Supporting Information to:
Matrix Isolation Studies of Photochemical and Thermal Reactions of 3- and 5-Membered Cyclic Hydrocarbons with $CrCl_2O_2$

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Table S1: Product Band Positions Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Cyclopentadiene and the Calculated[a] Bands of $CrCl_2O$-cyclopent-2-enone, $CrCl_2O$-cyclopent-3-enone, and $CrCl_2O$-cyclopenta-1,3-dienol

$CrCl_2O_2$ + cyclopentadiene (exp. freq.[b])	$CrCl_2O$-cyclopent-2-enone (calcd. freq.)	$CrCl_2O$-cyclopent-3-enone (calcd. freq.)	$CrCl_2O$-cyclopenta-1,3-dienol (calcd. freq.)	Assignment
	415	418	431	
449	506	454	456	Cr-Cl st.
541				
682	531	506	493	
727	667	654	524	
783	753	665	648	
821	754	771	667	
828	802	783	789	
919	841	800	852	
950	896	934	880	
1005	959	947	893	Cr-O st.
1016	978	954	927	
1069	999	963	931	
1122	1073	1080	979	
1170	1092	1090	1091	
1192	1130	1102	1094	
1227	1193	1146	1103	
1247	1199	1164	1134	
1271	1239	1261	1200	
1297	1298	1268	1242	
1352	1341	1337	1294	
1416	1408	1387	1352	
1446	1435	1396	1386	
1546				
1564				C=C st.
1602	1570	1620	1532	C=O st.
1687	1628	1671	1630	C=O st.
	2943	2929	2927	
	2964	2932	2956	
	2967	2948	3108	
	3000	2952	3131	
	3093	3098	3136	
	3137	3118		
3552			3577	O-H st.

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p). [b] Frequencies in cm^{-1}.

Table S2: Product Band Positions of the Merged Jet Codeposition of $CrCl_2O_2$ with Cyclopentadiene Compared to the Literature Spectrum of Cyclopent-3-enone, and the Calculated[a] Spectrum of 1,3-Cyclopentanedione

$CrCl_2O_2$ + cyclopentadiene (exp. freq.[b])		cyclopent-3-enone (lit. exp. freq.[c])	1,3-cyclopentanedione (calcd. freq.)
lower temp.	higher temp.		
		458	458
			516
			556
			573
		617	
627		623	
		644	
		674	664
703			
	727		
736	736		
	746		
769		766	765
772		772	780
	783	782	
	793		
822	822		
828			
856			
	864		862
			869
927	927		
	931		
	946		
954		957	
		983	971
	1018		
	1031		
1048			
			1079
			1122
1131	1131	1135	1130
1165	1165	1167	
	1176		1143
	1190		1202
1208			
	1214		1223
1219			
	1223		
	1235		1246
1263	1263	1266	
	1278		1271

	1302		
1352	1352		1358
1402	1404	1410	1411
	1428		1426
1496	1507		
1576	1576	1602	
1612	1612	1617	
	1743		1747
1759	1759		
1766	1766	1765	
1776		1774	
		1782	1783
		1902	
		2800	
2864	2864	2915	
		2921	
		2929	2941
		2934	2945
		2938	2958
		3074	2991
		3081	3005
		3089	3012
		3530	

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p). [b] Frequencies in cm^{-1}. [c] Vapor phase, see ref. 49.

Table S3: Product Band Positions Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Cyclopentene and the Calculated[a] Bands of $CrCl_2O$-cyclopentanone and a Representative $CrCl_2O$-cyclopentenol Complex

$CrCl_2O_2$ + cyclopentene (exp. freq.[b])	$CrCl_2O$-cyclopentanone (calcd. freq.)	$CrCl_2O$-cyclopentenol (calcd. freq.)
	417	429
447	445	435
484	502	470
737	576	525
778	595	602
787	712	655
799	807	785
825	823	818
846	870	855
858	889	880
916	937	892
928	946	938
952	999	1005
1007	1080	1036
1026	1138	1093
1072	1151	1112
1081	1162	1135
1157	1179	1181
1194	1231	1196
1207	1265	1208
1248	1279	1274
1304	1307	1284
1341	1309	1293
1366	1397	1343
1390	1404	1446
1437	1460	1452
1590	1472	1471
1678	1662	1684
	2923	2920
	2923	2922
	2948	2945
	2956	2962
	3001	2974
	3004	3011
	3007	3115
3554	3013	3590

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p). [b] Frequencies in cm^{-1}.

Table S4: Product Band Positions Arising from the Irradiation of Matrices Containing $CrCl_2O_2$ and Cyclopentane and the Calculated[a] Bands of $CrCl_2O$-cyclopentanol

$CrCl_2O_2$ + cyclopentane (exp. freq.[b])	$CrCl_2O$-cyclopentanol (calcd. freq.)	calcd. intensity (km/mol)
	403	65.5
447	425	77.9
	428	67.3
	538	14.3
	566	12.9
723	659	3.4
754	776	45.3
779	785	1.9
813	839	4.0
833	871	2.2
872	879	2.0
933	902	9.2
946	929	59.4
958	984	0.4
1016	1006	0.3
1050	1062	2.4
1006	1091	187.7
1141	1129	107.5
1163	1154	9.5
1171	1194	14.5
1189	1200	1.1
1245	1230	28.9
	1267	0.7
	1278	0.2
1301	1299	0.5
	1310	0.7
1326	1320	0.6
1338	1375	58.8
1356	1442	9.7
1439	1449	6.3
1470	1461	6.5
	1477	4.3
	2924	13.4
	2944	13.3
	2948	27.9
	2953	16.6
	2992	18.7
	2996	24.7
	3004	19.1
	3008	13.0
	3034	7.0
3573	3627	47.0

[a] Calculated values have been scaled by a factor of 0.97, B3LYP/6-311G++(d,2p). [b] Frequencies in cm^{-1}.

Table S5: Calculated (B3LYP/6-311G++(d,2p)) Relative Energies[a] of Possible Products (Uncomplexed and Complexed) from the $CrCl_2O_2$ and Cyclopentene Reaction

Uncomplexed Products	Rel. Energies	Complexed Products	Rel. Energies
$CrCl_2O$ + cyclopentene oxide	22.3 kcal/mol	$CrCl_2O$-cyclopentyl + HCl	16.0 kcal/mol
$CrCl_2O$ + 3,6-dihydro-2H-pyran	17.7	$CrCl_2O$-3,6-dihydro-2H-pyran	-8.4
$CrCl_2O$ + 3,4-dihydro-2H-pyran	13.5	$CrCl_2O$-3,4-dihydro-2H-pyran	-8.4
$CrCl_2O$ + 3-cyclopentenol	12.0	$CrCl_2O$-3-cyclopentenol	-13.0
$CrCl_2O$ + 2-cyclopentenol	11.7	$CrCl_2O$-1-cyclopentenol	-13.6
$CrCl_2O$ + 1-cyclopentenol	8.1	$CrCl_2O$-2-cyclopentenol	-16.7
$CrCl_2O$ + cyclopentanone	-5.8	$CrCl_2O$-cyclopentanone	-32.4

[a] Energies relative to the reactants, $CrCl_2O_2$ + cyclopentene.

Table S6: Calculated (B3LYP/6-311G++(d,2p)) Relative Energies[a] of Possible Products (Uncomplexed and Complexed) from the $CrCl_2O_2$ and Cyclopentane Reaction

Uncomplexed Products	Rel. Energies	Complexed Products	Rel. Energies
$CrCl_2O$ + tetrahydropyran	21.1 kcal/mol	$CrCl_2O$-cyclopentyl + HCl	15.4 kcal/mol
$CrCl_2O$ + cyclopentanol	10.7	$CrCl_2O$-tetrahydropyran	-6.6
		$CrCl_2O$-cyclopentanol	-15.9

[a] Energies relative to the reactants, $CrCl_2O_2$ + cyclopentane.

Table S7: Calculated (B3LYP/6-311G++(d,2p)) Relative Energies[a] of Possible Products (Uncomplexed and Complexed) from the $CrCl_2O_2$ and Cyclopropane Reaction

Uncomplexed Products	Rel. Energies	Complexed Products	Rel. Energies
$CrCl_2O$ + oxetane	18.3 kcal/mol	$CrCl_2O$-formaldehyde + ethene	-3.8 kcal/mol
$CrCl_2O$ + cyclopropanol	12.9	$CrCl_2O$-methoxyethene	-7.5
$CrCl_2O$ + methoxyethene	10.7	$CrCl_2O$-oxetane	-11.4
$CrCl_2O$ + 2-propenol	6.2	$CrCl_2O$-cyclopropanol	-11.9
$CrCl_2O$ + propanal	-9.2	$CrCl_2O$-2-propenol	-18.7
$CrCl_2O$ + acetone	-17.5	$CrCl_2O$-propanal	-33.5
		$CrCl_2O$-acetone	-43.4

[a] Energies relative to the reactants, $CrCl_2O_2$ + cyclopropane.

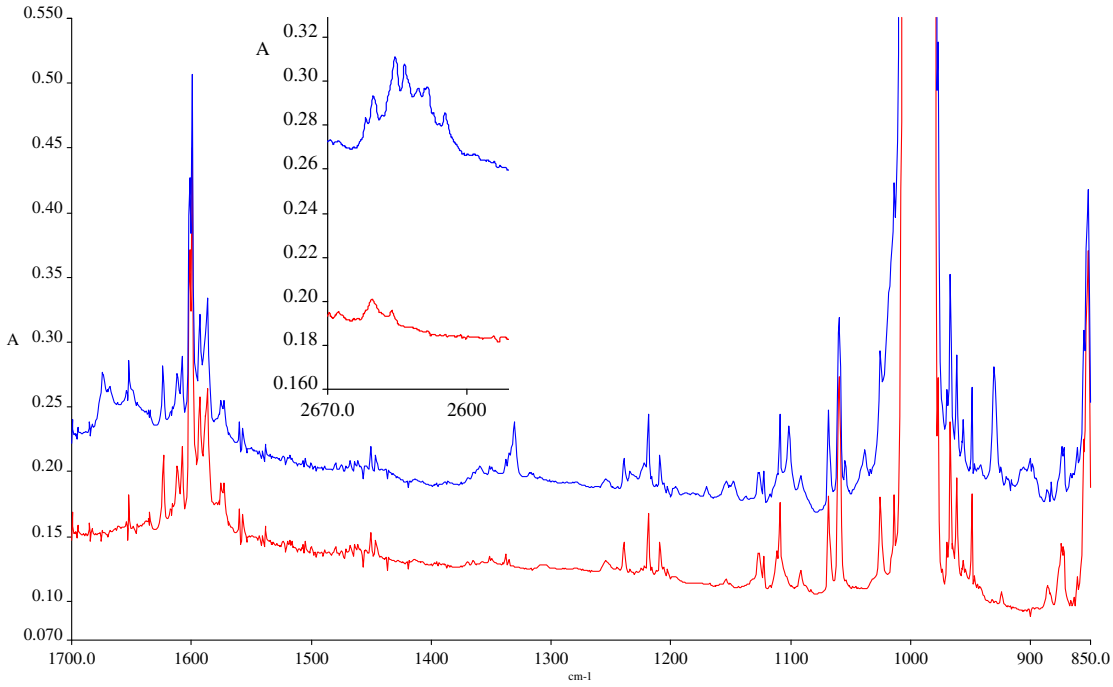
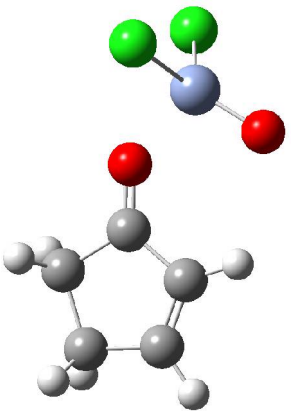


Figure S1: Infrared spectra of a matrix formed by the twin jet deposition of a sample of $Ar/CrCl_2O_2$ = 400 with a sample of Ar/cyclopentene-d_8 = 400. The lower trace is before irradiation, while the upper trace is after 1.0 h of irradiation with light of $\lambda > 300$ nm. The upper spectra is of the O-D stretch region.



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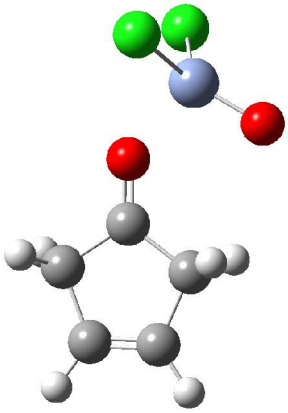

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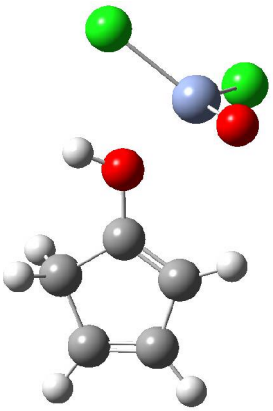

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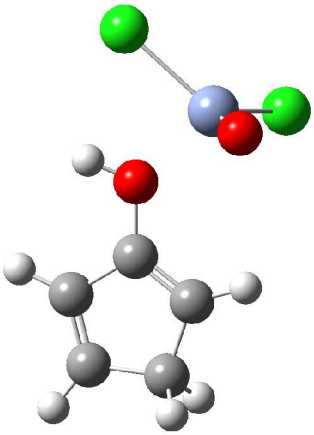

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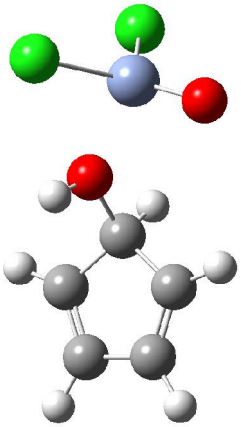

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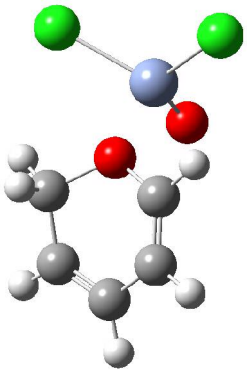

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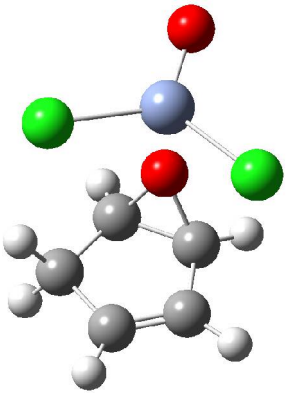
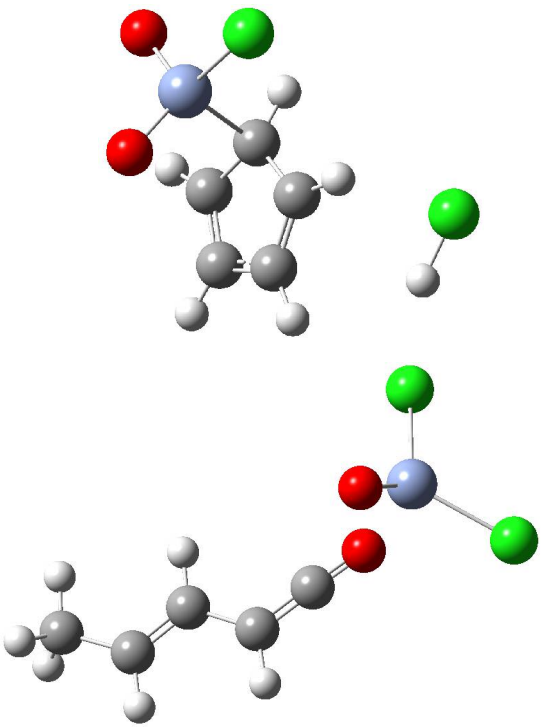


(g)



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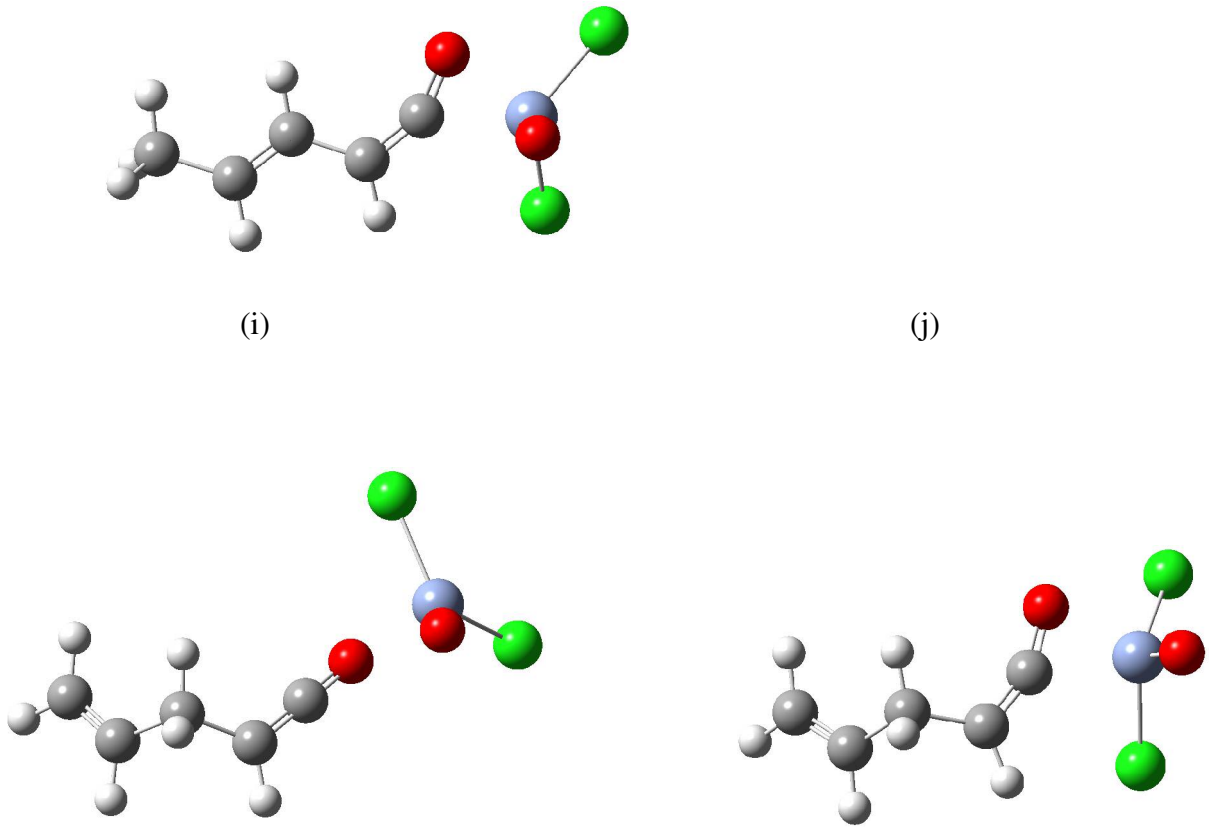
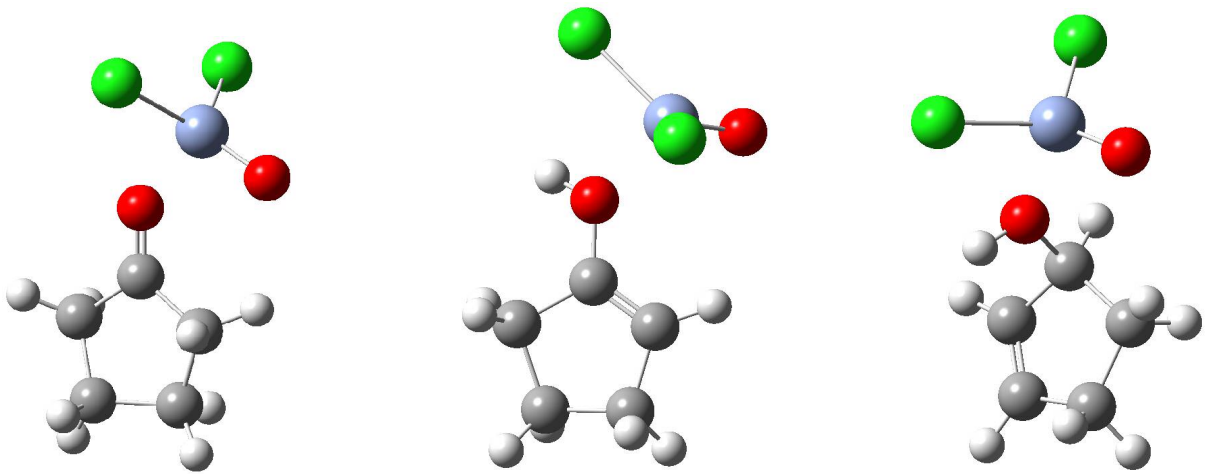


Figure S2. Calculated structures of the complexes of the photochemical reaction of $CrCl_2O_2$ and cyclopentadiene: (a) $CrCl_2O$-cyclopent-2-enone, (b) $CrCl_2O$-cyclopent-3-enone, (c) $CrCl_2O$-cyclopenta-1,3-dienol, (d) $CrCl_2O$-cyclopenta-1,4-dienol, (e) $CrCl_2O$-cyclopenta-1,4-dienol, (f) $CrCl_2O$-cyclopenta-2,4-dienol, (g) $CrCl_2O$-cyclopentadienyl + HCl, (h) $CrCl_2O$-2H-pyran, (i) $CrCl_2O$-penta-1,3-diene-1-one, η^1 (end on), (j) $CrCl_2O$-penta-1,3-diene-1-one, η^2 (C=O), (k) $CrCl_2O$-penta-1,4-diene-1-one, η^1 (end on), and (l) $CrCl_2O$-penta-1,4-diene-1-one, η^2 (C=O).



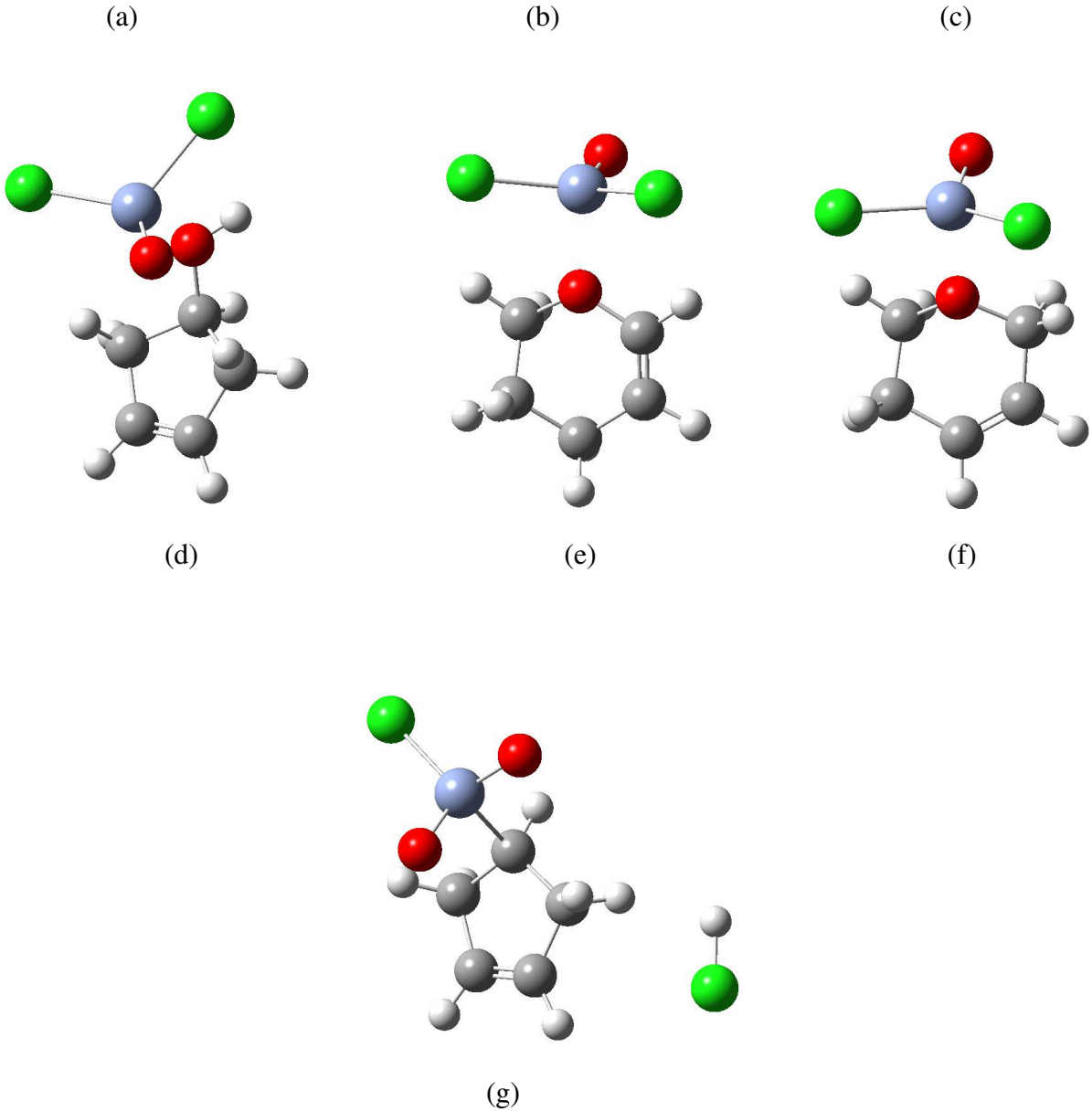
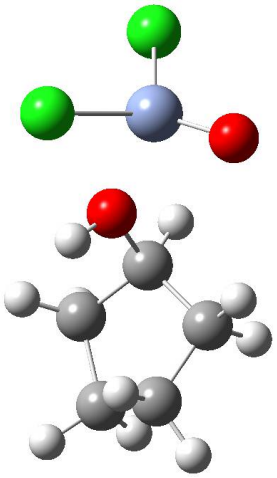


Figure S3. Calculated structures of the complexes of the photochemical reaction of $CrCl_2O_2$ and cyclopentene: (a) $CrCl_2O$-cyclopentanone, (b) $CrCl_2O$-1-cyclopentenol, (c) $CrCl_2O$-2-cyclopentenol, (d) $CrCl_2O$-3-cyclopentenol, (e) $CrCl_2O$-3,4-dihydro-2H-pyran, (f) $CrCl_2O$-3,6-dihydro-2H-pyran, and (g) $CrCl_2O$-cyclopentenyl + HCl.



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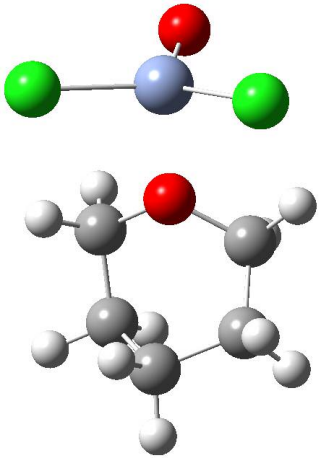

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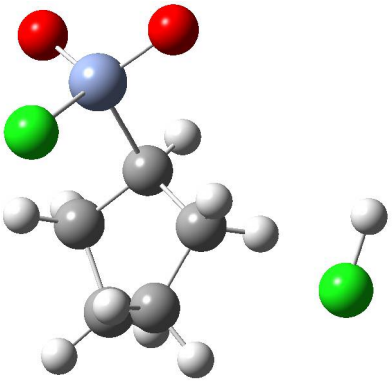
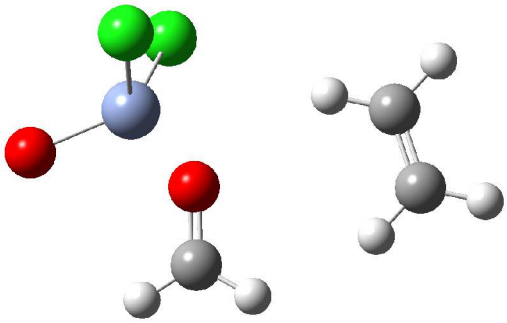


(c)

Figure S4. Calculated structures of the complexes of the photochemical reaction of $CrCl_2O_2$ and cyclopentane: (a) $CrCl_2O$-cyclopentanol, (b) $CrCl_2O$-tetrahydropyran, and (c) $CrCl_2O$-cyclopentyl + HCl.



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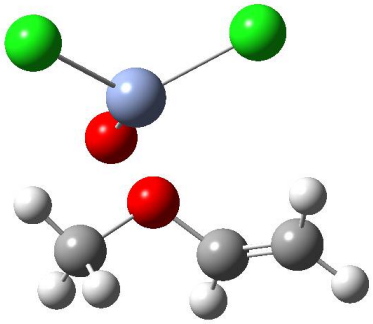

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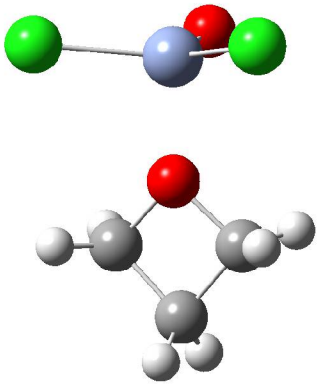

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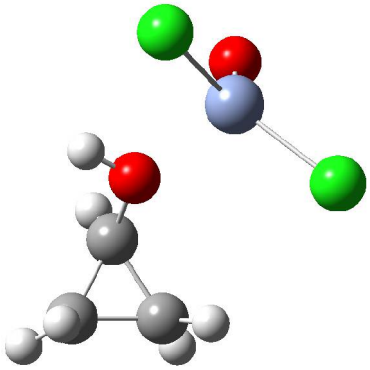

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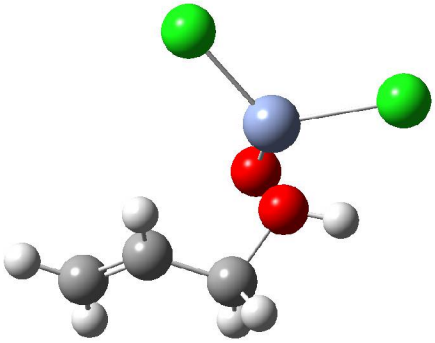

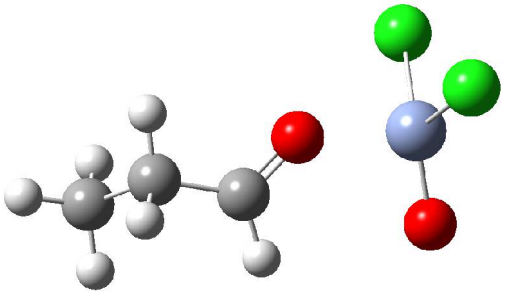

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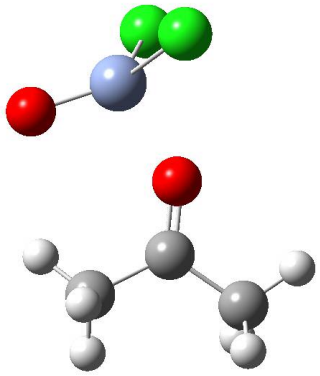

(g)

Figure S5. Calculated structures of the complexes of the photochemical reaction of $CrCl_2O_2$ and cyclopropane: (a) $CrCl_2O$-formaldehyde + ethene, (b) $CrCl_2O$-methoxyethene, (c) $CrCl_2O$-oetane, (d) $CrCl_2O$-cyclopropanol, (e) $CrCl_2O$-2-propenol, (f) $CrCl_2O$-propanal, and (g) $CrCl_2O$-acetone.

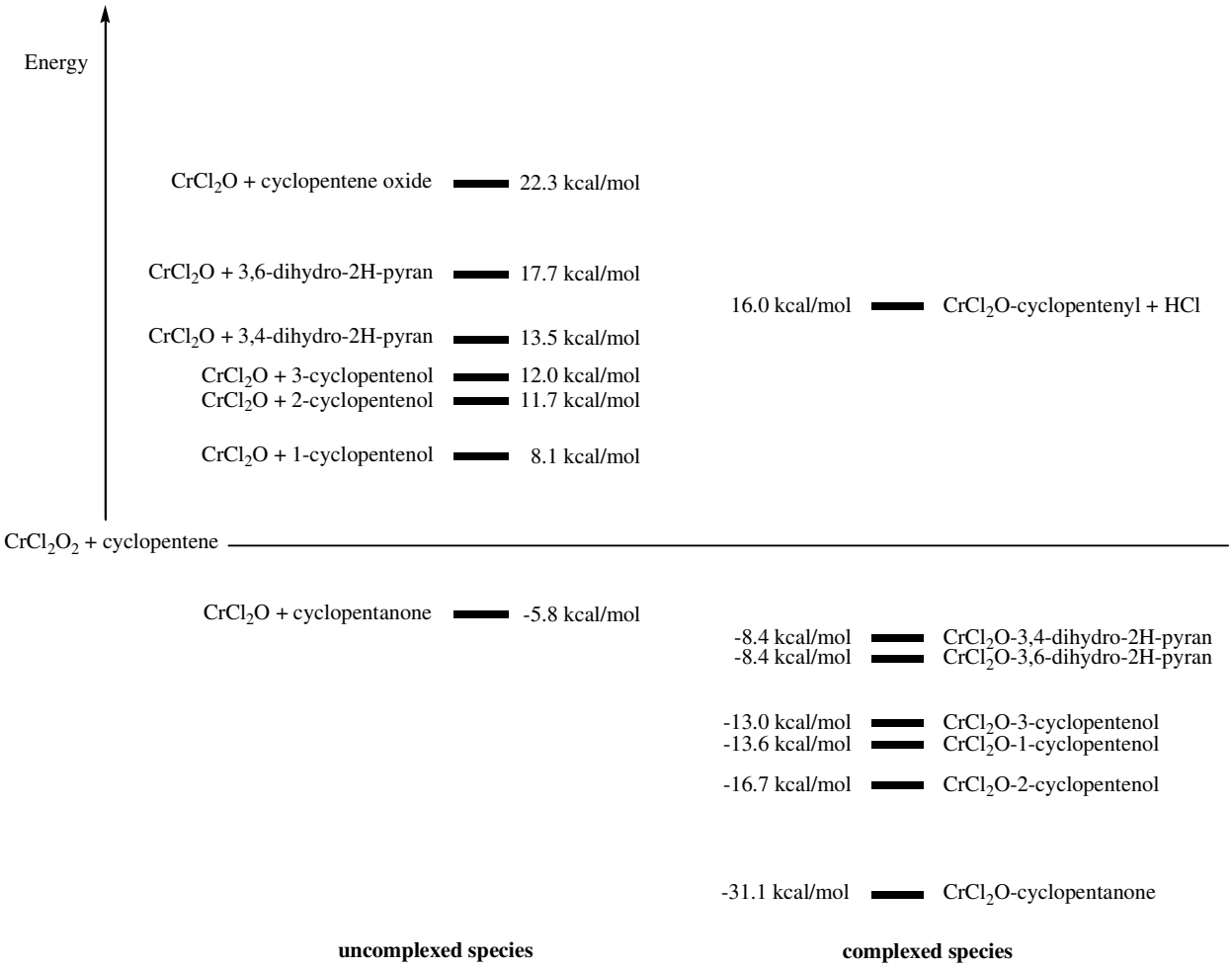

Figure S6. Relative energies of the uncomplexed and complexed products as compared to $CrCl_2O_2$ and cyclopentene.