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PHOSPHORUS PENTAFLUORIDE AS A LEWIS ACID: REACTIONS WITH TRIMETHYLSILYLATED NITROGEN HETEROCYCLES

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Dedicated to Professor Kurt Dehnicke on the occasion of his 60th birthday.

SUMMARY

The reaction of the N-trimethylsilyl-substituted heterocycles, trimethylsilylpyrazole, **1**, -imidazole, **3**, -5,6-dimethylbenzimidazole, **7**, and 1,3,4-triazole, **8** with phosphorus pentafluoride was studied. The reaction proceeded via the initial formation of 1:1 Lewis acid-base adducts between phosphorus pentafluoride and the nitrogen atom bearing the Me_3Si group. In the reaction of **1** with PF_5 the unusual bis-tetrafluorophosphate complex, **2** was directly formed by cleavage of Si-N bonds and elimination of Me_3SiF. The reaction of the trimethylsilylated triazole, **8** with PF_5 produced a mixture of substances. The dimer **5** was formed during thermolysis of **4**.
The products were characterized by ^1H, ^{13}C, ^{19}F, and ^{31}P n.m.r spectroscopy. A single crystal X-ray structure determination was conducted for the pyrazole-bridged bis-tetrafluorophosphate complex, **2**, in which the central six-membered ring (P_2N_4) adopts a boat conformation.

INTRODUCTION

A variety of acceptor-donor complexes of PF_5 have been reported; these include the $[PF_6]^-$ anion and some of its substituted derivatives, all involving hexa-coordinate (λ^6) phosphorus [1].

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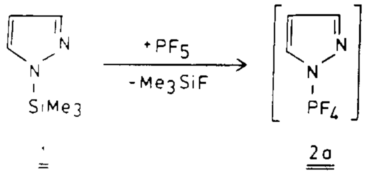
Neutral adducts of PF_5 with Lewis bases, e.g. ethers [2-3] and amines [4-7] have been described. PF_5 displays higher Lewis acidity than its alkyl- or aryl-substituted derivatives [8]. Special interest attaches to a group of λ^6-P-fluorophosphates where the hexa-coordination of phosphorus is the result of an intramolecular donor-acceptor interaction, in particular with nitrogen as the donor atom [9-11]. N.m.r. investigations [3, 7, 8, 12-20] and X-ray crystal structure determinations [7, 21-23] reveal essentially octahedral geometry, more or less strongly distorted, at λ^6P for both the neutral adducts and the ionic products. In the following we describe a series of donor-acceptor complexes involving λ^6P, arising from reactions between PF_5 and the N-trimethylsilyl derivatives of some nitrogen heterocycles.

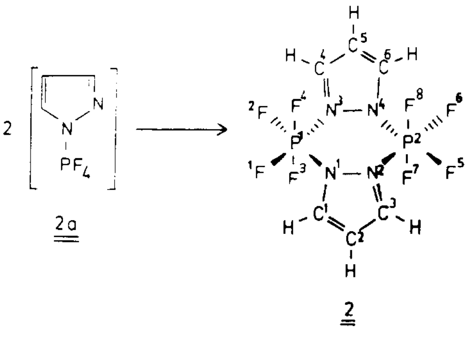
RESULTS AND DISCUSSION

Reaction of N-trimethylsilyl-pyrazole 1 with PF_5

This reaction was found to proceed in accord with eq. (1) with formation, ultimately, of the bis-tetrafluorophosphate complex, **2**.



(1)



We suggest that the reaction proceeds by initial cleavage of the SiN bond in **1** and formation of the tetrafluorophosphorane, **2a**, accompanied by elimination of fluorotrimethylsilane. The tetrafluorophosphorane, **2a** then dimerizes with formation of the stable bis-tetrafluorophosphate complex, **2**. This dimerization is thought to be due to charge delocalisation and formation of an energetically favourable six-membered ring system.

2 is a colourless solid, stable to air and moisture, which readily crystallizes from dichloromethane.

The ^1H n.m.r. spectrum of **2** exhibits broad signals for the protons bonded to the carbon atoms C^1 and C^3, which suggests coupling between ^1H, ^{19}F and ^{31}P. The ^1H n.m.r. resonance of the proton bonded to C^2 is a quintet, characterized by the coupling constant $^5J(FH)$. The ^{13}C n.m.r resonance of C^2 appears as a triplet, as a result of P-C coupling, $^3J(PC)$. The five lines of the ^{31}P n.m.r. spectrum of **2** were broad, suggesting ^{31}P-^{14}N coupling or, possibly, quadrupole effects, due to ^{14}N. Low temperature n.m.r. studies of **2** were impossible because of solubility problems.

The ^{19}F n.m.r. spectrum of **2** corresponds to the A_2BC part of an A_2BCX spin system. Its lineshape is similar to that of other PF species with $\lambda^6 P$ that involve intramolecular donor-acceptor interaction between nitrogen and phosphorus [11]. The signals corresponding to the fluorine atoms F^2, F^3 and F^4 are broader than those for F^1. This may result from ^{14}N-^{19}F spin-spin interaction.

The resonance of F^1, trans to a donor nitrogen atom (N^3), is split into a doublet of triplets, since F^1 is almost equivalent to F^2. No coupling ^{14}N-$^{19}F^1$ or ^1H-$^{19}F^1$ is observed. It is known that the coupling constants $^3J(^1H$-$^{19}F^{trans})$ in the anions, $[CH_3PF_5]^-$ [17] and $[HPF_5]^-$ [20] and $^2J(^{31}P$-$^{19}F^{trans})$ in $Me_3P{*}PF_5$ [18] are zero, apparently because of the angular dependence of the coupling constants [3].

X-ray crystal structure determination of **2**

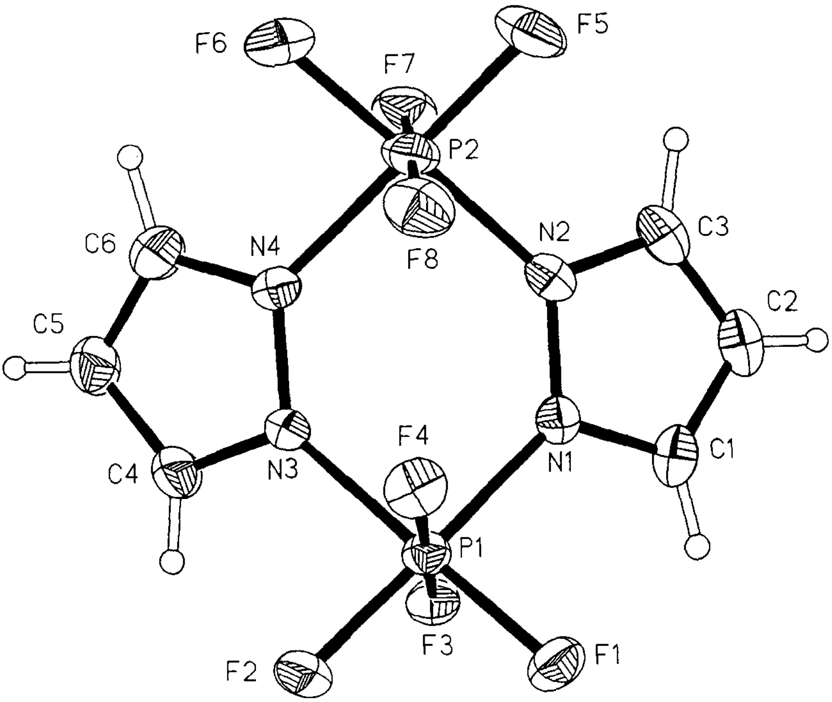
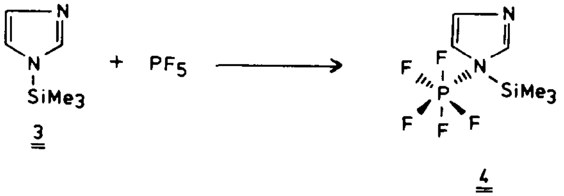


Fig. 1: The molecule of 2 in the crystal. The thermal ellipsoids correspond to 50% probability.

The X-ray crystal structure determination of **2** (Fig.1) confirmed that both phosphorus atoms are octahedrally coordinated. The characteristic feature of the structure of **2** is the flat boat conformation of the central six-membered ring, with the atoms P(1) and P(2) lying 60 and 49 pm, respectively, above the N_4 plane. The dihedral angle between the equatorial planes at the phosphorus atoms is 48°. A transannular P...P contact of 372 pm was observed. The five-membered pyrazole rings are planar within 1 pm, as is the coordination at the nitrogen atom. The mean values of the PN and PF bond lengths are 183.4 and 158.5 pm, respectively.

Reaction of N-trimethylsilyl-imidazole **3** with PF_5

This reaction was studied in order to establish whether **3** would react with PF_5 to produce a dimeric bis-tetrafluorophosphate complex comparable to **2**. As illustrated in eq. (2), the reaction took quite a different and unexpected course.



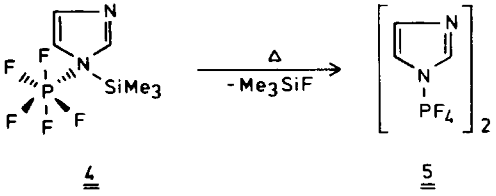
(2)

The product, **4** turned out to be a 1:1 donor-acceptor complex between the N-trimethylsilylated heterocycle, **3** and PF_5. Its mass spectrum revealed **3** as a base peak. This observation may be rationalized if one assumes that the observed 1:1 coordination between **3** and PF_5 is favoured over the SiN cleavage and formation of an eight-membered ring. The stability of the latter is less pronounced; the donor-acceptor interaction is thought to involve the sp^3-hybridized nitrogen atom N^1, which is more basic than the sp^2-hybridized nitrogen atom N^2 [24].

The unusual donor-acceptor complex, **4** is stable, melting without decomposition, although it is known that SiN bond cleavage to form a PN bond proceeds readily under mild conditions [25, 26]. Its ^{31}P n.m.r. spectrum is a sextet with broad signals. Because of the near identity of $^1J(PF^{cis})$ and $^1J(PF^{trans})$, the difference amounting to only 5.7 Hz, the expected doublet of quintets is not seen. We suggest that the line broadening results from ^{31}P-^{14}N and/or phosphorus-nitrogen quadrupole interaction. Because of solubility problems, low temperature n.m.r.experiments were impossible. The significant high field shift of δP (from -80.3 ppm in PF_5 [27] to -143.34 ppm) in **4** illustrates the change in coordination at phosphorus from λ^5 to λ^6. Because of the presence of two different fluorine environments, F^{cis} and F^{trans}, two doublets, characterized by $^1J(PF^{cis})$ and $^1J(PF^{trans})$, were observed in the ^{19}F n.m.r. spectrum of **4**. The resonance due to F^{cis} (at lower field) is split into a doublet, as a result of coupling with F^{trans}, while the resonance of F^{trans} (at higher field) is split into a quintet by coupling with the four cis-fluorine atoms.

Thermolysis of **4**

Compound **4** exhibits remarkable thermal stability which is quite unexpected, in view of the well-known facile cleavage of Si-N bonds by Lewis-acidic phosphorus fluorides [25, 26]. Formation of fluorotrimethylsilane was observed only upon heating **4** to 145°C, well above the melting point of 121°C. After 30 min of heating **4** to 145°C a solid product was recovered which, according to its ^1H n.m.r. spectrum, still contained ca. 10% unchanged **4**. When the thermolysis of **4** was conducted in vacuo (0.1 mm Hg) or at still higher temperature in order to drive the reaction to completion, a glassy, apparently polymeric solid was formed which was insoluble in common organic solvents (eq. 3).



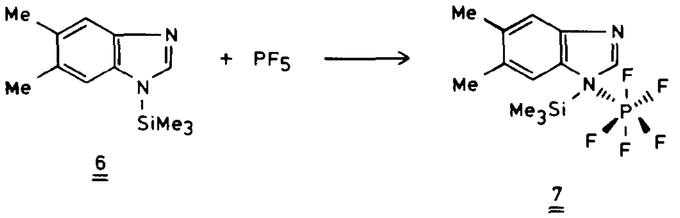
(3)

The n.m.r. spectra of **5** were similar to those of **2**. In the ^{31}P n.m.r. spectrum the expected quintet was observed. As in the case of **2** the line broadening may be due to ^{31}P-^{14}N coupling. Similar line broadening was seen in the ^{19}F n.m.r. spectrum of **5**, as a result of which the

$^2J(FF)$ coupling constant could not be determined. Because of the limited solubility of **5** low temperature n.m.r. studies were impossible.

Reaction of N-Trimethylsilyl-5.6-dimethylbenzimidazole **6** with PF_5

The reaction produced the 1:1 complex **7** in 86% yield, in accord with eq. (4).

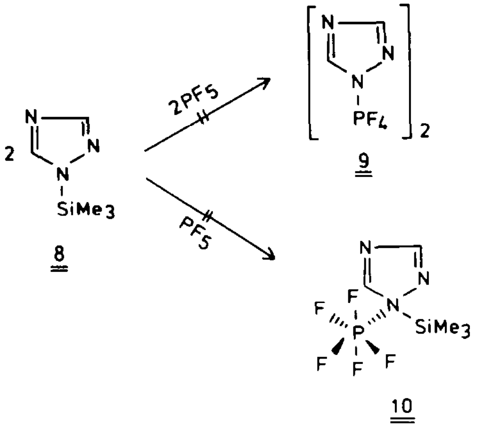


(4)

Like **4**, **7** was thermally stable, melting at 232°C without decomposition. The n.m.r spectra of **7** were nearly identical to those of **4**. The base peak in the mass spectrum of **7** corresponded to the starting silylated heterocycle, **6**, as in the case of **4**.

Reaction of 1-Trimethylsilyl-1.2.4-triazole **8** with PF_5

In this reaction, neither the tetrafluorophosphorane, **9a** nor the 1:1 complex **10** between **8** and PF_5 were formed (eq. 5).



(5)

A colourless solid was obtained after the volatile products were removed. Its ^{19}F solution n.m.r. spectrum indicated the presence of a mixture of products, most notably fluorotrimethylsilane. Its formation suggests that the crude product obtained in the reaction of **8** and PF_5 undergoes rapid transformation in solution. Because of its poor solubility in common organic solvents a ^{31}P n.m.r. spectrum of the product could not be recorded. The elemental analysis was inconclusive.

EXPERIMENTAL

All experiments were conducted with exclusion of moisture in an atmosphere of dry nitrogen. Solvents were dried by standard procedures [28, 29]. N.m.r. spectra: BRUKER AC 200: ^{1}H (200 MHz); ^{13}C (50 MHz); ^{19}F (188 MHz); ^{31}P (81 MHz); BRUKER AM 400: ^{13}C (100 MHz); JEOL JNMC 60 HL: ^{31}P (24.3 MHz); PERKIN ELMER R 24B : ^{1}H (60 MHz). N.m.r. reference substances: CD_3CN int. (^{1}H, ^{13}C); CCl_3F ext. (^{19}F); 85% H_3PO_4 ext. (^{31}P). High field shifts have a negative sign, low field shifts a positive sign.
Mass spectra were recorded by the Mass Spectrometry Laboratory of the chemical institutes of the Technische Universität Braunschweig on the instruments VARIAN MAT CH-7 and FINNIGAN MAT 8430. Signal intensities are listed in %, relative to the base peak (100%).
Materials: N-Trimethylsilyl pyrazole [30]; N-trimethylsilyl imidazole [30]; N-trimethylsilyl-5.6-dimethylbenzimidazole [31]; N-trimethylsilyl-1.2.4-triazole [30]; Phosphorus pentafluoride was used as obtained from U.S. Agrichemicals, Inc.

Reaction of N-trimethylsilyl-pyrazole, 1 with phosphorus pentafluoride: Synthesis of bis(1-pyrazolo-2-azonia-tetrafluorophosphate), 2

Phosphorus pentafluoride (12.96 g; 0.103 mole) was condensed at -196°C onto a solution of 14.47 g (0.103 mole) of 1 in 80 ml of dichloromethane in a heavy-wall glass tube fitted with a TEFLON® stopcock . The temperature of the reaction mixture was increased to room temperature within

1 h and stirring was continued for another 1.5 h. Compound **2** was precipitated as a colourless solid. The reaction mixture was pumped dry (0.1 mm Hg; 20^{0}C; 1 h), and the residue was recrystallized from 20 ml of dichloromethane.

Yield of **2** 16.29 g (91%); mp. 138^{0}C.

$C_6H_6F_8N_4P_2$ (347.96):

calc.	C 20.70	H 1.73	P 17.80
found	C 20.60	H 1.78	P 17.74

Mass spectrum: m/z (%) = 348 (1.5, $[M]^+$), 329 (0.7, $[M-F]^+$), 222 (23, $[M-PF_5]^+$), 203 (5, $[M-PF_6]^+$), 174 (12, $[M-C_3H_3N_2-PF_4]^+$), 155 (25, $[M-C_3H_3N_2-PF_5]^+$), 107 (100, $[PF_4]^+$).

N.m.r. spectra: ^1H (CD_3CN, 200.1 MHz): δ 6.68 (quintet, $^5J_{(HF)}$ 2.9 Hz, H-C=C), 8.36 (m, br, H-C=N). - ^{13}C (CD_3CN, 50.3 MHz): δ 107.42 (t, $^3J_{(CP)}$ 7.44 Hz, C^2), 142.25 (s, C^1C^3) - ^{19}F (CD_3CN, 188.3 MHz): δ -35.84 (ddd, $^1J_{(PF^{3.4})}$ 791.5 Hz, $^2J_{(F^{3.4}F^2)}$ 57.6 Hz, $F^{3.4}$), -57.9 (dt, $^1J_{(PF^1)}$ 788.0 Hz, $^2J_{(F^1F^{3.4})}$ 37.5 Hz, F^1), -58.0 (ddd, $^1J_{(PF^2)}$ 788.5 Hz, $^2J_{(F^1F^2)}$ 56.5 Hz, F^2). - ^{31}P (CD_3CN, 81.0 MHz): δ -154.72 (quintet, br).

Crystal Structure Analysis of 2

Crystal data: $C_6H_6N_4F_8P_2$, M = 348.1, monoclinic, space group $P2_1/c$, a = 767.2(3), b = 1908.5(7), c = 851.3(3) pm, β = 116.17(3)^0, U = 1.1187 nm^3, Z = 4, D_x = 2.067 Mg m^{-3}, $F(000)$ = 688, λ(Mo K_α) = 71.069 pm, μ = 0.48 mm^{-1}, T = -95^{0}C.

Data Collection and Reduction: A colourless tablet ca. 0.65 x 0.6 x 0.3 mm was mounted under inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low temperature attachment). 4601 intensities were measured to $2\Theta_{max}$ 55^0 (monochromated Mo K_α radiation), of which 2552 were independent (R_{int} 0.022) and 2230 observed (> $4\sigma(F)$). The orientation matrix was refined from diffractometer angles of 50 reflections in the 2Θ range 20-24^0.

Structure Solution and Refinement: The program system 'Siemens SHELXTL PLUS' was employed. The structure was solved by direct methods and refined anisotropically. Hydrogen atoms were refined freely. An extinction correction of the form $F_{corr} = F[1+xF^2/\sin 2\Theta]^{-0.25}$ was applied, whereby x refined to 3.1(3) x 10^{-6}; the weighting scheme was $w^{-1} = \sigma^2(F) + 0.0001F^2$. The final R value was 0.025, with wR 0.033; 206 parameters, S 1.9, max. Δ/σ 0.002, max. $\Delta\rho$ 0.27 x 10^{-6} e pm^{-3}. Atom coordinates are given in Table 1, bond lengths and angles in Table 2.

Further details of the structure determination (H atom coordinates, structure factors, temperature factors) have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD 55265.

TABLE 1

Atomic coordinates (x10^5) and equivalent isotropic displacement coefficients (pm^2) for compound 2

	x	y	z	U(eq)
P(1)	73090(5)	43113(2)	44310(5)	196(1)
P(2)	28965(6)	33996(2)	11932(5)	263(2)
F(1)	74514(14)	50086(4)	54814(11)	281(3)
F(2)	92166(12)	39935(4)	59578(11)	284(3)
F(3)	85549(12)	46443(4)	35404(11)	247(3)
F(4)	60092(13)	39520(4)	52113(10)	254(3)
F(5)	6826(13)	36195(6)	3844(13)	389(4)
F(6)	23854(14)	25895(5)	10050(14)	420(4)
F(7)	28328(14)	34117(5)	-7066(12)	351(4)
F(8)	30302(13)	34095(5)	30964(12)	313(4)
N(1)	51430(18)	46693(6)	26043(15)	209(4)
N(2)	35489(18)	43310(6)	13816(16)	230(5)
N(3)	70995(17)	35213(6)	31304(15)	207(4)
N(4)	54749(18)	31539(7)	20713(17)	256(5)
C(1)	49749(25)	53527(8)	21635(21)	272(6)
C(2)	32809(25)	54600(9)	6765(22)	304(6)
C(3)	24372(24)	48167(9)	2139(21)	299(6)
C(4)	86480(23)	31779(9)	31731(21)	285(6)
C(5)	80562(25)	25909(9)	21479(23)	351(7)
C(6)	60759(27)	25916(9)	14777(25)	383(7)

TABLE 2

Bond lengths (pm) and angles (°) for compound 2

P(1)-F(1)	158.0 (1)	P(1)-F(2)	158.8 (1)
P(1)-F(3)	159.1 (1)	P(1)-F(4)	157.8 (1)
P(1)-N(1)	183.5 (1)	P(1)-N(3)	183.5 (1)
P(2)-F(5)	158.2 (1)	P(2)-F(6)	158.6 (1)
P(2)-F(7)	159.7 (1)	P(2)-F(8)	157.8 (1)
P(2)-N(2)	183.4 (1)	P(2)-N(4)	184.1 (2)
N(1)-N(2)	136.9 (2)	N(1)-C(1)	134.7 (2)
N(2)-C(3)	135.2 (2)	N(3)-N(4)	136.6 (2)
N(3)-C(4)	134.3 (2)	N(4)-C(6)	135.1 (3)
C(1)-C(2)	137.2 (2)	C(2)-C(3)	136.3 (2)
C(4)-C(5)	136.9 (2)	C(5)-C(6)	136.7 (3)

F(1)-P(1)-F(2)	92.9(1)	F(1)-P(1)-F(3)	91.6(1)
F(2)-P(1)-F(3)	90.7(1)	F(1)-P(1)-F(4)	91.5(1)
F(2)-P(1)-F(4)	90.9(1)	F(3)-P(1)-F(4)	176.5(1)
F(1)-P(1)-N(1)	88.7(1)	F(2)-P(1)-N(1)	177.7(1)
F(3)-P(1)-N(1)	87.6(1)	F(4)-P(1)-N(1)	90.8(1)
F(1)-P(1)-N(3)	177.7(1)	F(2)-P(1)-N(3)	89.1(1)
F(3)-P(1)-N(3)	87.2(1)	F(4)-P(1)-N(3)	89.6(1)
N(1)-P(1)-N(3)	89.4(1)	F(5)-P(2)-F(6)	92.6(1)
F(5)-P(2)-F(7)	90.5(1)	F(6)-P(2)-F(7)	90.9(1)
F(5)-P(2)-F(8)	90.9(1)	F(6)-P(2)-F(8)	91.0(1)
F(7)-P(2)-F(8)	177.7(1)	F(5)-P(2)-N(2)	88.9(1)
F(6)-P(2)-N(2)	178.0(1)	F(7)-P(2)-N(2)	87.7(1)
F(8)-P(2)-N(2)	90.4(1)	F(5)-P(2)-N(4)	178.2(1)
F(6)-P(2)-N(4)	88.1(1)	F(7)-P(2)-N(4)	87.8(1)
F(8)-P(2)-N(4)	90.8(1)	N(2)-P(2)-N(4)	90.5(1)
P(1)-N(1)-N(2)	129.8(1)	P(1)-N(1)-C(1)	122.4(1)
N(2)-N(1)-C(1)	107.5(1)	P(2)-N(2)-N(1)	129.9(1)
P(2)-N(2)-C(3)	122.7(1)	N(1)-N(2)-C(3)	107.3(1)
P(1)-N(3)-N(4)	129.2(1)	P(1)-N(3)-C(4)	122.9(1)
N(4)-N(3)-C(4)	107.8(1)	P(2)-N(4)-N(3)	129.9(1)
P(2)-N(4)-C(6)	122.2(1)	N(3)-N(4)-C(6)	107.0(1)
N(1)-C(1)-C(2)	109.7(1)	C(1)-C(2)-C(3)	105.6(1)
N(2)-C(3)-C(2)	109.9(1)	N(3)-C(4)-C(5)	110.0(1)
C(4)-C(5)-C(6)	105.1(2)	N(4)-C(6)-C(5)	110.1(2)

Reaction of N-trimethylsilyl-imidazole, **3** with phosphorus pentafluoride: Preparation of the 1:1 Adduct **4** between **3** and PF_5

Phosphorus pentafluoride (11.0 g; 0.087 mole) was condensed onto the solution of 12.25 g (0.087 mole) of **3** in 80 ml of dichloromethane in a heavy-wall glass tube fitted with a TEFLON® stopcock at -196°C. The reaction mixture was allowed to reach room temperature within 1 h, and was then stirred magnetically for another 1.5 h. The solid residue left after all the volatile products were pumped off in vacuo (0.1 mm Hg, 20°C; 1 h) was recrystallized from 20 ml of dichloromethane.

The yield of **4** was 18.3 g (79%); mp. 121°C.

$C_6H_{12}F_5N_2PSi$ (266.24):

calc.	C 27.06	H 4.54	P 11.63
found	C 26.84	H 4.50	P 11.55

Mass spectrum: m/z (%) = 247 (30, $[M-F]^+$), 140 (100, $[M-PF_5]^+$), 126 (68, $[PF_5]^+$), 73 (76, $[Me_3Si]^+$), 68 (27, $[M-PF_5-Me_3Si+H]^+$).

N.m.r spectra: ^{1}H (CD_3CN, 200.1 MHz): δ 0.1 (s, Me_3Si), 7.22 (m, br), 8.40 (m, br): resonances due to imidazole hydrogen atoms cannot be assigned individually. - ^{19}F (CD_3CN, 188.3 MHz): δ -59.41 (dd, $^{1}J_{(PF^{cis})}$ 758.4 Hz, $^{2}J_{(FF)}$ 53.3 Hz, F^{cis}); -78.89 (dquintets, $^{1}J_{(PF^{trans})}$ 752.7 Hz, F^{trans}). - ^{31}P (CD_3CN, 81.0 MHz): δ -143.34 (sextet, br).

Thermolysis of complex **4**: Formation of the bis-tetrafluorophosphate complex, **5**

The experiment was conducted in a heavy-wall glass tube, fitted with a TEFLON® stopcock. The complex, **4** (3.39 g , 0.012 mole) was heated to 145°C over 30 min and maintained for another 30 min at that temperature until the evolution of gas ceased. Fluorotrimethylsilane (0.9 g) was pumped off (0.1 mm Hg, 20°C, 0.5 h), while the molten reaction mixture foamed and eventually solidified. According to its ^{1}H and ^{19}F n.m.r. spectra the product still contained ca. 10% of the starting material **4**, which could not be removed by recrystallisation.

Mass spectrum: m/z (%) = 174 (39, $[M-C_3H_3N_2PF_4]^+$), 155 (9, $[M-C_3H_3N_2PF_5]^+$), 107 (100, $[PF_4]^+$), 68 (6, $[C_3H_3N_2+H]^+$).

N.m.r. spectra: ^1H (CD_3CN, 200.1 MHz): δ 7.37 (m, br, H-C=C), 8.66 (m, br, H-C=N). - ^{19}F (CD_3CN, 188.3 MHz): δ -47.96 (m, br, $^1J_{(PF)}$ 797.2 Hz), -60.34 (m, br, $^1J_{(PF)}$ 759.5 Hz, $^2J_{(FF)}$ not resolved). - ^{31}P (CD_3CN), 81.0 MHz): δ -153.17 (quintet, br).

Reaction of N-trimethylsilyl-5,6-dimethylbenzimidazole, **6** with phosphorus pentafluoride: Synthesis of the 1:1 complex **7** between **6** and PF_5

Phosphorus pentafluoride (6.3 g, 0.05 mole) was condensed onto a solution of 10.0 g (0.045 mole) of **6** in 60 ml of dichloromethane in a heavy-wall glass tube, fitted with a TEFLON® stopcock, at -196°C. The reaction mixture was brought to room temperature within 1 h ; subsequently, stirring was continued at 70°C for 2 h. Half of the volatile products were removed in vacuo (0.1 mm Hg, 20°C, 0.5 h), whereupon **7** was precipitated as a colourless solid.

Yield 13.3 g (86%); mp. 232°C.

$C_{12}H_{18}F_5N_2PSi$ (344.26):

calc.	C 41.86	H 5.27	P 8.99
found	C 41.92	H 5.25	P 9.02

Mass spectrum: m/z (%) = 325 (2, $[M-F]^+$), 218 (100, $[M-PF_5]^+$), 146 (5, $[M-PF_5-Me_3Si+H]^+$), 107 (13, $[PF_4]^+$), 73 (16, $[Me_3Si]^+$).

N.m.r. spectra: ^1H (CD_3CN, 200.1 MHz): δ 0.66 (s, Me_3Si); 2.46 (s, Me), 7.53 (s, br, C_6H_2), 7.77 (s, br, C_6H_2); 8.55 (d, $^3J_{(PH)}$ 2.5 Hz, H-C=N). - ^{19}F (CD_3CN, 188.3 MHz): δ -56.82 (dd, $^1J_{(PF^{cis})}$ 762.7 Hz, $^2J_{(FF)}$ 55.2 Hz, F^{cis}); -78.15 (dquintets, $^1J_{(PF^{trans})}$ 750.2 Hz, F^{trans}). - ^{31}P (CD_3CN, 81.0 MHz): δ -141.6 (sextet, br).

Reaction of **8** with phosphorus pentafluoride: attempted preparation of the complex **10**

Phosphorus pentafluoride (10.95 g, 0.081 mole) was condensed onto a solution of 12.33 g (0.081 mole) of **8** in 50 ml of dichloromethane in a heavy-wall glass tube, fitted with a TEFLON® stopcock, at -196°C. A colourless solid was precipitated while the temperature of the reaction mixture was allowed to reach room temperature (1 h). According to the ^1H and ^{19}F n.m.r spectra of this precipitate (in acetonitrile as a solvent) a mixture of unidentifiable products was present.

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REFERENCES

1 R. Schmutzler, Adv. Fluorine Chem., **5** (1965) 31.

2 M. Webster, Chem. Rev., **66** (1966) 87.

3 L. Lunazzi, S. Brownstein, J. Magn. Res., **1** (1969) 119.

4 E. L. Muetterties, T. A. Bither, M. W. Farlow, D. D. Coffman, J. Inorg. Nucl. Chem., **16** (1960) 52.

5 D. H. Brown, G.-W. Fraser, D. W. A. Sharp; J. Chem. Soc. A, (1966) 171.

6 J. S. Harman, D. W. A. Sharp, J. Chem. Soc. A, (1970) 1138.

7 W. Storzer, D. Schomburg, G. V. Röschenthaler, R. Schmutzler, Chem. Ber., **116** (1983) 367.

8 F. N. Tebbe, E. L. Muetterties, Inorg. Chem. **6** (1967) 129.

9 K. P. John, W. S. Sheldrick, R. Schmutzler, J. Chem. Soc. A, (1974) 1841.

10 K. P. John, W. S. Sheldrick, R. Schmutzler, J. Chem. Soc. A, (1974) 2466.

11 R. Krebs, D. Schomburg, R. Schmutzler, Polyhedron, 8 (1989) 731.

12 E. L. Muetterties, W. Mahler, Inorg. Chem., 4 (1965) 119.

13 W. Wieker, A. R. Grimmer, L. Kolditz, Z. Chem., 7 (1967) 434.

14 W. McFarlane, J. F. Nixon, J. R. Swain, Mol. Phys., 19 (1970) 141.

15 H. Dreeskamp, C. Schumann, R. Schmutzler, J. Chem. Soc., Chem. Commun. (1970) 671.

16 J. F. Nixon, J. R. Swain, J. Chem. Soc. A, (1970) 2075.

17 W. Stadelmann, O. Stelzer, R. Schmutzler, Z. Anorg. Allg. Chem. **385** (1971) 142.

18 C. W. Schultz, R. W. Rudolph, J. Am. Chem. Soc., 93 (1971) 1889.

19 K. P. John, R. Schmutzler, Z. Naturf., **29b** (1974) 730.

20 A. H. Cowley, P. J. Wisian, M. Sanchez, Inorg. Chem., 16 (1977) 1451.

21 W. S. Sheldrick, J. Chem. Soc. A, (1974) 1402.

22 W. S. Sheldrick, M. J. C. Hewson, Z. Naturf., **29b** (1978) 834.

23 W. S. Sheldrick, J. A. Gibson, G. V. Röschenthaler, Z. Naturf. **33b** (1978) 1102.

24 P. Sykes, Reaktionsmechanismen in der Organischen Chemie, VCH Verlagsgesellschaft, Weinheim, 9th. edn., **1988**, p. 83.

25 M. Murray, R. Schmutzler, Z. Chem.,. 8 (1968) 241.

26 R. Schmutzler, J. Chem. Soc. A, (1973) 2687.

27 G. S. Reddy, R. Schmutzler, Z. Naturf., **25b** (1970) 1199.

28 Autorenkollektiv, *Organikum*, Reprint of the 15th edn., p. 783 ff., VEB Deutscher Verlag der Wissenschaften, Berlin 1977.

29 D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Paris, Braunschweig, Barnsley, 1966.

30 L. Birkofer, P. Richter, A. Ritter, Chem. Ber., 93 (1960) 2804.

31 A. T. Ayupova, Ch. Sh. Kadyrov, L. V. Nolchanov, S. S. Khalikov, Khim. Geterotsikl. Soedin. 6 (1984) 812; Chem. Abstr. 102 (1984) 6968t.