Comparison Between Tetrel Bonded Complexes Stabilized by σ and π Hole Interactions

Wiktor Zierkiewicz [1,*], Mariusz Michalczyk [1] and Steve Scheiner [2,*]

[1] Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, Wrocław 50370, Poland; mariusz.michalczyk@pwr.edu.pl

[2] Department of Chemistry and Biochemistry, Utah State University Logan, Utah 84322-0300, United States

* Correspondence: wiktor.zierkiewicz@pwr.edu.pl (W.Z.); steve.scheiner@usu.edu (S.S.); Tel.: +48-071-320-3455 (W.Z.); +1-435-797-7419 (S.S.)

Academic Editor: Steve Scheiner
Received: 30 May 2018; Accepted: 09 June 2018; Published: date

TABLE S1. NBO values of sum of the E(2) for LP(N)→σ*(T-X), (T= Si, Ge or Sn and X=H or F) orbital interaction and total charge transfer (CT) from NH_3 to $TH_{2-n}F_n$ in σ-hole bonded complexes obtained at the BLYP-D3(BJ)/def2-TVZPP level.

Lewis acid[a]	ΣE(2) [kcal/mol]	CT [me]
SiH_4	3.30	19
GeH_4	3.66	17
SnH_4	6.41	30
SiH_3F(a)	15.14	83
SiH_3F(b)	3.44	20
GeH_3F(a)	17.07	78
GeH_3F(b)	4.21	19
SnH_3F(a)	22.75	93
SnH_3F(b)	16.94	69
SiH_2F_2(a)	24.40	107
SiH_2F_2(b)	6.65	33
GeH_2F_2(a)	26.30	96
GeH_2F_2(b)	38.62	123
SnH_2F_2(a)	34.82	117
SnH_2F_2(b)	54.87	168

[a]NBO analysis performed using DFT functional for the MP2 optimized geometries.

GeH_4	

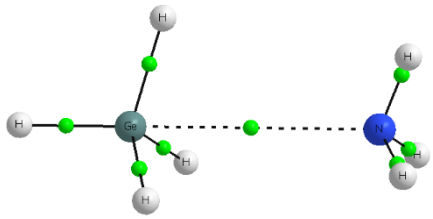
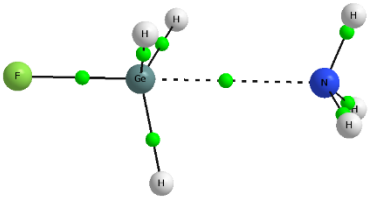
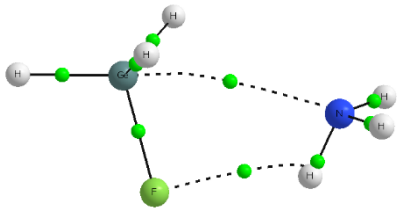
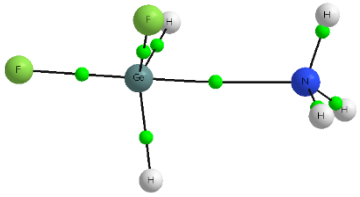
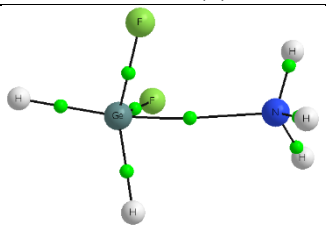
	
GeH_3F(a)	GeH_3F(b)
	
GeH_2F_2(a)	GeH_2F_2(b)
	

Figure S1. AIM diagrams showing the bond critical points (green dots) in Ge-containing complexes stabilized by σ-hole tetrel bonds.

TABLE S2. AIM data for σ-hole bonded complexes. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$ (both in atomic units) and total electron energy (H, kcal mol^{-1}). Calculations were performed at the MP2/aug-cc-pVDZ-PP level.

$NH_3\cdots$system	interaction	ρ	$\nabla^2\rho$	H
SiH_4	Si···N	0.008	0.025	0.51
GeH_4	Ge···N	0.007	0.023	0.53
SnH_4	Sn···N	0.011	0.033	0.40
SiH_3F(a)	Si···N	0.023	0.055	-2.12
SiH_3F(b)	Si···N	0.009	0.028	0.46
	F···N	0.010	0.049	0.95
GeH_3F(a)	Ge···N	0.024	0.077	-0.24
GeH_3F(b)	Ge···N	0.009	0.028	0.53
	F···H	0.013	0.053	0.40
SnH_3F(a)	Sn···N	0.027	0.089	-0.55
SnH_3F(b)	Sn···N	0.021	0.063	-0.21
	F···N	0.016	0.072	0.85
SiH_2F_2(a)	Si···N	0.032	0.055	-5.07
SiH_2F_2(b)	F···N	0.013	0.046	0.36
	F···N	0.013	0.047	0.33
	H···N	0.014	0.037	0.12
GeH_2F_2(a)	Ge···N	0.033	0.099	-2.14
GeH_2F_2(b)	Ge···N	0.041	0.114	-4.42
SnH_2F_2(a)	Sn···N	0.037	0.123	-1.52
SnH_2F_2(b)	Sn···N	0.050	0.182	-2.83

TABLE S3. NBO values of sum of the E(2) for LP(N)→σ*(T-X), (T= Si, Ge or Sn and X=H or F) orbital interaction and total charge transfer (CT) from NH_3 to $TH_{2-n}F_n{=}CH_2$ in π-hole bonded complexes obtained at the BLYP-D3(BJ)/def2-TVZPP level.

Lewis acid	ΣE(2) [kcal/mol]	CT [me]
$SiH_2{=}CH_2$	53.54 (42.89)	163
$GeH_2{=}CH_2$	32.81 (27.70)	118
$SnH_2{=}CH_2$	31.45 (23.88)	113
$SiHF{=}CH_2$	68.53 (44.69)	194
$GeHF{=}CH_2$	61.43 (37.38)	175
$SnHF{=}CH_2$	55.89 (26.78)	171
$SiF_2{=}CH_2$	75.96 (47.14)	197
$GeF_2{=}CH_2$	38.35 (24.04)	193
$SnF_2{=}CH_2$	63.06 (26.16)	179

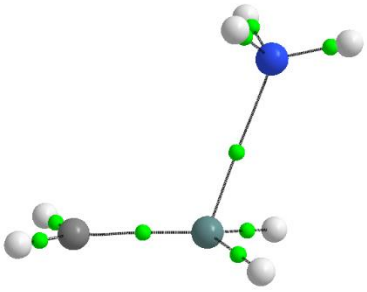
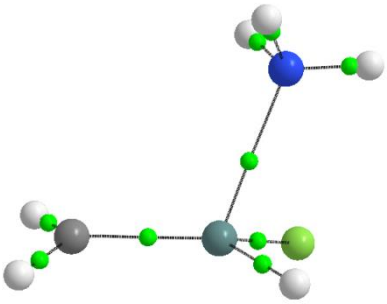
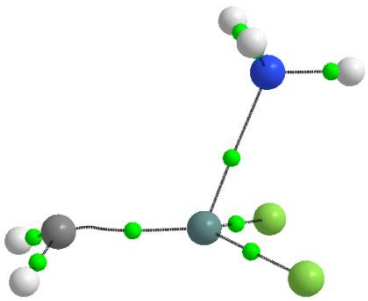
$GeH_2{=}CH_2$(c)	$GeHF{=}CH_2$ (c)	$GeF_2{=}CH_2$(c)
		

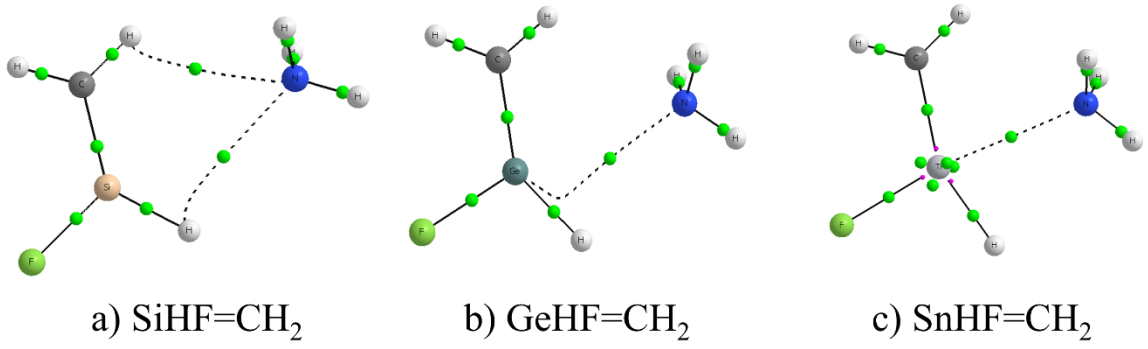
Figure S2. Bond critical points (green dots) in several Ge-containing complexes stabilized by π-hole tetrel bond.

TABLE S4. AIM data for π-hole bonded complexes. Bond critical point (BCP) properties: electron density ρ, Laplacian of electron density $\nabla^2\rho$ (both in atomic units) and total electron energy (H, kcal mol^{-1}). Calculations were performed at the MP2/aug-cc-pVDZ level.

Lewis acid	ρ	$\nabla^2\rho$	H
$SiH_2{=}CH_2$	0.046	0.123	-8.03
$GeH_2{=}CH_2$	0.035	0.092	-2.67
$SnH_2{=}CH_2$	0.033	0.102	-1.42
$SiHF{=}CH_2$	0.057	0.226	-7.65
$GeHF{=}CH_2$	0.060	0.172	-10.17
$SnHF{=}CH_2$	0.052	0.194	-2.96
$SiF_2{=}CH_2$	0.064	0.279	-7.90
$GeF_2{=}CH_2$	0.074	0.225	-14.07
$SnF_2{=}CH_2$	0.059	0.230	-3.87

Table S5. Geometry and energetics for d complexes

Lewis acid	E_{int}	E_{def} A	E_{def} B	R(N···T)	∠F-T···N	R(N···H1)	∠T-H1···N	R(N···H2)	∠C-H2···N	∠ C–T-H1
$SiHF=CH_2$	-2.50	0.32	0.00	3.394	165.1	2.892	96.8	2.724	118.9	132.9
$GeHF=CH_2$	-4.23	1.02	0.00	3.058	169.2	2.808	84.5	2.662	108.7	143.4
$SnHF=CH_2$	-8.88	2.53	0.00	2.759	172.2	2.864	76.1	2.745	99.2	156.5



a) $SiHF=CH_2$ b) $GeHF=CH_2$ c) $SnHF=CH_2$

Figure S3. AIM molecular diagram of $THF=CH_2/NH_3$ d dimers wherein the base occupies the d maximum of the MEP of the acid.

Table S6. NBO properties of d complexes

Lewis acid	E(2) [kcal/mol]	CT [me]
$SiHF{=}CH_2$	1.35 (0.92)[a]	11
$GeHF{=}CH_2$	5.09 (3.75)	30
$SnHF{=}CH_2$	14.59 (7.77)	73

[a]the largest value of the contribution in this donation

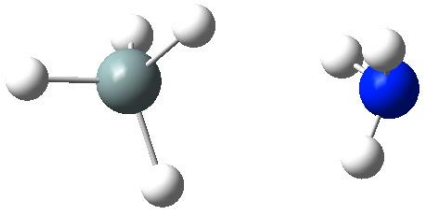
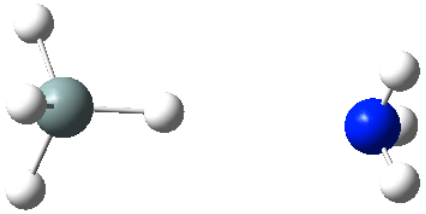
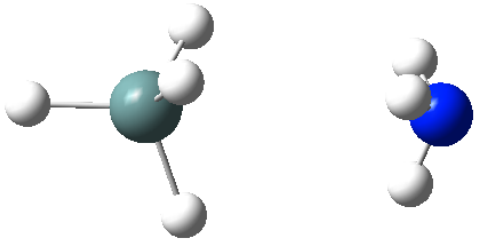
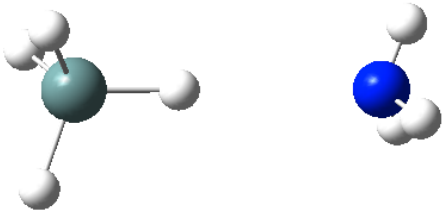
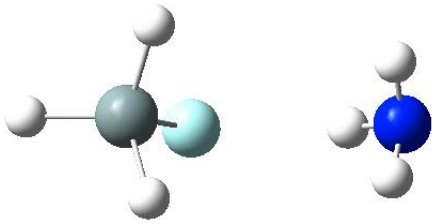
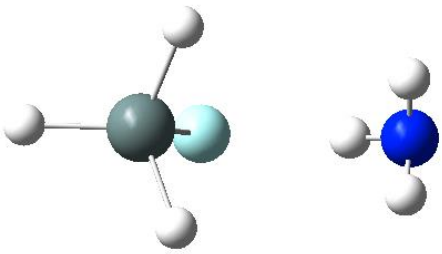
Table S7. AIM parameters of d complexes

Lewis acid	interaction	ρ	$\nabla^2\rho$	H
$SiHF{=}CH_2$	H···N	0.007	0.025	0.60
	H···N	0.008	0.026	0.72
$GeHF{=}CH_2$	Ge···N	0.012	0.035	0.56
$SnHF{=}CH_2$	Sn···N	0.023	0.073	-0.25

Table S8. EDA/BLYP-D3(BJ)/ZORA/TZ2P decomposition of the interaction energy of π-hole bonded complexes d into Pauli repulsion (E_{Pauli}), electrostatic (E_{elec}), orbital interaction (E_{oi}) and dispersion (E_{disp}) terms. All energies in kcal/mol. The relative values in percent express the contribution of each to the sum of all attractive terms.

Lewis acid	E_{int}	E_{Pauli}	E_{elec}	%	E_{oi}	%	E_{disp}	%
$SiHF{=}CH_2$	-2.92	5.48	-4.38	52	-1.77	21	-2.25	27
$GeHF{=}CH_2$	-4.55	11.16	-9.22	59	-3.67	23	-2.81	18
$SnHF{=}CH_2$	-8.67	28.32	-23.49	64	-10.06	27	-3.43	9

Table S9. Secondary minima for dimers of NH_3 with σ-hole donors. Data obtained at the MP2/aug-cc-pVDZ-PP level of theory. E_{int} corrected for BSSE (in kcal/mol). Distances are in Å.

TH_nF_n System	E_{int}	R(N···X)	structure
SiH_4 (b)	-0.50	3.600	
SiH_4 (c)	-0.06	3.078	
GeH_4 (b)	-0.46	3.610	
GeH_4 (c)	-0.08	2.940	
SiH_3F(c)	-1.00	3.307	
SnH_3F(c)	-1.76	3.169	

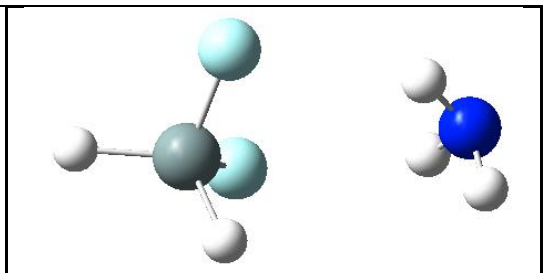
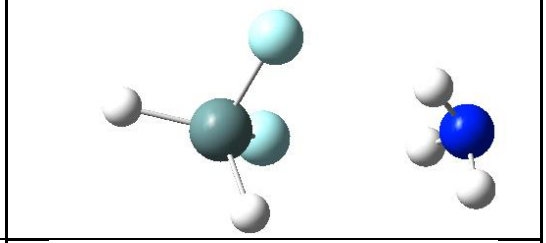
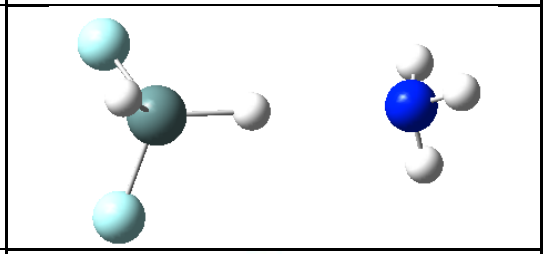
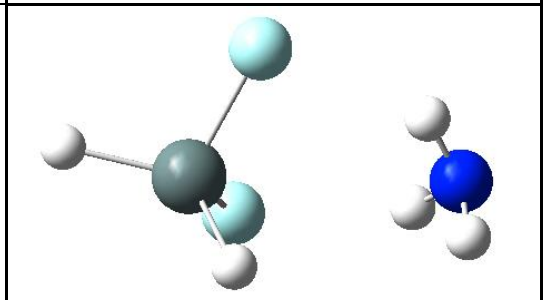
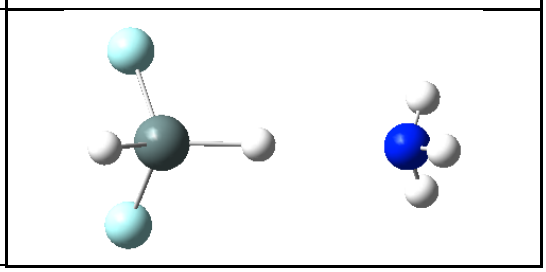
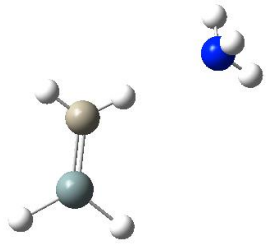
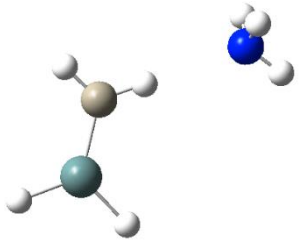
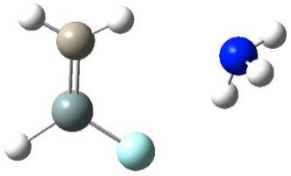
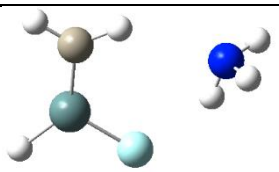
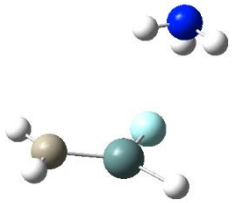
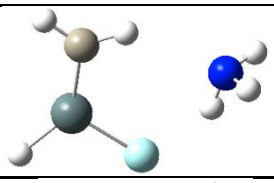
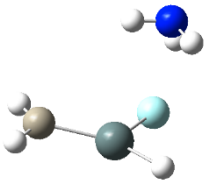
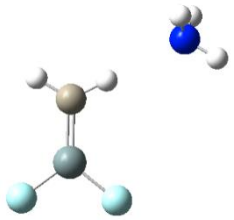
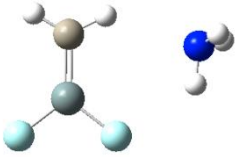
SiH_2F_2(c)	-0.95	3.404	
GeH_2F_2(c)	-1.32	3.337	
GeH_2F_2(d)	-1.72	2.590	
SnH_2F_2(c)	-1.90	3.249	
SnH_2F_2(d)	-1.73	2.596	

Table S10. Secondary minima for dimers of NH_3 with π-hole donors. Data obtained at the MP2/aug-cc-pVDZ-PP level of theory. E_{int} corrected for BSSE (in kcal/mol). Distances are in Å.

TH_nF_n System	E_{int}	R(N···X)	structure
SiH_2=CH_2 (b)	-1.65	2.500	
GeH_2=CH_2 (b)	-1.16	2.473	
SiHF=CH_2 (e)	-2.10	2.648	
GeHF=CH_2 (e)	-2.98	2.549	
GeHF=CH_2 (f)	-1.27	3.263	
SnHF=CH_2 (e)	-3.79	2.554	
SnHF=CH_2 (f)	-1.93	3.155	

$SiF_2=CH_2$ (b)	-1.88	2.405	
$SiF_2=CH_2$ (c)	-2.32	2.612	
$GeF_2=CH_2$ (b)	-3.64	2.600