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

Hydrogen Bonds and Halogen Bonds in Complexes of Carbones L→C←L as Electron Donors to HF and ClF, for L = CO, N_2, HNC, PH_3, and SH_2

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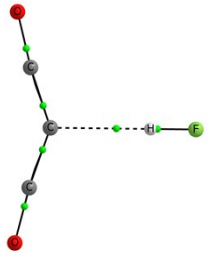
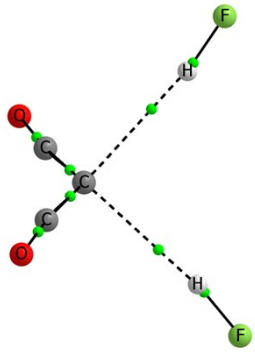
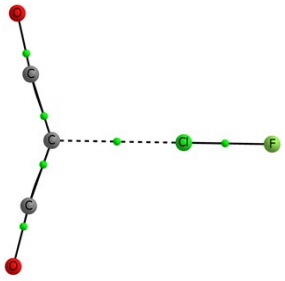
Table S1. Structures (Å, deg), total energies (au), and molecular graphs of complexes of OC→C←CO with one and two HF and ClF molecules.

	occco MP2= -264.29338266 NIMAG= 0 C X,1,1. C,1,r1,2,a1 C,1,r1,2,a1,3,180.,0 O,1,r2,2,a2,4,180.,0 O,1,r2,2,a2,3,180.,0 r1=1.278099 r2=2.448793 a1=95.966 a2=95.133
	occco_hf_c2v MP2= -364.63865271 NIMAG= 0 C,0.,0.,0.28834188 C,0.,1.22477998,0.70779174 C,0.,-1.22477998,0.70779174 O,0.,2.35481081,0.98938332 O,0.,-2.35481081,0.98938332 H,0.,0.,-1.76735027 F,0.,0.,-2.69848166
	occco_2hf MP2= -464.98179312 NIMAG= 0 C,0.,0.,0.3504254809 C,0.,1.2032127612,0.8554973592 C,0.,-1.2032127612,0.8554973592 O,0.,2.3129354785,1.1951814587 O,0.,-2.3129354785,1.1951814587 H,-1.5312063788,0.,-1.0935531994 H,1.5312063788,0.,-1.0935531994 F,-2.2943101987,0.,-1.6232500574 F,2.2943101987,0.,-1.6232500574
	occco_clf MP2= -823.66354607 NIMAG= 0 C,0.,0.,0.4392692222 C,0.,1.2271109383,0.8555149771 C,0.,-1.2271109383,0.8555149771 O,0.,2.3587629508,1.1293137208 O,0.,-2.3587629508,1.1293137208 Cl,0.,0.,-2.0601043485 F,0.,0.,-3.7319622285

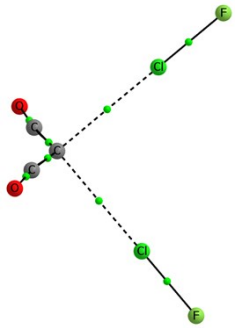
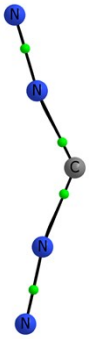
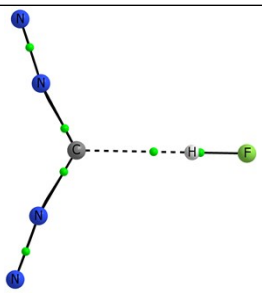
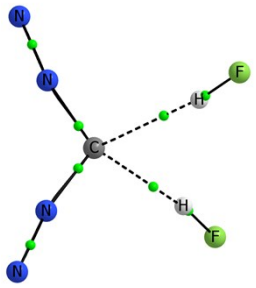
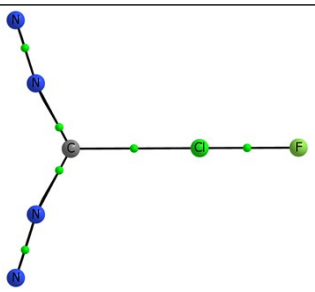
	occco_2clf MP2= -1383.03276020 NIMAG= 0 C,0.,0.,0.6226376912 C,0.,1.2176798287,1.0861864783 C,0.,-1.2176798287,1.0861864783 O,0.,2.3386460841,1.3893269997 O,0.,-2.3386460841,1.3893269997 Cl,-1.8632267091,0.,-1.167328749 Cl,1.8632267091,0.,-1.167328749 F,-3.0640898633,0.,-2.3154403102 F,3.0640898633,0.,-2.3154403102

Table S2. Structures (Å, deg), total energies (au), and molecular graphs of complexes of NN→C←NN with one and two HF and ClF molecules.

	n2cn2 MP2= -256.56479818 NIMAG= 0 C X,1,1. N,1,r1,2,a1 N,1,r1,2,a1,3,180.,0 N,1,r2,2,a2,4,180.,0 N,1,r2,2,a2,3,180.,0 r1=1.26707563 r2=2.42717611 a1=114.27859507 a2=109.60147599
	n2cn2_hf_c2v MP2= -356.91190534 NIMAG= 0 C,0.,0.,0.12040519 N,0.,1.12833163,0.74731132 N,0.,-1.12833163,0.74731132 N,0.,2.21901314,1.12240416 N,0.,-2.21901314,1.12240416 H,0.,0.,-1.84822557 F,0.,0.,-2.78335803
	n2cn2_2hf MP2= -457.25669476 NIMAG= 0 C,0.0000000348,0.23432971,0. N,0.0000001377,0.91712429,1.11636807 N,0.0000001377,0.91712429,-1.11636807 N,0.0000001999,1.32970398,2.18522301 N,0.0000001999,1.32970398,-2.18522301 H,-1.42190871,-1.18048332,0. H,1.4219083531,-1.1804837486,0. F,-2.20083722,-1.69447812,0. F,2.2008367081,-1.6944787834,0.
	n2cn2_clf MP2= -815.94038615 NIMAG= 0 C,0.,0.,0.3274875081 N,0.,1.1373100471,0.933216079 N,0.,-1.1373100471,0.933216079 N,0.,2.2356897269,1.2816031898 N,0.,-2.2356897269,1.2816031898 Cl,0.,0.,-1.9074965694 F,0.,0.,-3.6213769262

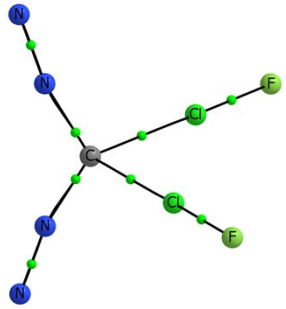
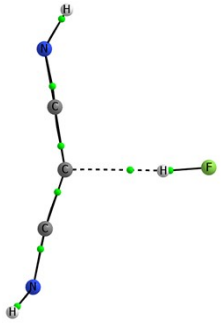
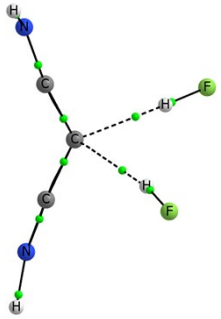
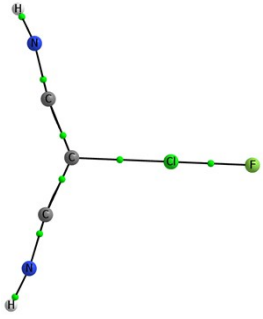
	n2cn2_2clf MP2= -1375.31392417 NIMAG= 0 C,0.0000000001,0.,0.3461521923 N,0.0000000001,1.1251504367,1.0186234049 N,0.0000000001,-1.1251504367,1.0186234049 N,0.0000000002,2.2063803792,1.3949269225 N,0.0000000002,-2.2063803792,1.3949269225 Cl,-1.8509820125,0.,-1.0505355792 Cl,1.8509820123,0.,-1.0505355796 F,-3.2272028758,0.,-2.0422253554 F,3.2272028753,0.,-2.0422253562

Table S3. Structures (Å, deg), total energies (au), and molecular graphs of complexes of HNC→C←CNH with one and two HF and ClF molecules.

	hncccnh MP2= -224.49828538 NIMAG= 0 C,0.,0.,-0.0727410902 C,-1.2777541366,0.015305167,0.0077287239 C,1.2777541366,-0.015305167,0.0077287239 N,-2.4959363321,-0.088106447,-0.0479416778 N,2.4959363321,0.088106447,-0.0479416778 H,-3.1391210905,0.4521763263,0.5140337039 H,3.1391210905,-0.4521763263,0.5140337039
	hncccnh_hf_2 MP2= -324.84631720 NIMAG= 0 C,0.025855665,-0.3979920643,-0.0317893391 C,0.1841603418,-0.6401983839,1.2290566534 C,0.21511312,-0.7137646619,-1.2725233241 N,0.2282660238,-0.9093448869,2.4105826751 N,0.1795367962,-0.9170026582,-2.4689658497 H,0.6329667368,-0.3835777431,3.1697390467 H,0.9381958626,-1.1491725868,-3.0906529625 H,-0.4561089312,1.5467894875,0.0446170894 F,-0.6209856151,2.4611864976,0.1549360107
	hncccnh_clf_cs MP2= -783.87597986 NIMAG= 0 C,0.02688357,0.85464306,0. C,-0.02246988,1.3796153,1.20599586 C,-0.02246988,1.3796153,-1.20599586 N,0.08903734,1.73637556,2.34731754 N,0.08903734,1.73637556,-2.34731754 H,-0.56066104,1.93162951,3.09076707 H,-0.56066104,1.93162951,-3.09076707 Cl,0.00602361,-1.30361233,0. F,-0.01330197,-3.07334689,0.
	hncccnh_2hf MP2= -425.19351407 NIMAG= 0 C,0.1694741939,0.4133533394,0. C,0.0681299915,0.9258423686,1.205488668 C,0.0681299915,0.9258423686,-1.205488668 N,0.1320682366,1.2910133393,2.3477813064 N,0.1320682366,1.2910133393,-2.3477813064 H,-0.5227183113,1.4396504955,3.0953767211 H,-0.5227183113,1.4396504955,-3.0953767211 H,1.3780930569,-1.1356032572,0. H,-1.3313288755,-0.9408341046,0. F,1.9905693891,-1.8448503324,0. F,-2.1548686351,-1.3836076298,0.

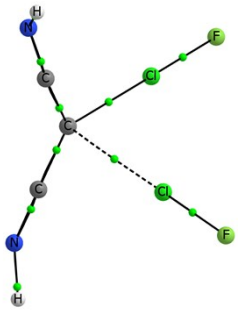
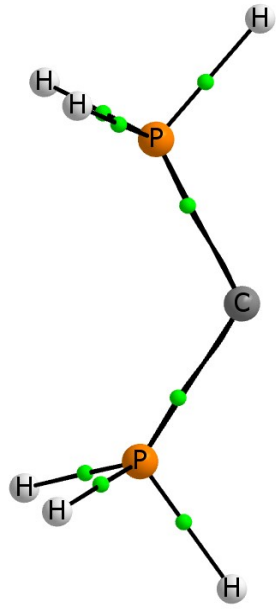
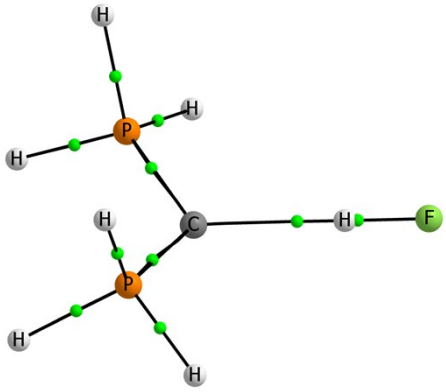
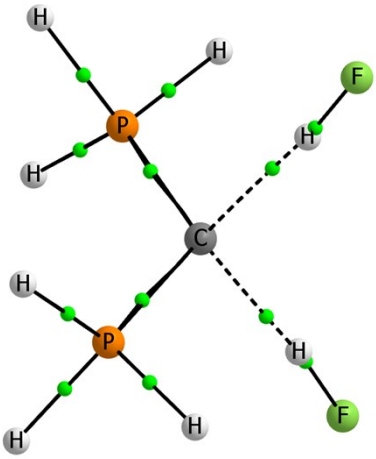
	hncccnh_2clf MP2= -1343.24816531 NIMAG= 0 C,0.3357542363,0.5939811706,0. C,0.1217887327,1.0867625783,1.2084329851 C,0.1217887327,1.0867625783,-1.2084329851 N,0.0996139036,1.4617184883,2.3427688888 N,0.0996139036,1.4617184883,-2.3427688888 H,-0.5275600911,1.4355898664,3.1281612559 H,-0.5275600911,1.4355898664,-3.1281612559 Cl,1.7702191452,-1.0960962607,0. Cl,-1.7797177138,-0.8296738095,0. F,2.9074618733,-2.4161139948,0. F,-3.1690571101,-1.7666616793,0.

Table S4. Structures (Å, deg), total energies (au), and molecular graphs of complexes of $H_3P{\rightarrow}C{\leftarrow}PH_3$ with one and two HF and ClF molecules.

	ph3cph3 MP2= -723.24780957 NIMAG= 0 C X,1,1. P,1,r1,2,a1 P,1,r1,2,a1,3,180.,0 H,3,r2,1,a2,2,0.,0 H,4,r2,1,a2,2,0.,0 H,3,r3,1,a3,2,d3,0 H,3,r3,1,a3,2,-d3,0 H,4,r3,1,a3,2,d3,0 H,4,r3,1,a3,2,-d3,0 r1=1.65748192 r2=1.40235366 r3=1.42132697 a1=119.87711784 a2=112.22000049 a3=121.80824346 d3=117.38873328
	ph3cph3_hf MP2= -823.61200529 NIMAG= 0 C,0.,-0.3319616825,-0.1966273382 P,1.458436208,-0.0443277036,-0.9383488443 P,-1.458436208,-0.0443277036,-0.9383488443 H,2.5269454885,-0.138816188,-0.0390045554 H,-2.5269454885,-0.138816188,-0.0390045554 H,1.9400601182,-0.8814524035,-1.9754472824 H,1.7174967,1.211075746,-1.5397666355 H,-1.7174967,1.211075746,-1.5397666355 H,-1.9400601182,-0.8814524035,-1.9754472824 H,0.,-1.4738086288,1.1148845846 F,0.,-2.1038252147,1.847770359
	ph3cph3_hf2 MP2= -923.97263358 NIMAG= 0 C,0.,0.,-0.0618881618 P,1.4586416725,0.,-0.8875404704 P,-1.4586416725,0.,-0.8875404704 H,2.5366944211,0.,0.0018151859 H,-2.5366944211,0.,0.0018151859 H,1.7969573545,-1.080127172,-1.7323299583 H,1.7969573545,1.080127172,-1.7323299583 H,-1.7969573545,1.080127172,-1.7323299583 H,-1.7969573545,-1.080127172,-1.7323299583 H,0.,-1.4779508483,0.9342302452 F,0.,-2.3277938952,1.3860682585 H,0.,1.4779508483,0.9342302452 F,0.,2.3277938952,1.3860682585

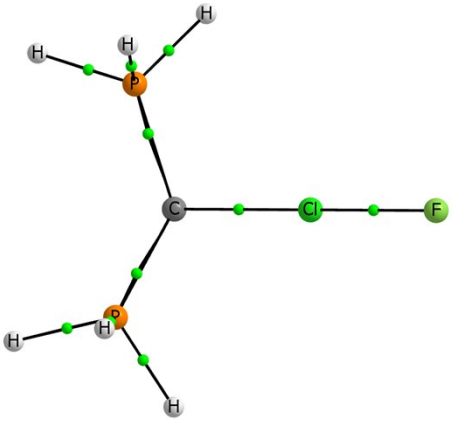
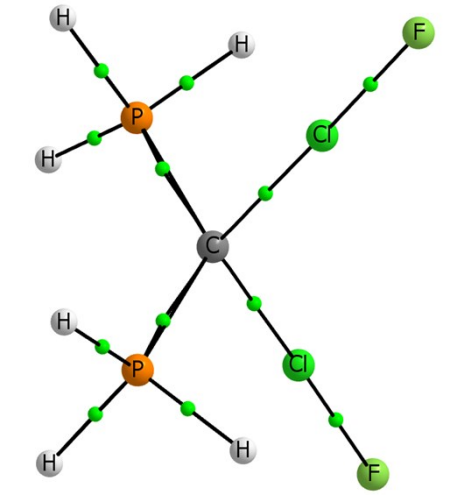
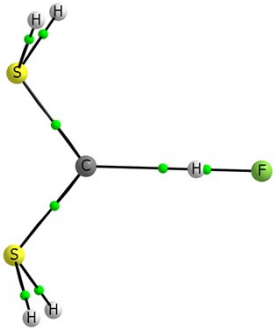
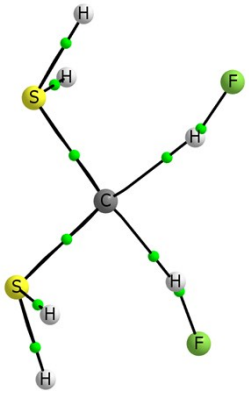
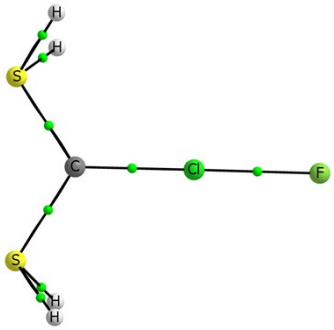
	ph3cph3_clf_cs MP2= -1282.66020425 NIMAG= 0 C,-0.5702208707,0.7820187856,0. P,0.0877149421,1.2013921191,1.4940238996 P,0.0877149421,1.2013921191,-1.4940238996 H,-0.6418889533,0.5951188924,2.5189372346 H,-0.6418889533,0.5951188924,-2.5189372346 H,1.4091888811,0.823366933,1.8154764299 H,0.0736271937,2.5629495925,1.8454539394 H,0.0736271937,2.5629495925,-1.8454539394 H,1.4091888811,0.823366933,-1.8154764299 Cl,-0.1644036178,-1.22931212,0. F,0.2116043722,-3.0850092358,0.
	ph3cph3_clf2 MP2= -1842.06423199 NIMAG= 0 C,0.,0.,-0.197510476 P,1.5473265889,0.,-0.9366014009 P,-1.5473265889,0.,-0.9366014009 H,2.4886749959,0.,0.0920023721 H,-2.4886749959,0.,0.0920023721 H,1.8634832179,-1.112175768,-1.7293150167 H,1.8634832179,1.112175768,-1.7293150167 H,-1.8634832179,1.112175768,-1.7293150167 H,-1.8634832179,-1.112175768,-1.7293150167 Cl,0.,-1.8044991034,0.7579002304 F,0.,-3.4682002611,1.5930108333 Cl,0.,1.8044991034,0.7579002304 F,0.,3.4682002611,1.5930108333

Table S5. Structures (Å, deg), total energies (au), and molecular graphs of complexes of $H_2S{\rightarrow}C{\leftarrow}SH_2$ with one and two HF and ClF molecules.

	sh2csh2 MP2= -835.64105675 NIMAG= 0 C,0.,0.,0.9156757047 S,0.,1.321528952,-0.1985578964 S,0.,-1.321528952,-0.1985578964 H,-0.9564879678,2.1958664427,0.2168109512 H,0.9564879678,-2.1958664427,0.2168109512 H,0.9564879678,2.1958664427,0.2168109512 H,-0.9564879678,-2.1958664427,0.2168109512
	sh2csh2_hf MP2= -936.01013497 NIMAG= 0 C,0.,0.,0.9640528482 S,0.,1.3418492879,-0.0945105931 S,0.,-1.3418492879,-0.0945105931 H,-0.9617198222,2.1946574259,0.3453265972 H,0.9617198222,-2.1946574259,0.3453265972 H,0.9617198222,2.1946574259,0.3453265972 H,-0.9617198222,-2.1946574259,0.3453265972 H,0.,0.,2.6228632357 F,0.,0.,3.6066024262
	sh2csh2_2hf_2 MP2= -1036.37304874 NIMAG= 0 C,0.,0.,0.1223139218 S,1.342779589,0.2488535012,-0.9319605674 S,-1.342779589,-0.2488535012,-0.9319605674 H,1.9729297489,1.3313596823,-0.4158558868 H,-1.9729297489,-1.3313596823,-0.4158558868 H,2.3271173107,-0.5758722217,-0.4997453782 H,-2.3271173107,0.5758722217,-0.4997453782 H,-0.1990084851,-1.3265015897,1.1693142726 H,0.1990084851,1.3265015897,1.1693142726 F,-0.547177965,-2.1459717069,1.5655800979 F,0.547177965,2.1459717069,1.5655800979
	sh2csh2_clf_2_cs MP2= -1395.07297178 NIMAG= 0 C,0.5410515897,-0.4385920457,0. S,1.385213613,0.0866048172,1.3952385412 S,1.385213613,0.0866048172,-1.3952385412 H,0.687808939,1.1415365109,1.9255657793 H,0.8604759567,-0.7551203492,-2.3085802082 H,0.8604759567,-0.7551203492,2.3085802082 H,0.687808939,1.1415365109,-1.9255657793 Cl,-1.2794012454,-0.1709949123,0. F,-3.2122183692,0.2215653473,0.

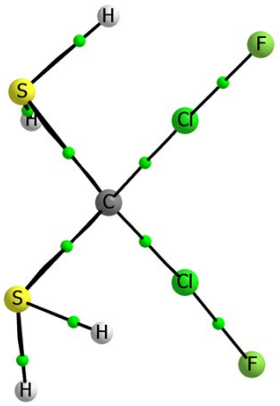
	sh2csh2_2clf_2_cs MP2= -1954.47793911 NIMAG= 0 C,-0.2777685223,0.0499668431,0. S,-1.3187088323,-0.0673553052,-1.4708006374 S,-1.3187088323,-0.0673553052,1.4708006374 H,-1.2037371574,1.2074080245,-1.9201681324 H,-0.3239526424,-0.5464710293,2.246524511 H,-0.3239526424,-0.5464710293,-2.246524511 H,-1.2037371574,1.2074080245,1.9201681324 Cl,0.6029390113,-1.7281147203,0. Cl,0.6265188278,1.7230393204,0. F,1.4745926442,-3.3788087609,0. F,1.4187797445,3.4468264846,0.

Table S6. Paramagnetic spin orbit (PSO), diamagnetic spin orbit (DSO), Fermi contact (FC), and spin-dipole (SD) components and total ^{2h}J(F-C) (Hz) for coupling across hydrogen bonds in complexes with one and two HF molecules, and ^{1x}J(Cl-C) (Hz) for coupling across halogen bonds in complexes with 1 and 2 ClF molecules.

L = CO	PSO	DSO	FC	SD	^{2h}J(F-C)
HF	-1.7	0.2	18.2	0.2	16.8
2HF	-1.8	0.2	14.5	0.2	13
					^{1x}J(Cl-C)
ClF	1.8	0	27.6	0.3	29.7
2ClF	1.6	0.1	22.4	0.3	24.3

L = NN	PSO	DSO	FC	SD	^{2h}J(F-C)
HF	-0.9	0.2	62.1	0.4	61.8
2HF	-1.3	0.2	45.4	0.1	44.4
					^{1x}J(Cl-C)
ClF	1.3	0.1	64.6	0.1	66.1
2ClF	1.6	0.1	52.9	0.2	54.7

L = HNC	PSO	DSO	FC	SD	^{2h}J(F-C)
HF	-2.1	0.1	19.1	0.2	17.3
2HF	-2.0	0.2	37.2	0.1[a]	35.5
	-2.7	0.2	23.9	0.2[a]	21.5[b]
					^{1x}J(Cl-C)
ClF	3.3	0.1	52.2	0.9	56.5
2ClF	2.9	0.1	53.2	0.9[a]	57.1
	2.4	0.1	20.3	0.9[a]	23.7[b]

L = PH_3	PSO	DSO	FC	SD	^{2h}J(F-C)
HF	-2.8	0.3	139	0	136.5
2HF	-3.7	0.3	98.5	0.8	95.2
					^{1x}J(C-Cl)
ClF	7.7	0.1	33.7	3.3	44.8
2ClF	4.8	0.1	46.8	2	53.7

L = SH_2	PSO	DSO	FC	SD	^{2h}J(F-C)
HF	0.0	0.3	289.2	0.8	290.3
2HF	-1.5	0.3	166.4	-0.9	164.3
					^{1x}J(C-Cl)
ClF	-0.8	0.1	3.6	0.6	3.5

a) Estimated.
b) For the interaction at the longer intermolecular distance.