Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Implications of Monomer Deformation for Tetrel and Pnicogen Bonds

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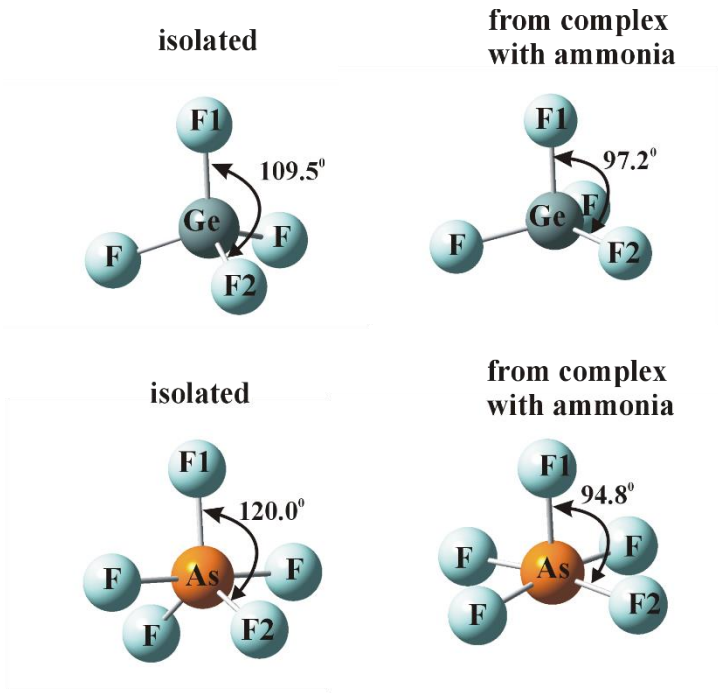


Fig. S1. The structures of isolated GeF_4 and AsF_5 and their internal geometry within the complex with NH_3, highlighting changes in internal bond angles.

TABLE S1. EDA/BLYP-D3/ZORA/TZ2P decomposition of the total DFT-D interaction energy of complexes into Pauli repulsion (E_{Pauli}), electrostatic (E_{elstat}), orbital interaction (E_{oi}) and dispersion (E_{disp}) terms. All energies in kcal mol^{-1}. The relative values in percent express the contribution of each to the sum of all attractive energy terms.

	ΔE	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
NH_3···SiF_4	-24.62	97.18	-75.74	62	-42.32	35	-3.74	3
NH_3···GeF_4	-27.52	108.66	-85.08	63	-47.40	35	-3.70	3
NH_3···SnF_4	-32.29	95.94	-83.03	65	-41.30	32	-3.90	3
NH_3··· PF_5	-38.34	143.77	-98.84	54	-78.79	43	-4.48	2
NH_3··· AsF_5	-41.38	127.33	-94.17	56	-70.06	42	-4.48	3
NH_3··· SbF_5	-43.13	102.76	-86.77	59	-54.45	37	-4.68	3
pyrazine···SiF_4	-20.60	77.77	-59.47	61	-32.96	34	-5.94	6
pyrazine···GeF_4	-26.84	98.73	-75.25	60	-44.19	35	-6.13	5
pyrazine···SnF_4	-32.52	92.52	-77.07	62	-41.38	33	-6.59	5
pyrazine··· PF_5	-37.44	126.89	-86.35	53	-70.66	43	-7.32	4
pyrazine··· AsF_5	-42.24	119.57	-86.58	54	-67.77	42	-7.46	5
pyrazine··· SbF_5	-44.82	100.46	-81.91	56	-55.51	38	-7.86	5
NCH···SiF_4	-2.98	5.73	-5.35	61	-1.40	16	-1.97	23
NCH··· GeF_4	-6.29	22.90	-18.00	62	-8.46	29	-2.73	9
NCH···SnF_4	-14.71	51.03	-39.29	60	-23.23	35	-3.22	5
NCH··· PF_5	-2.42	3.03	-3.21	59	-0.62	11	-1.62	30
NCH··· AsF_5	-14.93	48.91	-34.32	54	-26.01	41	-3.51	5
NCH··· SbF_5	-21.41	55.00	-42.05	55	-30.54	40	-3.82	5

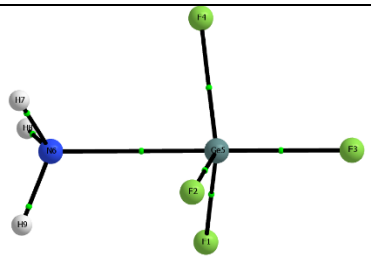
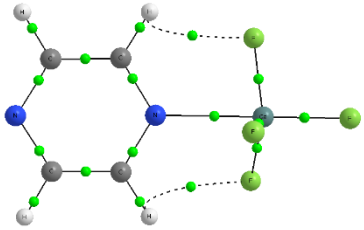
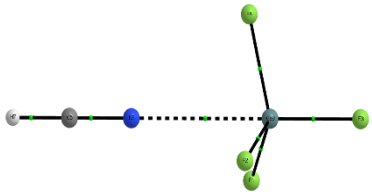
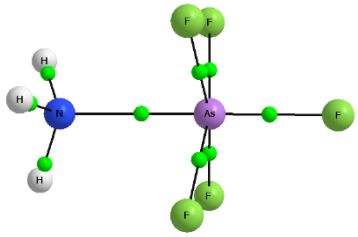
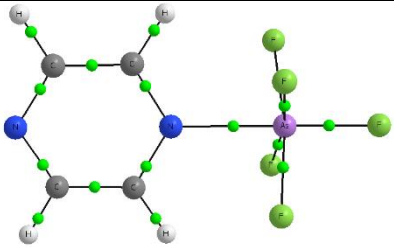
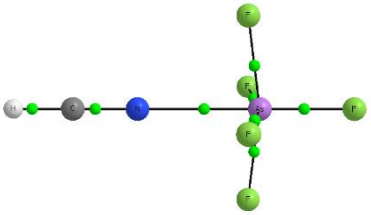
NH_3···GeF_4	pyrazine···GeF_4	NCH···GeF_4
		
NH_3···AsF_5	pyrazine···AsF_5	NCH···AsF_5
		

Fig. S2 AIM graphs computed at the MP2/cc-pVTZ level of theory.

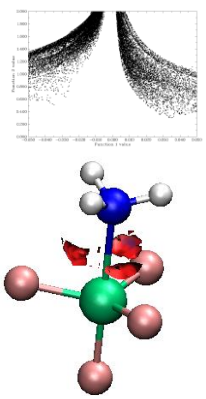
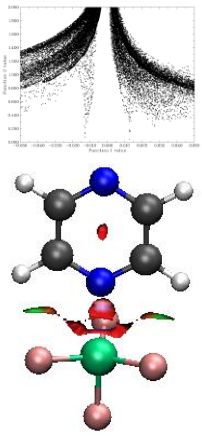
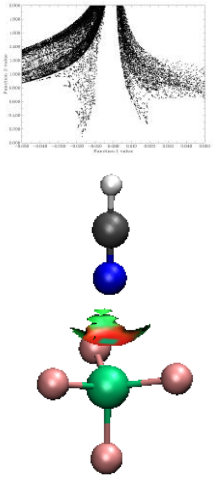
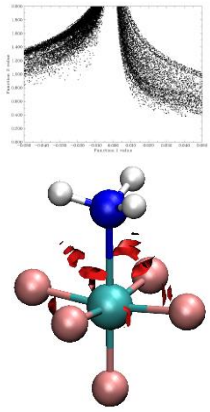
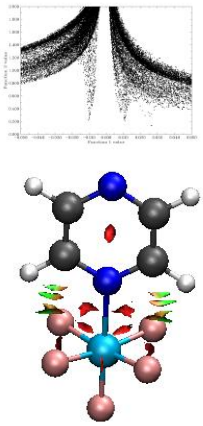
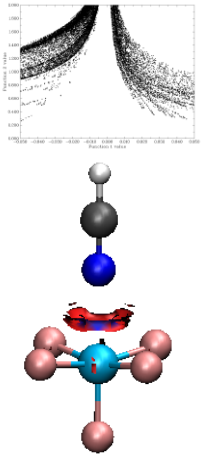
NH_3···GeF_4	pyrazine···GeF_4	NCH···GeF_4
		
NH_3···AsF_5	pyrazine···AsF_5	NCH···AsF_5
		

Fig. S3. Noncovalent interaction regions (bonding isosurfaces are illustrated in green while brown and red represent repulsive forces).

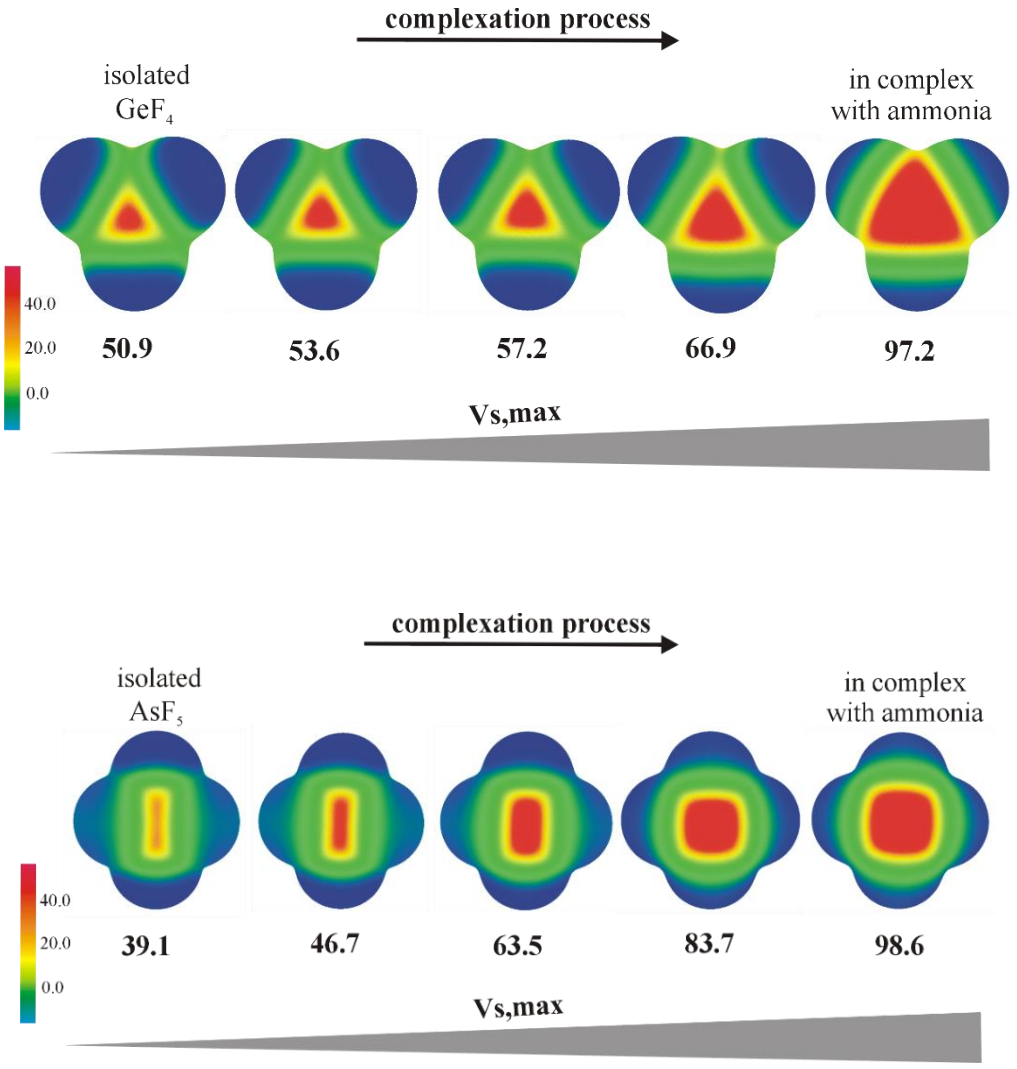


Fig. S4. MEP of GeF_4 (upper) and AsF_5 (lower) as their geometries deform to accommodate an approaching NH_3 molecule.

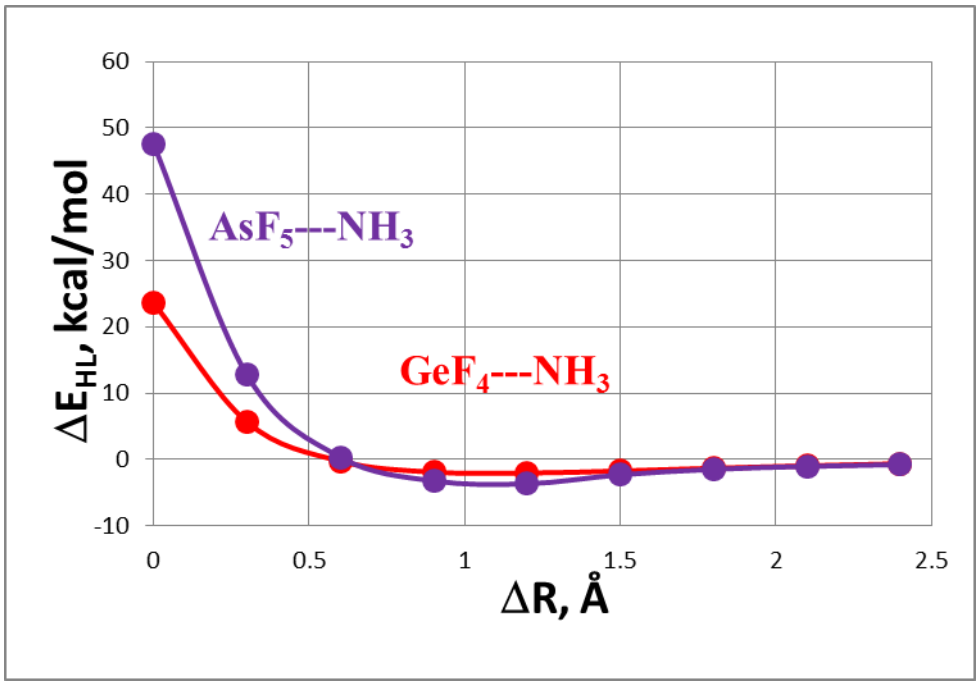


Fig. S5. ΔE_{HL} for $GeF_4\cdots NH_3$ and $AsF_5\cdots NH_3$ as the R(T/Z··N) distance is stretched from its equilibrium value.

TABLE S2. EDA/BLYP-D3/ZORA/TZ2P decomposition of the total DFT-D interaction energy (kcal/mol) in $GeF_4\cdots NH_3$ as the R(Ge··N) distance is stretched from its equilibrium value. Geometries from MP2 calculations.

	Distance [Å]	ΔE	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
R_e	2.107	-27.52	108.68	-85.09	62	-47.41	35	-3.70	3
R_e+0.3	2.407	-21.12	50.15	-44.50	62	-23.40	33	-3.38	5
R_e+0.6	2.707	-14.02	23.55	-23.80	63	-10.82	29	-2.95	8
R_e+0.9	3.007	-9.41	11.20	-13.10	64	-5.05	25	-2.46	12
R_e+1.2	3.307	-6.43	5.17	-7.21	62	-2.46	21	-1.93	17
R_e+1.5	3.607	-4.49	2.40	-4.13	60	-1.32	19	-1.43	21
R_e+1.8	3.907	-3.09	1.18	-2.49	58	-0.76	18	-1.01	24
R_e+2.1	4.207	-2.11	0.63	-1.58	57	-0.47	17	-0.70	25
R_e+2.4	4.507	-1.42	0.38	-1.02	57	-0.29	16	-0.48	27

TABLE S3. EDA/BLYP-D3/ZORA/TZ2P decomposition of the total DFT-D interaction energy (kcal/mol) in $AsF_5\cdots NH_3$ as the R(As··N) distance is stretched from its equilibrium value. Geometries from MP2 calculations.

	Distance [Å]	ΔE	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
R_e	2.017	-36.85	163.6	-116.11	58	-79.69	40	-4.65	2
R_e+0.3	2.317	-31.93	72	-59.27	57	-40.44	39	-4.22	4
R_e+0.6	2.617	-23.11	31.52	-31.18	57	-19.8	36	-3.67	7
R_e+0.9	2.917	-15.91	13.76	-16.99	57	-9.66	33	-3.01	10
R_e+1.2	3.217	-10.89	6.03	-9.7	57	-4.89	29	-2.33	14
R_e+1.5	3.517	-6.17	3.33	-5.63	59	-2.1	22	-1.77	19
R_e+1.8	3.817	-3.82	1.8	-3.28	58	-1.04	19	-1.29	23
R_e+2.1	4.117	-2.55	0.95	-2	57	-0.59	17	-0.91	26
R_e+2.4	4.417	-1.75	0.53	-1.29	57	-0.36	16	-0.63	28

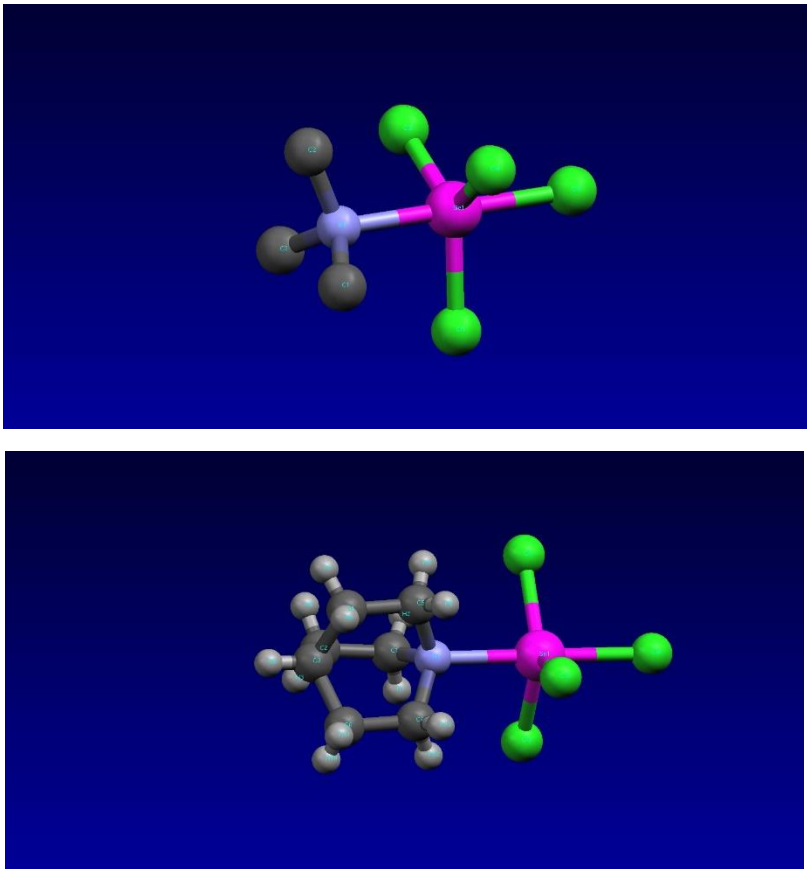


Fig S6. X-ray structures of complexes of $GeCl_4$ with a) NMe_3,[1] and b) quinuclidine.[2]

References

[1] M. S. Bilton and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1972, 722.

[2] W. A. Grigsby, T. S. Morien, C. L. Raston, B. W. Skelton and A. H. White, *Australian Journal of Chemistry*, 2004, **57**, 507.