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Gas-phase structures of aminodifluorophosphines determined using electron diffraction data and computational techniques

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Table S1 Calculated coordinates (MP2/6-311+G*) for $(PF_2)_2NH$, **1**.[a]

Atom	*x*	*y*	*z*	*x*	*y*	*z*
	Conformer 1			Conformer 2		
F(1)	1.191304	2.207765	0.317265	0.238235	2.127617	1.193300
P(2)	0.000000	1.487595	–0.496470	0.672879	1.130863	0.000000
N(3)	0.000000	0.000000	0.306499	–0.714215	0.141188	0.000000
H(4)	0.000000	0.000000	1.327023	–1.617129	0.609400	0.000000
P(5)	0.000000	–1.487600	–0.496470	–0.803535	–1.546773	0.000000
F(6)	–1.191300	2.207765	0.317265	0.238235	2.127617	–1.193300
F(7)	–1.191300	–2.207770	0.317265	0.238235	–1.869787	–1.190799
F(8)	1.191304	–2.207770	0.317265	0.238235	–1.869787	1.190799

[a] All coordinates are in Å.
Energy (conformer 1) = –1135.730774 Hartrees (corrected for ZPE).
Energy (conformer 2) = –1135.730246 Hartrees (corrected for ZPE).

Table S2 Calculated coordinates (MP2/6-311+G*) for $N(PF_2)_3$, **2**.[a]

Atom	*x*	*y*	*z*
F(1)	–2.224081	0.000000	1.197249
P(2)	–1.526447	0.824086	0.000000
N(3)	0.000000	0.000000	0.000000
P(4)	0.049545	–1.733985	0.000000
F(5)	–2.224081	0.000000	–1.197249
P(6)	1.476903	0.909899	0.000000
F(7)	1.112041	1.926111	–1.197249
F(8)	1.112041	1.926111	1.197249
F(9)	1.112041	–1.926111	–1.197249
F(10)	1.112041	–1.926111	1.197249

[a] All coordinates are in Å.
Energy = –1675.413140 Hartrees (corrected for ZPE).

Table S3 Calculated coordinates (MP2/6-311+G*) for $(PF_2)_2N(CH_3)$, **3**.[a]

Atom	*x*	*y*	*z*
F(1)	0.000000	0.197714	0.000000
P(2)	–0.350633	1.641093	0.000000
N(3)	–1.432932	1.765135	0.000000
C(4)	0.077857	2.111656	0.883753
F(5)	0.077857	2.111656	–0.883753
H(6)	0.141730	–0.673522	–1.444226
H(7)	0.141730	–0.673522	1.444226
H(8)	1.143700	0.310612	–2.244236
H(9)	1.143700	0.310612	2.244236

[a] All coordinates are in Å.
Energy = –1174.876073 Hartrees (corrected for ZPE).

Table S4 Calculated coordinates (MP2/6-311+G*) for $(PF_2)N(CH_3)_2$, **4**.[a]

Atom	*x*	*y*	*z*
F(1)	0.806615	–1.157644	1.181750
P(2)	–0.287281	–0.892397	0.000000
N(3)	–0.359339	0.758955	0.000000
C(4)	0.806615	1.638409	0.000000
F(5)	0.806615	–1.157644	–1.181750
C(6)	–1.649603	1.439324	0.000000
H(7)	–2.461609	0.709458	0.000000
H(8)	–1.749187	2.069649	0.889646
H(9)	–1.749187	2.069649	–0.889646
H(10)	1.722692	1.048265	0.000000
H(11)	0.800375	2.273722	–0.891241
H(12)	0.800375	2.273722	0.891241

[a] All coordinates are in Å.
Energy = –674.325963 Hartrees (corrected for ZPE).

Table S5 Calculated coordinates (MP2/6-311+G*) for $(PF_2)_2N(SiH_3)$, **5**.[a]

Atom	*x*	*y*	*z*
N(1)	0.000000	0.032862	0.000000
Si(2)	1.558362	0.966990	0.000000
H(3)	1.247875	2.407303	0.000000
H(4)	2.283153	0.573417	1.219905
H(5)	2.283153	0.573417	–1.219905
P(6)	–0.809254	–0.397499	–1.432682
P(7)	–0.809254	–0.397499	1.432682
F(8)	0.341230	–1.262883	–2.162204
F(9)	0.341230	–1.262883	2.162204
F(10)	–0.527543	0.963046	–2.261954
F(11)	–0.527543	0.963046	2.261954

[a] All coordinates are in Å.
Energy = –1425.916665 Hartrees (corrected for ZPE).

Table S6 Calculated coordinates (MP2/6-311+G*) for $(PF_2)N(SiH_3)_2$, **6**.[a]

Atom	*x*	*y*	*z*
F(1)	0.448546	–0.022328	–0.014131
P(2)	1.979641	–0.916111	–0.051546
N(3)	2.613023	–0.909885	1.284910
Si(4)	1.686348	–2.301396	–0.475629
F(5)	2.883335	–0.249390	–1.014964
Si(6)	0.515793	1.759151	0.117663
H(7)	0.568377	2.366618	–1.228139
H(8)	1.776392	2.057792	0.836200
H(9)	–0.650854	2.246945	0.873854
H(10)	–0.996167	–0.858720	–0.149474
H(11)	–1.805630	0.193818	–1.092772
H(12)	–1.751037	–0.413391	1.219345

[a] All coordinates are in Å.
Energy = –1176.410768 Hartrees (corrected for ZPE).

Table S7 Calculated coordinates (MP2/6-311+G*) for $(PF_2)_2N(GeH_3)$, **7**.[a]

Atom	*x*	*y*	*z*
N(1)	0.000000	0.345760	0.000000
Ge(2)	0.150968	–1.583908	0.000000
H(3)	1.652005	–1.903379	0.000000
H(4)	–0.559790	–2.043292	1.278446
H(5)	–0.559790	–2.043292	–1.278446
P(6)	–0.028422	1.239345	–1.435633
P(7)	–0.028422	1.239345	1.435633
F(8)	–1.314291	0.579610	–2.163563
F(9)	–1.314291	0.579610	2.163563
F(10)	1.063694	0.368965	–2.262268
F(11)	1.063694	0.368965	2.262268

[a] All coordinates are in Å.
Energy = –3212.340503 Hartrees (corrected for ZPE).

Table S8 Calculated coordinates (MP2/6-311+G*) for $(PF_2)_2H(SiH_3)$, **8**.[a]

Atom	*x*	*y*	*z*	*x*	*y*	*z*
	Conformer 1			Conformer 2		
F(1)	–1.277250	–1.058928	–0.744811	–1.685340	1.190126	–0.206605
P(2)	–1.115763	–0.042228	0.510584	–0.826723	0.000008	0.490017
N(3)	0.511608	–0.197864	0.834609	0.521368	–0.000087	–0.487631
Si(4)	1.910563	0.012673	–0.234181	2.200075	0.000006	0.047439
F(5)	–1.072533	1.289045	–0.421928	–1.685434	–1.190069	–0.206556
H(6)	0.692475	–0.402325	1.810236	0.338477	–0.000151	–1.488620
H(7)	2.479756	1.370297	–0.093976	2.158222	–0.000512	1.523446
H(8)	2.924839	–0.981404	0.178869	2.895378	–1.202569	–0.459129
H(9)	1.458283	–0.216579	–1.616969	2.895095	1.203124	–0.458233

[a] All coordinates are in Å.
Energy (conformer 1) = –886.225399 Hartrees (corrected for ZPE).
Energy (conformer 2) = –886.225209 Hartrees (corrected for ZPE).

Table S9 Nozzle-to-plate distances (mm), weighting functions (nm^{-1}), scale factors, correlation parameters and electron wavelengths (pm) used in the electron diffraction studies of compounds **1**–**8**.

Compound	Nozzle-to-plate distance[a]	Δs	s_{min}	sw_1	sw_2	s_{max}	Scale factor[b]	Correlation parameter	Electron wavelength[c]
1	288.3	2	34	54	124	146	0.797(11)	0.469	5.719
	128.2	4	52	72	292	340	0.847(9)	0.126	5.707
2	580.0	2	20	32	80	98	0.504(5)	–0.206	5.847
	190.0	4	68	80	260	280	0.505(10)	0.125	5.852
3	500.0	2	28	48	134	156	1.590(14)	–0.014	5.673
	250.0	4	100	120	256	300	1.505(26)	–0.126	5.673
4	500.0	2	28	48	126	148	1.656(30)	0.136	5.791
	250.0	4	104	124	220	252	1.520(71)	–0.023	5.791
5	285.6	2	20	40	80	100	0.900(13)	0.446	5.854
	128.4	4	44	64	220	240	0.960(18)	0.348	5.854
6	284.3	2	24	44	122	144	0.727(13)	0.496	5.799
	128.5	4	60	80	220	260	0.806(14)	0.146	5.799
7	288.3	2	22	42	120	140	0.724(24)	0.442	5.811
	128.2	4	120	140	230	248	0.750(35)	0.363	5.811
8	500.0	2	32	52	122	144	1.327(13)	0.281	5.659
	250.0	4	100	120	200	240	1.324(33)	–0.066	5.659

[a] Determined by reference to the scattering pattern of benzene recorded immediately before or after the sample plates; values taken from the original studies.
[b] Values in parentheses are the estimated standard deviations.
[c] Values taken from the original studies.

Table S10 Relative energies (kJ mol^{-1}) of the two conformers of bis(difluoro-phosphino)amine, **1**.

Level/basis set	Conformer 1	Conformer 2
RHF/3-21G*	0	0.6
RHF/6-31G*	0	0.9
MP2/6-31G*	0	1.3
MP2/6-31+G*	0	1.3
MP2/6-311G*	0	1.9
MP2/6-311+G*	0	1.4

Table S11 Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)_2NH$, **1**, from the GED study.[a, b]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P average	169.3(3)	169.7	—
p_2	N–P difference	1.4(2)	1.4	1.4(2)
p_3	P–F mean	157.8(1)	161.4	—
p_4	N–H mean	102.0(13)	101.9	101.9(14)
p_5	N–P–F average	97.8(6)	98.8	—
p_6	N–P–F difference 1	1.1(6)	0.7	0.7(6)
p_7	N–P–F difference 2	1.3(6)	1.5	1.5(6)
p_8	F–P–F mean	96.9(5)	95.2	—
p_9	P–N–H average	119.6(3)	116.6	116.6(10)
p_{10}	P–N–H difference 1	1.3(6)	1.3	1.3(5)
p_{11}	P–N–H difference 2	3.9(11)	4.0	4.0(10)
p_{12}	P–N–P–F(6)	124.3(10)	131.6	—
p_{13}	P′–N′–P′–F′(6)	144.0(77)	131.6	—
p_{14}	Weight conformer 1	0.46(3)[c]	0.38	—
Dependent parameters				
p_{15}	N–P–F(1)	97.5(5)	98.8	—
p_{16}	N′–P′–F′(1)	97.3(9)	98.0	—
p_{17}	N′–P′–F′(6)	98.6(7)	99.5	—
p_{18}	N–P	168.6(3)	169.1	—
p_{19}	N′–P′	170.0(3)	170.4	—
p_{20}	P–N–H	121.3(5)	118.4	—
p_{21}	P′(2)–N′–H′	120.0(6)	117.1	—
p_{22}	P′(5)–N′–H′	117.4(8)	114.4	—
p_{23}	P–N–P	117.4(9)	123.3	—
p_{24}	P′–N′–P′	122.5(7)	128.5	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits. [b] *Z*′ denotes an atom from the second conformer. [c] Standard deviation obtained from values of *R* factor as the weight was varied. See Figure 3.

Table S12 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)_2NH$, **1**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	F(1)–P(2)	157.7(1)	5.2(2)	—
u_2	P(2)–N(3)	168.6(6)	4.7(tied to u_1)	—
u_3	F(1)...F(6)	239.4(8)	9.4(tied to u_4)	—
u_4	F(1)...N(3)	244.7(4)	13.3(7)	—
u_5	P(2)...P(5)	286.5(5)	10.0(9)	—
u_6	F(1)...P(5)	392.5(4)	10.5(7)	—
u_7	F(1)...F(8)	487.1(13)	13.5(14)	17.2(17)
u_8	F(1)...F(7)	424.3(9)	13.0(10)	10.4(10)
u_9	P′(5)–F′(7)	157.7(1)	5.3(tied to u_1)	—
u_{10}	F′(1)–P′(2)	158.2(1)	5.2(tied to u_1)	—
u_{11}	N′(3)–P′(5)	168.6(5)	4.7(tied to u_1)	—
u_{12}	P′(2)–N′(3)	170.0(5)	4.8(tied to u_1)	—
u_{13}	F′(7)...F′(8)	239.4(10)	10.0(tied to u_4)	—
u_{14}	F′(1)...N′(3)	245.5(14)	13.5(tied to u_4)	—
u_{15}	N′(3)...F′(7)	246.7(10)	13.0(tied to u_1)	—
u_{16}	P′(2)...P′(5)	295.3(9)	7.7(tied to u_5)	—
u_{17}	P′(2)...F′(7)	309.4(54)	16.8(14)	16.6(17)
u_{18}	F′(1)...F′(8)	376.1(29)	23.7(33)	33.1(33)
u_{19}	F′(1)...F′(7)	342.1(12)	20.4(19)	18.5(19)

[a] Estimated standard deviations, as obtained in the least squares refinement, are given in parentheses. Atom pairs u_9 to u_{19} inclusive relate to the second conformer; atoms from conformer 2 denoted by Z′. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S13 Least-squares correlation matrix (×100) for $(PF_2)_2NH$, **1**.[a]

	p_1	p_6	p_8	p_{12}	p_{13}	u_4	u_5	k_1	k_2
p_5		52	–77	52		–70			
p_6					54				
p_8				–60		66			
p_9	60								
p_{11}							–60		
u_1								72	54
u_4								50	50
k_1									70

[a] Only elements with absolute values ≥ 50% are shown; k_1 and k_2 are scale factors.

Table S14 Refined and calculated geometric parameters (r_{h1} structure) for $N(PF_2)_3$, **2**, from the GED study.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	169.2(3)	173.5	—
p_2	P–F	156.4(1)	161.2	—
p_3	N–P–F	99.2(6)	98.0	—
p_4	F–P–F	98.1(9)	95.9	—
p_5	F(1)–P(2)–N–P(4)	41.5(15)	48.6	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S15 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $N(PF_2)_3$, **2**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	F(5)–P(2)	156.4(1)	3.9(3)	—
u_2	P(4)...P(2)	292.2(5)	9.6(5)	—
u_3	N(3)–P(2)	169.1(3)	5.0(5)	4.7(5)
u_4	P(4)...F(1)	313.4(10)	20.9(9)	16.4(16)
u_5	P(6)...F(5)	393.4(6)	19.2(16)	—
u_6	F(1)...F(5)	236.0(15)	7.9(13)	—
u_7	F(5)...N(3)	247.5(10)	9.7(14)	—
u_8	F(7)...F(5)	388.9(14)	24.1(27)	26.4(26)
u_9	F(8)...F(5)	452.7(10)	22.1(12)	15.9(16)

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S16 Least-squares correlation matrix (×100) for $N(PF_2)_3$, **2**.[a]

	p_4	p_5	u_3	u_4	u_6	u_7	u_8	k_1
p_1				58				
p_2			50					
p_3	–72	79			–83	–71		
p_4		–52			62	90		
p_5					–72	–56		
u_1			65					63
u_5							–86	
u_6						59		

[a] Only elements with absolute values ≥ 50% are shown; k_1 is a scale factor.

Table S17 Energy differences (kJ mol^{-1}) between the two conformers of $(PF_2)NH(CH_3)$, **3**, for the various calculations.

Level/Basis Set	Conformer 1	Conformer 2
RHF/3-21G*	0	5.2
RHF/6-31G*	0	5.5
MP2/6-31G*	0	6.2
MP2/6-31+G*	0	6.9
MP2/6-311G*	0	6.4
MP2/6-311+G*	0	7.1

Table S18 Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)NH(CH_3)$, **3**, from the GED study.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	165.2(9)	165.3	165.3(12)
p_2	P–F average	163.6(3)	162.9	162.9(3)
p_3	P–F difference	0.3(1)	0.3	0.3(1)
p_4	N–C	150.7(4)	144.8	—
p_5	N–H	100.8(19)	101.0	—
p_6	C–H mean	109.8(8)	109.1	—
p_7	N–P–F average	100.6(3)	100.5	—
p_8	N–P–F difference	1.4(7)	1.1	1.1(7)
p_9	F–P–F	92.6(4)	93.3	—
p_{10}	P–N–C	127.5(6)	126.5	—
p_{11}	P–N–H	115.3(3)	115.3	115.3(3)
p_{12}	H–C–H mean	107.8(9)	108.8	108.8(10)
p_{13}	C–N–P–F(5)	–29.0(48)	–44.3	—
p_{14}	CH_3 torsion	–91.2(207)	—	—
p_{15}	CH_3 tilt	–1.5(20)	—	–2.0(20)
p_{16}	H(6) drop	15.8(20)	—	16.0(20)
Dependent parameters				
p_{17}	P–F(1)	163.3(4)	162.6	—
p_{18}	P–F(5)	163.9(4)	163.2	—
p_{19}	N–P–F(1)	99.1(7)	99.4	—
p_{20}	N–P–F(5)	102.0(7)	101.6	—
p_{21}	C–N–H	115.5(8)	116.6	—
p_{22}	N–C–H(7)	110.3(13)	111.8	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S19 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)NH(CH_3)$, **3**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	F(1)–P(2)	163.2(4)	5.2(1)	4.1(4)
u_2	N(3)–P(2)	165.1(9)	5.7(tied to u_1)	—
u_3	P(2)–F(5)	163.9(4)	5.4(tied to u_1)	—
u_4	N(3)–C(4)	150.7(4)	4.9(4)	4.7(5)
u_5	C(4)–H(7)	109.6(8)	8.0(7)	7.5(8)
u_6	C(4)–H(8)	109.6(8)	7.9(tied to u_5)	—
u_7	C(4)–H(9)	109.6(8)	7.9(tied to u_5)	—
u_8	F(1)...N(3)	249.7(13)	6.2(8)	—
u_9	F(1)...C(4)	320.0(35)	14.8(15)	15.1(15)
u_{10}	F(1)...F(5)	236.5(5)	6.2(6)	—
u_{11}	P(2)...C(4)	281.0(6)	8.5(7)	—
u_{12}	F(5)...N(3)	255.6(13)	6.5(tied to u_8)	—
u_{13}	C(4)...F(5)	298.0(31)	16.8(tied to u_9)	—

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S20 Least-squares correlation matrix (×100) for $(PF_2)NH(CH_3)$, **3**.[a]

	p_1	p_5	p_7	p_9	p_{10}	p_{14}	p_{15}	u_1	u_5	u_8	u_{11}	k_1	k_2
p_1					–51			–55					
p_2	–98	–74	55		50			54					
p_4													–54
p_5									67				
p_6							–70						
p_7	–60			–51	50						–54		
p_8										–78			
p_9	71												
p_{13}						65					54		
u_1												51	
k_1													60

[a] Only elements with absolute values ≥ 50% are shown; k_1 and k_2 are scale factors.

Table S21a Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)N(CH_3)_2$, **4**, from the GED study, including rotational constants.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	164.9(11)	165.3	165.3(14)
p_2	P–F	159.2(4)	163.2	—
p_3	N–C average	146.5(7)	146.0	—
p_4	N–C difference	0.2(1)	0.2	0.2(1)
p_5	C–H mean	108.9(8)	109.5	—
p_6	N–P–F	101.4(4)	101.0	—
p_7	F–P–F	95.3(5)	92.8	—
p_8	P–N–C average	122.6(5)	122.4	—
p_9	P–N–C difference	4.0(8)	4.2	4.2(9)
p_{10}	H–C–H mean	109.0(7)	109.0	109.0(8)
p_{11}	C(4)–N–P–F(5)	–52.1(8)	–47.5	—
p_{12}	$C(4)H_3$ torsion	–0.3(148)	0.0	—
p_{13}	$C(6)H_3$ torsion	1.2(171)	0.0	—
Dependent parameters				
p_{14}	C(4)–N	146.5(7)	146.0	—
p_{15}	C(6)–N	146.6(7)	145.9	—
p_{16}	P–N–C(4)	124.6(5)	124.5	—
p_{17}	P–N–C(6)	120.6(7)	120.3	—
p_{18}	C–N–C	114.8(10)	115.2	—
p_{19}	N–C–H(10)	110.0(7)	110.2	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S21b Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)N(CH_3)_2$, **4**, from the GED study, excluding rotational constants.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	164.3(11)	165.3	165.3(14)
p_2	P–F	159.4(4)	163.2	—
p_3	N–C average	146.3(7)	146.0	—
p_4	N–C difference	0.2(1)	0.2	0.2(1)
p_5	C–H mean	109.7(8)	109.5	—
p_6	N–P–F	102.2(5)	101.0	—
p_7	F–P–F	95.7(8)	92.8	—
p_8	P–N–C average	123.5(7)	122.4	—
p_9	P–N–C difference	4.3(9)	4.2	4.2(9)
p_{10}	H–C–H mean	108.7(7)	109.0	109.0(8)
p_{11}	C(4)–N–P–F(5)	–57.3(28)	–47.5	—
p_{12}	$C(4)H_3$ torsion	0.0(19)	0.0	0.0(20)
p_{13}	$C(6)H_3$ torsion	0.3(19)	0.0	0.0(20)
Dependent parameters				
p_{14}	C(4)–N	146.2(7)	145.9	—
p_{15}	C(6)–N	146.4(7)	146.0	—
p_{16}	P–N–C(4)	125.7(8)	124.5	—
p_{17}	P–N–C(6)	121.3(9)	120.3	—
p_{18}	C–N–C	113.0(14)	115.2	—
p_{19}	N–C–H(10)	110.2(7)	110.2	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S22 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)N(CH_3)_2$, **4**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	C(6)–H(7)	108.5(8)	8.8(tied to u_4)	—
u_2	C(4)–H(10)	108.6(8)	8.8(tied to u_4)	—
u_3	C(6)–H(8)	108.5(8)	9.0(tied to u_4)	—
u_4	C(4)–H(11)	108.5(8)	8.9(10)	—
u_5	N(3)–C(4)	146.5(7)	4.6(4)	4.6(5)
u_6	N(3)–C(6)	146.7(7)	4.7(tied to u_5)	—
u_7	F(1)–P(2)	159.1(4)	5.0(6)	—
u_8	P(2)–N(3)	164.6(11)	4.1(4)	4.2(4)
u_9	F(1)...F(5)	235.4(11)	6.7(6)	6.6(7)
u_{10}	F(1)...N(3)	250.3(8)	9.3(8)	9.2(9)
u_{11}	P(2)...C(4)	264.7(40)	7.9(6)	8.0(8)
u_{12}	P(2)...C(6)	270.2(30)	7.6(tied to u_{11})	—
u_{13}	F(1)...C(6)	293.5(43)	11.0(16)	—
u_{14}	P(2)...H(11)	329.4(45)	29.9(26)	29.0(29)
u_{15}	P(2)...H(8)	330.1(104)	34.5(tied to u_{14})	—
u_{16}	F(1)...C(4)	363.8(25)	16.7(20)	—

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S23 Least-squares correlation matrix (×100) for $(PF_2)N(CH_3)_2$, **4**.[a]

	p_1	p_2	p_6	p_8	p_{11}	u_7
p_1		–84	–58	–51		–73
p_2						57
p_3	–54					66
p_7					–90	
p_{11}				–51		

[a] Only elements with absolute values > 50% are shown.

Table S24 Energy differences (kJ mol^{-1}) between the two conformers of $(PF_2)_2N(SiH_3)$, **5**, for the various calculations.

Level/basis set	Conformer 1	Conformer 2
RHF/3-21G*	0	7.0
RHF/6-31G*	0	4.0
MP2/6-31G*	0	5.4
MP2/6-311G*	0	5.7
MP2/6-311+G*	0	5.3

Table S25 Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)_2N(SiH_3)$, **5**, from the GED study.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	169.0(4)	170.1	—
p_2	P–F average	157.0(1)	161.6	—
p_3	P–F difference	0.4(3)	0.4	0.4(2)
p_4	N–Si	177.7(10)	181.7	—
p_5	Si–H mean	142.9(16)	147.3	—
p_6	N–P–F average	100.6(4)	99.0	—
p_7	N–P–F difference	2.4(3)	2.4	2.4(3)
p_8	F–P–F	97.4(5)	95.5	—
p_9	P(6)–N–Si	121.9(3)	122.6	—
p_{10}	H–Si–H mean	111.5(8)	111.6	111.6(8)
p_{11}	Si–N–P(6)–F(8)	58.5(11)	58.7	—
p_{12}	SiH_3 torsion	16.2(21)	0.0	—
Dependent parameters				
p_{13}	P(6)–F(8)	156.8(2)	161.8	—
p_{14}	P(6)–F(10)	157.2(2)	162.3	—
p_{15}	N–P(6)–F(8)	101.8(4)	100.4	—
p_{16}	N–P(6)–F(10)	99.4(4)	97.9	—
p_{17}	P–N–P	116.1(6)	116.2	—
p_{18}	N–Si–H(3)	107.3(9)	106.5	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S26 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)_2N(SiH_3)$, **5**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	N(1)–Si(2)	177.7(10)	5.0(5)	4.9(5)
u_2	N(1)–P(6)	169.0(4)	4.4(4)	4.5(5)
u_3	Si(2)–H(3)	142.8(17)	8.3(9)	8.4(8)
u_4	Si(2)–H(4)	142.8(17)	8.3(tied to u_3)	—
u_5	P(6)–F(8)	156.7(2)	4.5(3)	—
u_6	P(6)–F(10)	157.1(2)	4.5(tied to u_5)	—
u_7	N(1)...F(8)	252.6(6)	9.1(tied to u_8)	—
u_8	N(1)...F(10)	248.4(6)	9.2(12)	—
u_9	Si(2)...P(6)	302.5(4)	9.0(5)	—
u_{10}	Si(2)...F(8)	329.2(13)	16.9(14)	—
u_{11}	Si(2)...F(10)	306.8(16)	18.6(15)	17.6(18)
u_{12}	P(6)...P(7)	286.2(7)	7.1(6)	6.8(7)
u_{13}	P(6)...F(9)	381.7(12)	16.9(6)	—
u_{14}	P(6)...F(11)	391.5(7)	13.8(tied to u_{13})	—
u_{15}	F(8)...F(9)	424.2(33)	22.6(24)	24.0(24)
u_{16}	F(8)...F(10)	235.6(10)	7.2(10)	—
u_{17}	F(8)...F(11)	495.1(11)	19.7(19)	—
u_{18}	F(10)...F(11)	451.7(19)	15.2(29)	—

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S27 Least-squares correlation matrix (×100) for $(PF_2)_2N(SiH_3)$, **5**.[a]

	p_1	p_9	u_1	u_5	u_8	u_{12}	u_{16}	k_1	k_2
p_1			55	–76					
p_4	–63	–91		65	56		56	54	
p_5								–55	
p_6							–58		
p_8					93		77	57	
p_9	65			–64	–55		–56		
u_5								52	
u_8							85	63	
u_9						71			
u_{16}								57	
k_1									69

[a] Only elements with absolute values > 50% are shown; k_1 and k_2 are scale factors.

Table S28 Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)N(SiH_3)_2$, **6**, from the GED study.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	166.1(10)	167.5	—
p_2	P–F average	158.7(3)	162.7	—
p_3	P–F difference	0.4(4)	0.3	0.3(4)
p_4	N–Si average	175.9(3)	178.1	—
p_5	N–Si difference	1.4(1)	1.4	1.4(1)
p_6	Si–H mean	146.0(5)	147.8	—
p_7	N–P–F average	101.3(6)	100.1	—
p_8	N–P–F difference	1.5(10)	2.4	2.4(12)
p_9	F–P–F	96.3(4)	94.6	—
p_{10}	P–N–Si average	119.8(5)	120.9	—
p_{11}	P–N–Si difference	–1.2(11)	3.0	3.0(15)
p_{12}	H–Si–H mean	111.0(9)	110.3	110.3(10)
p_{13}	Si(4)–N–P–F(5)	–55.5(29)	–59.3	—
p_{14}	$Si(4)H_3$ torsion	52.7(203)	86.0	—
p_{15}	$Si(6)H_3$ torsion	61.0(96)	20.0	—
Dependent parameters				
p_{16}	P–F(1)	158.9(3)	162.9	—
p_{17}	P–F(5)	158.5(3)	162.5	—
p_{18}	N–P–F(1)	100.5(9)	98.8	—
p_{19}	N–P–F(5)	102.1(7)	101.3	—
p_{20}	Si–N–Si	120.4(10)	118.1	—
p_{21}	N–Si(4)	176.6(3)	178.8	—
p_{22}	N–Si(6)	175.2(3)	177.3	—
p_{23}	P–N–Si(4)	119.2(5)	119.4	—
p_{24}	P–N–Si(6)	120.4(9)	122.4	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S29 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)N(SiH_3)_2$, **6**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	F(1)–P(2)	158.6(3)	4.4(tied to u_3)	—
u_2	N(3)–P(2)	167.9(10)	4.6(4)	4.4(4)
u_3	P(2)–F(5)	158.2(3)	4.3(4)	—
u_4	N(3)–Si(4)	176.1(4)	5.4(tied to u_5)	—
u_5	N(3)–Si(6)	174.7(4)	5.2(5)	—
u_6	Si(4)–H(10)	145.9(6)	8.2(7)	8.5(9)
u_7	Si(4)–H(11)	145.9(6)	8.2(tied to u_6)	—
u_8	Si(4)–H(12)	145.9(6)	8.2(tied to u_6)	—
u_9	Si(6)–H(7)	145.9(6)	8.2(tied to u_6)	—
u_{10}	Si(6)–H(8)	145.9(6)	8.2(tied to u_6)	—
u_{11}	Si(6)–H(9)	145.9(6)	8.2(tied to u_6)	—
u_{12}	F(1)...N(3)	248.4(12)	8.2(6)	7.1(7)
u_{13}	F(1)...Si(4)	301.5(38)	18.1(tied to u_{20})	—
u_{14}	F(1)...F(5)	236.2(8)	7.6(9)	—
u_{15}	F(1)...Si(6)	396.5(18)	11.7(tied to u_{21})	—
u_{16}	P(2)...Si(4)	295.8(8)	9.0(tied to u_{17})	—
u_{17}	P(2)...Si(6)	294.5(13)	9.2(5)	—
u_{18}	N(3)...F(5)	251.7(12)	8.1(tied to u_{12})	—
u_{19}	Si(4)...F(5)	316.5(33)	15.2(15)	17.4(17)
u_{20}	Si(4)...Si(6)	305.8(11)	7.5(7)	—
u_{21}	F(5)...Si(6)	391.0(33)	17.6(10)	—

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S30 Least-squares correlation matrix (×100) for $(PF_2)N(SiH_3)_2$, **6**.[a]

	p_1	p_{10}	u_5	u_6	u_{12}	u_{17}	u_{19}	u_{20}	u_{21}	k_1	k_2
p_1		–65	72								
p_2				–69							
p_4	–81		–55								
p_7	–68		–51								
p_9					66						
p_{10}						75		59			
p_{11}								–52			
p_{13}		58				62	59	55	63		
u_3				67							
u_5										50	
u_{17}								76			
u_{19}								52			
k_1											67

[a] Only elements with absolute values ≥ 50% are shown; k_1 and k_2 are scale factors.

Table S31 Energy differences (kJ mol^{-1}) between the two conformers of $(PF_2)_2N(GeH_3)$, **7**, for the various calculations.

Level/basis set	Conformer 1	Conformer 2
RHF/3-21G*	0	11.9
RHF/6-31G*	0	8.0
MP2/6-31G*	0	9.2
MP2/6-31+G*	0	8.8
MP2/6-311G*	0	8.7
MP2/6-311+G*	0	7.8

Table S32 Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)_2N(GeH_3)$, **7**, from the GED study.[a]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	N–P	169.7(3)	169.1	—
p_2	P–F average	159.7(2)	162.1	—
p_3	P–F difference	0.6(5)	0.5	0.5(5)
p_4	N–Ge	190.8(5)	193.6	—
p_5	Ge–H mean	154.0(8)	153.4	153.4(9)
p_6	N–P–F average	99.8(3)	99.1	—
p_7	N–P–F difference	2.1(4)	2.4	2.4(4)
p_8	F–P–F	96.6(7)	95.0	—
p_9	P(6)–N–Ge	122.7(1)	121.9	—
p_{10}	H–Ge–H mean	112.3(14)	113.0	113.0(15)
p_{11}	Ge–N–P(6)–F(8)	59.5(8)	58.3	—
p_{12}	GeH_3 torsion	8.8(44)	9.0	—
Dependent parameters				
p_{13}	P(6)–F(8)	159.5(3)	161.8	—
p_{14}	P(6)–F(10)	160.0(3)	162.3	—
p_{15}	N–P(6)–F(8)	100.9(4)	100.4	—
p_{16}	N–P(6)–F(10)	98.8(4)	97.9	—
p_{17}	P–N–P	114.5(3)	116.2	—
p_{18}	N–Ge–H(3)	106.5(16)	106.5	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

Table S33 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)_2N(GeH_3)$, **7**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	N(1)–Ge(2)	190.7(5)	6.5(6)	—
u_2	N(1)–P(6)	169.7(3)	4.6(4)	4.4(4)
u_3	Ge(2)–H(3)	153.8(8)	8.9(9)	8.8(9)
u_4	Ge(2)–H(4)	153.8(8)	8.8(tied to u_3)	—
u_5	P(6)–F(8)	159.4(3)	4.9(2)	—
u_6	P(6)–F(10)	159.9(3)	5.0(tied to u_5)	—
u_7	N(1)...F(8)	253.4(6)	9.5(12)	—
u_8	N(1)...F(10)	250.0(7)	9.4(tied to u_7)	—
u_9	Ge(2)...P(6)	315.7(4)	8.1(4)	7.2(7)
u_{10}	Ge(2)...F(8)	340.5(10)	11.8(9)	—
u_{11}	Ge(2)...F(10)	314.8(11)	15.5(16)	18.2(18)
u_{12}	P(6)...P(7)	285.0(5)	6.1(8)	—
u_{13}	P(6)...F(9)	380.2(11)	12.5(9)	—
u_{14}	P(6)...F(11)	394.1(8)	10.1(tied to u_{13})	—
u_{15}	F(8)...F(10)	238.4(12)	6.8(8)	—
u_{16}	F(8)...F(11)	497.3(11)	12.0(14)	—

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S34 Least-squares correlation matrix (×100) for $(PF_2)_2N(GeH_3)$, **7**.[a]

	p_9	u_2	u_5	u_7	u_{10}	u_{11}	u_{12}	u_{13}	u_{15}	k_2
p_1			–60							
p_2		66								
p_4	–64									51
p_6							–51		–70	
p_8				91						
p_{11}					–64			–61		
u_9						–63	–52			
u_{11}							59			

[a] Only elements with absolute values > 50% are shown; k_2 is a scale factor.

Table S35 Energy differences (kJ mol^{-1}) between the two conformers of $(PF_2)NH(SiH_3)$, **8**, for the calculations at different levels of theory.

Level/basis set	Conformer 1	Conformer 2
RHF/3-21G*	0	4.8
RHF/6-31G*	0	4.1
MP2/6-31G*	0	1.7
MP2/6-311G*	0	0.4
MP2/6-311+G*	0	0.5

Table S36 Refined and calculated geometric parameters (r_{h1} structure) for $(PF_2)NH(SiH_3)$, **8**, from the GED study.[a,b]

No.	Parameter	GED (r_{h1})	MP2/6-311+G*	Restraint
Independent parameters				
p_1	P–F average	159.3(2)	162.4	—
p_2	P–F difference 1	0.3(2)	0.3	0.3(3)
p_3	P–F difference 2	0.2(1)	0.2	0.2(2)
p_4	N–P–F average	99.2(4)	100.1	—
p_5	N–P–F difference 1	0.8(5)	0.8	0.8(6)
p_6	N–P–F difference 2	1.6(4)	1.6	1.6(4)
p_7	F–P–F mean	95.4(5)	94.2	—
p_8	F(5)–P(2)–N(3)–Si(4)	–20.1(39)	–41.3	—
p_9	F′(1)–P′(2)–N′(3)–Si′(4)	127.6(26)	131.9	—
p_{10}	H–Si–H mean	110.1(9)	110.3	110.3(10)
p_{11}	Si–H mean	147.7(3)	147.7	147.7(3)
p_{12}	SiH_3 torsion 1	–36.0(48)	2.0	—
p_{13}	SiH_3 torsion 2	26.3(47)	60.0	—
p_{14}	SiH_3 rock 1	1.9(19)	2.0	2.0(20)
p_{15}	SiH_3 rock 2	–1.7(19)	–2.0	–2.0(20)
p_{16}	N–H mean	101.4(6)	101.5	101.5(6)
p_{17}	N–Si average	175.0(7)	176.8	—
p_{18}	N–Si difference	1.1(1)	1.1	1.1(1)
p_{19}	N–P mean	168.0(9)	166.6	—
p_{20}	P–N–Si average	127.5(5)	128.2	—
p_{21}	P–N–Si difference	3.2(16)	3.6	3.4(17)
p_{22}	P–N–H average	113.7(8)	113.9	113.9(8)
p_{23}	P–N–H difference	3.3(13)	3.2	3.2(14)
p_{24}	Weight conformer 1	0.54(+2/–5)[c]	0.54	—
Dependent parameters				
p_{25}	P–F(1)	159.2(3)	162.4	—
p_{26}	P–F(5)	159.5(2)	162.6	—
p_{27}	P′–F′	159.3(2)	162.5	—
p_{28}	N–P–F(1)	100.0(5)	100.9	—
p_{29}	N–P–F(5)	98.4(6)	99.3	—
p_{30}	N′–P′–F′	99.2(5)	100.1	—
p_{31}	N–Si	175.6(7)	177.3	—
p_{32}	N′–Si′	174.4(7)	176.2	—
p_{33}	P–N–Si	129.1(8)	130.0	—
p_{34}	P′–N′–Si′	125.9(11)	126.4	—
p_{35}	P–N–H	112.1(10)	112.4	—
p_{36}	P′–N′–H′	115.4(10)	115.6	—

[a] Distances are in pm, angles in degrees. See text for parameter definitions and Figure 2 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits. [b] *Z*′ denotes an atom from the second conformer. [c] Error determined from *R*-factor plot (Figure 4) as the weight was varied.

Table S37 Selected interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of $(PF_2)NH(SiH_3)$, **8**.[a]

No.	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	F(1)–P(2)	159.2(3)	3.9(3)	4.0(4)
u_2	P(2)–N(3)	167.9(10)	4.3(4)	4.3(4)
u_3	P(2)–F(5)	159.4(2)	3.9(tied to u_1)	—
u_4	N(3)–Si(4)	175.6(7)	4.4(4)	4.7(5)
u_5	Si(4)–H(7)	147.5(3)	8.8(8)	8.6(9)
u_6	Si(4)–H(8)	147.5(3)	8.8(tied to u_5)	—
u_7	Si(4)–H(9)	147.5(3)	8.8(tied to u_5)	—
u_8	F(1)...N(3)	250.4(7)	8.2(8)	—
u_9	F(1)...Si(4)	354.7(40)	19.2(33)	—
u_{10}	F(1)...F(5)	235.6(10)	7.4(tied to u_{20})	—
u_{11}	P(2)...Si(4)	308.3(10)	11.3(5)	—
u_{12}	N(3)...F(5)	247.4(9)	8.8(tied to u_8)	—
u_{13}	Si(4)...F(5)	303.8(28)	21.6(20)	21.5(22)
u_{14}	F′(1)–P′(2)	159.3(2)	3.9(tied to u_1)	—
u_{15}	P′(2)–N′(3)	167.9(10)	4.4(tied to u_2)	—
u_{16}	N′(3)–Si′(4)	174.5(7)	4.4(tied to u_4)	—
u_{17}	Si′(4)–H′(7)	147.5(3)	8.6(tied to u_5)	—
u_{18}	Si′(4)–H′(8)	147.5(3)	8.7(tied to u_5)	—
u_{19}	F′(1)...N′(3)	249.0(8)	8.5(tied to u_8)	—
u_{20}	F′(1)...F′(5)	235.5(10)	7.3(6)	6.7(7)
u_{21}	P′(2)...Si′(4)	303.0(15)	11.7(tied to u_{11})	—

[a] Estimated standard deviations, as obtained in the least-squares refinement, are given in parentheses. Atom pairs u_{14} to u_{21} inclusive relate to the second conformer; atoms from conformer 2 are denoted by Z'. [b] Amplitudes not refined were fixed at the values obtained using the RHF/6-31G* force field.

Table S38 Least-squares correlation matrix (×100) for $(PF_2)NH(SiH_3)$, **8**.[a]

	p_{17}	p_{19}	u_1	u_8	u_{20}	k_2
p_1	67	–77	56			
p_4	51	–70	56			
p_7				80		
p_{17}		–79	61			
p_{19}			–78			
u_8					54	
k_1						53

[a] Only elements with absolute values > 50% are shown; k_1 and k_2 are scale factors.

Figure S1 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)_2NH$, **1**, as a mixture of two conformers. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_P-f_P)(Z_F-f_F)$.

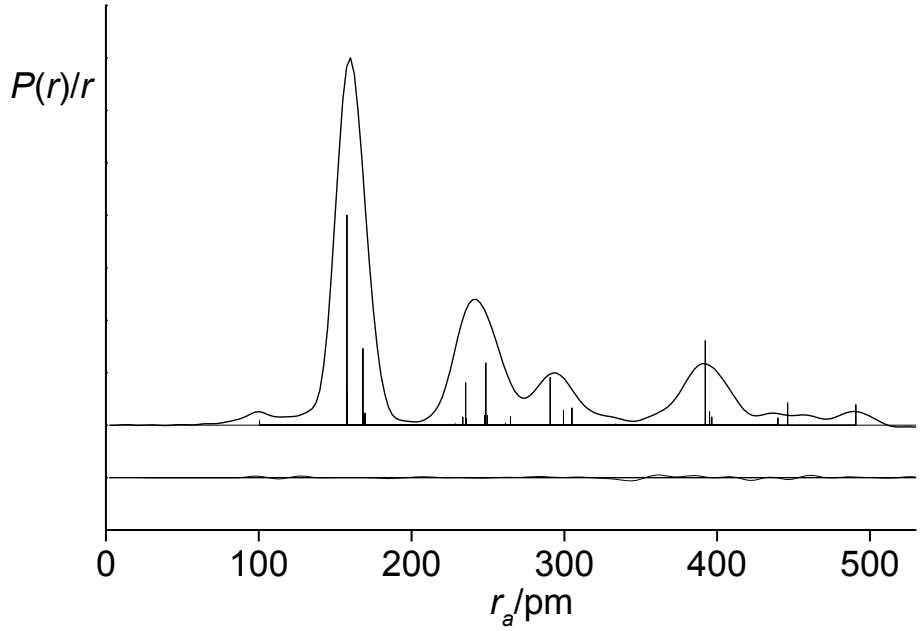

Figure S2 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $N(PF_2)_3$, **2**. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_P-f_P)(Z_F-f_F)$.

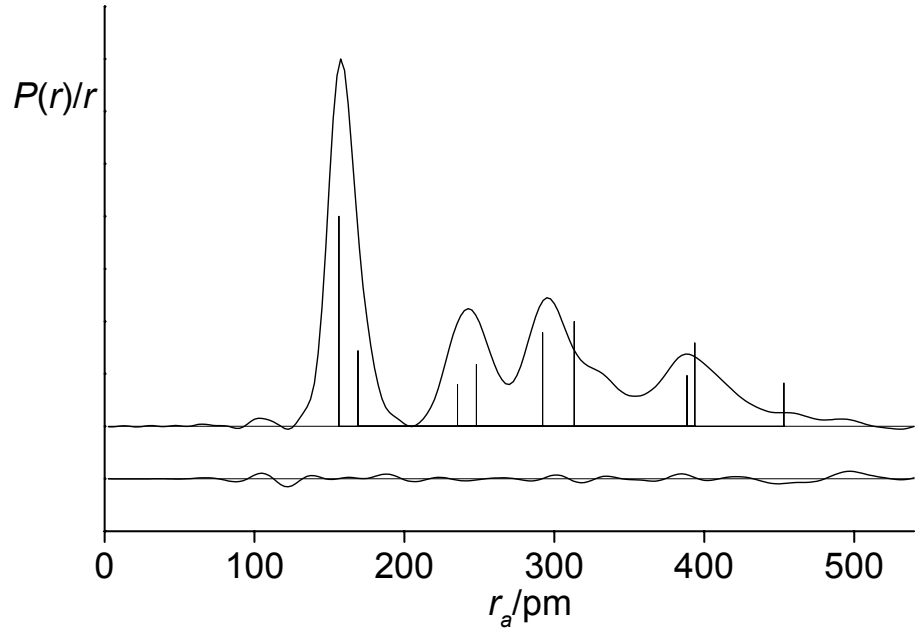

Figure S3 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)NH(CH_3)$, **3**. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_P-f_P)(Z_F-f_F)$.

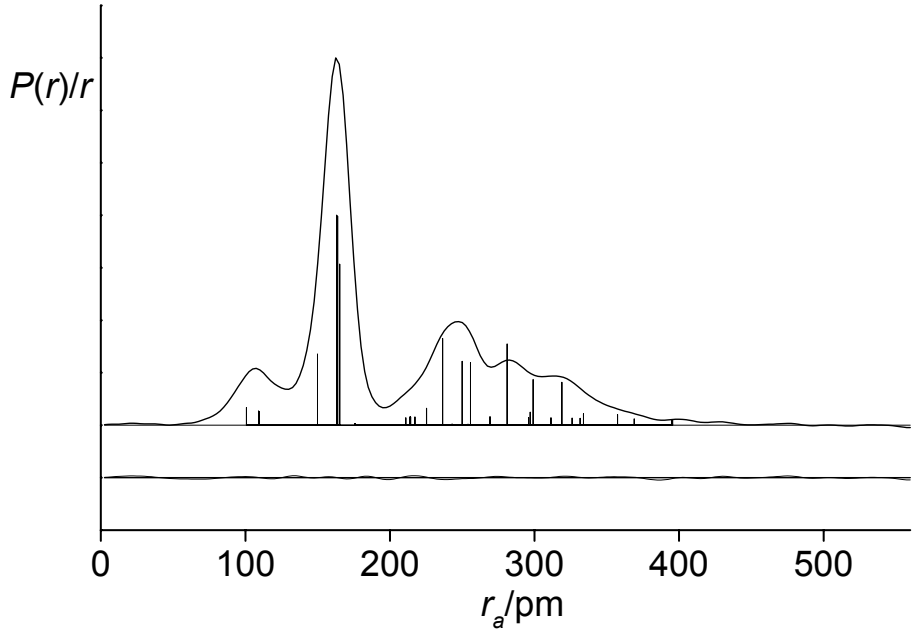

Figure S4 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)N(CH_3)_2$, **4**. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_P-f_P)(Z_F-f_F)$.

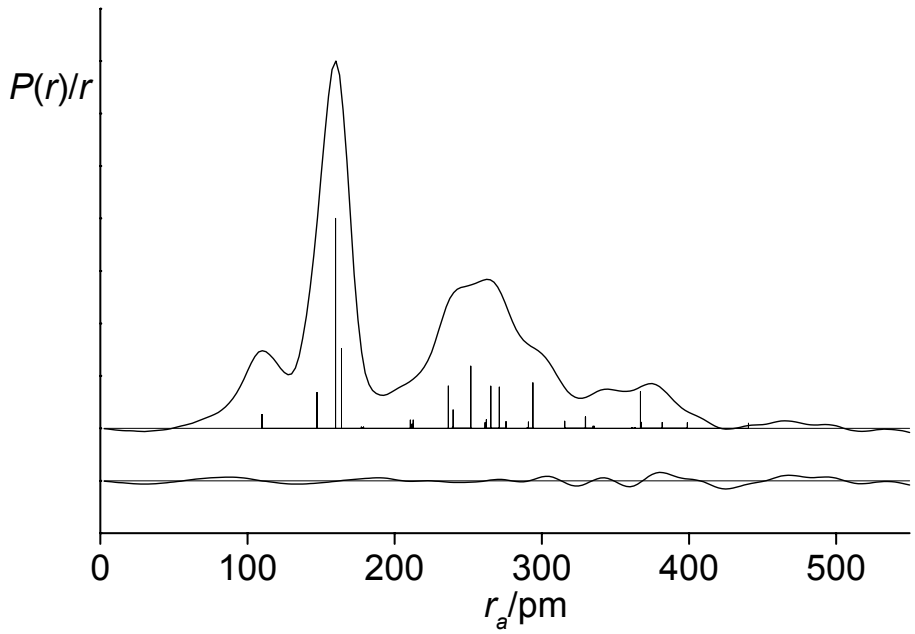

Figure S5 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)_2N(SiH_3)$, **5**. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_P-f_P)(Z_F-f_F)$.

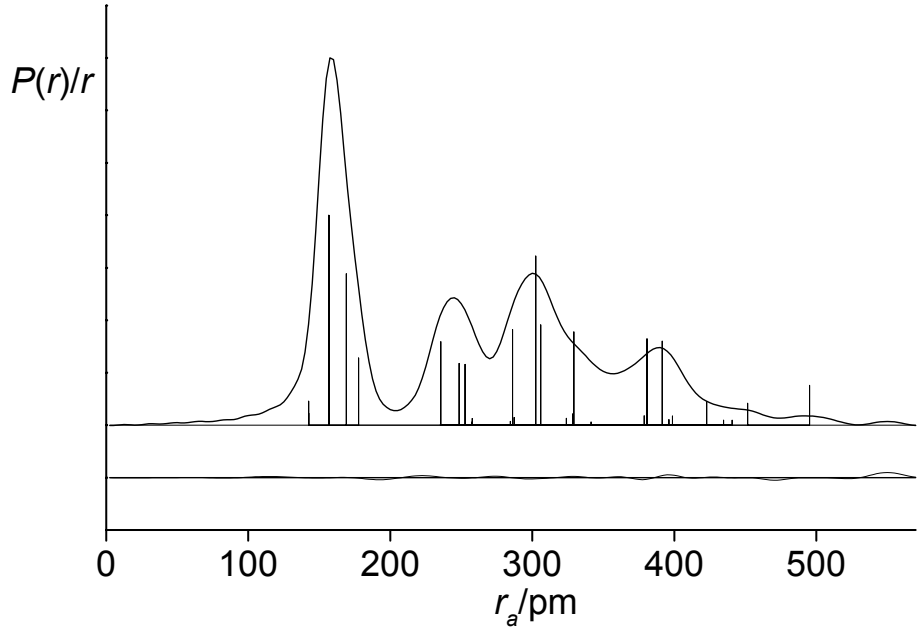

Figure S6 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)N(SiH_3)_2$, **6**. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_{Si}-f_{Si})(Z_F-f_F)$.

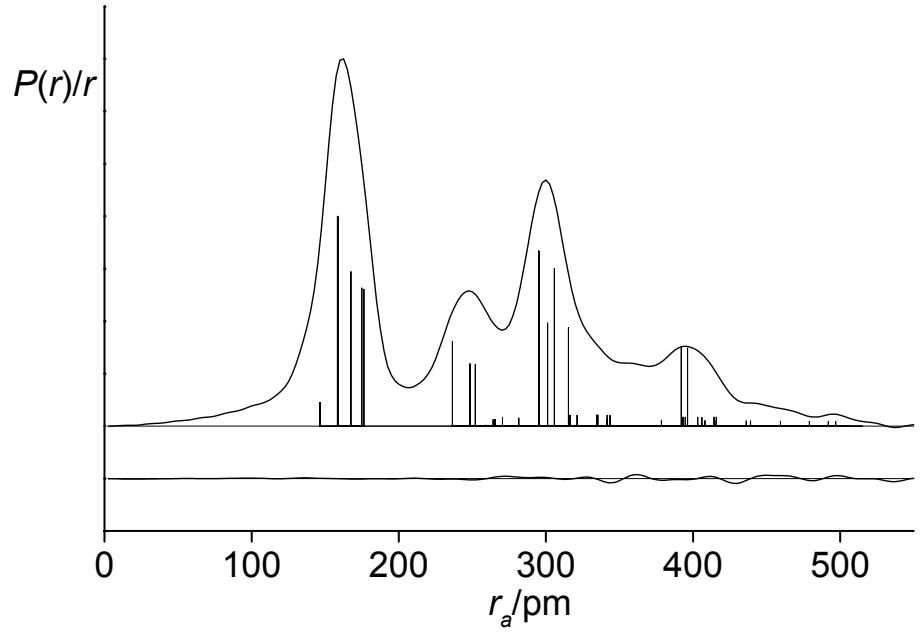

Figure S7 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)_2N(GeH_3)$, **7**. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_{Ge}-f_{Ge})(Z_F-f_F)$.

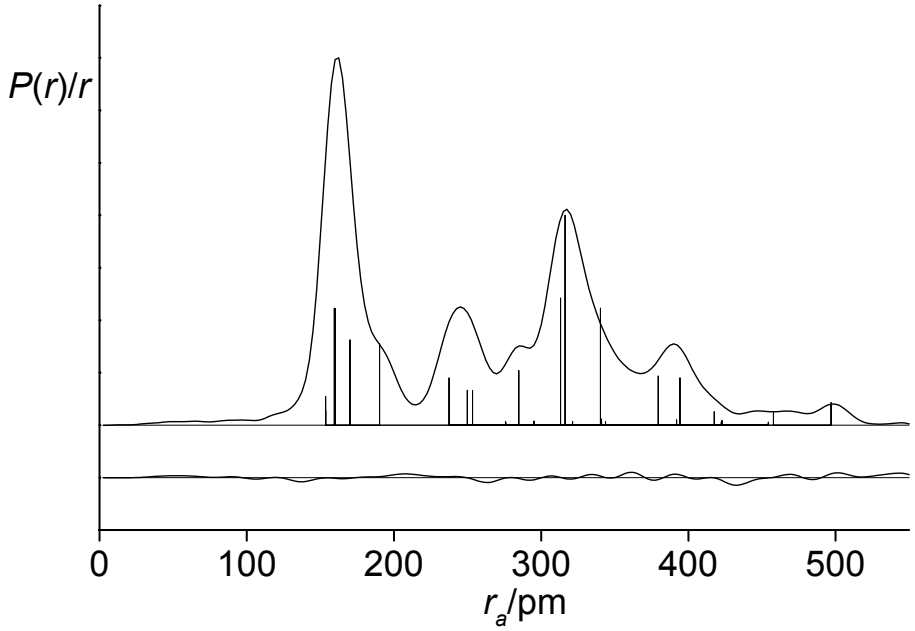

Figure S8 Experimental radial-distribution curve and theoretical–experimental difference curve for the refinement of $(PF_2)NH(SiH_3)$, **8**, as a mixture of two conformers. Before Fourier inversion the data were multiplied by $s.\exp(-0.00002s^2)/(Z_P-f_P)(Z_F-f_F)$.