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

Supporting Information

Spectroscopic characterization of heteronuclear iron-chromium carbonyl cluster anions

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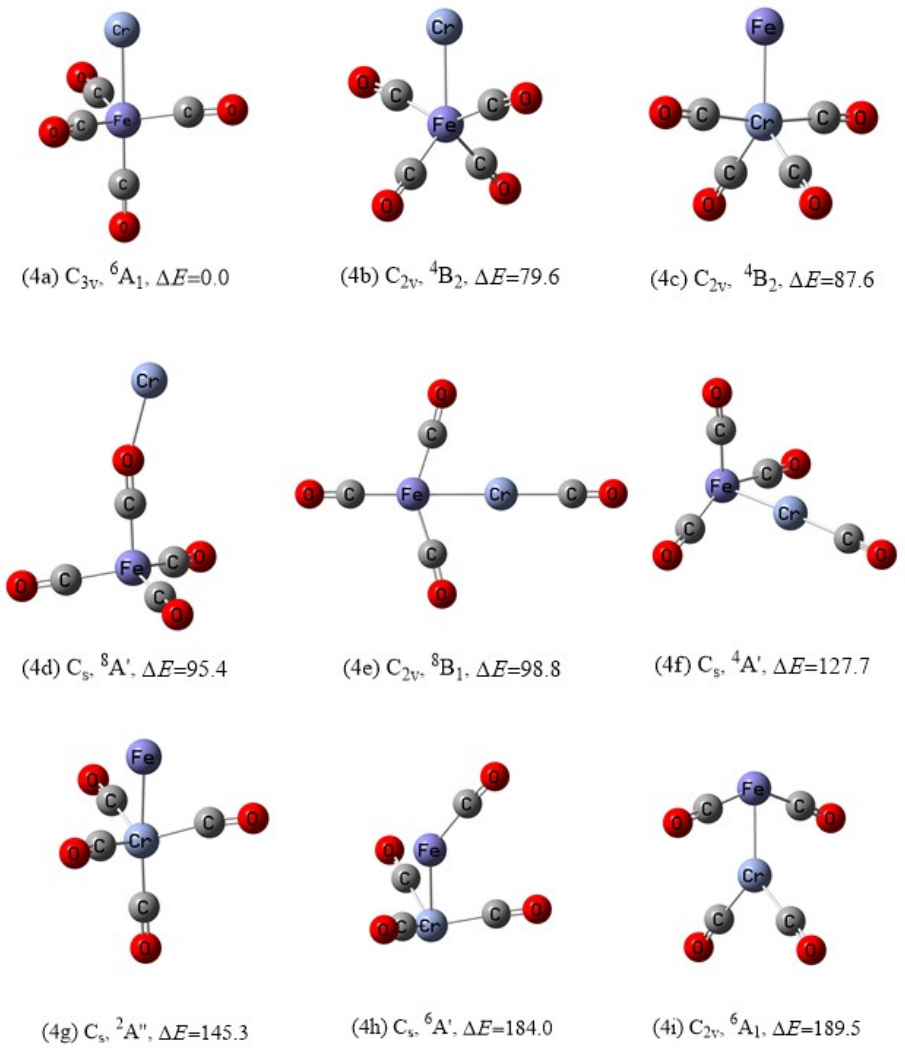


Fig. S1 Optimized structures of the $CrFe(CO)_4^-$ isomers calculated at the B3LYP/6-311+G(d) level, including the symmetry, electronic state, and the relative energy with ZPE correction of each isomer (ΔE in kJ/mol).

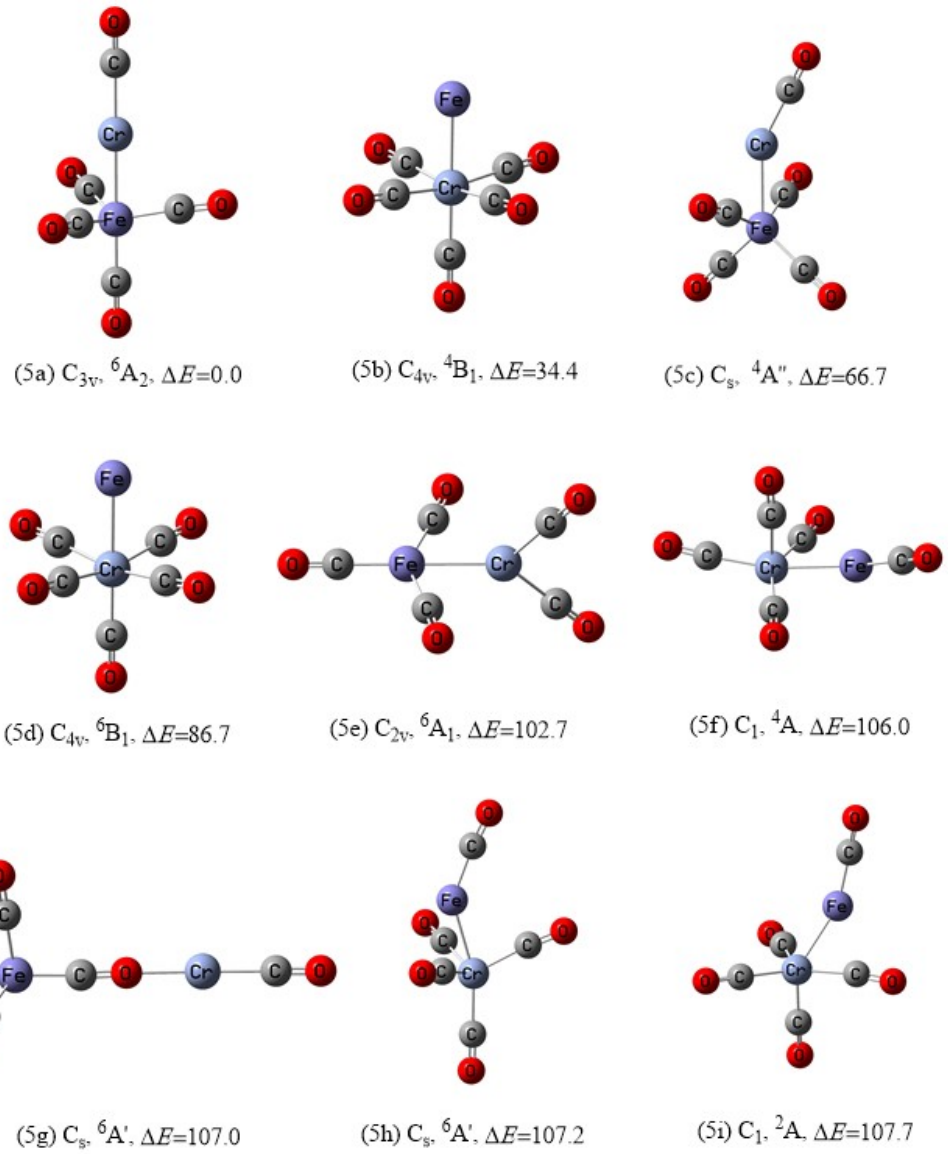


Fig. S2 Optimized structures of the nine lowest-energy isomers of the $CrFe(CO)_5^-$ cluster anions calculated at the B3LYP/6-311+G(d) level, including the symmetry, electronic state, and the relative energy with ZPE correction of each isomer (ΔE in kJ/mol).

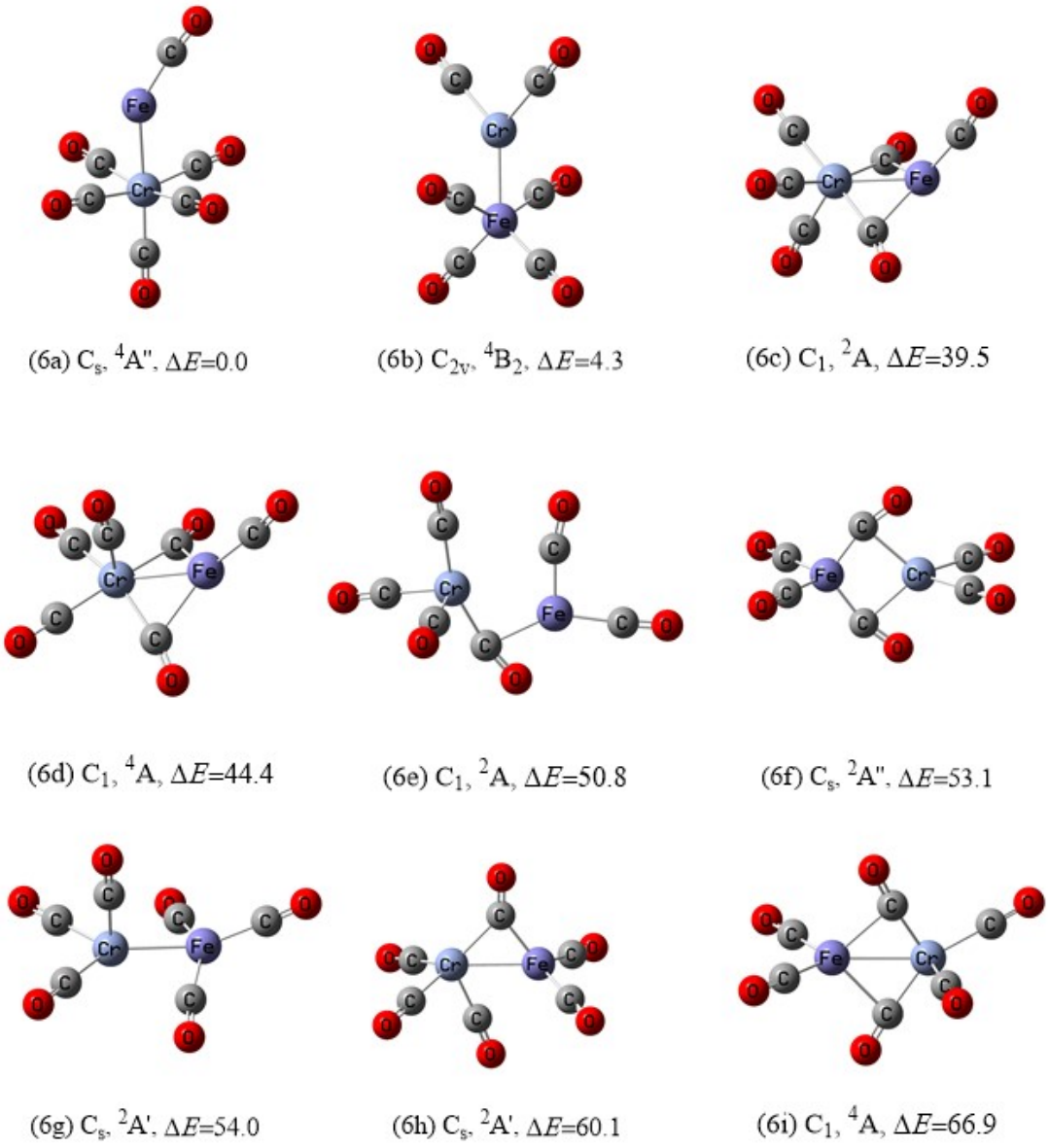


Fig. S3 Optimized structures of the nine lowest-energy isomers of the $CrFe(CO)_6^-$ cluster anions calculated at the B3LYP/6-311+G(d) level, including the symmetry, electronic state, and the relative energy with ZPE correction of each isomer (ΔE in kJ/mol).

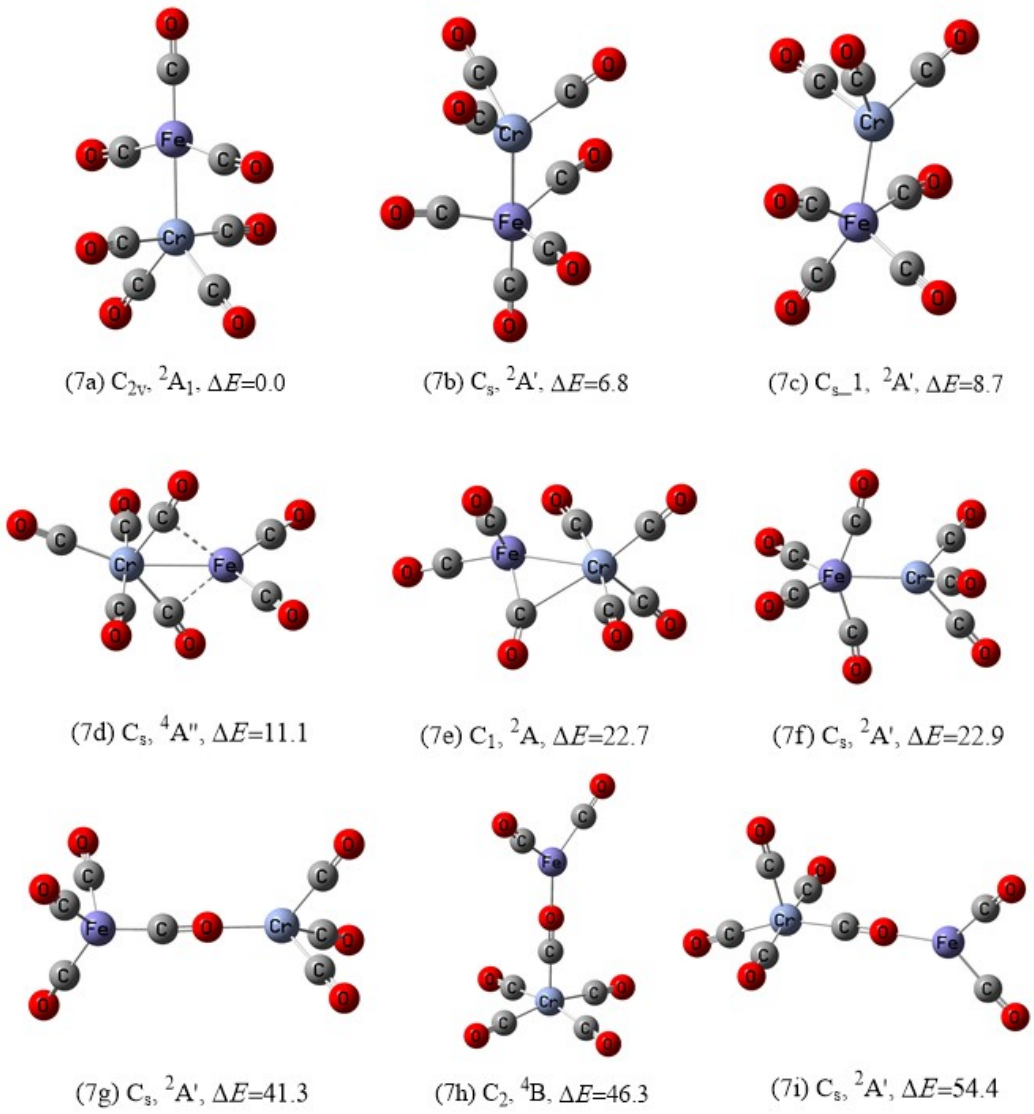


Fig. S4 Optimized structures of the nine lowest-energy isomers of the $CrFe(CO)_7^-$ cluster anions calculated at the B3LYP/6-311+G(d) level, including the symmetry, electronic state, and the relative energy with ZPE correction of each isomer (ΔE in kJ/mol).

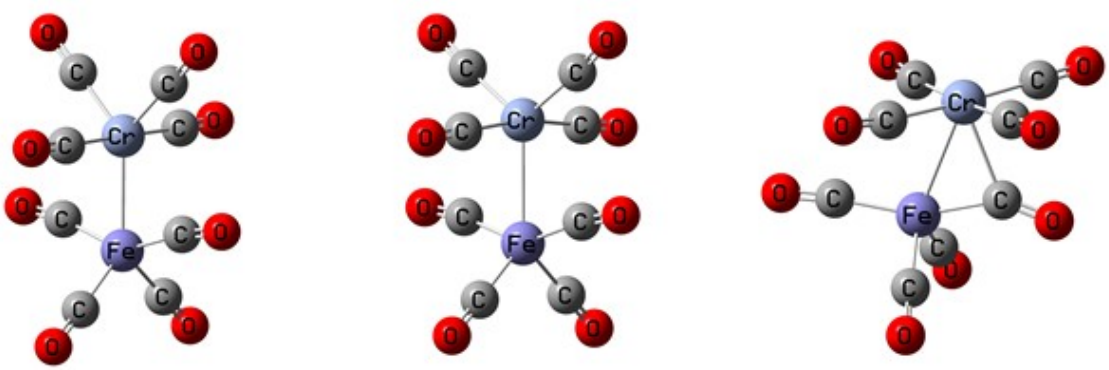
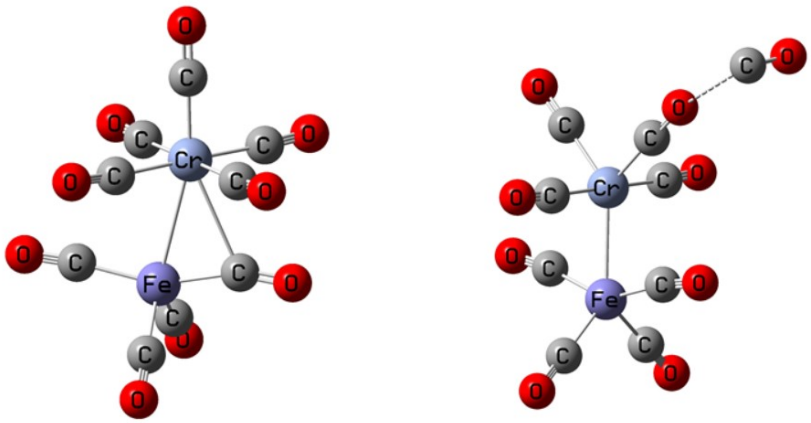


Fig. S5 Optimized structures of the $CrFe(CO)_8^-$ isomers calculated at the B3LYP/6-311+G(d) level, including the symmetry, electronic state, and the relative energy with ZPE correction of each isomer (ΔE in kJ/mol).



(9a) C_s, ^{2}A", ΔE=0.0 (9b) C_1 ^{2}A, ΔE=85.9

Fig. S6 Optimized structures of the $CrFe(CO)_9^-$ isomers calculated at the B3LYP/6-311+G(d) level, including the symmetry, electronic state, and the relative energy with ZPE correction of each isomer (ΔE in kJ/mol).

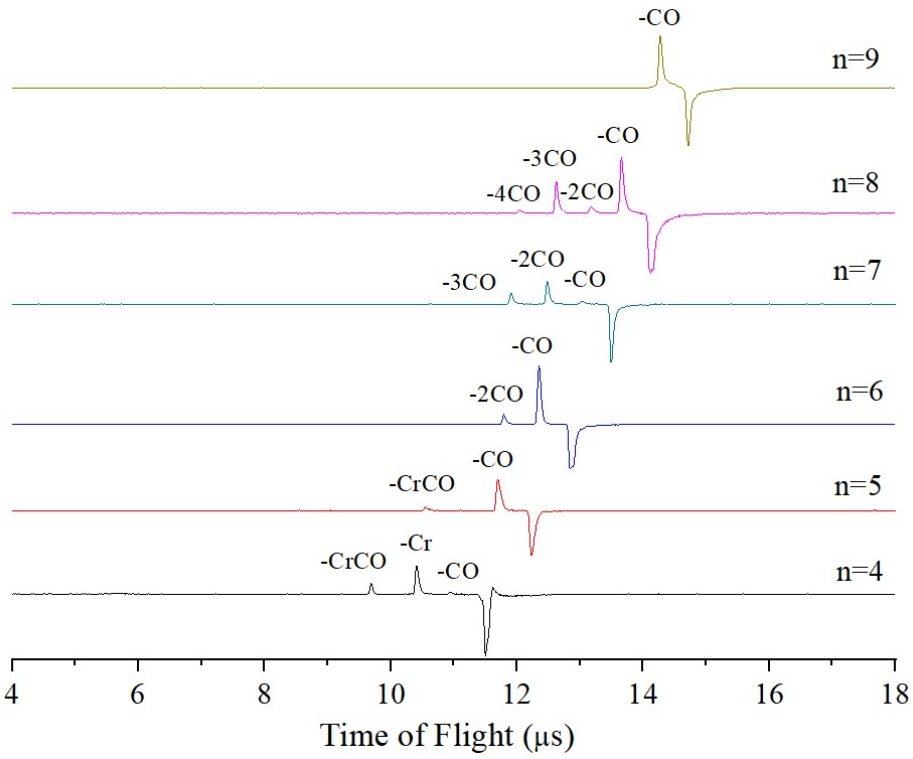
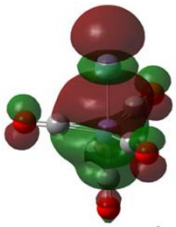
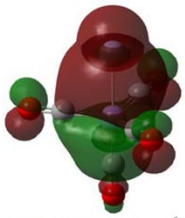


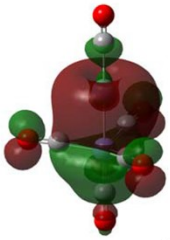
Fig. S7 The photo-fragmentation mass spectra of the $CrFe(CO)_n^-$ (n=4-9) cluster anions (difference in mass spectra for a selected anion recorded with and without the photodissociation laser). The negative peak demonstrates the depletion of the mass-selected anion, whereas the positive peaks show the produced fragment anions.



$CrFe(CO)_4^-$, C_{3v}, $^6A_1$
α–MO: SOMO-7



$CrFe(CO)_4^-$, C_{3v}, $^6A_1$
β–MO: HOMO-2



$CrFe(CO)_5^-$, C_{3v}, $^6A_2$
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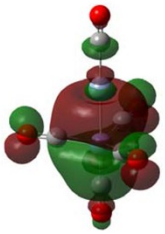

$CrFe(CO)_5^-$, C_{3v}, $^6A_2$
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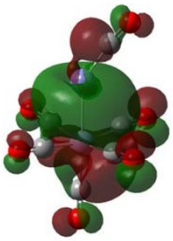

$CrFe(CO)_6^-$, C_s, $^4A''$
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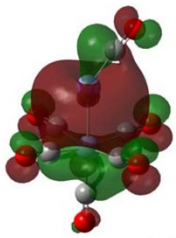
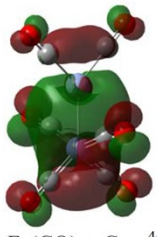
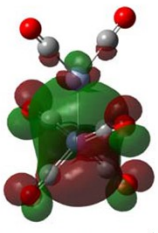


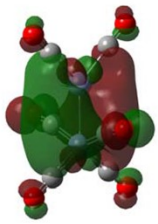
$CrFe(CO)_6^-$, C_s, $^4A''$
β–MO: HOMO



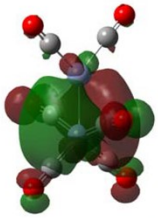
$CrFe(CO)_6^-$, C_{2v}, $^4B_2$
α–MO: SOMO-1



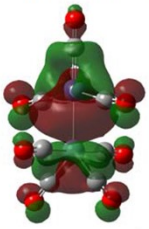
$CrFe(CO)_6^-$, C_{2v}, $^4B_2$
β–MO: HOMO-2



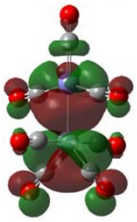
$CrFe(CO)_6^-$, C_{2v}, $^4B_2$
α–MO: SOMO



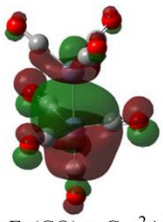
$CrFe(CO)_6^-$, C_{2v}, $^4B_2$
β–MO: HOMO-1



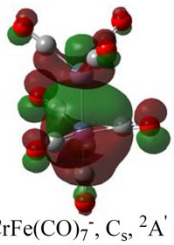
$CrFe(CO)_7^-$, C_{2v}, $^2A_1$
α–MO: SOMO-3



$CrFe(CO)_7^-$, C_{2v}, $^2A_1$
β–MO: HOMO-3



$CrFe(CO)_7^-$, C_s, $^2A'$
α–MO: SOMO-4



$CrFe(CO)_7^-$, C_s, $^2A'$
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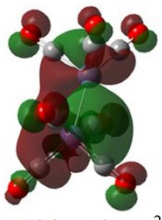
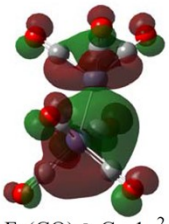
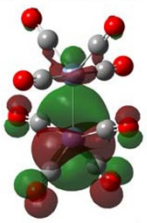


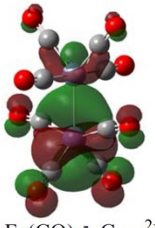
$CrFe(CO)_7^-$, C_s_1, $^2A'$
α–MO: SOMO-4



$CrFe(CO)_7^-$, C_s_1, $^2A'$
β–MO: HOMO-3



$CrFe(CO)_8^-$, C_{2v}, $^2B_1$
α–MO: SOMO-6



$CrFe(CO)_8^-$, C_{2v}, $^2B_1$
β–MO: HOMO-6

Fig. S8 The frontier bonding orbitals accounting for the Cr-Fe binding of the observed $CrFe(CO)_n^-$ (n = 4-8) cluster anions.

Table S1. Bonding characters of the most table isomer (9a) for the $CrFe(CO)_9^-$ anion calculated at the B3LYP/6-311+G(d) Levels .

Structures	Cr-Fe		NBO Group Charge		Natural Charge		NBO net spin[a] /e	
	R (Å)	WBI	$Fe(CO)_4$	$Cr(CO)_5$	Fe	Cr	Fe	Cr
$CrFe(CO)_9^-$ (*9a*)	2.914	0.28	-0.34	-0.66	-1.41	-2.49	1.01	0.01

[a] Net spin population on the Fe and Cr atoms.