Supporting Information

Using One Halogen Bond to Change the Nature of a Second Bond in Ternary Complexes with P···Cl and F···Cl Halogen Bonds

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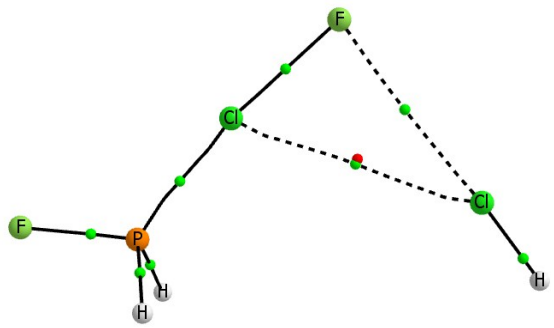
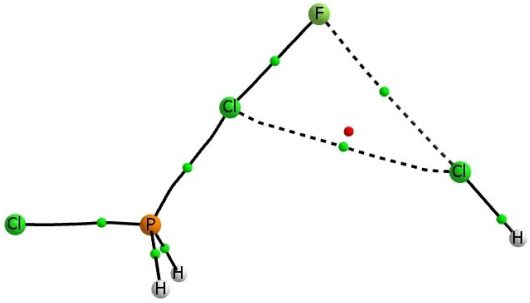
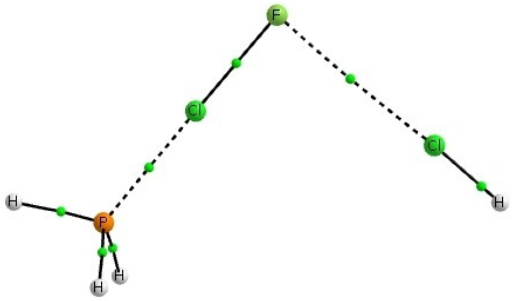
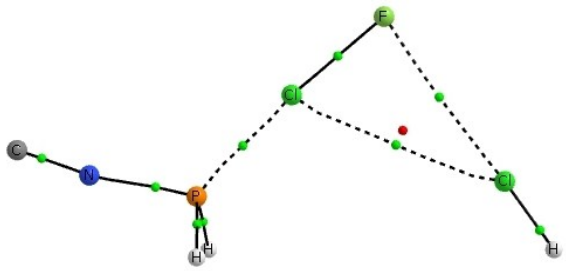
Table S1. Structures, total energies, and molecular graphs of complexes H_2XP:ClF:ClH

	H_2FP:ClF:ClH MP2= -1461.53190070 NIMAG= 0 P,-0.1354584351,0.,0.3548463755 F,0.6647508564,0.,-1.0053949402 H,-0.979939281,-1.10298525,0.1923316095 H,-0.979939281,1.10298525,0.1923316095 Cl,0.7908089992,0.,2.160376541 F,1.3585861702,0.,3.9897294972 Cl,-1.5963346657,0.,4.6915071869 H,-2.8450675071,0.,4.9554050094
	H_2ClP:ClF:ClH MP2= -1821.50428870 NIMAG= 0 P,-0.2989016725,0.,0.6230470801 Cl,1.5393313678,0.,-0.2259233601 H,-0.9126364913,1.0909188923,-0.005344724 H,-0.9126364913,-1.0909188923,-0.005344724 Cl,-0.6498291541,0.,2.683334895 F,-1.2685720422,0.,4.4599947104 Cl,-4.0964626482,0.,3.2366726196 H,-5.2632170942,0.,2.7199811231
	H_3P:ClF:ClH MP2= -1362.35827812 NIMAG= 1 P,-0.0443023957,0.,0.1417481925 H,0.9906809107,0.,-0.8031713653 H,-0.8180396474,-1.0860650543,-0.2874737699 H,-0.8180396474,1.0860650543,-0.2874737699 Cl,0.5201484172,0.,2.2299888002 F,0.9791525465,0.,4.0365199519 Cl,-1.9295325044,0.,4.8415093566 H,-3.1672276045,0.,5.1511261751
	$H_2(NC)P$:ClF:ClH MP2= -1454.41232710 NIMAG= 0 P,-0.2166927524,0.,0.6838355341 N,1.3587417748,0.,0.0685984181 H,-0.764326953,1.0915801062,-0.0009374689 H,-0.764326953,-1.0915801062,-0.0009374689 Cl,-0.6223552329,0.,2.7768400311 F,-1.1806916769,0.,4.5366619948 Cl,-4.0765943306,0.,3.4020020395 H,-5.2608338182,0.,2.9270803259 C,2.5159538026,0.,-0.2035295877

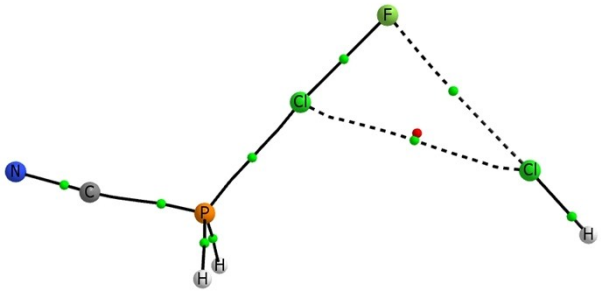
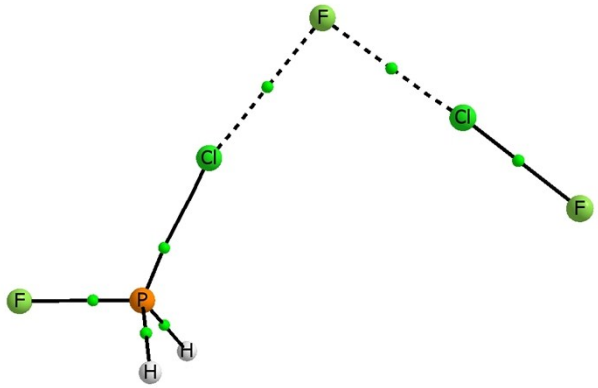
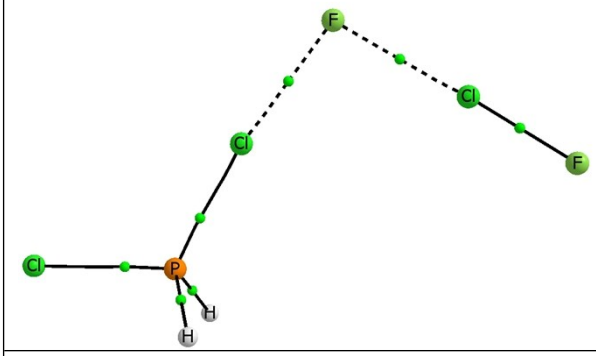
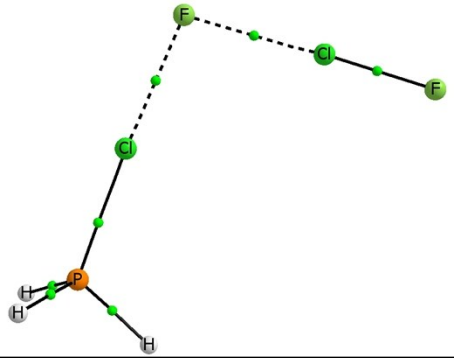
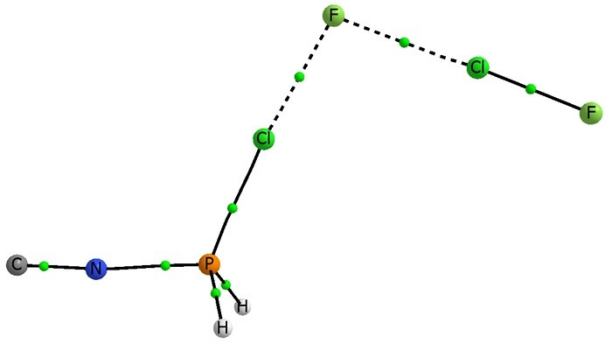
	H_2(CN)P:ClF:ClH MP2= -1454.43857581 NIMAG= 0 P,-0.2234787363,0.,0.6503048269 C,1.4568206888,0.,0.0933935124 H,-0.7322293475,1.0876160332,-0.0726949633 H,-0.7322293475,-1.0876160332,-0.0726949633 Cl,-0.6942853652,0.,2.7926780928 F,-1.2179998557,0.,4.5393643151 Cl,-4.1590013658,0.,3.5168888392 H,-5.36256751,0.,3.0938016121 N,2.6015333879,0.,-0.1771159234

Table S2. Structures, total energies, and molecular graphs of complexes H_2XP:ClF:ClF

	H_2FP:ClF:ClF MP2= -1560.59913757 NIMAG= 0 P,-0.1981458936,0.,0.3019870297 F,0.8021698519,0.,-0.8906597494 H,-0.9836106757,.1276972133,0.0762364626 H,0.9836106757,1.1276972133,0.0762364626 Cl,0.5709421164,0.,2.0728108847 F,0.9303443674,0.,4.2124917335 Cl,-1.077635173,0.,4.6807652796 F,-2.7818467189,0.,5.0018205133
	H_2ClP:ClF:ClF MP2= -1920.56846518 NIMAG= 0 P,-0.2898928489,0.,0.4840364781 Cl,1.6678876465,0.,0.1128689216 H,-0.7769150969,1.1141872102,-0.2019249696 H,-0.7769150969,-1.1141872102,-0.2019249696 Cl,-0.8473209508,0.,2.3732649926 F,-1.7392832761,0.,4.2729836646 Cl,-3.7444015051,0.,3.618888388 F,-5.3573640843,0.,3.0284574485
	H_3P:ClF:ClF MP2= -1461.42213587 NIMAG= 0 P,2.7420228687,0.5963274257,0. H,2.4476400717,1.9611960642,0. H,3.5756672641,0.4102495408,1.1054135244 H,3.5756672641,0.4102495408,-1.1054135244 Cl,1.1045076087,-0.5488793505,0. F,-0.6728271431,-1.6398966661,0. Cl,-2.0361167966,-0.0228604573,0. F,-3.0993412502,1.3237344272,0.
	$H_2(NC)P$:ClF:ClF MP2= -1553.47343488 NIMAG= 0 P,-0.232522847,0.,0.5041490869 N,1.4166494914,0.,0.2255505456 H,-0.6707203453,1.1142329269,-0.2138586676 H,-0.6707203453,-1.1142329269,-0.2138586676 Cl,-0.810990698,0.,2.4090306628 F,-1.5983790568,0.,4.2785092516 Cl,-3.706580285,0.,3.7639627292 F,-5.3424063981,0.,3.3016553827 C,2.6034611267,0.,0.1344778949

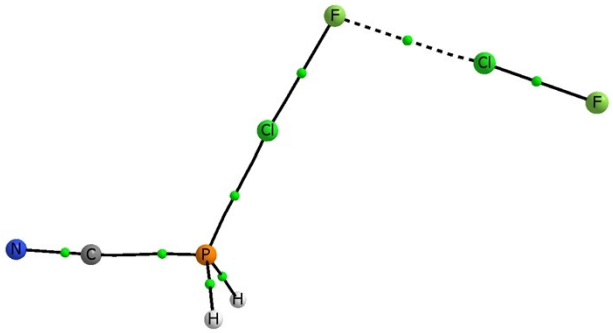
	H_2(CN)P:ClF:ClF MP2= 1553.49710454 NIMAG= 0 P,-0.2167030763,0.,0.4908282514 C,1.5272751376,0.,0.2248805689 H,-0.6357719618,1.1041694547,-0.2588874883 H,-0.6357719618,-1.1041694547,-0.2588874883 Cl,-0.8664239453,0.,2.4496903672 F,-1.6084231677,0.,4.244012967 Cl,-3.8426310649,0.,3.8473812426 F,-5.4858593216,0.,3.5005746437 N,2.6993795259,0.,0.1241269672

Table S3. NBO charges in H_2XP:ClF:ClF complexes with chlorine-transferred halogen bonds

H_2XP, X =	H_2XP-Cl^+	F^-	Cl(3)-F(3)
F	+0.874	-0.677	-0.197
Cl	+0.827	-0.663	-0.164
H	+0.818	-0.659	-0.159
NC	+0.779	-0.650	-0.129

Table S4. Components of spin-spin coupling constants $^{1x}J(P\text{-}Cl_2)$ and $^{1x}J[(F(2)\text{-}Cl(3)]$ across halogen bonds and $^{1}J(F_2\text{-}Cl_2)$ (Hz) for ternary complexes $H_2XP{:}ClF{:}ClH$

X =	PSO	DSO	FC	SD	$^{1x}J(P\text{-}Cl_2)$
F	-37.3	0.1	17.4	-1.3	-21.2
Cl	-28.7	0.1	203.3	-1.9	172.7
H	-14.1	0.0	191.4	-0.4	177.0
NC	-23.8	0.1	241.7	-2.3	215.6
CN	-15.7	0.0	323.6	-2.6	305.3
X =					$^{1x}J(F_2\text{-}Cl_3)$
F	0.1	0.1	18.7	-0.2	18.6
Cl	0.0	0.1	15.0	-0.2	14.8
H	0.1	0.1	21.3	-0.1	21.3
NC	-0.1	0.1	13.3	-0.1	13.2
CN	-0.1	0.1	13.4	-0.1	13.3
X =					$^{1}J(Cl_2\text{-}F_2)$
F	132.8	0.1	354.3	40.6	527.9
Cl	193.1	0.1	304.6	65.6	563.5
H	236.9	0.1	288.8	85.0	610.8
NC	222.3	0.1	280.6	81.8	584.9
CN	279.8	0.1	225.9	109.4	615.2

Table S5. Components of spin-spin coupling constants J(P-Cl_2), J[F(2)-Cl(2)], and ^{1x}J[F(2)-Cl(3)] (Hz) for ternary complexes H_2XP:ClF:ClF

X =	PSO	DSO	FC	SD	^{1}J(P-Cl_2)
F	-44.0	0.1	-170.9	1.4	-213.4
Cl	-36.9	0.1	-132.8	1.3	-168.4
H	-22.5	0.0	-129.9	4.2	-148.1
NC	-33.7	0.1	-117.9	1.3	-150.2
CN	-23.8	0.1	2.6	0.8	-20.3[a]

X =					^{1x}J(F_2-Cl_3)
F	156.4	0.2	287.8	45.0	489.3
Cl	131.8	0.2	278.7	36.4	447.0
H	129.2	0.2	280.3	35.5	445.2
NC	103.3	0.2	256.2	27.0	386.7
CN	67.7	0.1	213.4	16.3	297.5

X =					^{1x}J(Cl_2-F_2)
F	34.9	0.2	255.6	3.4	294.1
Cl	60.9	0.2	300.6	10.4	372.0
H	74.1	0.2	319.0	14.6	407.9
NC	82.9	0.2	340.5	18.4	442.0
CN	147.9	0.2	346.4	44.0	538.5[b]

a) ^{1x}J(P-Cl_2) in this complex.
b) ^{1}J(Cl_2-F_2) in this complex.