshielding caused solely through an inductive effect of $(CF_3)_2P$- would be expected to be greater that that caused by the less electronegative $CF_3P<$ group. However, the NH and NMe protons of the bis(hydrazino)phosphines are as effectively deshielded as those of the mono(hydrazino)phosphines. If (p-d)π bonding is effective across the P-N bond, deshielding of the hydrazino protons may arise from both inductive, and (p-d)π bonding effects. Figure III.15 indicates the operation of these effects for the bis(hydrazino)phosphines (a), and the mono(hydrazino)phosphines (b).

If (p-d)π bonding is represented as being synergic in character, its extent will be influenced by the electronegativities of the R_2P and NR_2 moieties. On the Allred-Rochow scale, phosphorus has an electronegativity of 2.06, and nitrogen, 3.07. Although the degree of polarity of the P-N bond in $(CF_3)_2PNHNMe_2$ would be difficult to predict, owing to the electronegative CF_3 groups on phosphorus, removal of one CF_3 group would

Figure III.15

H^1 NMR Shielding Mechanisms for the Phosphinohydrazines



(a) (b)

α; deshielding of the R' protons through withdrawal of electrons via an inductive mechanism.

β; deshielding of the R' protons resulting from effective withdrawal of the nitrogen lone pair via (p-d)π bonding.

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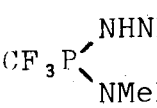
leave a less electronegative phosphorus, allowing the nitrogen atom a larger share of the σbonding electrons in $CF_3P(NHNMe_2)_2$ than in $(CF_3)_2PNHNMe_2$. Back-bonding through a P-N (p-d)π bond would be expected to be more extensive in $CF_3P(NHNMe_2)_2$ than in $(CF_3)_2PNHNMe_2$. Thus, enhanced (p-d)π bonding in the $CF_3P(NRNR_2)_2$ system, together with anisotropic contributions from two, rather than one P-N bond, may account for the equivalent deshielding effects of $(CF_3)_2P-$ and $CF_3P<$ on the $-NRNR_2$ protons.

(ii) Spin-Spin Coupling Constants

The mechanism for spin-spin coupling between two magnetically nonequivalent hydrogen nuclei has been suggested to involve coupling via bonding electrons, and depends on the electron density at each nucleus (p.63 of ref.31). Since only the s wave function has a finite density at the nucleus, the magnitude of the coupling may be said to depend on the amount of s character between the interacting nuclei; the magnitude of C^{13}-H^{1} coupling has been correlated with the hybridization of the carbon atom, and the resultant s character of the C-H bond (p.1012 of ref.31). For heavier nuclei, additional coupling directly through space is also possible, although the magnitude of this coupling is not as large as that arising from the indirect coupling (pp.185 and 875 of ref.31).

The PNCH and PNH coupling constants observed for the (trifluoromethyl)phosphinohydrazines are noted in Table II.46 and Table III.4. The observed values for J_{PNCH} are similar to those found for the chloro- and fluoro-phosphinohydrazines (68) and compare well for those noted for other PNMe systems (69-71). H.A. Bent (72) suggests that in a molecule, s character is concentrated in bonds directed towards more electropositive substituents

and so, J_{PNCH} coupling constants should increase as the substituent R in $(CF_3)_2PN(Me)R$ increases in electronegativity. This correlates with the J_{PNCH} coupling constants found for $(CF_3)_2PNMeNMe_2$ (J_{PNCH}, 3.6 cps) and $(CF_3)_2PNMeNH_2$ (J_{PNCH}, 8.5 cps), but does not explain the equivalent, and larger coupling constants in $CF_3P(NMeNMe_2)_2$ (IX) (J_{PNCH}, 7.0 cps), CF_3P  PCF_3 (X) (J_{PNCH}, 13.0 cps), and $CF_3P(NHNMe)_2PCF_3$ (XI) (J_{PNCH}, 14.0 cps). It has been proposed that the hybridization at phosphorus may be a decisive factor in changes in J_{PH} (72); the cyclic nature of compounds X and XI may impose a larger N-P-N bond angle (increasing s character in the P-N bond) than would be required for the long chain phosphinohydrazines. The cyclic phosphinohydrazine $ClP(NMeNMe)_2PCl$ has a value for J_{PNCH} of 16.5 cps (66). By similar arguments, the steric requirements of the methyl groups in $CF_3P(NMeNMe_2)_2$ may be greater than the requirements of the methyl groups in $(CF_3)_2PNMeNMe_2$. This would tend to increase the N-P-N bond angle in the former compound, which would be reflected in the larger J_{PNCH} coupling constant observed.

J_{PNH} for $CF_3(NHNMe_2)_2$ was found to be 20 cps, certainly larger than coupling constants noted for some

other aminophosphine systems [$(C_6H_5)_2P(NHBu^t)$, J_{PNCH}, 11.5 cps; $C_6H_5P(Cl)(NHBu^t)$, J_{PNH}, 15.1 cps (74)] but are comparable to J_{PNH} found for some phosphorus V hydrazine compounds [$(C_6H_5)P(S)(NHNMe_2)_2$, J_{PNH}, 27.3 cps; $(C_6H_5)_2P(X)(NHNMe_2)$, X=S, J_{PNH}, 21.5 cps, X=O, J_{PNH}, 18.8 cps (58)] . The coupling constants for compound X (J_{PNH}, 40 cps) and compound XI (J_{PNH}, 43 cps) are larger still, and may reflect the stereochemical requirements of the ring system.

Long range F-H coupling is observed in compounds V and IX (J_{FCPNCH}, 0.7 cps). The coupling is the same in both compounds. If the primary mechanism for this coupling operates via the bonding electrons, the coupling would be expected to be different for V and IX, as it is with J_{PNCH} coupling to the same protons. Through space F-H coupling (31, p.190) may be responsible for the coupling observed.

F^{19} NMR Data

Factors which influence the F^{19} chemical shift are not completely understood at the present, although it is generally agreed that the paramagnetic contribution to the shielding term is most important (p.874 of ref.31). This arises for fluorine because the electron distribution about the nucleus is not spherical. Thus, the ionic character of the R-F bond has been correlated to the F^{19} chemical

shift; qualitatively similar to the deshielding of the H^1 nucleus, an increase in the electronegativity of R, produces deshielding of the F^{19} nucleus. A notable exception occurs in the fluorochlorocarbons where the fluorine nuclei are shielded in a manner opposite to that predicted from electronegativity considerations (31, p.883) The presence of the double bonded structures (a), and (b) have been postulated; the greater importance of structure (a) would offer an explanation for the deviation. Thus,

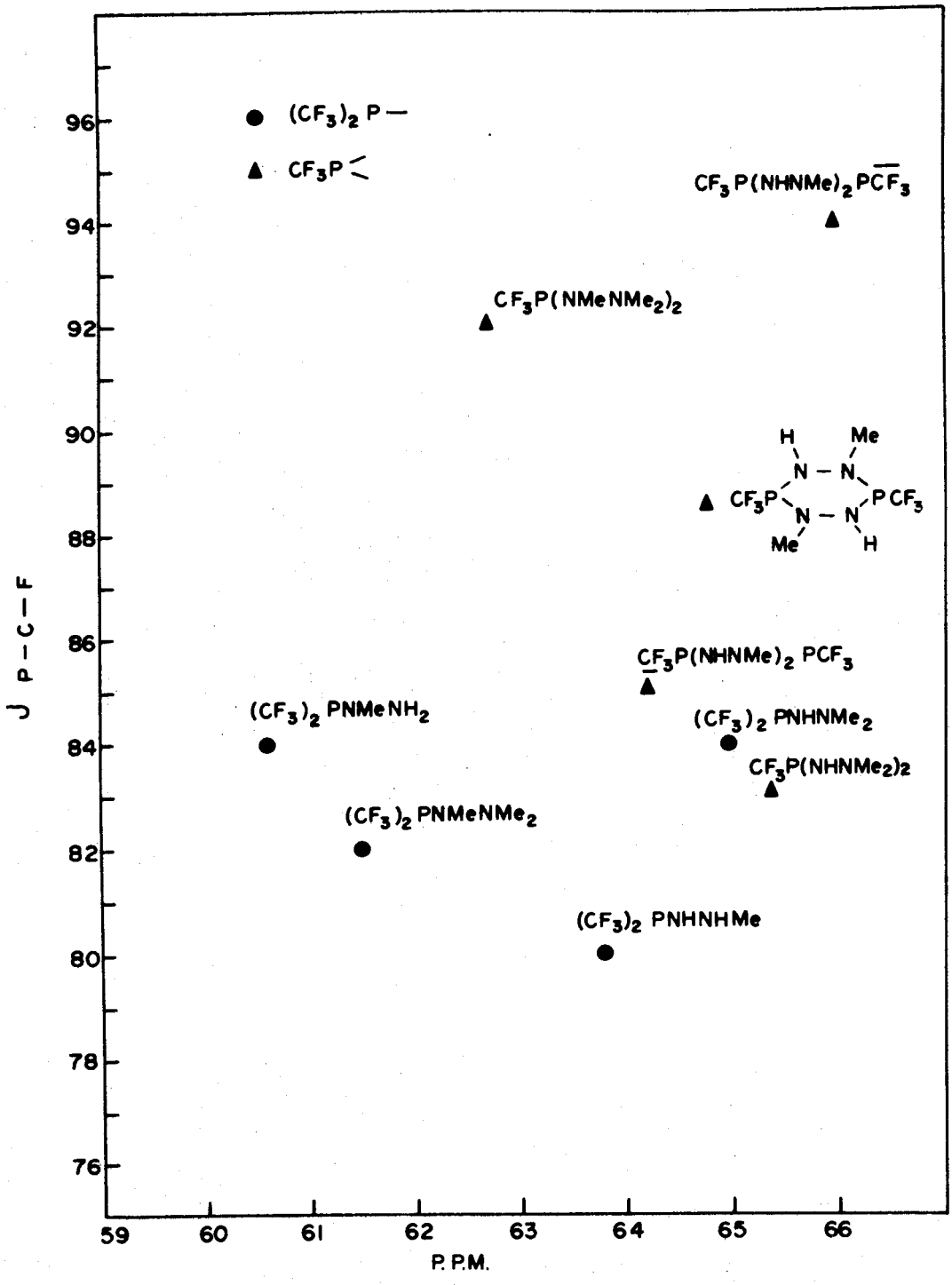
(a) (b)

the electronegativity of substituents, dispersion forces from solvent molecules and neighbouring substituents (31, p.874), and multiple bonding situations as noted above, may all have an effect on the F^{19} chemical shifts.

The fluorine chemical shifts of the (trifluoromethyl) phosphinohydrazines vary from 60.6 to 66.0 ppm and while the $CF_3P(NRNR^1R^{11})_2$ fluorines appear generally to be more shielded than the $(CF_3)_2PNRNR^1R^{11}$ fluorines, as would be expected from electronegativity considerations, the trends within each series do not seem to follow a predictable sequence.

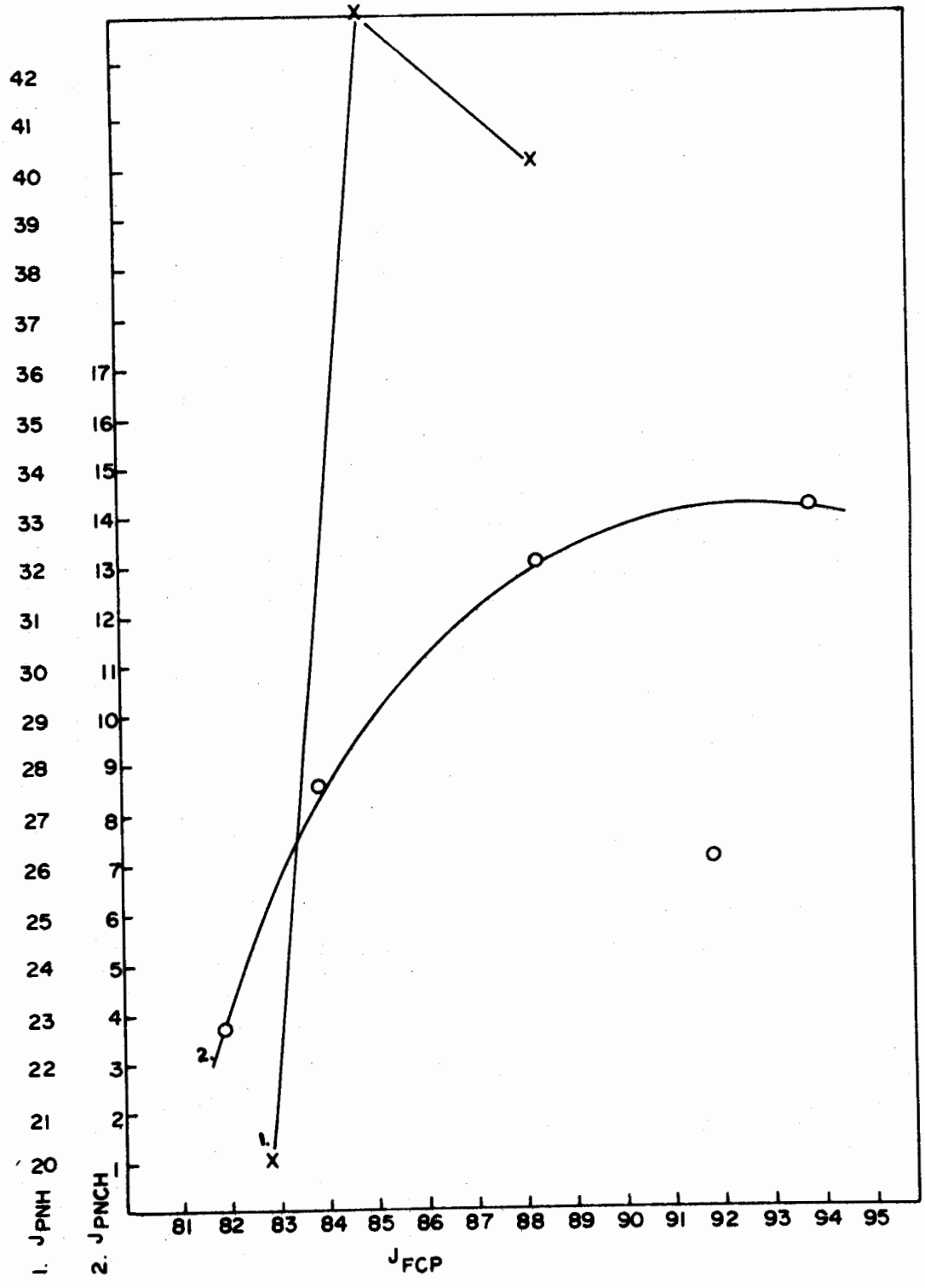
The observed J_{PCF} coupling constants vary over a

range from 80 to 94 cps and are generally larger for the $CF_3P(NRNR^1R^{11})_2$ compounds than for the $(CF_3)_2PNRNR^1R^{11}$ compounds. This is contrary to what is expected from electronegativity considerations alone. Packer (53) observed a qualitative direct relationship between J_{PCF} and the electronegativity of X in $(CF_3)_2PX$ compounds. This condition would be satisfied for the (trifluoromethyl)phosphinohydrazines only if $-NRNR^1R^{11}$ were more electronegative than CF_3. Figure III.16 plots the chemical shift of the CF_3 group against J_{PCF} for the (trifluoromethyl)phosphinohydrazines. While within each series ($(CF_3)_2P-$ and $CF_3P<$), J_{PCF} tends to decrease with an increase in F^{19} chemical shifts, on comparing the two series, there is a general increase in both J_{PCF} and the F^{19} chemical shifts from $(CF_3)_2PNRNR^1R^{11}$ to $CF_3P(NRNR^1R^{11})_2$. The chemical shift direction can be explained from electronegativity arguments. The coupling constant values may indicate that the hybridization about phosphorus, as well as substituant electronegativity effects, influence J_{PCF}. If the hybridization at phosphorus is an important factor in determining J_{PCF}, then J_{PCF} should show a positive correlation with J_{PNCH} and J_{PNH}. This trend is qualitatively observed, as noted in Figure III.17. It is noted that the hybridization at phosphorus is not due to substituent electronegativity effects, but due to



VARIATION OF ^{19}F CHEMICAL SHIFTS WITH J_{FCP} IN COMPOUNDS IV TO XI

Figure III.16



VARIATION OF J_{PNH} AND J_{PNCH} WITH J_{FCP} IN COMPOUND $\overline{IV}-\overline{XI}$

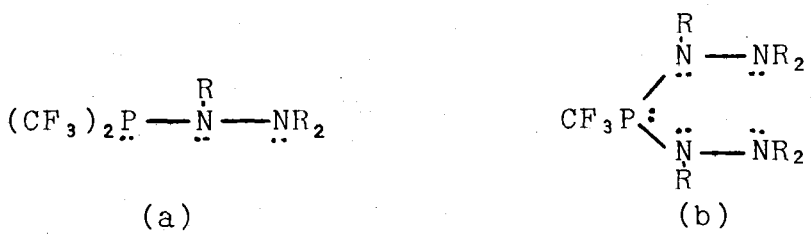
Figure III.17

steric requirements imposed by the substituents, or from hybridization requirements imposed by (p-d)π bonding.

D. Preparation of (Trifluoromethyl)phosphinohydrazineboranes

I. Introduction

The phosphinohydrazines, compounds IV to VII, are potentially tribasic; lone pairs from the two nitrogens are able to serve in σ donor fashion, and phosphorus has possible σ donating, as well as a π accepting function. The bishydrazinophosphines, compounds VIII and IX, have five basic sites on the molecular skeleton. (Figure III.18)



(a) (b)

Figure III.18

(a) bis(trifluoromethyl)phosphinohydrazines

(b) bis(hydrazino)trifluoromethylphosphines

To determine the σ donor functionality, as well as the most basic atom or atoms for the (trifluoromethyl)phosphinohydrazines, BX_3 (X = Me, F, Cl) adducts were prepared for compounds IV to VIII.

Previous studies of adduct formation with aminophos-

phines have shown that the donor site, to boron (75-78), aluminum (79,80), carbonium (81,82,83,70), phosphorus (84), and various transition metal (85-89) species, is always the phosphorus atom. Reactions of chloramine with aminophosphines give products which also show the more basic site to be phosphorus (90). Similarly, studies on the phosphinohydrazines, $R_nP(NR^1NMe_2)_{(3-n)}$, (n = 1, 2: R = C_6H_5; R^1 = H, Me), have shown the phosphorus atom to be more basic, towards Me^+ (91); the site of chloramination of these phosphinohydrazines is at phosphorus (91-93). Attempts to chloraminate (92) or alkylate (91) $(C_6H_5)P(O)NHNMe_2$ failed, indicating that both nitrogens of the hydrazinophosphineoxide are deactivated towards electron acceptor species.

$(C_6H_5)_2PNHNMe_2$ forms a 2:1 complex with Pt^{II}, 1:1 complexes with Hg^{II} and Pt^{IV}, and both 1:1 and 2:1 complexes with Pd^{II} (94); the functionality of the phosphinohydrazine in these complexes is still uncertain. Studies of transition metal complexes of (phosphinoamino)pyridines, where the two nitrogens are separated by a carbon atom, indicate that both phosphorus and the terminal nitrogen may coordinate to the metal in chelate fashion (95).

The (trifluoromethyl)phosphinohydrazineborane adducts (compounds XI to XXI) were prepared by the reaction of BX_3 (X = Me, F, Cl) with the appropriate (trifluoromethyl)

phosphinohydrazine dissolved in an inert solvent. H^1 and F^{19} NMR spectra were measured soon after the preparation of each adduct. These spectra are included in Tables III.6 ans III.7.

While the P-N bond in some aminophosphines is cleaved by BMe_3, BF_3 and BCl_3 (96), increased P-N bond stability is expected for the (trifluoromethyl)phosphinohydrazines, owing to the CF_3 groups attached to phosphorus (52, 97). Accordingly, BMe_3 and BF_3 complexes of compounds IV to VIII were found to be stable against cleavage, while adducts prepared using BCl_3 indicated further reaction only after about a week.

From the molar quantities of BF_3 used in reactions with $(CF_3)_2PNHNMe_2$ and $CF_3P(NHNMe_2)_2$, the formulations suggested for the products are $(CF_3)_2PNHNMe_2.BF_3$ (compound XII) and $CF_3P(NHNMe_2)_2.2BF_3$ (compound XXI). The F^{19} NMR spectrum for compound XXI indicates the equivalence of the two BF_3 groups; the integrated ratios of BF_3:CF_3 is 2:1. For the (trifluoromethyl)phosphinohydrazines, reduced σ donor character is expected for the phosphorus atom; MeCl does not react with $(CF_3)_3P$ (98), and neither $MeP(CF_3)_2$ nor $(CF_3)_3P$ show adduct formation with BF_3 at temperatures down to $-78^{\circ}C$ (99). Thus, the reaction stoichiometry and the NMR spectra suggest that for the (trifluoromethyl)phosphinohydrazines, adduct formation occurs

Table III.6 H^1 NMR Data for (trifluoromethyl)phosphinohydrazine boranes (a)

Compound	Solvent	>N-H	-NH	>N-Me	-NMe_2	BMe_3
$(CF_3)_2PNHNMe_2.BMe_3$	$CDCl_3$	5.64			7.43	9.45
$(CF_3)_2PNHNMe_2.BF_3$	$CDCl_3$	4.12 J_{PNH}, 11			7.07	
$(CF_3)_2PNHNMe_2.BCl_3$	$CDCl_3$	2.85			6.67	
$(CF_3)_2PNMeNMe_2.BMe_3$	$CFCl_3$			7.14 J_{PNCH}, 2.8 JFCPNCH0.7	7.50	9.32
$(CF_3)_2PNMeNMe_2.BF_3$	$CFCl_3$			6.80 J_{PNCH}, 2.0 J_{FCPNCH} 0.7	**7.15**	
$(CF_3)_2PNMeNMe_2.BCl_3$	$CFCl_3$			6.40 J_{FCPNCH},0.7	6.49(b) J (?), 1.4	
$(CF_3)_2PNMeNH_2.BMe_3$	$CDCl_3$		6.00	6.89 J_{PNCH}, 8.5		9.45
$(CF_3)_2PNMeNH_2.BF_3$	$CDCl_3$		3.80	6.72 J_{PNCH}, 4.8		
$(CF_3)_2PNHNHMe.BMe_3$	$CDCl_3$	PNH 5.03 NNH 5.47		7.27		10.02
$(CF_3)_2PNHNHMe.BF_3$	$CDCl_3$	PNH 3.92 NNH 4.52		7.08(c)		
$CF_3P(NHNMe_2)_2.2BF_3$	C_6H_5Cl	3.97 J_{PNH}, 9			6.93	

Table III.7 F^{19} NMR Data for (trifluoromethyl)phosphinohydrazine boranes (a)

Compound	Solvent	$-CF_3$	BF_3
$(CF_3)_2PNHNMe_2.BMe_3$	$CDCl_3$	65.0 J_{PCF}, 83	
$(CF_3)_2PNHNMe_2.BF_3$	$CDCl_3$	63.7 J_{PCF}, 88.5	163.4
$(CF_3)_2 PNHNMe_2.BCl_3$	$CDCl_3$	62.7 J_{PCF}, 89	
$(CF_3)_2PNMeNMe_2.BMe_3$	$CFCl_3$	61.5 J_{PCF}, 85.5	
$(CF_3)_2PNMeNMe_2.BF_3$	$CFCl_3$	59.6 J_{PCF}, 88.5	153.4
$(CF_3)_2PNMeNMe_2.BCl_3$	$CFCl_3$	58.1 J_{PCF}, 93.3	
$(CF_3)_2PNMeNH_2.BMe_3$	$CDCl_3$	60.6 J_{PCF}, 83.7	
$(CF_3)_2PNMeNH_2.BF_3$	$CDCl_3$	59.8 J_{PCF}, 89.5	148.5
$(CF_3)_2PNHNHMe.BMe_3$	$CDCl_3$	63.5 J_{PCF}, 82.7	
$(CF_3)_2PNHNHMe.BF_3$	$CDCl_3$	62.9(b) J_{PCF}, 86.5	159.0
$CF_3P(NHNMe_2)_2.2BF_3$	C_6H_5Cl	70.9 J_{PCF}, 92.5	162.1

Table III.6

(a) Chemical shifts reported in τ , relative to tetramethylsilane, 10.0 τ , as internal reference; coupling constants reported in cps.

(b) Doublet; splitting unassigned; see discussion.

(c) Temperature dependent splitting; see discussion.

Table III.7

(a) Chemical shifts reported in ppm above $CFCl_3$ (internal reference); coupling constants reported in cps.

(b) Temperature dependent signals; at +39°C, spectrum is doublet of quartets, J_{FF}, 8.0; see discussion.

at one of the nitrogens, rather than at the phosphorus centre.

2. Reactions of $(CF_3)_2PNHNMe_2$ with BX_3

(a) $(CF_3)_2PNHNMe_2.BMe_3$ (Compound XI)

The reaction between $(CF_3)_2PNHNMe_2$ and excess BMe_3 gives $(CF_3)_2PNHNMe_2.BMe_3$ (compound XI), and free BMe_3 . The formulation of a 1:1 adduct was based on the amount of BMe_3 recovered from the reaction, as well as on the H^1 NMR spectrum of the adduct, which showed peaks corresponding to BMe_3 (9.45 τ), NMe_2 (7.43 τ), and NH (5.63 τ), with an intensity ratio of 9:6:1 respectively. Comparing the position of the complexed BMe_3 peak to that for uncomplexed BMe_3 (9.23 τ (100)) suggests that a weak adduct is formed; experiments with space filling models indicate that steric interactions may be largely responsible for the stability of the adduct. The F^{19} spectrum showed a doublet arising from coupling between the CF_3 fluorines and the P^{31} nucleus (δ midpoint, 65.0 ppm; J_{PCF}, 83 cps).

(b) $(CF_3)_2PNHNMe_2.BF_3$ (Compound XII)

The reaction between $(CF_3)_2PNHNMe_2$ and excess BF_3 gives $(CF_3)_2PNHNMe_2.BF_3$ (compound XII). The formulation for the adduct was based on the quantity of BF_3 recovered from the reaction, and on the NMR spectra of the adduct. The H^1 and F^{19} NMR spectra for compound XII are assigned

as follows:

H^1: NMe_2, 7.07 τ ; NH, δ midpoint, 4.12 τ, J_{PNH} 11 cps; F^{19}: CF_3; δ midpoint 63.7 ppm, J_{PCF}, 88.5 cps: BF_3, 163.4 ppm. The integrated intensities were measured for the H^1 spectrum, NMe_2 :NH = 6:1, and for the F^{19} spectrum, CF_3:BF_3 = 2:1. The chemical shift for uncomplexed BF_3 is 127 ppm relative to $CFCl_3$ (p.945 of ref.31)

(c) $(CF_3)_2PNHNMe_2.BCl_3$ (Compound XIII)

The quantity of BCl_3 recovered from a reaction of $(CF_3)_2PNHNMe_2$ with excess BCl_3 suggested the formation of the 1:1 adduct $(CF_3)_2PNHNMe_2.BCl_3$ (compound XIII). The H^1 NMR spectrum of the adduct showed peaks corresponding to NMe_2 (6.67 τ),and NH (2.85 τ),with intensities of 6:1 respectively. The F^{19} spectrum showed a doublet corresponding to CF_3 (δ midpoint, 62.7 ppm, J_{PCF}, 89 cps). $(CF_3)_2PCl$, which would be expected from a reaction as in equation 3-39 was not detected. ($(CF_3)_2PCl$, δ midpoint, 61.4 ppm, J_{PCF}, 85.1 (53)). After about a week, however,

$$BCl_3 + (CF_3)_2PNHNMe_2 \rightarrow (CF_3)_2PCl + Cl_2BNHNMe_2 \qquad (3\text{-}39)$$

the product changed to a dark brown oil; the observation of NMR spectra for this product was restricted by its high viscosity.

3. Reactions of $(CF_3)_2PNMeNMe_2$ with BX_3

(a) $(CF_3)_2PNMeNMe_2.BMe_3$ (Compound XIV)

BMe_3 , and an excess of $(CF_3)_2PNMeNMe_2$ were allowed to react for one hour, after which time, the H^1 NMR spectrum showed peaks corresponding to NMe (δ midpoint, 7.14 τ, J_{PNCH}, 2.8 cps, J_{FCPNCH}, 0.7 cps), NMe_2 (7.50 τ), and BMe_3 (9.32 τ). The areas under the peaks indicated a deficiency in the proportion of BMe_3 required for a 1:1 adduct, in accord with the mole quantities of reactants used. The position of the BMe_3 peak is close to that for uncomplexed BMe_3 , and thus is in accord with the formation of a weak adduct.

(b) $(CF_3)_2PNMeNMe_2.BF_3$ (Compound XV)

Compound XV was isolated from a reaction of $(CF_3)_2$ $PNMeNMe_2$ with excess BF_3. The quantity of BF_3 recovered from the reaction indicated the formulation of compound XV to be $(CF_3)_2PNMeNMe_2.BF_3$. Supporting evidence for a 1:1 adduct comes from the F^{19} NMR spectrum in which the integrated intensities of $CF_3:BF_3$ = 2:1 (CF_3;δ midpoint, 59.6 ppm, J_{PCF}, 88.5 cps; BF_3, 153.4 ppm). The H^1 NMR spectrum showed peaks corresponding to NMe_2 (7.15 τ) and NMe (δ midpoint 6.80 τ , P_{PNCH}, 2.0 cps, J_{FPNCH}, 0.7 cps). intensities, NMe_2:NMe = 2:1.

(c) $(CF_3)_2PNMeNMe_2.BCl_3$ (Compound XVI)

$(CF_3)_2PNMeNMe_2$ was allowed to react with an excess of BCl_3. The amount of BCl_3 recovered from the reaction

indicated that $(CF_3)_2PNMeNMe_2$ reacts with BCl_3 in 1:1 molar proportions to give the adduct $(CF_3)_2PNMeNMe_2.BCl_3$ (compound XVI). The H^1 NMR spectrum for compound XVI showed a septet at 6.40 τ corresponding to the NMe protons. No spin coupling to phosphorus was observed; the septet arises from coupling to the F^{19} nuclei of the two equivalent CF_3 groups (J_{FCPNCH}, 0.7 cps), most likely via a through space mechanism (31, p.190). The resonance absorption corresponding to the NMe_2 protons, appeared as two peaks (δ midpoint 6.49 τ) with a splitting of 1.4 cps. This splitting may arise from different rotational isomers. The possibility of the reaction 3-40 which would give rise to an additional peak was precluded since no peaks corresponding to $(CF_3)_2PCl$ appeared in the F^{19} spectrum.

$$BCl_3 + (CF_3)_2PNMeNMe_2 \rightarrow (CF_3)_2PCl + Cl_2BNMeNMe_2 \quad (3\text{-}40)$$

The F^{19} spectrum for compound XVI showed a doublet corresponding to the CF_3 groups on phosphorus (δ midpoint, 58.1 ppm, J_{PCF}, 93.3 cps).

4. NMR Correlations and the site of adduct formation in the (trifluoromethyl) phosphinohydrazines

In each of the adducts, compounds XI to XVI, a 1:1 complex with BX_3 (X = Me, F, Cl) is formed. Since evidence supports one of the nitrogens as being the donor site, the

problem remains as to which of the two nitrogen atoms coordinates with the boron atom.

The site of adduct formation could not be inferred from observed spin-spin coupling, as neither the H^1 nor F^{19} NMR spectra revealed any fine structure arising from coupling to boron, or to the substituents on boron. Nor was BF coupling observed for the BF_3 adducts. This is in contrast to the well resolved 1:1:1:1 quartets observed for the methylhydrazine.BF_3 adducts, and methylamine.BF_3 adducts (1). The absence of such coupling could be due to exchange phenomena. However, the BF_3 adduct of $(CF_3)_2PNMeNH_2$ (Section III.D.5(b)) which included a small quantity of $(CF_3)_2PNHNHMe.BF_3$, showed BF_3 F^{19} NMR absorptions corresponding to both adducts, in the same intensity ratio as the CF_3 F^{19} signals for the respective compounds. If intermolecular exchange were fast, only one BF_3 peak would be observed. More likely, the collapse of the 1:1:1:1 multiplet is caused by quadrupolar relaxation of the boron, which is situated in an unsymmetrical electric field. Such a system might be one in which the boron is situated at some position between the two nitrogens of the hydrazine moiety; in this arrangement, the boron would effectively be five coordinate.

If we use the arguments developed for the BX_3 adducts of the methylhydrazines, in order to determine the more

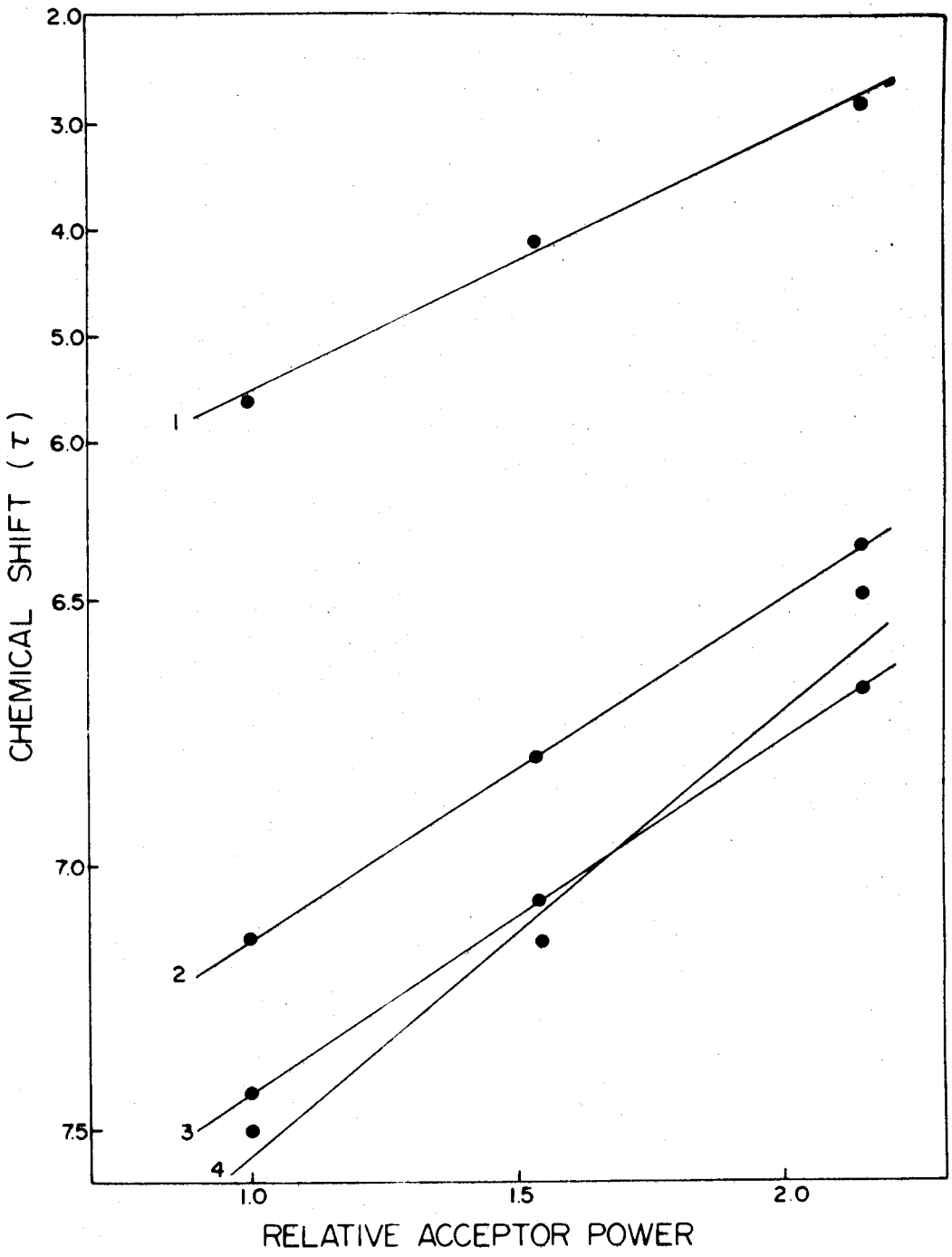
basic of the two nitrogen atoms, the chemical shifts of the protons on the hydrazine moiety are plotted against the relative acceptor power of BX_3. These curves for compounds XI to XVI are shown in Figure III.19. Again, to distinguish the more basic of the two nitrogen atoms, the expected sensitivity order is: adjacent protons > protons remote by one bond > protons remote by two bonds. The slopes of the curves are collected in Table III.8.

A comparison of the slopes obtained for the (trifluoromethyl)phosphinohydrazine boranes with the slopes obtained for the methylhydrazineboranes (Table III.3), quickly reveals that not only are the protons on the (trifluoromethyl)phosphinohydrazines more sensitive to deshielding effects, but that the slope values suggest that either, or both, nitrogen atoms are participating in coordinate bond formation to the borane. This is surprising in view of the fact that only one BX_3 molecule is coordinated to the (trifluoromethyl)phosphinohydrazine.

Table III.8

Slope values (arbitrary units, τ /relative acid strength, x 10^2) from Figure III.19

	NMe_2	NMe	NH
$(CF_3)_2PNHNMe_2$	66	-	240
$(CF_3)_2PNMeNMe_2$	83	64	-



DESHIELDING EFFECTS FOR 1. $(CF_3)_2PNHNMe_2$; 2. $(CF_3)_2PNMeNMe_2$; 3. $(CF_3)_2PNHNMe_2$; 4. $(CF_3)_2PNMeNMe_2$

Figure III.19

Obviously, the (trifluoromethyl)phosphinohydrazineborane system is more complex than that of the alkylated hydrazineboranes; P-N (p-d)π interactions, permissible in the former system may be influenced drastically by adduct formation.

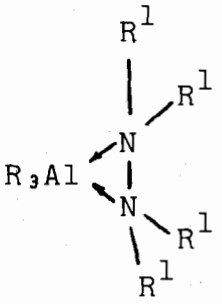
It is difficult to assess the contribution of P-N (p-d)π bonding to the deshielding of the protons on the hydrazine moiety, although its possibility has been mentioned (Section III.C.1.). If this deshielding mechanism is indeed operative, modifications to the electronic structure,with increasing (p-d)π bonding, should be reflected as an increase in the deshielding of protons attached to the nitrogen nearest the phosphorus atom (middle nitrogen). If the borane coordinates to the middle nitrogen, the (p-d)π bonding interaction between that nitrogen and the phosphorus atom would vanish. Thus, the deshielding of protons on the middle nitrogen caused by borane addition would be partly compensated by the reduction in (p-d)π bonding. This of course does not explain the extent and equivalence of the deshielding of both middle and terminal nitrogen methyl groups in $(CF_3)_2PNMeNMe_2.BX_3$, and would suggest that borane addition occurs at the terminal nitrogen. This is favored sterically for BMe_3 and BCl_3, but less so for BF_3.

If one assumes borane addition to the terminal nitrogen, the equivalent deshielding of middle and terminal nitrogen methyl protons is still difficult to explain, unless P-N (p-d)π bonding is increased in these systems. A possible mechanism assumes the presence of a secondary bonding interaction across the N-N bond. If some double bond character, utilizing the nitrogen lone pair orbitals and the C-N and P-N bonding orbitals, is present across the N-N bond in the (trifluoromethyl)phosphinohydrazines, as has been suggested to explain the short N-N bond length in $(CF_3)_2NN(CF_3)_2$ (101), then utilization of the lone pair of the terminal in the formation of a coordinate bond to boron, may release the lone pair of the middle nitrogen to strengthen the P-N (p-d)π interaction.

A second explanation for the equivalent deshielding of protons on the middle and terminal nitrogens assumes that the boron lies at some position between the two nitrogens.

Hydrazine has been proposed to act as a bidentate ligand towards $(iPrO)_3Al$ (102); in this complex, the aluminum atom is five coordinate, and assumes a position midway between the nitrogen atoms. The equivalent structure for $Me_3Al.(Me_2NNMe_2)$, proposed by Fetter and Bartocha (103), and supported by NMR measurements(104), and for

$Et_3Al.(Me_2NNMe_2)$ (105), is shown in Figure III.19.



R = R^1 = Me (103) (104)

R = Et, R^1 = Me (105)

R = iPrO, R^1 = H (102)

Figure III.20 Bidentate hydrazines.

Experiments with space filling models of the (trifluoromethyl)phosphinohydrazineborane adducts indicate that steric hindrance is lower for all three boranes, BMe_3, BF_3 and BCl_3, if the boron atom is at a position between the nitrogen atoms, than if the boron is coordinated to one specific nitrogen. Support for this stereochemical arrangement also comes from the observed collapse of the B-F spin multiplets for all of the BF_3 adducts.

5. Reactions of $(CF_3)_2PNMeNH_2$ with BX_3

(a) $(CF_3)_2PNMeNH_2.BMe_3$ (compound XVII)

Equimolar quantities of $(CF_3)_2PNMeNH_2$ and BMe_3 were allowed to react at room temperature to give the adduct $(CF_3)_2PNMeNH_2.BMe_3$ (compound XVII). The H^1 NMR spectrum showed peaks corresponding to BMe_3 (9.45 τ), NMe (∂ mid-point, 6.89 τ , J_{PNCH} 8.5 cps) and NH (6.00 τ) with integrated intensities of 9:3:2 respectively. The position

of the BMe_3 peak suggests the adduct to be weak. The F^{19} spectrum showed a doublet corresponding to CF_3 groups attached to phosphorus (δ midpoint, 60.6 ppm., J_{PCF}, 83.7 cps).

(b) $(CF_3)_2PNMeNH_2.BF_3$ (compound XVIII)

Equimolar quantities of $(CF_3)_2PNMeNH_2$ and BF_3 were allowed to react at room temperature to give the adduct $(CF_3)_2PNMeNH_2.BF_3$ (compound XVIII). The NMR spectra were assigned as follows: H^1: NMe, δ midpoint 6.72 τ, J_{PNCH}, 4.8 cps; NH_2, 3.80 τ ; integrated intensities, NMe:NH_2 = 3:2; F^{19}: CF_3, δ midpoint, 59.8 ppm, J_{PCF}, 89.5 cps; BF_3, 148.5 ppm; integrated intensities, BF_3:CF_3 = 1:2

6. Reactions of $(CF_3)_2PNHNHMe$ with BX_3

(a) $(CF_3)_2PNHNHMe.BMe_3$ (compound XIX)

Equimolar quantities of $(CF_3)_2PNHNHMe$ and BMe_3 were allowed to react at room temperature to give the adduct $(CF_3)_2PNHNHMe.BMe_3$ (compound XIX). The NMR spectra were assigned: H^1: BMe_3, 10.02 τ ; NMe, 7.27 τ; PN-H, 5.03 τ; NN-H, 5.47 τ; integrated intensities, BMe_3:NMe:PN-H:NN-H = 9:3:1:1; F^{19}: CF_3, δ midpoint, 63.5 ppm, J_{PCF}, 82.7 cps.

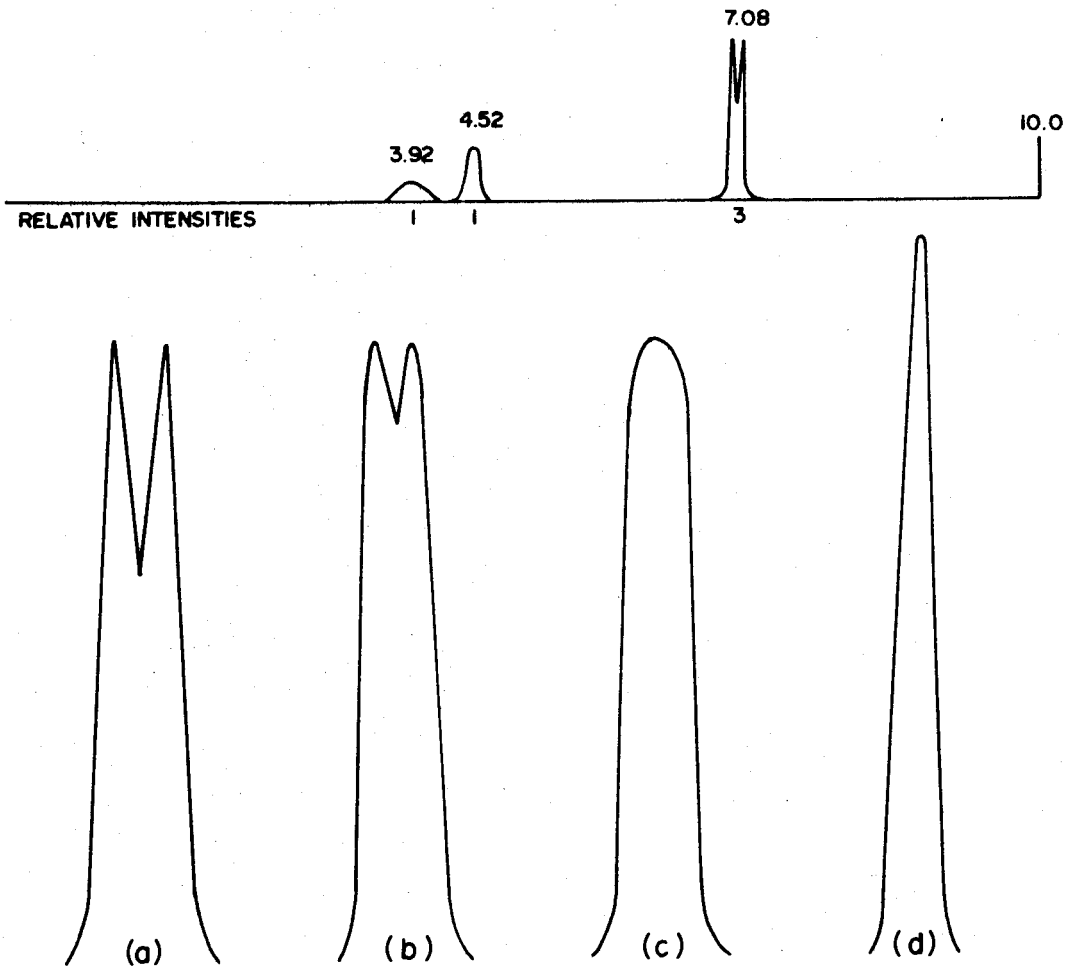
In this instance, the chemical shift of the BMe_3 protons indicates compound XIX to be more stable than compounds XI, XIV and XVII. Why this should be so is not completely clear, unless the BMe_3 adds to the terminal

nitrogen atom. In this case there may be less steric hindrance than for addition to the terminal nitrogen compounds XI and XIV; a more basic terminal nitrogen atom is compared to the NH_2 terminal nitrogen atom in compound XVII may be responsible for the greater stability of compound XIX.

(b) $(CF_3)_2PNHNHMe.BF_3$ (Compound XX)

$(CF_3)_2PNHNHMe.BF_3$ (compound XX), was prepared from the reaction of equimolar quantities of $(CF_3)_2PNHNHMe$ and BF_3 . NMR measurements on compound XX showed temperature dependence of both the H^1 and F^{19} spectra (Figures III.21 and III.22). At +38°C the H^1 spectrum consisted of a doublet (δ midpoint, 7.08τ) corresponding to the NMe protons, with a splitting of 5.0 cps (coalescence temperature = 49°C), and two broad signals corresponding to the PN-H (3.92 τ) and NN-H (4.52 τ) amino protons, with intensities of 3:1:1 respectively. The F^{19} spectrum at 38°C consisted of two doublets of quartets centered at ∂ midpoint, 62.9 ppm. The analysis of the spectrum (Figure III.23) is consistent with two magnetically nonequivalent CF_3 groups. Mutual coupling between the CF_3 groups gives rise to two quartets (J_{FCPCF}, 8.0 cps), and coupling of the CF_3 fluorines to the P^{31} nucleus ultimately gives rise to the observed spectrum. The coupling of the P^{31} nucleus to the fluorines

TEMPERATURE VARIATION OF THE H^1 AND ^{19}F NMR SPECTRA FOR $(CF_3)_2PNNNHMe \cdot BF_3$



NMe PEAK ; (a) at 38°C , (b) at 47.5°C ,

(c) at COALESCENCE TEMPERATURE 49.0°C, (d) at 56°C

Figure III.21

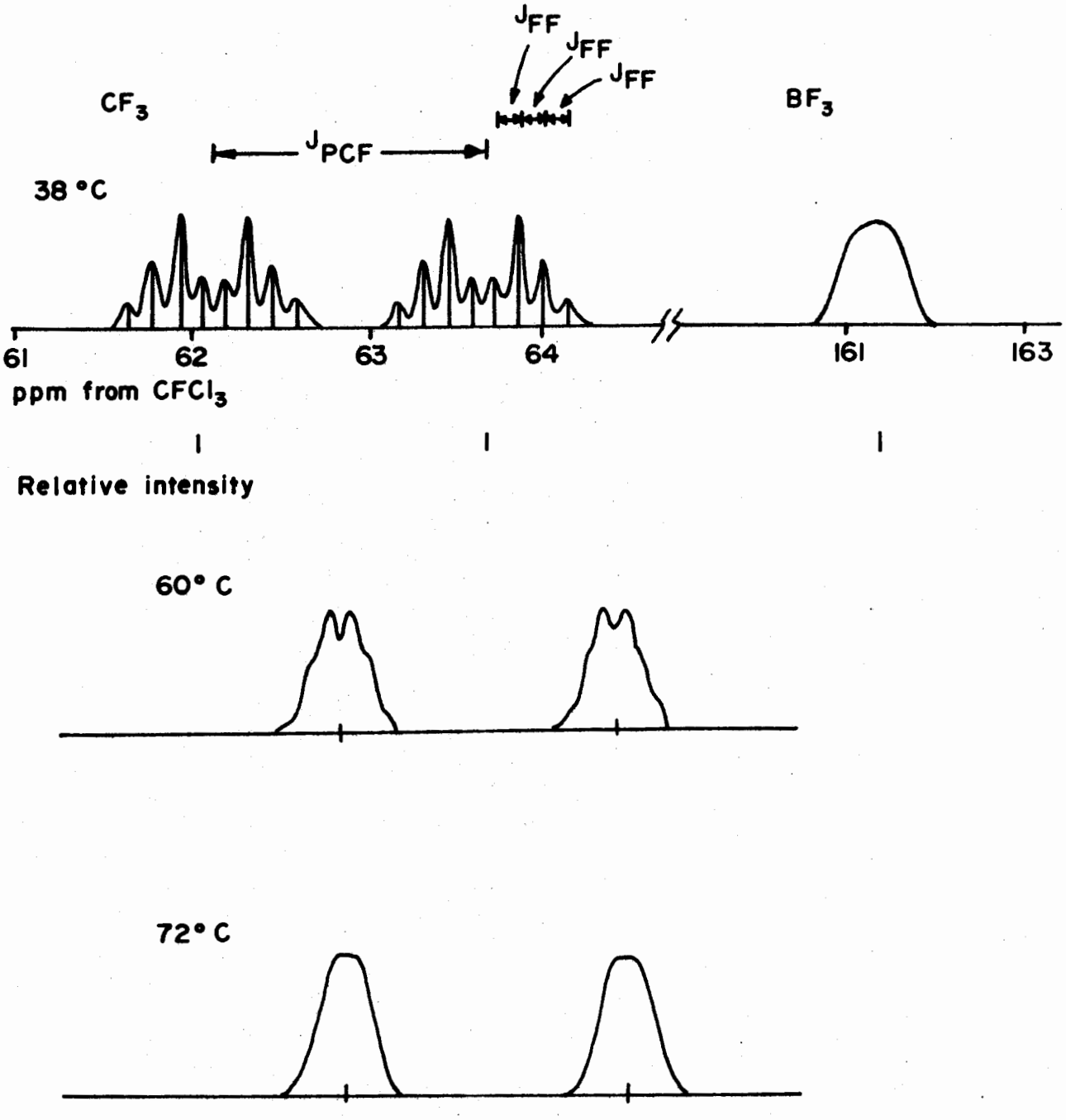
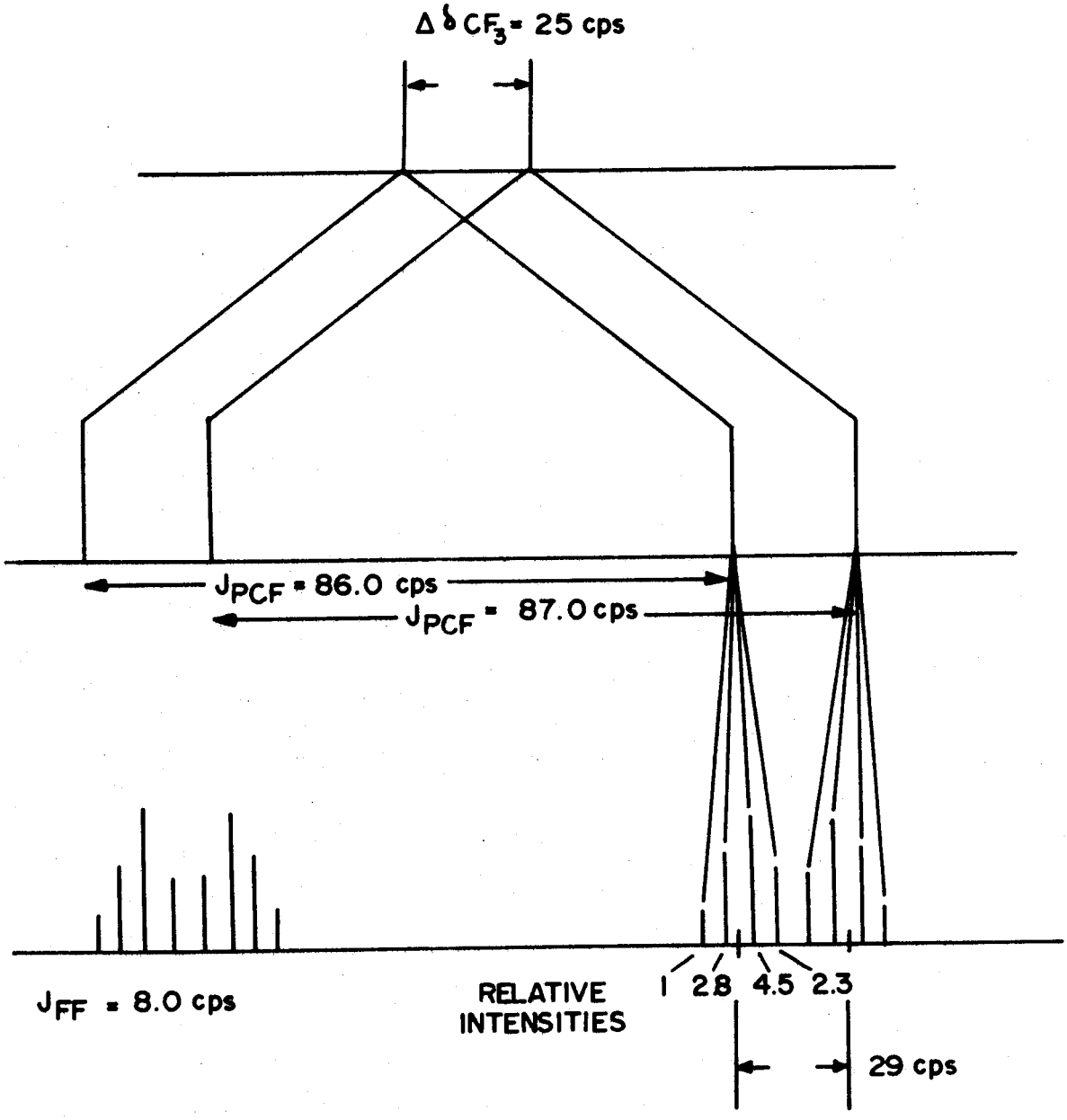


Figure III.22 Temperature Variation of the F^{19} NMR Spectrum for $(CF_3)_2PNNHMe.BF_3$



SPLITTING PATTERN OF TWO MAGNETICALLY NONEQUIVALENT CF_3 GROUPS ATTACHED TO PHOSPHORUS IN $(CF_3)_2PNHNMe \cdot BF_3$

Figure III.23

of the nonequivalent CF_3 groups is almost identical (CF_3(A), J_{PCF}, 86.0 cps, CF_3(B), J_{PCF}, 87.0 cps). At higher temperatures each doublet of quartets coalesced (coalescence temperature (calc) = 72 ± 2°C) to show only the coupling due to phosphorus (J_{PCF}, 86.5 cps). BF_3 was observed as a single broad line (159.0 ppm); the intensity ratio of CF_3:BF_3 was 2:1.

The observed F^{19} spectrum could arise from restricted rotation about the P-N bond; the splitting observed for the NMe group in the H^1 spectrum could arise either from spin coupling to the HNMe amino proton, or from restricted rotation about the N-N bond. If the latter mechanism is assumed, the free energy of activation for the rotation about the N-N bond can be calculated from the Eyring equation (26) (equation 3.41):

$$k_r = \frac{K_B\ T}{h}\ \exp(-\Delta G^{\ddagger}/RT) \qquad (3\text{-}41)$$

k_r = rate constant
K_B = Boltzmann's constant
h = Planck's constant
R = gas constant
T = temperature in °K
$\Delta G^{\ddagger}$ = free energy of activation. Thus,

$$\Delta G^{\ddagger} = 4.57\ T\ (10.32 + \log\ T/K_r) \qquad (3\text{-}42)$$

kc, the rate constant at the coalescence temperature Tc, can be approximated from equation 3-43;

$kc = \pi\Delta\nu / 2$ (3-43)

$\Delta\nu$ = line separation without exchange.

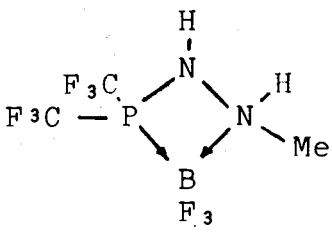
If the separate signals are coupled to each other, kc is better approximated from equation 3-44;

$kc = \pi(\Delta\nu^2 + 6 - J^2)^{\frac{1}{2}} / 2$ (3-44)

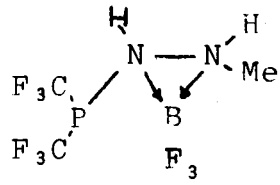
J = coupling constant.

Thus, from equations 3-42 and 3-43, the free energy of activation for rotation about the N-N bond, $\Delta G^{\ddagger}$ N-N = 17.3 ± 0.8 Kcal/mole. Similarly, from the F^{19} spectrum, and using equations 3-42 and 3-44, $\Delta G^{\ddagger}$ P-N = 17.4 ± 0.2 Kcal/mole.

The equivalence of the values of the free energies of activation suggests that rotational isomerism, rather than spin-spin coupling is responsible for the splitting in the H^1 spectrum, and that a single mechanism is responsible for the rotational barriers about the P-N and N-N bonds. Arguments can be presented for two possible structures causing the observed effects. Structure (a), in which boron coordination to the phosphorus atom and the terminal nitrogen atom, locks the configuration of the PNN skeleton, and structure (b), in which the boron is situated at a point between the



(a)



(b)

two nitrogens, rotation about the P-N bond being slowed due to increased (p-d)π bonding in the adduct.

7. $CF_3P(NHNMe_2)_2.2BF_3$ (Compound XXI)

Compound XXI was isolated from the reaction of $CF_3P(NHNMe_2)_2$ with excess BF_3 . The quantity of BF_3 recovered from the reaction indicated the formulation for cpd XXI to be $CF_3P(NHNMe_2)_2.2BF_3$. Supporting evidence for a 2:1 adduct comes from the F^{19} NMR spectrum in which the integrated intensities of BF_3:CF_3 = 2:1. (CF_3;δ midpoint, 70:9 ppm; J_{PCF}, 92.5 cps; BF_3, 153.4 ppm.) The H^1 NMR spectrum showed peaks corresponding to NMe_2 (6.93τ) and NH (δ midpoint 3.97 τ , J_{PNH}, 9 cps) with integrated intensities of NMe_2:NH = 6:1.

8, General Correlations

In the F^{19} NMR spectra, a qualitative correlation was observed between J_{PCF} and the Lewis acid strength of the coordinating boranes. Within each series of (trifluoromethyl)phosphinohydrazine.BX_3 adducts, J_{PCF} increases as X varies from Me to F to Cl. At the same time, the chemical

shifts of the respective CF_3 groups indicate deshielding in the same order. This is in agreement with trends found by Packer (53) for $(CF_3)_2PX$ compounds where J_{PCF} increases with increasing electronegativity of X, and also suggests inductive effects to be operative. At the same time however, in the H^1 NMR spectra, the J_{PNCH} coupling constants for the $(CF_3)_2PNMeNRR^1.BX_3$ adducts, decrease as X varies from Me to F to Cl, quite opposite to what might have been expected. J_{PNCH} for F_2PNMe_2 has been reported (106) to be 9.25 cps. The crystal structure (107) shows the $PNMe_2$ arrangement to be planar, suggesting sp^2 hybridization of the nitrogen atom. Deformations from this planar arrangement might be expected to be reflected in a decrease in J_{PNCH}. While the $P-N\begin{smallmatrix}R\\N\end{smallmatrix}$ arrangement in the(trifluoromethyl)phosphinohydrazines may not be planar, the PNN bond angle may be greater than the tetrahedral angle (109° 28'); coordination in some fashion to BX_3 may tend to decrease the PNN bond angle, being reflected in a decrease in J_{PNCH}.

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