Supporting Information

How Many Pnicogen Bonds can be Formed to a Central Atom Simultaneously?

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Table S1. Structural parameters in isolated ZF_3 (Z = P, As, Sb, Bi) calculated at the MP2/aug-cc-pVDZ level of theory.

	R(Z-F), Å	Σθ(F-Z-F), degs
PF_3	1.630	291.2
AsF_3	1.745	288.2
SbF_3	1.918	284.5
BiF_3	2.016	286.6

Table S2. Deformation energies (E_{def}, kcal/mol) of ZF_3 complexes with HCN and CN anion calculated at the MP2/aug-cc-pVDZ level of theory.

	ZF_3	base	total
	$HCN\cdots ZF_3$		
$HCN\cdots PF_3$	0.08	0.00	0.08
$HCN\cdots AsF_3$	0.15	0.01	0.16
$HCN\cdots SbF_3$	0.26	0.01	0.27
$HCN\cdots BiF_3$	0.26	0.02	0.28
	$H_3N\cdots ZF_3$		
$H_3N\cdots PF_3$	0.41	0.00	0.41
$H_3N\cdots AsF_3$	0.92	0.02	0.90
$H_3N\cdots SbF_3$	1.36	0.03	1.39
$H_3N\cdots BiF_3$	1.09	0.02	1.11
	$NC^-\cdots ZF_3$		
$NC^-\cdots PF_3$	54.68	0.30	54.98
$NC^-\cdots AsF_3$	46.59	0.27	46.86
$NC^-\cdots SbF_3$	35.83	0.22	36.05
$NC^-\cdots BiF_3$	33.74	0.18	33.92

Table S3. AIM descriptors of the neutral and anionic complexes. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$, ellipticity ε, and total electron energy H, were obtained at the MP2/ aug-cc-pVDZ level. Data in atomic units.

	interaction	ρ	$\nabla^2\rho$	ε	H
$HCN\cdots ZF_3$					
$HCN\cdots PF_3$	N···P	0.012	+0.033	0.041	-0.001
$HCN\cdots AsF_3$	N···As	0.016	+0.042	0.035	-0.0004
$HCN\cdots SbF_3$	N···Sb	0.020	+0.049	0.049	0.0003
$HCN\cdots BiF_3$	N···Bi	0.022	+0.062	0.040	-0.0003
$H_3N\cdots ZF_3$					
$H_3N\cdots PF_3$	N···P	0.022	+0.048	0.044	-0.001
$H_3N\cdots AsF_3$	N···As	0.033	+0.062	0.050	+0.003
$H_3N\cdots SbF_3$	N···Sb	0.036	+0.083	0.073	+0.004
$H_3N\cdots BiF_3$	N···Bi	0.033	+0.095	0.041	+0.001
$NC^-\cdots ZF_3$					
$NC^-\cdots PF_3$	N···P	0.131	+0.143	0.097	+0.099
$NC^-\cdots AsF_3$	N···As	0.122	+0.063	0.047	+0.075
$NC^-\cdots SbF_3$	N···Sb	0.090	+0.180	0.040	+0.031
$NC^-\cdots BiF_3$	N···Bi	0.082	+0.176	0.028	+0.023

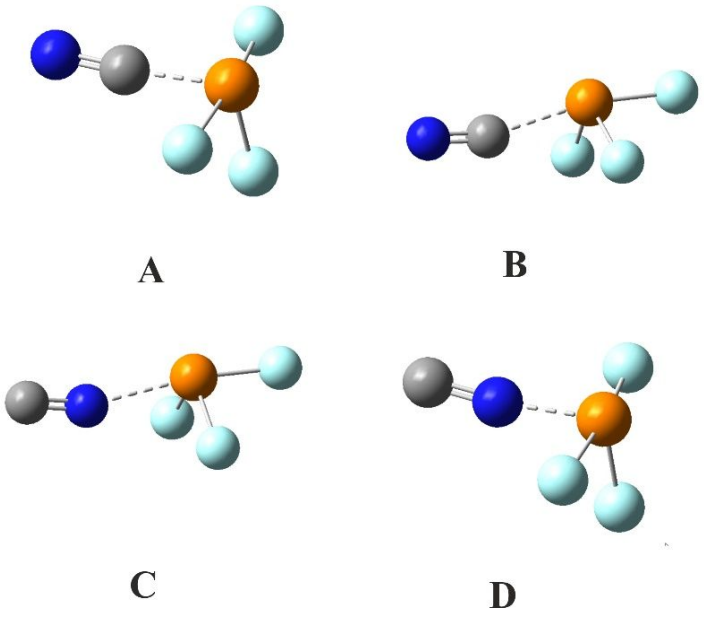


Fig S1. MP2/aug-cc-pVDZ optimized geometries of complexes of CN^- anion with ZF_3

Table S4. Electronic and Gibbs free energy differences (ΔE_{el} and ΔG [a], in kcal/mol) between indicated geometries and global minimum, calculated at the MP2/aug-cc-pVDZ.

	B	C	D
$NC^-\cdots PF_3$	3.93 (3.09)	5.82 (4.60)	11.70 (11.45)
$NC^-\cdots AsF_3$	3.79 (3.09)	5.82 (4.84)	10.73 (10.38)
$NC^-\cdots SbF_3$	1.75 (1.31)	3.75 (3.05)	7.51 (7.18)
$NC^-\cdots BiF_3$	1.50 (0.97)	2.30 (1.32)	8.11 (6.88)

[a] Gibbs free energies in parentheses.

Table S5. Deformation energies (E_{def}, kcal/mol) of ZF_3 complexes with CN^- anion calculated at the MP2/aug-cc-pVDZ level of theory.

	ZF_3	base	total
B			
$NC^-\cdots PF_3$	11.13	0.08	11.21
$NC^-\cdots AsF_3$	9.55	0.09	9.64
$NC^-\cdots SbF_3$	7.57	0.09	7.66
$NC^-\cdots BiF_3$	5.82	0.06	5.88
C			
$CN^-\cdots PF_3$	6.45	0.01	6.46
$CN^-\cdots AsF_3$	6.36	0.02	6.38
$CN^-\cdots SbF_3$	5.54	0.02	5.56
$CN^-\cdots BiF_3$	4.43	0.01	4.44
D			
$CN^-\cdots PF_3$	52.98	0.11	53.08
$CN^-\cdots AsF_3$	45.23	0.08	45.32
$CN^-\cdots SbF_3$	34.87	0.07	34.93
$CN^-\cdots BiF_3$	33.39	0.06	33.45

Table S6. $V_{s,max}$ of dimers calculated at the MP2/aug-cc-pVDZ level of theory.

Dimer	(Z-F) σ-hole	π-hole
$HCN\cdots ZF_3$		
$HCN\cdots PF_3$	24.2	-1.7
$HCN\cdots AsF_3$	30.9	-5.9
$HCN\cdots SbF_3$	36.7	-5.4
$HCN\cdots BiF_3$	47.9	-3.4
$NH_3\cdots ZF_3$		
$H_3N\cdots PF_3$	21.7	-4.4
$H_3N\cdots AsF_3$	26.3	-11.1
$H_3N\cdots SbF_3$	33.4	-10.0
$H_3N\cdots BiF_3$	46.9	-6.6
$NC^-\cdots ZF_3$		
$CN^-\cdots PF_3$	-81.1	-86.5
$CN^-\cdots AsF_3$	-69.9	-76.2
$CN^-\cdots SbF_3$	-59.1	-64.5
$CN^-\cdots BiF_3$	-40.7	-47.3

Table S7. Pairwise interaction energies, and energies of cooperativity (E_{coop}) in ZF_3 complexes with two HCN or CN^- bases calculated at the MP2/aug-cc-pVDZ level of theory.

	E_{tot}	E1	E2	E3	E_{coop}
$(HCN)_2\cdots PF_3$	-4.70	-2.93	-2.93	0.78	0.38
$(HCN)_2\cdots AsF_3$	-7.51	-4.48	-4.49	0.83	0.63
$(HCN)_2\cdots SbF_3$	-11.06	-6.48	-6.48	0.78	1.12
$(HCN)_2\cdots BiF_3$	-14.57	-8.16	-8.12	0.80	0.91
$(H_3N)_2\cdots PF_3$	-8.66	-5.23	-5.22	1.02	0.77
$(H_3N)_2\cdots AsF_3$	-14.88	-8.85	-8.85	1.21	1.61
$(H_3N)_2\cdots SbF_3$	-23.28	-13.71	-13.72	1.15	3.00
$(H_3N)_2\cdots BiF_3$	-27.45	-15.25	-15.22	1.07	1.95
$(CN^-)_2\cdots SbF_3$	-4.29	-45.30	-45.28	75.64	10.65
$(CN^-)_2\cdots BiF_3$	-12.92	-46.69	-46.69	70.18	10.28

E1=L_a-ZF_3, E2=ZF_3-L_b, E3= L_a-L_b where L refers to bases

Table S8. AIM descriptors of the neutral and anionic trimers. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$, ellipticity ε, and total electron energy H, were obtained at the MP2/ aug-cc-pVDZ level. Data in atomic units.

	interaction	ρ	$\nabla^2\rho$	ε	H
$(HCN)_2\cdots ZF_3$					
$(HCN)_2\cdots PF_3$	N···P	0.011	+0.031	0.049	+0.001
$(HCN)_2\cdots AsF_3$	N···As	0.014	+0.038	0.042	+0.001
$(HCN)_2\cdots SbF_3$	N···Sb	0.017	+0.042	0.055	+0.000
$(HCN)_2\cdots BiF_3$	N···Bi	0.020	+0.057	0.047	+0.000
$(H_3N)_2\cdots ZF_3$					
$(H_3N)_2\cdots PF_3$	N···P	0.017	+0.041	0.058	0.0002
$(H_3N)_2\cdots AsF_3$	N···As	0.025	+0.051	0.053	-0.001
$(H_3N)_2\cdots SbF_3$	N···Sb	0.030	+0.067	0.072	-0.002
$(H_3N)_2\cdots BiF_3$	N···Bi	0.030	+0.084	0.040	-0.001
	F···N	0.014	+0.063	10.820	0.001
$(NC^-)_2\cdots ZF_3$					
$(NC^-)_2\cdots SbF_3$	N···Sb	0.047	+0.071	0.067	+0.009
$(NC^-)_2\cdots BiF_3$	N···Bi	0.037	+0.074	0.034	+0.003

Table S9. $V_{s,max}$ of trimers calculated at the MP2/aug-cc-pVDZ level of theory.

Isolated molecule	$V_{S,max}$ (Z-F) σ-hole	$V_{S,max}$ π-hole
$(HCN)_2\cdots ZF_3$		
$(HCN)_2\cdots PF_3$	14.2	-11.6
$(HCN)_2\cdots AsF_3$	20.3	-16.5
$(HCN)_2\cdots SbF_3$	25.8	-17.3
$(HCN)_2\cdots BiF_3$	27.7	-15.2
$(H_3N)_2\cdots ZF_3$		
$(NH_3)_2\cdots PF_3$	13.2	-12.9
$(NH_3)_2\cdots AsF_3$	16.1	-21.3
$(NH_3)_2\cdots SbF_3$	16.1	-24.9
$(NH_3)_2\cdots BiF_3$	34.6	-21.7
$(NC^-)_2\cdots ZF_3$		
$(CN)_2\cdots SbF_3$	-147.3	-195.6
$(CN)_2\cdots BiF_3$	-119.7	-178.7

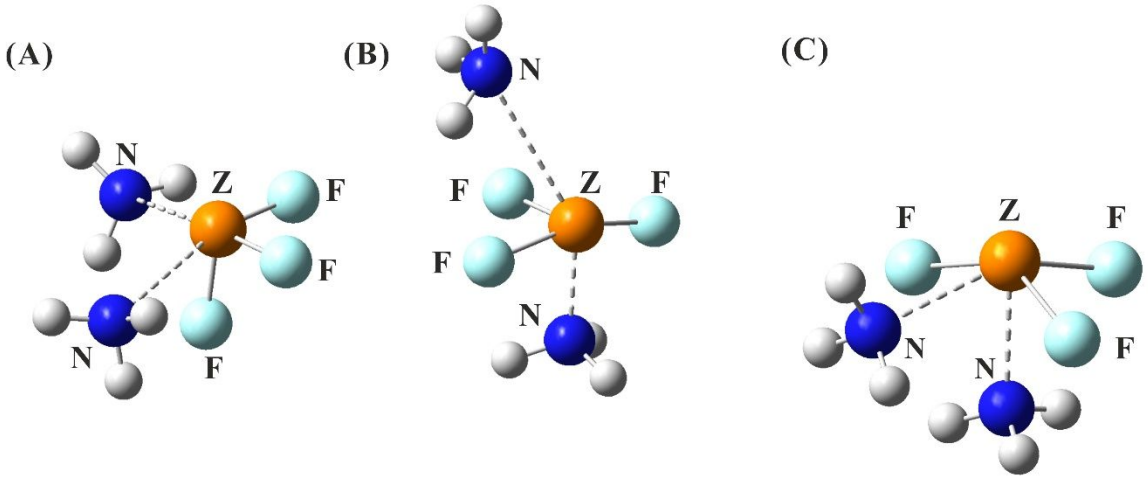


Fig S2. Three minima located on the potential energy surface of $(NH_3)_2\cdots ZF_3$.

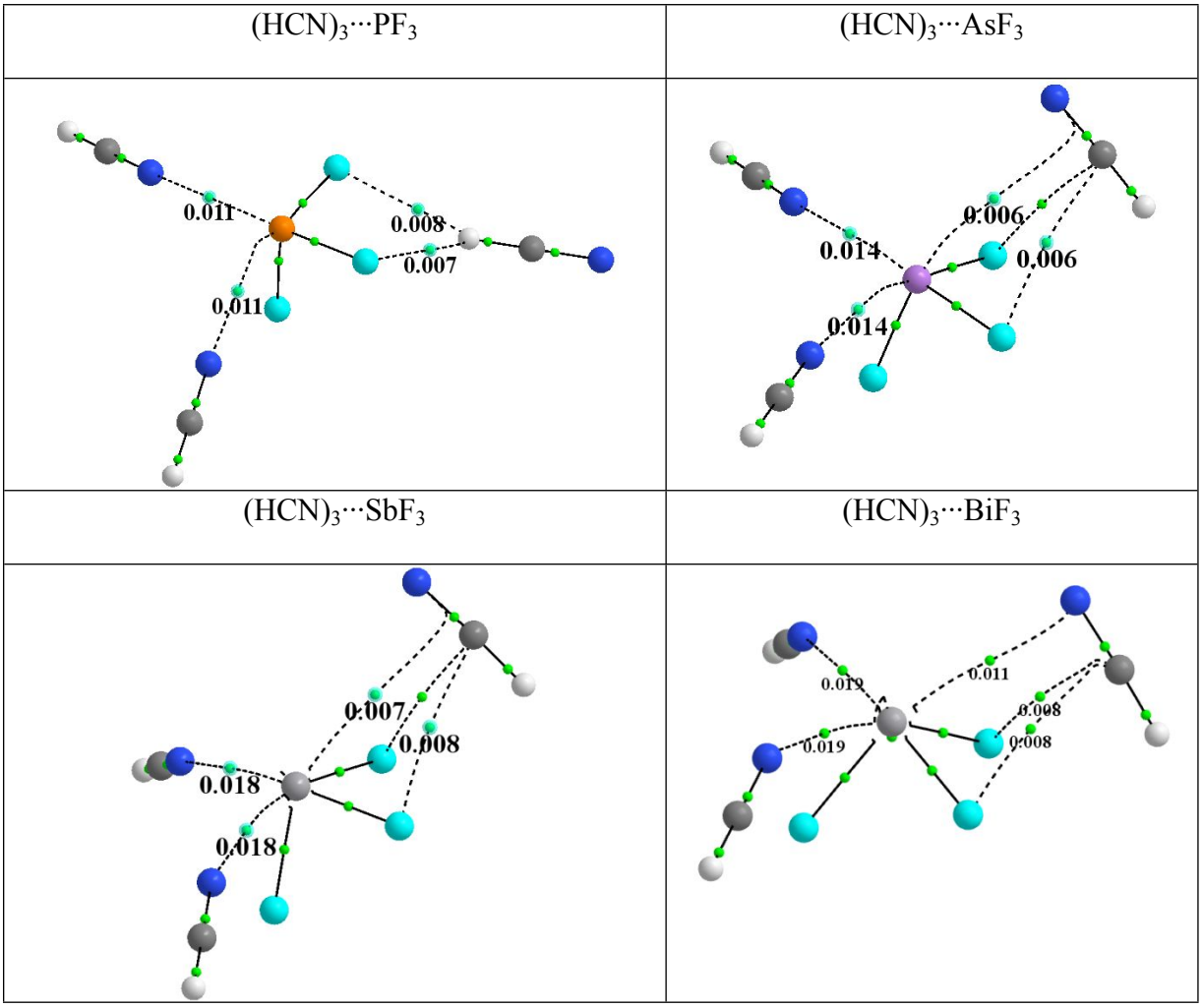
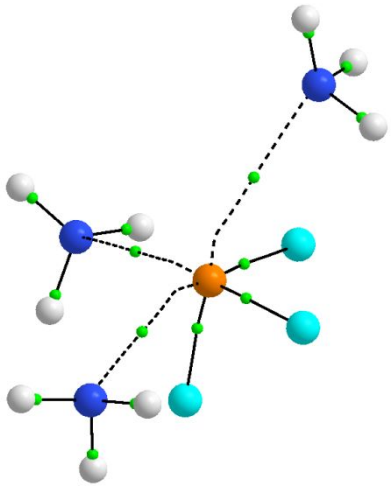
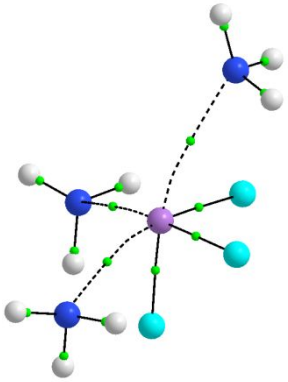
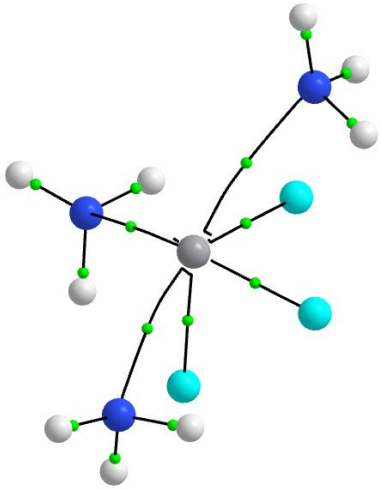


Fig S3. AIM molecular diagrams of MP2/aug-cc-pVDZ optimized structures of $(HCN)_3\cdots ZF_3$. Green dots represent bond critical points. Numbers refers to electron densities at BCPs (in a.u.)

$(NH_3)_3\cdots PF_3$	
$(NH_3)_3\cdots AsF_3$	
$(NH_3)_3\cdots SbF_3$	

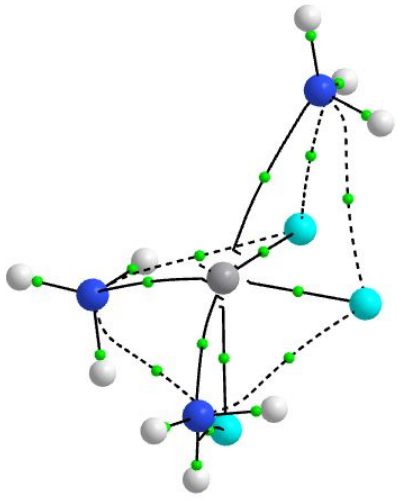
$(NH_3)_3\cdots BiF_3$	

Fig S4. AIM molecular diagrams of MP2/aug-cc-pVDZ optimized structures of $(H_3N)_3\cdots ZF_3$. Green dots represent bond critical points.

Table S10. AIM descriptors of the tetramers containing ZF_3 and 3 NH_3 molecules. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$, ellipticity ε, and total electron energy H, were obtained at the MP2/ aug-cc-pVDZ level. Data in atomic units.

	interaction	ρ	$\nabla^2\rho$	ε	H
$(NH_3)_3\cdots PF_3$	N···P	0.015	+0.038	0.050	+0.0004
$(NH_3)_3\cdots AsF_3$	N···As	0.021	+0.046	0.035	-0.0006
$(NH_3)_3\cdots SbF_3$	N···Sb	0.026	+0.053	0.051	-0.002
$(NH_3)_3\cdots BiF_3$	N···Bi	0.027	+0.075	0.036	-0.001

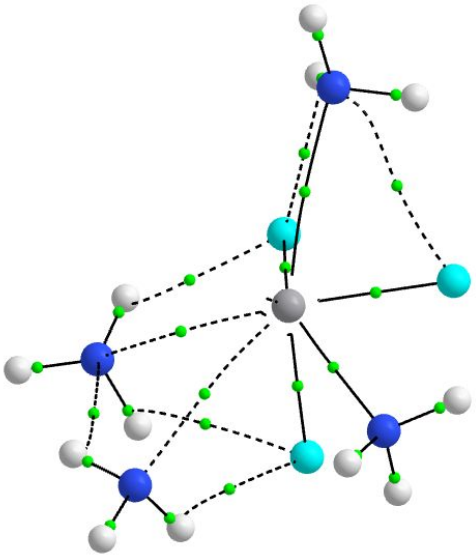
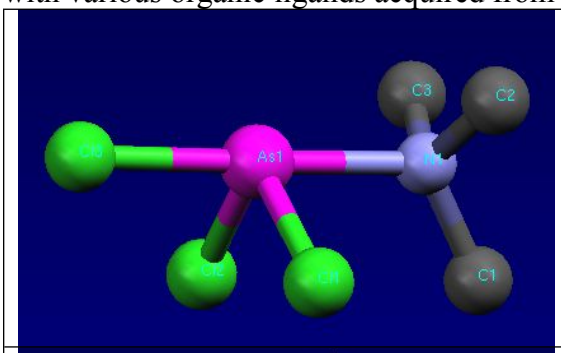
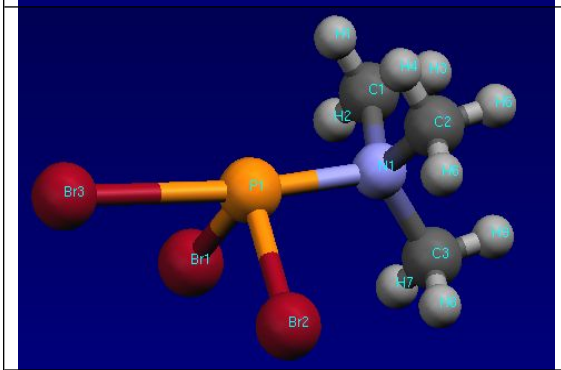
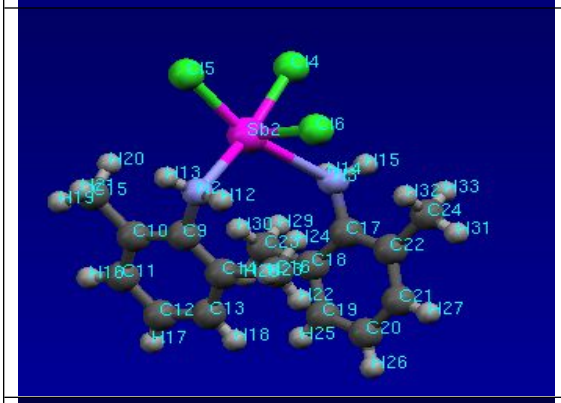
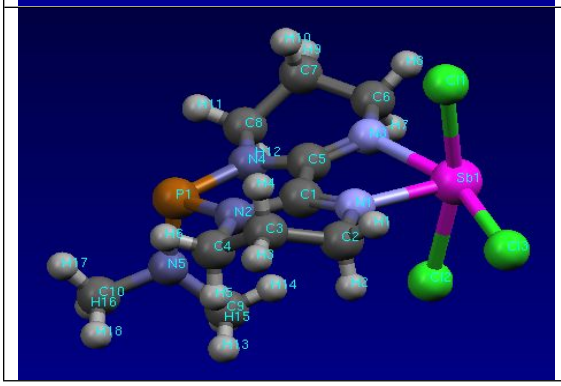
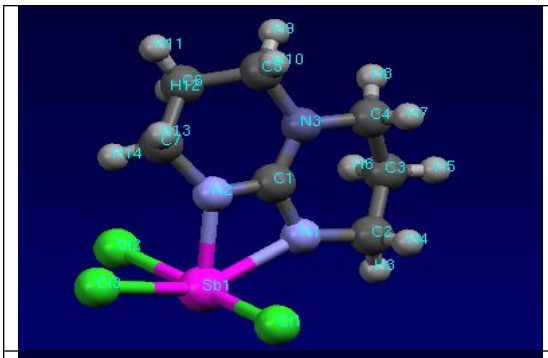
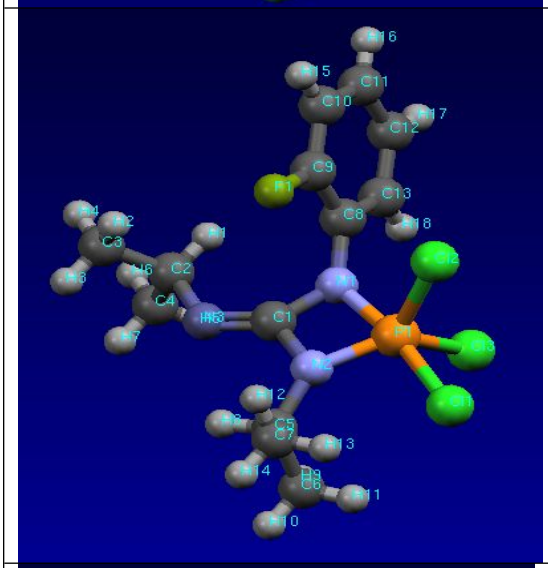
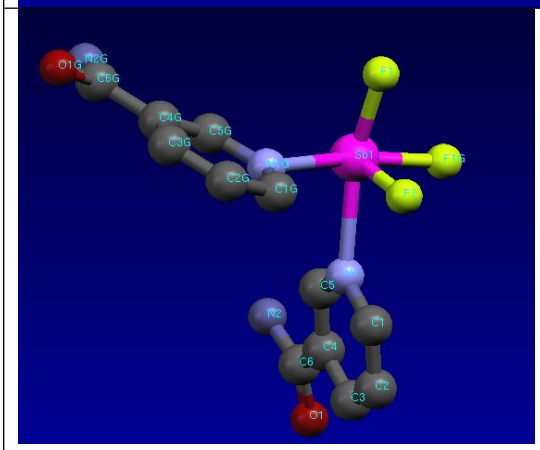
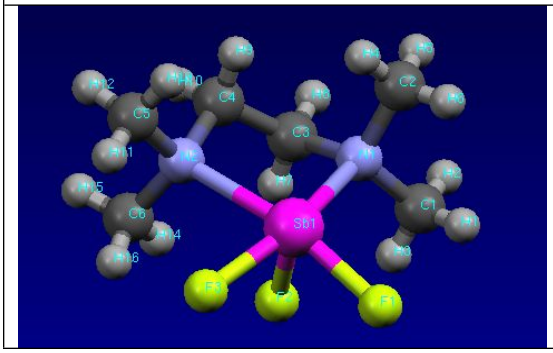


Fig S5. AIM molecular diagram of $(NH_3)_4\cdots BiF_3$.

Fig S6. Crystal structures of tetra and penta-coordinated Z (Z=P, As, Sb) atoms in complexes with various organic ligands acquired from CSD.

	ASCTMA [82] R(N···As)= 2.287 Å
	MEWXOB [83] R(N···P)= 1.978 Å
	SAVFAX [84] R(N···Sb)= 2.596 Å
	RIFLOJ [85] R(N···Sb)= 2.171, 2.375 Å

		TANVUB [86] R(N···Sb)= 2.076, 2.260 Å
		XEXDEJ [87] R(N···P)= 1.650, 1.783 Å
		YUXPUC [88] R(N···Sb)= 2.470, 2.470 Å
		ZARMEN [89] R(N···Sb)= 2.465, 2.484 Å