DFT Study of the Geometry and Energy Order of the Low Singlet and Triplet States of d^4-[η^5-CpMo(CO)$_2$X] 16-Electron Complexes (X = Halogen, CN, H, and CH_3)

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Supplemental Material

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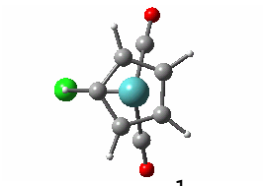
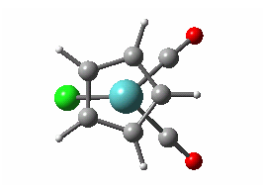
Table 1: Calculated relative energy of the four low energy states of $[CpMo(CO)_2Cl]$.[a]

	$^1A'$-a	$^1A'$-b	$^3A''$	$^3A'$
B3LYP	-502.760735218	-502.791271888	-502.789220264	-502.755459029
BPW91	-502.810859649	-502.842767664	-502.836310719	-502.802813784
CCSD(T)	-501.2147222	-501.2486338	-501.2432942	-501.2097279
CASSCF	-499.3984796787	-499.4388678795	-499.3969683084	-499.4267392467

CpMo(CO)2Cl: Geometry, Energy, Electronic State	CpMo(CO)2Cl: Cartesian Coordinates
 **Singlet: ^{1}A′-a** d^4 = $(1a')^2(1a'')^2$ E(B3LYP)= -502.760735218 **CCSD(T)=** **[-501.2147222]**	42 0.000000 0.258511 0.000000 6 -1.242106 -1.874137 0.000000 6 -1.587301 -1.133969 1.158730 6 -2.161059 0.100277 0.718270 1 -0.724539 -2.823084 0.000000 1 -1.451929 -1.448488 2.183520 1 -2.567974 0.874264 1.356900 6 -1.587301 -1.133969 -1.158730 6 -2.161059 0.100277 -0.718270 1 -1.451929 -1.448488 -2.183520 1 -2.567974 0.874264 -1.356900 17 1.817660 -1.311817 0.000000 6 0.864514 1.128527 -1.609200 8 1.245181 1.595110 -2.595710 6 0.864514 1.128527 1.609200 8 1.245181 1.595110 2.595710 xx -1.83681 -0.596395 0.0 xx -2.161059 0.100277 0.0
 **Singlet: ^{1}A′-b** d^4 = $(1a')^2(1a'')^2$ E(B3LYP)= -502.791271888 **CCSD(T)=** **[-501.2486338]**	42 0.000000 0.149216 0.000000 6 -0.676399 -2.087142 0.000000 6 -1.252065 -1.469041 1.148335 6 -1.252065 -1.469041 -1.148335 6 -2.252895 -0.540896 0.702550 6 -2.252895 -0.540896 -0.702550 1 -1.038876 -1.718830 2.178736 1 -1.038876 -1.718830 -2.178736 1 -2.867190 0.082073 1.339483 1 -2.867190 0.082073 -1.339483 1 0.058415 -2.879644 0.000000 6 1.539802 -0.097299 1.207570 6 1.539802 -0.097299 -1.207570 8 2.442260 -0.283391 -1.912958 8 2.442260 -0.283391 1.912958 17 -0.216597 2.484120 0.000000 xx -1.449627 -1.32876 0. xx -2.252895 -0.540896 0.

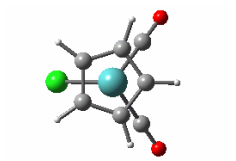
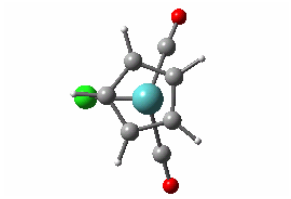
CpMo(CO)2Cl: Geometry, Energy, Electronic State	CpMo(CO)2Cl: Cartesian Coordinates
 **Triplet: ^{3}A″** d^4 = $(1a')^2(1a'')^1(2a')^1$ E(B3LYP)= -502.789220264 **CCSD(T)= [-501.2432942]**	42 0.000000 0.123179 0.000000 6 -0.666990 -2.145793 0.000000 1 -1.713683 -2.417652 0.000000 6 1.472328 -1.664907 0.714250 6 0.157154 -1.964729 1.154115 6 1.472328 -1.664907 -0.714250 6 0.157154 -1.964729 -1.154115 1 2.323592 -1.455475 1.347681 1 -0.164251 -2.053392 2.183057 1 2.323592 -1.455475 -1.347681 1 -0.164251 -2.053392 -2.183057 17 1.595280 1.854688 0.000000 6 -1.212865 0.857841 -1.428566 8 -1.920139 1.179279 -2.285171 6 -1.212865 0.857841 1.428566 8 -1.920139 1.179279 2.285171 xx 0.453418 -1.89394 0.0 xx 1.472328 -1.664907 0.0
 **Triplet: ^{3}A′** d^4 = $(1a'')^2(1a')^1(2a')^1$ E(B3LYP)= -502.755459029 **CCSD(T)= [-501.2097279]**	42 0.000000 0.195720 0.000000 6 -0.761364 -2.082557 0.000000 6 -1.274772 -1.436805 1.152917 6 -2.124829 -0.361284 0.714362 1 -0.039057 -2.887196 0.000000 1 -1.070218 -1.712630 2.178405 1 -2.708381 0.288446 1.352101 6 -1.274772 -1.436805 -1.152917 6 -2.124829 -0.361284 -0.714362 1 -1.070218 -1.712630 -2.178405 1 -2.708381 0.288446 -1.352101 17 2.310281 -0.611996 0.000000 6 0.418630 1.194966 -1.750144 8 0.541332 1.728254 -2.764582 6 0.418630 1.194966 1.750144 8 0.541332 1.728254 2.764582 xx -1.576720 -1.053241 0. xx -2.124829 -0.361284 0.

Table 2: Absolute energies of the four low energy states in $CpMo(CO)_2X$ defined by the specified configuration of the d^4 electrons. These are the energies used to give the relative energy of each species in Table 1 in the Text. All values obtained at the B3LYP level, and do not include ZPE term corrections.

X	$^1A'$-a	$^1A'$-b	$^3A'$	$^3A''$
	$(1a')^2(1a'')^2$	$(1a')^2(2a')^2$	$(1a'')^2(1a')^1(2a')^1$	$(1a')^2(1a'')^1(2a')^1$
F	-587.6282803	-587.655622305	-587.613558094	-587.654195778
Cl	-502.760735218	-502.791271888	-502.755459029	-502.7892203
Br	-500.978003536	-501.007598998	-500.97415889	-501.005878808
I	-499.194722509	-499.223068399	-499.192516636	-499.221420404
CN	-580.614575705	-580.6202788	-580.605747397	-580.625067946
CN- C_1	-580.625042901			
H	-488.3620328	-488.342729823	-488.340381133	-488.357100299
CH_3	-527.664882398	-527.668980921	-527.649134757	-527.674923459
CH_3 Agostic	-527.682163274			