Electronic Supplementary Material (ESI) for Faraday Discussions.

Negative Hyperconjugation and Red-, Blue- or Zero-Shift in X-Z---Y Complexes

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Supporting Information

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Table S1 Complexes of FCl---Y showing Proper, F_3CCl---Y and O_2NCl---Y showing Pro-improper X-Z bond length change during complex formation. Bond length changes (Å) are shown in the parenthesis. Calculations are done at MP2(full)/6-311+g(d,p) level of theory

Proper	Pro-improper	Pro-improper/improper
FCl---NMe_3[1] (+0.158)	F_3CCl---NCH[2] (-0.0082)	O_2NCl---FLi (-0.092)
FCl---NH_3[1] (+0.082)	F_3CCl---OH_2[3] (-0.0070)	O_2NCl---OH_2[5] (-0.052)
FCl---C_2H_4[4] (+0.051)	F_3CCl---NH_3[3] (-0.0066)	O_2NCl-OMe_2[5] (-0.041)
FCl---OMe_2[5] (+0.035)	F_3CCl---OMe_2[5] (-0.0050)	O_2NCl---NCH[2] (-0.027)
FCl---OH_2[4] (+0.018)	F_3CCl---C6H6[5] (-0.0037)	O_2NCl---PH_3[5] (-0.024)
FCl---NF3[1] (+0.006)	F_3CCl---NMe_3[5] (-0.0006)	O_2NCl---NH_3[2] (-0.013)
FCl---H_2[4] (+0.003)	F_3CCl---N^tBu[5] (+0.0008)	O_2NCl---NMe_3[5] (+0.009))

Table S2 Representative examples for substantiating the arguments in figure 10. Calculations are done at MP2(full)/6-311+g(d,p) level of theory.

	Complex	d(Z---Y) (Å)	Δ(X-Z) (Å)	‹(X-Hal---Y) (degree)	$B.E_{ZPE-BSSE}$ (kcal/mol)
Chalcog	$FSH---NH_3$[5]	2.529	+0.0212	176.57	-2.43
	$CF_3SMe---OH_2$[8]	3.215	-0.0021	173.38	-1.59
	$NO_2SMe---NH_3$[6]	3.108	-0.0034	176.05	-2.50
Pnicoge	FPH_2---NH_3[7]	2.662	+0.0267	165.94	-3.61
	$Cl_3SiPH_2---NH_3$[8]	3.257	-0.0002	157.17	-1.05
	$Br_3SiPH_2---FLi$[8]	2.793	-0.0013	154.33	-4.07

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3. W. Wang, N.-B. Wong, W. Zheng and A. Tian, *J. Phys. Chem. A*, 2004, **108**, 1799-1805.
4. B. Raghavendra and E. Arunan, *J. Phys. Chem. A*, 2007, **111**, 9699-9706.
5. U. Adhikari and S. Scheiner, *J. Phys. Chem. A*, 2012, **116**, 3487-3497.
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8. This study.

All the geometries are optimized at MP2(full)/aug-cc-pVTZ level of theory.

(1) FCl---NH3 (Equilibrium Geometry)

Total Energy including ZPVE = -615.865426 a.u
$N_{img} = 0$

Cl	0.000000000	0.000000000	0.213572000
F	0.000000000	0.000000000	1.926771000
N	0.000000000	0.000000000	-1.993628000
H	0.000000000	0.948979000	-2.338757000
H	0.821840000	-0.474489000	-2.338757000
H	-0.821840000	-0.474489000	-2.338757000

(2) FCl---NH3 (Cl---F = 2.0 Å)

Cl	0.000000000	0.000000000	1.253504000
F	0.000000000	0.000000000	3.010861000
N	0.000000000	0.000000000	-0.746496000
H	-0.000268000	0.950574000	-1.091595000
H	0.823356000	-0.475055000	-1.091595000
H	-0.823088000	-0.475520000	-1.091595000

(3) FCl---NH3 (Cl---F = 2.2 Å)

Cl	0.000000000	0.000000000	1.393820000
F	0.000000000	0.000000000	3.108273000
N	0.000000000	0.000000000	-0.806180000
H	-0.000268000	0.949141000	-1.150940000
H	0.822114000	-0.474338000	-1.150940000
H	-0.821846000	-0.474802000	-1.150940000

(4) FCl---NH3 (Cl---F = 2.4 Å)

Cl	0.000000000	0.000000000	1.535740000
F	0.000000000	0.000000000	3.219833000
N	0.000000000	0.000000000	-0.864260000
H	-0.000267000	0.946068000	-1.216074000
H	0.819452000	-0.472803000	-1.216074000
H	-0.819185000	-0.473265000	-1.216074000

(5) FCl---NH3 (Cl---F = 2.6 Å)

Cl	0.000000000	0.000000000	1.675953000
F	0.000000000	0.000000000	3.340677000
N	0.000000000	0.000000000	-0.924047000
H	-0.000266000	0.943218000	-1.283165000
H	0.816984000	-0.471379000	-1.283165000
H	-0.816718000	-0.471840000	-1.283165000

(6) FCl---NH3 (Cl---F = 2.8 Å)

Cl	0.000000000	0.000000000	1.813385000

F	0.000000000	0.000000000	3.467493000
N	0.000000000	0.000000000	-0.986615000
H	-0.000266000	0.941414000	-1.350392000
H	0.815421000	-0.470477000	-1.350392000
H	-0.815155000	-0.470937000	-1.350392000

(7) FCl---NH3 (Cl---F = 3.0 Å)

Cl	0.000000000	0.000000000	1.949423000
F	0.000000000	0.000000000	3.597198000
N	0.000000000	0.000000000	-1.050577000
H	-0.000265000	0.940164000	-1.417653000
H	0.814338000	-0.469852000	-1.417653000
H	-0.814073000	-0.470312000	-1.417653000

(8) FCl---NH3 (Cl---F = 3.2 Å)

Cl	0.000000000	0.000000000	2.084634000
F	0.000000000	0.000000000	3.728562000
N	0.000000000	0.000000000	-1.115366000
H	-0.000265000	0.939256000	-1.484918000
H	0.813552000	-0.469399000	-1.484918000
H	-0.813287000	-0.469858000	-1.484918000

(9) FCl---NH3 (Cl---F = 3.4 Å)

Cl	0.000000000	0.000000000	2.219273000
F	0.000000000	0.000000000	3.860795000
N	0.000000000	0.000000000	-1.180727000
H	-0.000265000	0.938604000	-1.552089000
H	0.812987000	-0.469073000	-1.552089000
H	-0.812722000	-0.469531000	-1.552089000

(10) FCl---NH3 (Cl---F = 3.6 Å)

Cl	0.000000000	0.000000000	2.353460000
F	0.000000000	0.000000000	3.993497000
N	0.000000000	0.000000000	-1.246540000
H	-0.000265000	0.938162000	-1.619117000
H	0.812605000	-0.468852000	-1.619117000
H	-0.812340000	-0.469310000	-1.619117000

(11) FCl---NH3 (Cl---F = 3.8 Å)

Cl	0.000000000	0.000000000	2.487874000
F	0.000000000	0.000000000	4.126085000
N	0.000000000	0.000000000	-1.312126000
H	-0.000265000	0.937598000	-1.686257000
H	0.812116000	-0.468570000	-1.686257000
H	-0.811851000	-0.469028000	-1.686257000

(12) FCl---NH3 (Cl---F = 4.0 Å)

Cl	0.000000000	0.000000000	2.621549000
F	0.000000000	0.000000000	4.259200000

N	0.000000000	0.000000000	-1.378451000
H	-0.000265000	0.937417000	-1.753078000
H	0.811959000	-0.468480000	-1.753078000
H	-0.811695000	-0.468938000	-1.753078000

(13) FCl---NH3 (Cl---F = 4.2 Å)

Cl	0.000000000	0.000000000	2.755144000
F	0.000000000	0.000000000	4.392365000
N	0.000000000	0.000000000	-1.444856000
H	-0.000264000	0.937279000	-1.819862000
H	0.811840000	-0.468411000	-1.819862000
H	-0.811576000	-0.468869000	-1.819862000

(14) FCl---NH3 (Cl---F = 4.4 Å)

Cl	0.000000000	0.000000000	2.888673000
F	0.000000000	0.000000000	4.525555000
N	0.000000000	0.000000000	-1.511327000
H	-0.000264000	0.937178000	-1.886612000
H	0.811752000	-0.468360000	-1.886612000
H	-0.811488000	-0.468818000	-1.886612000

(15) FCl---NH3 (Cl---F = 4.6 Å)

Cl	0.000000000	0.000000000	3.022147000
F	0.000000000	0.000000000	4.658754000
N	0.000000000	0.000000000	-1.577853000
H	-0.000264000	0.937109000	-1.953328000
H	0.811692000	-0.468325000	-1.953328000
H	-0.811428000	-0.468783000	-1.953328000

(16) FCl---NH3 (Cl---F = 4.8 Å)

Cl	0.000000000	0.000000000	3.155573000
F	0.000000000	0.000000000	4.791953000
N	0.000000000	0.000000000	-1.644427000
H	-0.000264000	0.937067000	-2.020011000
H	0.811656000	-0.468304000	-2.020011000
H	-0.811391000	-0.468762000	-2.020011000

(17) FCl---NH3 (Cl---F = 5.0 Å)

Cl	0.000000000	0.000000000	3.288962000
F	0.000000000	0.000000000	4.925150000
N	0.000000000	0.000000000	-1.711038000
H	-0.000264000	0.937045000	-2.086669000
H	0.811637000	-0.468294000	-2.086669000
H	-0.811373000	-0.468752000	-2.086669000

(18) CF_3Cl---NH_3 (Equilibrium Geometry)

Total Energy including ZPVE = -853.488400 a.u
$N_{img} = 0$

C	-1.094797000	-0.000013000	-0.000070000
F	-1.567707000	-0.610852000	1.079334000
F	-1.566842000	-0.629852000	-1.068878000
F	-1.567812000	1.240150000	-0.011228000
Cl	0.642546000	0.000409000	0.000592000
N	3.683466000	-0.000091000	-0.000186000
H	4.060073000	-0.934001000	0.078081000
H	4.060554000	0.398338000	-0.848242000
H	4.061854000	0.534410000	0.768763000

(19) CF_3Cl---NH_3 (Cl---N = 2.0 Å)

C	2.284331000	-0.000411000	-0.000105000
F	2.773184000	-1.110827000	0.560827000
F	2.773620000	1.040380000	0.681049000
F	2.773282000	0.069041000	-1.242187000
Cl	0.485816000	-0.000005000	0.000071000
N	-1.514184000	0.000026000	0.000248000
H	-1.908085000	-0.053686000	0.934079000
H	-1.907660000	0.835666000	-0.420419000
H	-1.907426000	-0.782042000	-0.513371000

(20) CF_3Cl---NH_3 (Cl---N = 2.2 Å)

C	2.355341000	-0.000416000	-0.000064000
F	2.839300000	-1.109209000	0.560468000
F	2.839419000	1.039368000	0.679887000
F	2.839259000	0.068568000	-1.240588000
Cl	0.590214000	-0.000296000	0.000059000
N	-1.609786000	-0.000014000	0.000103000
H	-2.000285000	-0.054116000	0.933395000
H	-2.000165000	0.835378000	-0.419629000
H	-2.000421000	-0.781121000	-0.513441000

(21) CF_3Cl---NH_3 (Cl---N = 2.4 Å)

C	2.435518000	-0.000377000	-0.000082000
F	2.915612000	-1.108386000	0.560216000
F	2.915941000	1.038649000	0.679432000
F	2.916282000	0.068352000	-1.239535000
Cl	0.685905000	-0.000091000	-0.000568000
N	-1.714095000	-0.000055000	0.000031000
H	-2.100284000	-0.054295000	0.933824000
H	-2.100824000	0.835687000	-0.419528000
H	-2.101176000	-0.781341000	-0.513600000

(22) CF_3Cl---NH_3 (Cl---N = 2.6 Å)

C	2.520103000	-0.000400000	-0.000051000
F	2.997224000	-1.107803000	0.559948000
F	2.997287000	1.038221000	0.679026000
F	2.997443000	0.068301000	-1.239005000
Cl	0.778266000	-0.000351000	-0.000235000
N	-1.821734000	-0.000055000	-0.000016000
H	-2.204794000	-0.054324000	0.934146000
H	-2.205162000	0.836120000	-0.419696000
H	-2.205756000	-0.781566000	-0.513925000

(23) CF_3Cl---NH_3 (Cl---N = 2.8 Å)

C	2.606471000	-0.000406000	-0.000047000
F	3.081633000	-1.107551000	0.559837000
F	3.081834000	1.037957000	0.678813000
F	3.081806000	0.068241000	-1.238740000
Cl	0.867906000	-0.000241000	-0.000105000
N	-1.932094000	-0.000057000	-0.000039000
H	-2.311098000	-0.054428000	0.935024000
H	-2.311506000	0.836934000	-0.420081000
H	-2.312075000	-0.782306000	-0.514473000

(24) CF_3Cl---NH_3 (Cl---N = 3.0 Å)

C	2.694715000	-0.000421000	-0.000054000
F	3.167675000	-1.107328000	0.559744000
F	3.167802000	1.037761000	0.678676000
F	3.167860000	0.068215000	-1.238492000
Cl	0.957378000	-0.000312000	-0.000160000
N	-2.042622000	-0.000045000	-0.000041000
H	-2.419467000	-0.054445000	0.935457000
H	-2.419912000	0.837339000	-0.420239000
H	-2.420552000	-0.782620000	-0.514699000

(25) CF_3Cl---NH_3 (Cl---N = 3.2 Å)

C	2.783937000	-0.000435000	-0.000060000
F	3.255199000	-1.107183000	0.559683000
F	3.255249000	1.037636000	0.678592000
F	3.255384000	0.068205000	-1.238331000
Cl	1.046638000	-0.000386000	-0.000206000
N	-2.153362000	-0.000035000	-0.000041000
H	-2.529518000	-0.054435000	0.935562000
H	-2.529978000	0.837448000	-0.420264000
H	-2.530671000	-0.782673000	-0.514744000

(26) CF_3Cl---NH_3 (Cl---N = 3.4 Å)

C	2.873848000	-0.000444000	-0.000064000
F	3.342612000	-1.107064000	0.559623000
F	3.342643000	1.037515000	0.678515000
F	3.342809000	0.068189000	-1.238192000

Cl	1.135703000	-0.000409000	-0.000231000
N	-2.264297000	-0.000024000	-0.000038000
H	-2.639594000	-0.054433000	0.935723000
H	-2.640068000	0.837600000	-0.420323000
H	-2.640777000	-0.782786000	-0.514823000

(27) CF_3Cl---NH_3 (Cl---N = 3.6 Å)

C	2.963285000	-0.000454000	-0.000067000
F	3.431128000	-1.107038000	0.559605000
F	3.431146000	1.037479000	0.678492000
F	3.431321000	0.068180000	-1.238158000
Cl	1.224602000	-0.000429000	-0.000238000
N	-2.375398000	-0.000014000	-0.000035000
H	-2.750512000	-0.054423000	0.935750000
H	-2.750988000	0.837633000	-0.420327000
H	-2.751706000	-0.782792000	-0.514831000

(28) CF_3Cl---NH_3 (Cl---N = 3.8 Å)

C	3.052695000	-0.000463000	-0.000070000
F	3.519778000	-1.107022000	0.559590000
F	3.519782000	1.037452000	0.678473000
F	3.519958000	0.068172000	-1.238137000
Cl	1.313487000	-0.000451000	-0.000236000
N	-2.486513000	-0.000002000	-0.000033000
H	-2.861544000	-0.054410000	0.935753000
H	-2.862020000	0.837645000	-0.420322000
H	-2.862746000	-0.782778000	-0.514827000

(29) CF_3Cl---NH_3 (Cl---N = 4.0 Å)

C	3.142066000	-0.000473000	-0.000072000
F	3.608518000	-1.107011000	0.559576000
F	3.608507000	1.037430000	0.678457000
F	3.608677000	0.068164000	-1.238125000
Cl	1.402365000	-0.000473000	-0.000226000
N	-2.597634000	0.000009000	-0.000030000
H	-2.972648000	-0.054397000	0.935740000
H	-2.973119000	0.837645000	-0.420313000
H	-2.973853000	-0.782752000	-0.514817000

(30) CF_3Cl---NH_3 (Cl---N = 4.2 Å)

C	3.231389000	-0.000483000	-0.000075000
F	3.697317000	-1.107004000	0.559564000
F	3.697284000	1.037414000	0.678443000
F	3.697448000	0.068158000	-1.238117000
Cl	1.491241000	-0.000501000	-0.000214000
N	-2.708759000	0.000021000	-0.000028000
H	-3.083789000	-0.054382000	0.935721000
H	-3.084254000	0.837640000	-0.420301000
H	-3.084998000	-0.782720000	-0.514803000

(31) CF_3Cl---NH_3 (Cl---N = 4.4 Å)

C	3.320659000	-0.000494000	-0.000077000
F	3.786156000	-1.106996000	0.559553000
F	3.786084000	1.037402000	0.678431000
F	3.786255000	0.068155000	-1.238111000
Cl	1.580114000	-0.000544000	-0.000206000
N	-2.819886000	0.000033000	-0.000025000
H	-3.194944000	-0.054365000	0.935702000
H	-3.195402000	0.837637000	-0.420288000
H	-3.196159000	-0.782685000	-0.514789000

(32) CF_3Cl---NH_3 (Cl---N = 4.6 Å)

C	3.409879000	-0.000505000	-0.000080000
F	3.875020000	-1.106986000	0.559545000
F	3.874889000	1.037395000	0.678422000
F	3.875084000	0.068155000	-1.238105000
Cl	1.668987000	-0.000604000	-0.000206000
N	-2.931013000	0.000047000	-0.000022000
H	-3.306097000	-0.054346000	0.935687000
H	-3.306547000	0.837638000	-0.420276000
H	-3.307323000	-0.782652000	-0.514775000

(33) CF_3Cl---NH_3 (Cl---N = 4.8 Å)

C	3.499055000	-0.000518000	-0.000083000
F	3.963898000	-1.106976000	0.559539000
F	3.963698000	1.037391000	0.678415000
F	3.963926000	0.068158000	-1.238100000
Cl	1.757860000	-0.000673000	-0.000212000
N	-3.042140000	0.000062000	-0.000018000
H	-3.417246000	-0.054326000	0.935676000
H	-3.417689000	0.837644000	-0.420264000
H	-3.418485000	-0.782620000	-0.514762000

(34) CF_3Cl---NH_3 (Cl---N = 5.0 Å)

C	3.588200000	-0.000530000	-0.000087000
F	4.052786000	-1.106967000	0.559534000
F	4.052515000	1.037388000	0.678409000
F	4.052779000	0.068161000	-1.238095000
Cl	1.846736000	-0.000742000	-0.000218000
N	-3.153264000	0.000077000	-0.000015000
H	-3.528396000	-0.054306000	0.935666000
H	-3.528832000	0.837650000	-0.420253000
H	-3.529646000	-0.782588000	-0.514750000

(35) NO_2Cl---NH_3 (Equilibrium Geometry)

Total Energy including ZPVE = -721.022833 a.u
$N_{img} = 0$

Cl	0.432957000	0.000068000	0.000937000
N	-1.393103000	-0.000028000	-0.000016000
O	-1.896621000	1.090176000	-0.000518000
O	-1.896460000	-1.090261000	-0.000517000
N	3.162720000	0.000012000	-0.000630000
H	3.531834000	0.823426000	-0.454144000
H	3.533912000	-0.019352000	0.938466000
H	3.531313000	-0.804446000	-0.487443000

(36) NO_2Cl---NH_3 (Cl---N = 2.0 Å)

Cl	-0.860208000	-0.053445000	0.013354000
N	1.022560000	-0.004436000	0.001329000
O	1.591346000	-1.023297000	0.267810000
O	1.513453000	1.057138000	-0.277605000
N	-2.859744000	-0.012221000	0.000417000
H	-3.248590000	-0.614910000	-0.713777000
H	-3.256658000	-0.283724000	0.890761000
H	-3.150168000	0.939448000	-0.197765000

(37) NO_2Cl---NH_3 (Cl---N = 2.2 Å)

Cl	-0.744328000	0.042651000	-0.009515000
N	1.105497000	-0.001426000	0.001873000
O	1.586468000	-1.025069000	0.365565000
O	1.657779000	1.001008000	-0.362454000
N	-2.944162000	0.015761000	-0.005838000
H	-3.273425000	-0.579672000	-0.753062000
H	-3.267034000	-0.376628000	0.867329000
H	-3.368803000	0.927928000	-0.119374000

(38) NO_2Cl---NH_3 (Cl---N = 2.4 Å)

Cl	-0.635906000	-0.000699000	-0.001161000
N	1.198817000	0.000564000	0.000407000
O	1.713803000	-1.029203000	0.356677000
O	1.712641000	1.031301000	-0.354802000
N	-3.035907000	0.000453000	-0.003505000
H	-3.399807000	-0.577144000	-0.748677000
H	-3.402806000	-0.355427000	0.868272000
H	-3.398845000	0.934707000	-0.132686000

(39) NO_2Cl---NH_3 (Cl---N = 2.6 Å)

Cl	-0.529897000	-0.001481000	-0.000835000
N	1.297067000	0.000708000	0.000634000
O	1.805459000	-1.029349000	0.355810000

O	1.803325000	1.032158000	-0.353648000
N	-3.129893000	-0.000319000	-0.003995000
H	-3.499494000	-0.576660000	-0.746710000
H	-3.500446000	-0.353408000	0.866897000
H	-3.494131000	0.932903000	-0.133628000

(40) NO_2Cl---NH_3 (Cl---N = 2.8 Å)

Cl	-0.427413000	-0.002992000	-0.000997000
N	1.398855000	0.000864000	0.000754000
O	1.902437000	-1.032868000	0.344420000
O	1.898470000	1.036843000	-0.341993000
N	-3.227414000	-0.001071000	-0.003846000
H	-3.600195000	-0.582999000	-0.740194000
H	-3.601617000	-0.343946000	0.869207000
H	-3.591132000	0.930721000	-0.142826000

(41) NO_2Cl---NH_3 (Cl---N = 3.0 Å)

Cl	-0.326879000	-0.002215000	-0.000644000
N	1.502302000	0.000845000	0.000636000
O	2.000732000	-1.029793000	0.354684000
O	1.997793000	1.033130000	-0.352725000
N	-3.326875000	-0.000982000	-0.003826000
H	-3.700639000	-0.576028000	-0.744843000
H	-3.702076000	-0.351508000	0.865548000
H	-3.692367000	0.931103000	-0.134303000

(42) NO_2Cl---NH_3 (Cl---N = 3.2 Å)

Cl	-0.227156000	-0.003875000	-0.000585000
N	1.606246000	0.000872000	0.000163000
O	2.101989000	-1.045869000	0.302122000
O	2.096751000	1.050208000	-0.301358000
N	-3.427154000	-0.001670000	-0.003294000
H	-3.803495000	-0.610317000	-0.715496000
H	-3.804440000	-0.308530000	0.881449000
H	-3.790751000	0.923734000	-0.178477000

(43) NO_2Cl---NH_3 (Cl---N = 3.4 Å)

Cl	-0.127837000	-0.006384000	-0.001226000
N	1.710080000	0.001087000	0.000519000
O	2.204042000	-1.038822000	0.323815000
O	2.196105000	1.044983000	-0.321912000
N	-3.527834000	-0.002381000	-0.003964000
H	-3.907560000	-0.596793000	-0.726189000
H	-3.905390000	-0.323924000	0.875338000
H	-3.889615000	0.926787000	-0.161857000

(44) NO_2Cl---NH_3 (Cl---N = 3.6 Å)

Cl	-0.028707000	-0.012291000	-0.001655000
N	1.813570000	0.001296000	0.000752000

O	2.308460000	-1.048810000	0.283825000
O	2.293573000	1.058529000	-0.281268000
N	-3.628693000	-0.003799000	-0.003769000
H	-4.012567000	-0.620564000	-0.704715000
H	-4.009219000	-0.291284000	0.885971000
H	-3.984425000	0.921475000	-0.194615000

(45) NO_2Cl---NH_3 (Cl---N = 3.8 Å)

Cl	0.070486000	-0.006730000	0.001430000
N	1.916706000	0.000733000	0.000707000
O	2.406432000	-1.068947000	0.205460000
O	2.397611000	1.074343000	-0.204436000
N	-3.729506000	-0.001981000	-0.003236000
H	-4.107707000	-0.666268000	-0.662619000
H	-4.110666000	-0.232675000	0.902629000
H	-4.091366000	0.906077000	-0.255410000

(46) NO_2Cl---NH_3 (Cl---N = 4.0 Å)

Cl	0.169717000	-0.004285000	0.000601000
N	2.019424000	0.000683000	0.000926000
O	2.505809000	-1.046067000	0.304737000
O	2.500210000	1.050082000	-0.302712000
N	-3.830280000	-0.001678000	-0.003887000
H	-4.208043000	-0.608127000	-0.717007000
H	-4.210065000	-0.309642000	0.879262000
H	-4.194781000	0.923587000	-0.177395000

(47) NO_2Cl---NH_3 (Cl---N = 4.2 Å)

Cl	0.269062000	-0.006100000	-0.002764000
N	2.121750000	0.000603000	0.001548000
O	2.607175000	-1.058119000	0.260142000
O	2.600635000	1.062865000	-0.254693000
N	-3.930933000	-0.001681000	-0.004875000
H	-4.311977000	-0.634892000	-0.692554000
H	-4.308403000	-0.274558000	0.890708000
H	-4.295318000	0.916435000	-0.212986000

(48) NO_2Cl---NH_3 (Cl---N = 4.4 Å)

Cl	0.368460000	-0.005029000	-0.000022000
N	2.223764000	0.000376000	0.000872000
O	2.707661000	-1.060346000	0.252165000
O	2.701769000	1.063858000	-0.249996000
N	-4.031536000	-0.001299000	-0.003937000
H	-4.410629000	-0.640684000	-0.686957000
H	-4.410889000	-0.266885000	0.893060000
H	-4.396609000	0.914561000	-0.220660000

(49) NO_2Cl---NH_3 (Cl---N = 4.6 Å)

Cl	0.467958000	0.002271000	0.000579000

N	2.325480000	0.000163000	0.001360000
O	2.804105000	-1.065333000	0.240641000
O	2.806718000	1.064565000	-0.237571000
N	-4.132039000	0.000186000	-0.004340000
H	-4.506132000	-0.649519000	-0.680329000
H	-4.509767000	-0.258468000	0.895358000
H	-4.504332000	0.910687000	-0.231173000

(50) NO_2Cl---NH_3 (Cl---N = 4.8 Å)

Cl	0.567521000	-0.001315000	-0.012166000
N	2.426919000	0.000418000	0.002459000
O	2.905260000	-1.069694000	0.219278000
O	2.906697000	1.071365000	-0.206770000
N	-4.232471000	-0.000486000	-0.006352000
H	-4.614908000	-0.663683000	-0.664354000
H	-4.602834000	-0.238001000	0.902212000
H	-4.604193000	0.905947000	-0.249782000

(51) NO_2Cl---NH_3 (Cl---N = 5.0 Å)

Cl	0.667025000	0.001041000	-0.011898000
N	2.528148000	0.000098000	0.002146000
O	3.004576000	-1.077841000	0.179368000
O	3.008229000	1.077653000	-0.167557000
N	-4.332967000	0.000641000	-0.004924000
H	-4.709549000	-0.685889000	-0.641883000
H	-4.706238000	-0.207997000	0.909444000
H	-4.707233000	0.896846000	-0.280172000

Coordinates of the equilibrium geometries of the complexes in Table S1. Calculations are done at MP2(full)/6-311+g(d,p) level of theory.

(1) FCl---NMe_3

F	-2.946354000	0.000099000	-0.000507000
Cl	-1.111275000	0.000218000	0.000240000
N	0.967849000	0.000029000	-0.000079000
C	1.397752000	-1.288681000	-0.548971000
H	0.999205000	-2.088367000	0.076570000
H	0.994727000	-1.394466000	-1.556977000
H	2.493636000	-1.347298000	-0.576847000
C	1.397813000	0.168642000	1.390358000
H	0.996605000	1.108536000	1.771518000
H	0.997103000	-0.653345000	1.984786000
H	2.493617000	0.176845000	1.454881000
C	1.398907000	1.119549000	-0.841345000
H	0.996290000	0.981227000	-1.845544000
H	1.001051000	2.046139000	-0.425646000
H	2.494847000	1.168868000	-0.881960000

(2) FCl---NH_3

Cl	0.000000000	0.000000000	0.213572000
F	0.000000000	0.000000000	1.926771000
N	0.000000000	0.000000000	-1.993628000
H	0.000000000	0.948979000	-2.338757000
H	0.821840000	-0.474489000	-2.338757000
H	-0.821840000	-0.474489000	-2.338757000

(3) FCl---OMe2

F	-2.777087000	-0.000227000	0.174487000
Cl	-1.093783000	-0.000157000	-0.112697000
O	1.254912000	-0.000097000	-0.411229000
C	1.817190000	1.173877000	0.156145000
H	2.895922000	1.206981000	-0.033543000
H	1.334273000	2.024415000	-0.323108000
H	1.633697000	1.208046000	1.236998000
C	1.818726000	-1.173330000	0.156221000
H	1.634252000	-1.208089000	1.236869000
H	1.337531000	-2.024495000	-0.323526000
H	2.897622000	-1.204660000	-0.032593000

(4) FCl---OH2

Cl	-0.319813000	-0.002141000	-0.016438000
O	2.260779000	0.000776000	-0.072070000
H	2.713470000	-0.753470000	0.313117000
H	2.705230000	0.762197000	0.308601000
F	-2.007569000	0.002384000	0.026033000

(5) F_3CCl---OH_2

C	1.083683000	0.001074000	-0.000001000
F	1.550510000	1.249328000	-0.002438000
F	1.562929000	-0.620346000	-1.077061000
F	1.562912000	-0.616129000	1.079489000
Cl	-0.654122000	-0.009719000	0.000007000
O	-3.628617000	0.003257000	-0.000004000
H	-4.226849000	-0.747040000	0.000003000
H	-4.213408000	0.764080000	0.000002000

(6) F_3CCl---NH_3

C	1.098568000	0.000062000	0.000019000
F	1.575461000	-1.110981000	0.562002000
F	1.574749000	1.042493000	0.681384000
F	1.575213000	0.069142000	-1.243238000
Cl	-0.639987000	-0.000505000	-0.000126000
N	-3.709372000	0.000185000	-0.000005000
H	-4.091025000	-0.054349000	0.937793000
H	-4.091431000	0.839727000	-0.421185000
H	-4.092372000	-0.784337000	-0.515876000

(7) F_3CCl---OMe_2

C	2.009732000	0.000222000	0.000452000
F	2.468214000	1.248212000	0.092525000
F	2.493772000	-0.535644000	-1.119530000
F	2.491057000	-0.693357000	1.031518000
Cl	0.270501000	-0.020752000	-0.003094000
O	-2.621634000	-0.006001000	-0.002481000
C	-3.444710000	-1.152516000	0.001346000
H	-2.789126000	-2.023640000	-0.001660000
H	-4.079917000	-1.180894000	0.896967000
H	-4.088146000	-1.180941000	-0.888376000
C	-3.394802000	1.174823000	0.001253000
H	-4.028159000	1.230462000	0.896889000
H	-2.702395000	2.016997000	-0.001820000
H	-4.036402000	1.230712000	-0.888482000

(8) F_3CCl---C6H6

C	-2.451277000	-0.042182000	-0.000001000
F	-3.143474000	1.095115000	-0.003181000
F	-2.801112000	-0.737934000	1.079828000
F	-2.800093000	-0.743336000	-1.076666000
Cl	-0.739840000	0.276781000	0.000001000
C	2.537040000	-0.723576000	1.211149000
C	2.510451000	0.675232000	1.212375000
C	2.496859000	1.375693000	0.000970000
C	2.510462000	0.676906000	-1.211402000
C	2.537037000	-0.721903000	-1.212108000
C	2.550765000	-1.421948000	-0.000963000
H	2.545421000	-1.267295000	2.151626000
H	2.498233000	1.217778000	2.153592000
H	2.474670000	2.462016000	0.001720000
H	2.498253000	1.220752000	-2.151868000
H	2.545414000	-1.264323000	-2.153336000
H	2.569381000	-2.508158000	-0.001713000

(9) F_3CCl---NMe_3

C	-2.242368000	0.000195000	-0.000427000
F	-2.720518000	-0.390478000	-1.181452000
F	-2.721260000	1.217314000	0.255901000
F	-2.710099000	-0.832599000	0.929368000
Cl	-0.498399000	0.007876000	-0.008189000
N	2.413637000	0.001188000	-0.002233000
C	2.844408000	-0.534008000	1.278603000
H	2.453560000	0.090492000	2.086356000
H	2.453303000	-1.547434000	1.402643000
H	3.946061000	-0.571624000	1.368097000
C	2.880877000	1.366633000	-0.173138000
H	2.513216000	1.763194000	-1.123337000
H	2.493542000	1.990136000	0.636902000
H	3.984301000	1.435756000	-0.169399000

C	2.873344000	-0.841707000	-1.093382000
H	2.476197000	-1.852533000	-0.967433000
H	2.509939000	-0.441743000	-2.043770000
H	3.976534000	-0.903262000	-1.139510000

(10) F_3CCl---N^tBu

C	3.696212000	0.032888000	0.063412000
F	4.310524000	0.527330000	1.134632000
F	4.168590000	0.666209000	-1.007344000
F	4.014765000	-1.257378000	-0.039061000
Cl	1.965919000	0.228023000	0.184235000
N	-1.160385000	0.011990000	0.018514000
C	-1.533403000	1.194416000	-0.857834000
C	-0.931028000	1.083523000	-2.273107000
C	-3.054568000	1.441078000	-0.997710000
C	-0.889731000	2.518092000	-0.378949000
H	0.160428000	1.045468000	-2.220566000
H	-1.287415000	0.246128000	-2.865483000
H	-1.205002000	1.998283000	-2.810766000
H	-3.522157000	1.651551000	-0.037193000
H	-3.223393000	2.315904000	-1.642289000
H	-3.573934000	0.592843000	-1.434220000
H	-1.078587000	3.270839000	-1.174664000
H	-1.293682000	2.927243000	0.552715000
H	0.195557000	2.404000000	-0.297056000
C	-1.330885000	-1.344245000	-0.670782000
C	-2.652618000	-1.493088000	-1.457785000
C	-0.148227000	-1.675970000	-1.609227000
C	-1.279945000	-2.554654000	0.286019000
H	-3.519138000	-1.302346000	-0.827920000
H	-2.706025000	-0.814022000	-2.308547000
H	-2.721944000	-2.514433000	-1.851353000
H	0.766934000	-1.768928000	-1.027844000
H	-0.350570000	-2.655450000	-2.056317000
H	0.024851000	-0.978796000	-2.418178000
H	-1.448152000	-3.448592000	-0.334449000
H	-0.294406000	-2.659771000	0.740680000
H	-2.040191000	-2.556702000	1.067550000
C	-1.716969000	0.055959000	1.429683000
C	-1.778398000	1.475038000	2.029631000
C	-3.156084000	-0.487701000	1.578968000
C	-0.747325000	-0.643186000	2.406718000
H	-0.790867000	1.935499000	2.080683000
H	-2.462089000	2.150211000	1.510894000
H	-2.151694000	1.349863000	3.058765000
H	-3.261375000	-1.547678000	1.342023000
H	-3.478207000	-0.360508000	2.623746000
H	-3.846468000	0.070319000	0.946251000
H	-1.139402000	-0.523039000	3.422762000

H	-0.572576000	-1.697795000	2.243220000
H	0.214492000	-0.128770000	2.367678000

(11) O_2NCl---OH_2

Cl	-0.414350000	-0.022679000	-0.011848000
N	1.439454000	0.007872000	0.003725000
O	1.918873000	1.109789000	0.034637000
O	1.955576000	-1.077233000	-0.018880000
O	-3.305825000	-0.045171000	-0.038811000
H	-3.772788000	0.719935000	-0.381953000
H	-3.808435000	-0.288574000	0.741717000

(12) O_2NCl-OMe_2

Cl	0.457326000	-0.001196000	-0.287416000
N	2.287905000	0.013423000	0.068489000
O	2.733885000	1.098158000	0.325798000
O	2.813172000	-1.065783000	0.004366000
O	-2.292282000	-0.057223000	-0.432892000
C	-2.689472000	-1.153810000	0.365740000
H	-2.279042000	-2.054397000	-0.089949000
H	-2.301959000	-1.056523000	1.388361000
H	-3.783495000	-1.233195000	0.407195000
C	-2.773682000	1.157825000	0.103538000
H	-2.388920000	1.318531000	1.119641000
H	-2.424509000	1.960706000	-0.546036000
H	-3.871226000	1.165942000	0.133608000

(13) O_2NCl---NCH

Cl	-0.027774000	-0.000446000	0.000241000
N	3.038388000	-0.001235000	-0.002275000
N	-1.886796000	0.000215000	0.000103000
O	-2.382593000	-1.093748000	0.000015000
O	-2.381820000	1.094562000	0.000010000
C	4.208358000	0.000889000	0.001118000
H	5.276170000	0.002879000	0.004194000

(14) O_2NCl---PH_3

Cl	0.230100000	-0.001583000	0.004473000
N	2.112591000	0.000465000	-0.000932000
O	2.601959000	-1.093741000	-0.002352000
O	2.599594000	1.095728000	-0.002341000
P	-3.226565000	-0.000352000	0.000427000
H	-3.955944000	1.099613000	-0.490347000
H	-3.964763000	-0.956974000	-0.722565000
H	-3.993083000	-0.129598000	1.174536000

(15) O_2NCl---NH_3

Cl	-0.427515000	-0.000817000	0.002042000
N	1.423449000	0.000204000	-0.000285000

O	1.929451000	-1.093201000	-0.000939000
O	1.928254000	1.094166000	-0.000939000
N	-3.242732000	0.000090000	-0.000389000
H	-3.615712000	-0.773547000	-0.539733000
H	-3.631430000	-0.074315000	0.933357000
H	-3.611774000	0.851972000	-0.408589000

(16) O_2NCl---NMe_3

Cl	0.571470000	0.000064000	0.004452000
N	2.486381000	-0.000001000	0.000391000
O	2.996973000	-1.094560000	-0.000799000
O	2.996987000	1.094540000	-0.000729000
N	-1.843411000	-0.000005000	0.000474000
C	-2.264906000	1.222156000	-0.668165000
H	-1.866683000	2.085035000	-0.129371000
H	-1.866478000	1.232603000	-1.685286000
H	-3.363800000	1.303136000	-0.713212000
C	-2.276377000	-0.034655000	1.389510000
H	-3.376007000	-0.037327000	1.472954000
H	-1.882354000	-0.934114000	1.868291000
H	-1.883302000	0.840448000	1.912182000
C	-2.264362000	-1.187612000	-0.728108000
H	-1.865871000	-1.147279000	-1.744476000
H	-1.865835000	-2.076056000	-0.232786000
H	-3.363243000	-1.266668000	-0.777242000

Coordinates of the equilibrium geometries of the complexes in Table S2. Calculations are done at MP2(full)/6-311+g(d,p) level of theory.

(1) FSH---NH_3

S	-0.317253000	-0.130080000	0.000014000
N	2.206105000	0.034800000	-0.000003000
H	2.547310000	-0.458101000	0.818432000
H	2.547040000	-0.461588000	-0.816451000
H	2.654066000	0.945580000	-0.002070000
H	-0.081482000	1.178637000	0.000051000
F	-2.003736000	0.070351000	-0.000019000

(2) CF_3SMe---OH_2

S	0.513835000	-0.350659000	-0.000324000
C	0.952308000	1.401072000	0.000012000
H	2.041549000	1.417068000	0.000088000
H	0.580016000	1.897363000	-0.895784000
H	0.579916000	1.897035000	0.895948000
C	-1.263759000	-0.142428000	0.000023000
F	-1.719117000	0.527514000	1.076032000
F	-1.719459000	0.528158000	-1.075436000
F	-1.843767000	-1.350266000	-0.000239000

O	3.728901000	-0.354234000	0.000151000
H	4.078642000	-0.833209000	-0.754730000
H	4.077101000	-0.834359000	0.755019000

(3) NO_2SMe---NH_3

S	-0.264033000	-0.242696000	-0.027376000
C	-0.537316000	1.525488000	-0.013388000
H	-1.624364000	1.616804000	-0.039514000
H	-0.145267000	1.979402000	0.895656000
H	-0.100210000	1.999455000	-0.891076000
N	-3.365480000	-0.445043000	0.019847000
H	-4.207565000	0.031257000	-0.286373000
H	-3.270161000	-1.266428000	-0.568229000
H	-3.548901000	-0.780201000	0.959912000
N	1.524900000	-0.233506000	0.006062000
O	2.033842000	-1.349529000	0.001385000
O	2.119777000	0.837000000	0.031940000

(4) FPH_2---NH_3

P	-0.374457000	0.000146000	-0.177126000
F	-2.017640000	-0.000124000	0.095226000
H	-0.078726000	-1.032593000	0.731313000
N	2.278596000	-0.000044000	0.038813000
H	2.702584000	-0.001118000	0.961036000
H	2.640046000	-0.813120000	-0.449015000
H	2.640424000	0.813918000	-0.447391000
H	-0.078878000	1.032141000	0.732233000

(5) Cl_3SiPH_2---NH_3

P	-1.574304000	0.002116000	-0.487336000
H	-1.862046000	-1.046241000	0.406315000
H	-1.862035000	1.042561000	0.415526000
Cl	1.466053000	-1.653647000	-0.833530000
Cl	1.057906000	-0.007804000	1.987668000
Cl	1.466143000	1.660032000	-0.820694000
Si	0.602803000	0.000043000	-0.005333000
N	-4.778718000	-0.000295000	0.097929000
H	-5.122266000	0.775298000	-0.457996000
H	-5.229497000	0.068816000	1.004019000
H	-5.129554000	-0.846600000	-0.337211000

(6) Br_3SiPH_2---FLi

P	2.045034000	-0.000506000	-0.604880000
H	2.355217000	1.050392000	0.275129000
H	2.355048000	-1.050504000	0.276248000
F	4.784508000	-0.000815000	-0.063096000
Li	6.365333000	0.001913000	-0.342728000
Si	-0.117961000	-0.000034000	-0.046018000
Br	-1.083437000	-1.804806000	-0.912287000

Br	-0.573041000	0.000761000	2.133236000
Br	-1.083262000	1.804324000	-0.913460000