Supplementary Material for

Halogen Bonding involving CO and CS with Carbon as the Electron Donor

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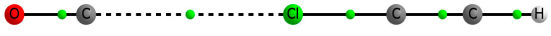
Table S1. Structures (Å), total energies (au), and molecular graphs of complexes OC:ClY

	OC:ClF MP2/AUG'-CC-PVTZ= -672.51018972 NIMAG= 0 C X 1 one O 1 r1 2 nin Cl 1 r2 2 nin 3 tra F 1 r3 2 nin 3 tra r1=1.13691199 r2=2.66247342 r3=4.31429744 one=1. nin=90. tra=180.
	OC:ClNC MP2/AUG'-CC-PVTZ= -665.43891428 NIMAG= 0 C X 1 one O 1 r1 2 nin Cl 1 r2 2 nin 3 tra N 1 r3 2 nin 3 tra C 1 r4 2 nin 3 tra r1=1.13729218 r2=2.99675982 r3=4.62484783 r4=5.81147763 one=1. nin=90. tra=180.
	OC:Cl_2 MP2/AUG'-CC-PVTZ= -1032.53268157 NIMAG= 0 C X 1 one O 1 r1 2 nin Cl 1 r2 2 nin 3 tra Cl 1 r3 2 nin 3 tra r1=1.13804715 r2=3.02005978 r3=5.02464523 one=1.

	nin=90. tra=180.
	OC:ClOH MP2/AUG'-CC-PVTZ= -648.51622783 NIMAG= 0 C,0.2067799453,0.,0.0160804631 O,1.3430918203,0.,-0.0486658133 Cl,-2.7952238146,0.,0.0545732002 O,-4.4951016769,0.,-0.0068927364 H,-4.7392707386,0.,0.9304234621
	OC:ClCN MP2/AUG'-CC-pVTZ =-665.51482092 NIMAG= 0 C X 1 one O 1 r1 2 nin Cl 1 r2 2 nin 3 tra C 1 r3 2 nin 3 tra N 1 r4 2 nin 3 tra r1=1.13791594 r2=3.22498693 r3=4.85774232 r4=6.03318381 one=1. nin=90. tra=180.
	OC:ClCCH MP2/AUG'-CC-PVTZ= -649.41957451 NIMAG= 0 C X 1 one O 1 r1 2 nin Cl 1 r2 2 nin 3 tra C 1 r3 2 nin 3 tra C 1 r4 2 nin 3 tra H 1 r5 2 nin 3 tra r1=1.13843245 r2=3.2878752 r3=4.92689611 r4=6.14098485 r5=7.20244288 one=1. nin=90.

	tra=180.
	OC:ClNH$_2$ MP2/AUG'-CC-PVTZ= -628.67445117 NIMAG= 0 C,0.4140444106,0.,0.0472411091 O,1.5445254707,0.,-0.0897721001 Cl,-2.8332989477,0.,0.0669332624 N,-4.5763675504,0.,-0.0603334621 H,-4.8636443746,0.810114332,0.4832273376 H,-4.8636443746,-0.810114332,0.4832273376

Table S2. Bond critical point data (ρ_{BCP}, $\nabla^2\rho_{BCP}$, and H_{BCP}, au) for OC:ClY complexes

ClY	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}
ClF	0.024	0.084	0.000
ClNC	0.012	0.047	0.002
ClCl	0.012	0.046	0.002
ClOH	0.012	0.047	0.002
ClCN	0.008	0.032	0.002
ClCCH	0.007	0.028	0.002
$ClNH_2$	0.007	0.030	0.002

Fig. S1. Plots of the electron densities (ρ_{BCP}) and the Laplacians ($\nabla^2\rho_{BCP}$) (au) at C···Cl bond critical points versus the C-Cl distance (Å) for OC:ClY complexes

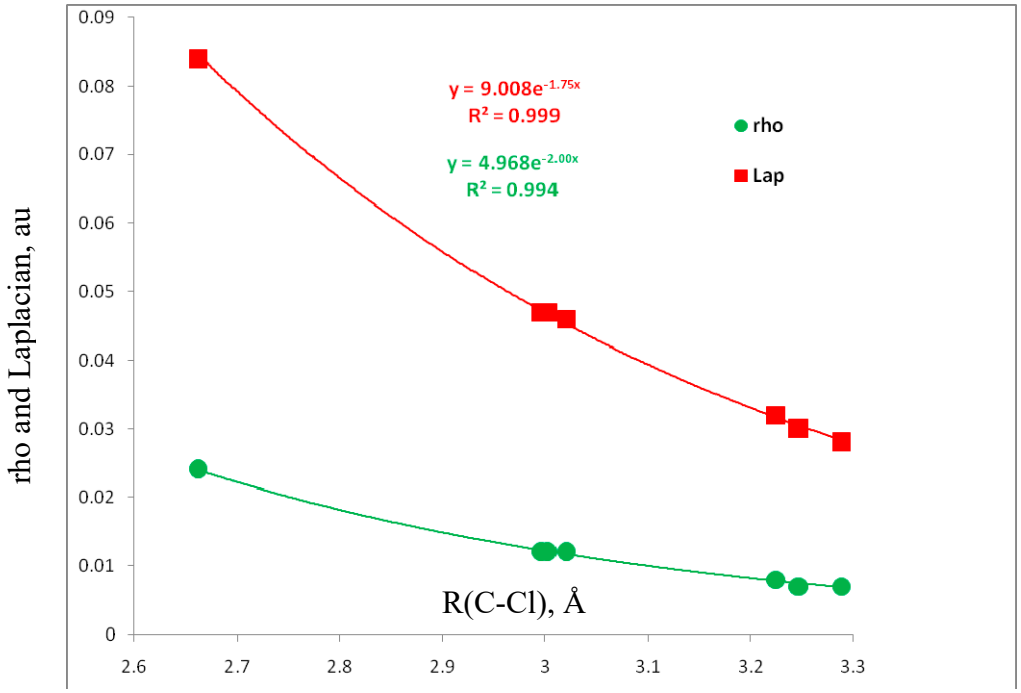


Table S3. Components of $^{1x}J(C\text{-}Cl)$ and $^{1}J(C\text{-}O)$ (Hz) for OC:ClY complexes

	PSO	DSO	FC	SD	$^{1x}J(C\text{-}Cl)$
OC:ClF	0.1	0.0	66.0	-0.3	65.9
OC:ClNC	0.1	0.0	31.6	0.0	31.7
OC:ClCl	0.2	0.0	28.5	-0.1	28.7
OC:ClOH	0.2	0.0	27.8	-0.1	27.9
OC:ClCN	0.0	0.0	16.7	0.0	16.7
OC:ClCCH	0.0	0.0	13.6	0.0	13.7
$OC:ClNH_2$	0.1	0.0	14.0	0.0	14.1

	PSO	DSO	FC	SD	$^{1}J(C\text{-}O)$
OC:ClF	12.8	0.1	13.1	-5.1	20.8
OC:ClNC	13.1	0.1	12.0	-5.0	20.2
OC:ClCl	13.3	0.1	12.0	-4.9	20.4
OC:ClOH	13.3	0.1	11.9	-4.9	20.5
OC:ClCN	13.3	0.1	11.9	-4.9	20.3
OC:ClCCH	13.4	0.1	11.8	-4.8	20.4
OC:ClNH2	13.5	0.1	11.7	-4.7	20.5
CO	13.6	0.1	11.8	-4.8	20.7

Table S4. Structures (Å), total energies (au), and molecular graphs of SC:ClY complexes stabilized by traditional halogen bonds

	SC:ClNC MP2/AUG'-CC-PVTZ= -987.96243507 NIMAG= 0 C X,1,one S,1,r1,2,nin Cl,1,r2,2,nin,3,tra,0 N,1,r3,2,nin,3,tra,0 C,1,r4,2,nin,3,tra,0 r1=1.53756654 r2=2.79539624 r3=4.43342209 r4=5.61980474 one=1. nin=90. tra=180.
	SC:Cl_2 MP2/AUG'-CC-PVTZ= -1355.05505377 NIMAG= 0 C X,1,one S,1,r1,2,nin Cl,1,r2,2,nin,3,tra,0 Cl,1,r3,2,nin,3,tra,0 r1=1.53893474 r2=2.76753341 r3=4.78663423 one=1. nin=90. tra=180.
	SC:ClCN MP2/AUG'-CC-PVTZ= -988.03689403 NIMAG= 0 C X,1,one S,1,r1,2,nin Cl,1,r2,2,nin,3,tra,0 C,1,r3,2,nin,3,tra,0 N,1,r4,2,nin,3,tra,0 r1=1.53989099 r2=3.09180632

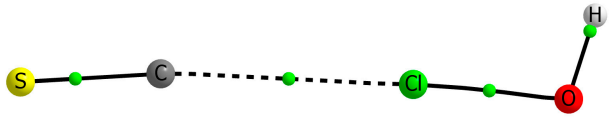
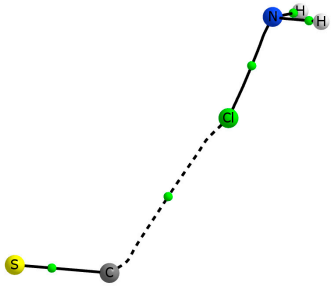
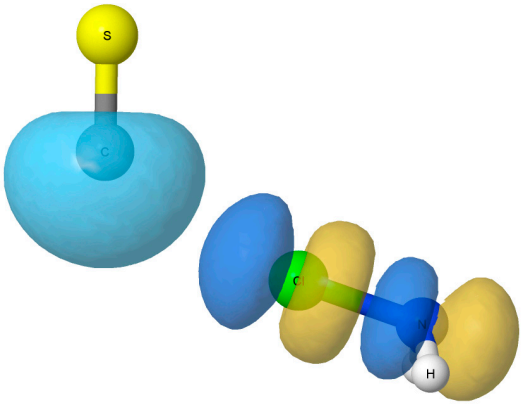
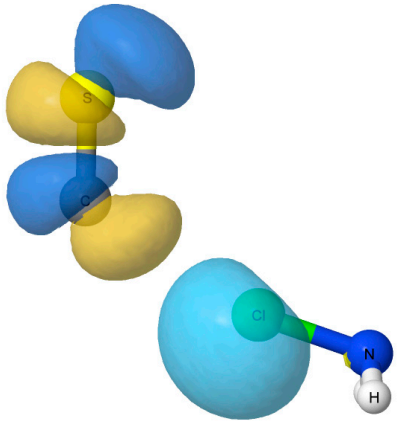
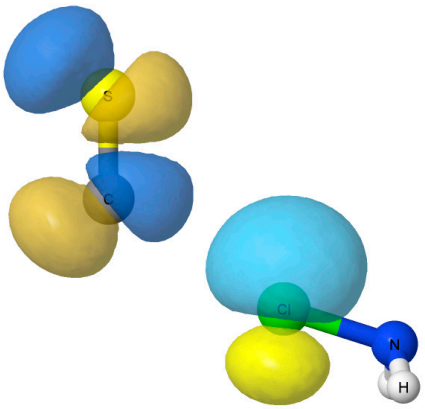
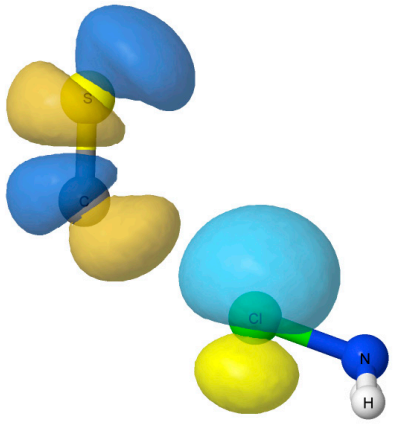
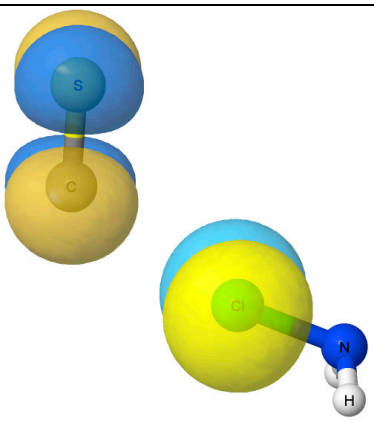
	r3=4.72583381 r4=5.90154998 one=1. nin=90. tra=180.
	SC:ClOH MP2/AUG'-CC-PVTZ= -971.03799286 NIMAG= 0 C,-0.0397056027,0.,0.0788470096 S,1.4930490506,0.,-0.0694526256 Cl,-2.8117144943,0.,0.0656498667 O,-4.5206641948,0.,-0.0310402195 H,-4.7809401233,0.,0.9015145444
	SC:ClCCH MP2/AUG'-CC-PVTZ= -971.94024694 NIMAG= 0 C X,1,one S,1,r1,2,nin Cl,1,r2,2,nin,3,tra,0 C,1,r3,2,nin,3,tra,0 C,1,r4,2,nin,3,tra,0 H,1,r5,2,nin,3,tra,0 r1=1.54143742 r2=3.18301357 r3=4.82282167 r4=6.03751802 r5=7.09884161 one=1. nin=90. tra=180.
	SC:ClNH$_2$ MP2/AUG'-CC-PVTZ= -951.19457076 NIMAG= 0 C,-0.80790239,-1.61348652,0. S,0.31676247,-2.66883094,0. Cl,-0.23290641,1.43016097,0. N,0.50617009,3.0164891,0. H,0.09706841,3.47723698,0.80934564 H,0.09706841,3.47723698,-0.80934564

Fig. S2. Orbitals involved in charge-transfer interactions in SC:$ClNH_2$[a,b]



a) The C_{lp}→σ*Cl-N charge-transfer. The charge-transfer energy is 5.1 kJ/mol.

	
2.6 kJ/mol	1.4 kJ/mol
	
2.0 kJ/mol	0.9 kJ/mol

b) The Cl_{lp}→π*C-S back donations and the corresponding charge-transfer energies

Table S5. Structures (Å), total energies (au), and molecular graphs of ion-pair complexes SC-Cl^{+}:$^{-}$Y

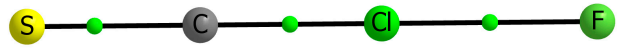
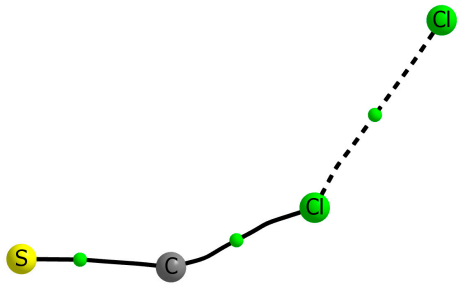
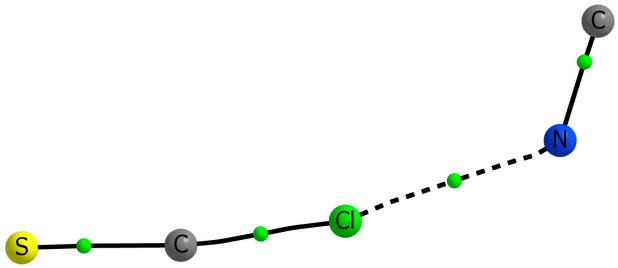
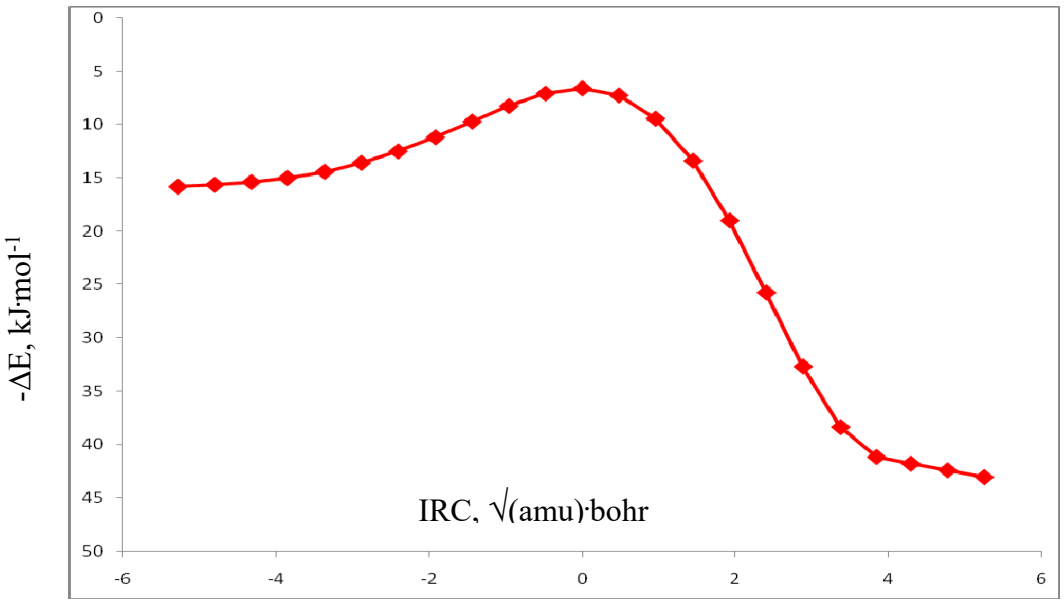
	SC-Cl^{+}:$^{-}$F MP2/AUG'-CC-PVTZ= -995.06710205 NIMAG= 0 C X,1,one S,1,r1,2,nin Cl,1,r2,2,nin,3,tra,0 F,1,r3,2,nin,3,tra,0 r1=1.53964055 r2=1.61335012 r3=3.53034882 one=1. nin=90. tra=180.
	SC-Cl^{+}:$^{-}$Cl MP2/AUG'-CC-PVTZ= -1355.06682708 NIMAG= 0 C,0.0286935074,1.3216878202,0. S,-1.1592774942,2.326245182,0. Cl,0.6801493973,-0.1601543928,0. Cl,0.2736085895,-2.5040686094,0.
	SC-Cl^{+}:$^{-}$NC MP2/AUG'-CC-PVTZ= -987.96278985 NIMAG= 0 C,-0.2675920233,-1.0282157739,0. S,-0.0301064942,-2.5424570055,0. Cl,-0.3110190858,0.5710337885,0. N,0.0951976604,2.7419744786,0. C,1.1535289428,3.2975325123,0.

Fig. S3. Plots along the intrinsic reaction coordinate (IRC) for the inter-conversion of complex and ion-pair on the SC:ClCl and SC:ClNC potential surfaces

SC:ClCl



SC:ClNC

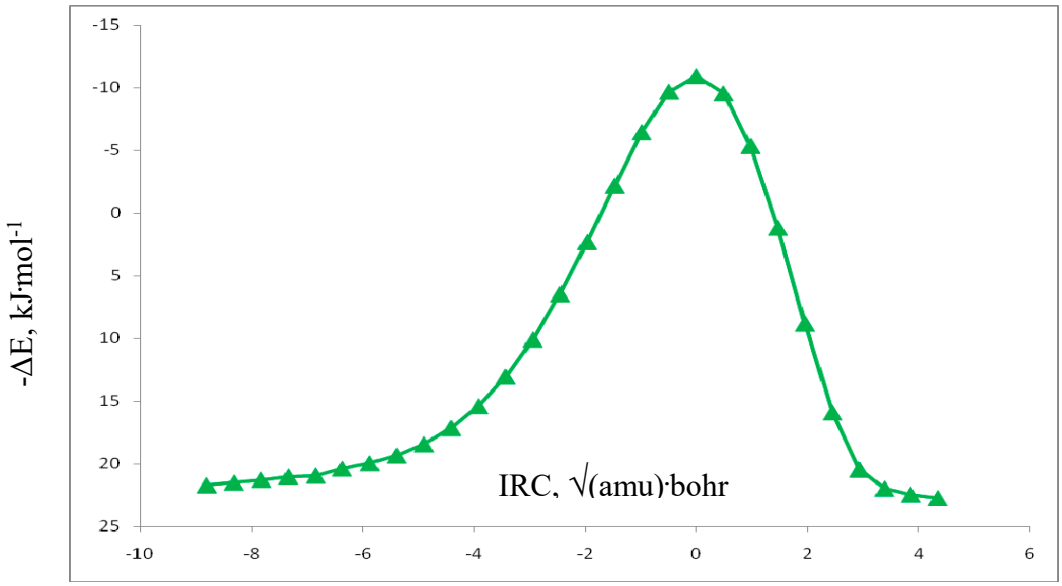


Table S6. Bond critical point data (ρ_{BCP}, $\nabla^2\rho_{BCP}$, and H_{BCP}, au) for SC:ClY complexes and $SCCl^+$:$^-$Y ion-pairs

SC:ClY, ClY =	ρ_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}
ClCl	0.022	0.069	0.001
ClNC	0.020	0.066	0.001
ClOH	0.021	0.069	0.001
ClCN	0.011	0.041	0.002
ClCCH	0.009	0.035	0.002
$ClNH_2$	0.010	0.036	0.002
$SCCl^+$:$^-$Y, Y=			
F	0.259	-0.394	-0.255
Cl	0.251	-0.385	-0.235
NC	0.266	-0.452	-0.266

Table S7. Components of ^{1x}J(C-Cl) for SC:ClY complexes and transition structures, ^{1}J(C-Cl) and ^{1x}J(Cl-A) for $SCCl^{+}:^{-}Y$ ion-pairs, and ^{1}J(Cl-A) for monomers ClF, ClCl, and ClNC

	SC:ClY complexes				
ClY =	PSO	DSO	FC	SD	^{1x}J(C-Cl)
ClCl	0.2	0.0	62.7	-0.3	62.6
ClNC	0.1	0.0	60.2	-0.2	60.2
ClOH	0.2	0.0	56.2	-0.2	56.1
ClCN	0.1	0.0	28.2	0.0	28.3
ClCCH	0.1	0.0	21.6	0.0	21.7
ClNH2	0.1	0.0	17.8	0.0	18.0

	SCCl+:-Y				
Y =					^{1}J(C-Cl)
F	-13.3	0.1	-62.2	-1.7	-77.1
Cl	-10.4	0.1	-51.8	0.3	-61.9
NC	-14.0	0.1	-77.1	-2.1	-93.1

					^{1x}J(Cl-A)
F	24.0	0.1	422.1	3.2	449.3
Cl	12.0	0.0	34.9	3.9	50.7
NC	-0.6	0.0	-47.9	-0.1	-48.6

	TS				^{1x}J(C-Cl)
ClCl TS	-3.0	0.0	144.3	-0.8	140.5
ClNC TS	-5.4	0.1	142.1	1.7	138.4

Monomers					^{1}J(Cl-A)
ClF	642.2	0.1	-99.3	255.4	798.4
ClCl	78.5	0.0	-9.8	30.9	99.6
ClNC	-5.2	0.0	41.2	-2.0	34.0

Table S8. Components of ^{1}J(S-C) for complexes, ion-pairs, transition structures, and the SC monomer

SC:ClY complexes					
ClY	PSO	DSO	FC	SD	^{1}J(S-C)
ClNC	-14.8	0.0	-24.8	4.0	-35.6
ClCl	-15.0	0.0	-25.6	3.8	-36.7
ClCN	-15.3	0.0	-25.1	3.7	-36.7
CLOH	-15.2	0.0	-25.7	3.7	-37.1
ClCCH	-15.7	0.0	-25.4	3.5	-37.5
ClNH2	-15.8	0.0	-26.1	3.5	-38.4
Ion-pairs					
ClF	-5.0	0.0	-30.7	4.7	-31.0
ClNC	-2.4	0.0	-28.3	5.8	-24.9
ClCl	-6.0	0.0	-36.9	3.0	-39.8
TS					
ClNC	-10.1	0.0	-31.7	1.1	-40.8
ClCl	-11.9	0.0	-32.6	4.7	-39.8
CS					
Monomer	-16.1	0.0	-26.5	3.3	-39.3