Supporting Information for

Lead-Chromium Carbonyl Complexes Incorporated with Group 8 Metals: Synthesis, Reactivity, and Theoretical Calculations

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Table S1. Cyclic Voltammetry (CV) of $[Et_4N]_2[Fe_3(CO)_9\{PbFe(CO)_4\}_2]$ ($[Et_4N]_2$[**5**]), $[Et_4N]_2[Fe_3(CO)_9\{PbCr(CO)_5\}_2]$ ($[Et_4N]_2$[**6**]), $[Et_4N]_2[Ru_3(CO)_9\{PbCr(CO)_5\}_2]$ ($[Et_4N]_2$[**7**]), $Fe_3(CO)_{12}$, and $Ru_3(CO)_{12}$.[a]

compound	reduction processes			
	E_p^{ox}/V[b]	E_p^{red}/V[c]	$E_{1/2}$/V	ΔE/mV
$[Et_4N]_2$[**5**]	−1.138	−1.310	−1.224	172
	- [d]	−1.666		
	−1.997	−2.211	−2.104	214
$[Et_4N]_2$[**6**]	−1.377	−1.536	−1.457	159
	- [d]	−1.727		
	−2.055	−2.169	−2.112	114
$[Et_4N]_2$[**7**]	- [d]	−1.809		
	- [d]	−2.042		
	- [d]	−2.254		
$Fe_3(CO)_{12}$	−0.436	−0.481	−0.459	45
	−0.753	−1.014	−0.884	261
	- [d]	−2.080		
$Ru_3(CO)_{12}$	−0.632	−0.843	−0.738	211
	−0.919	−1.116	−1.018	197
	−1.952	−2.085	−2.019	133

[a] All potentials vs SCE in 0.1 M Bu_4NClO_4/MeCN. [b] E_p^{ox} = oxidative peak potential. [c] E_p^{red} = reductive peak potential. [d] Difficult to determine.

Figure S1. The equatorial plane of the structure of $[Fe_3(CO)_9\{PbFe(CO)_4\}_2]^{2-}$ (**5**), showing the disorder of the iron atoms.

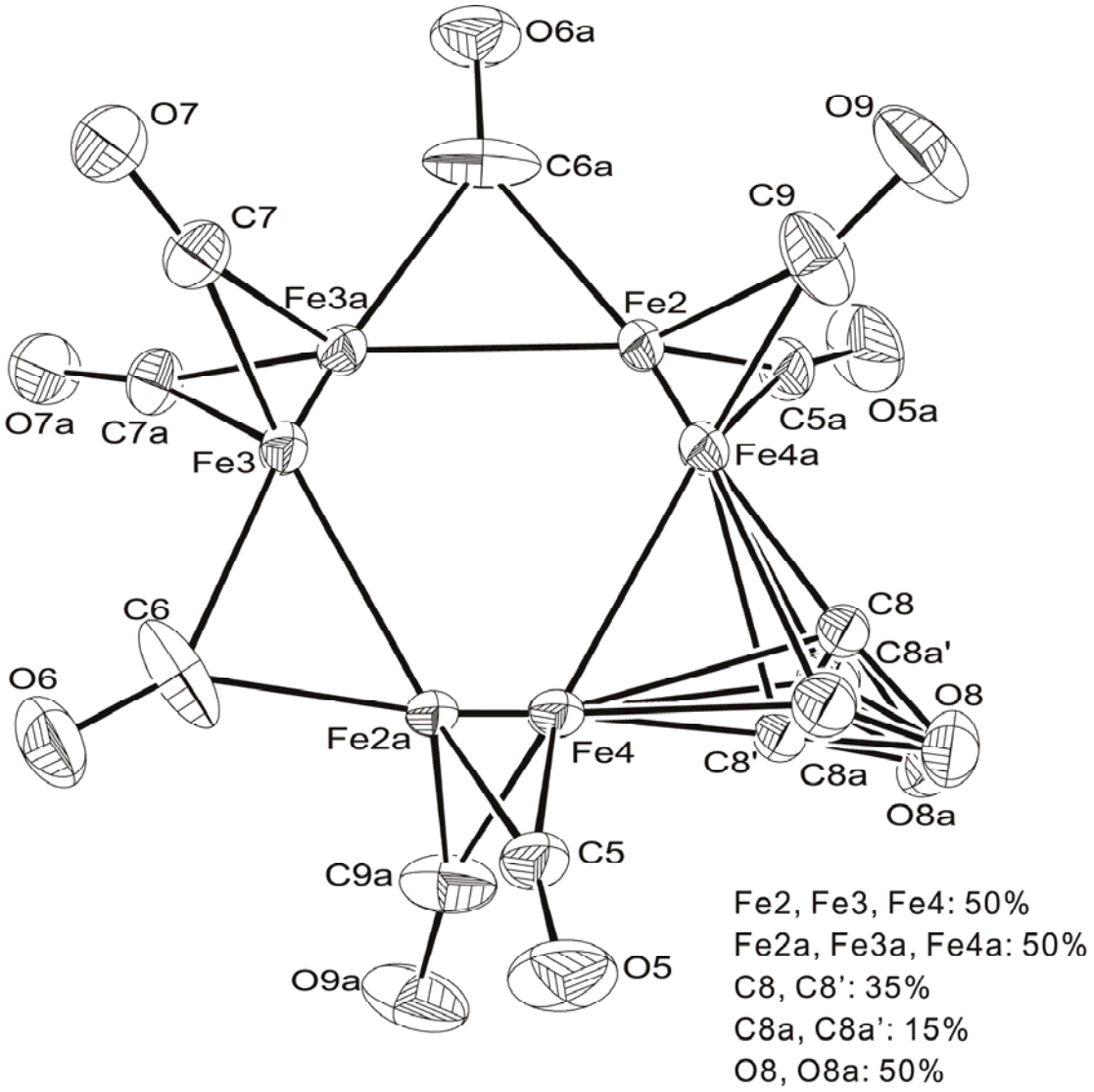
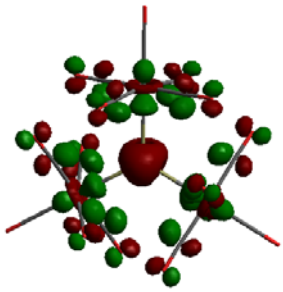
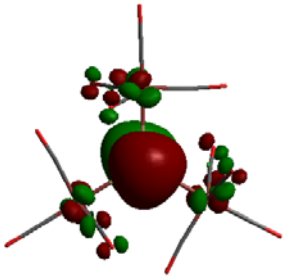
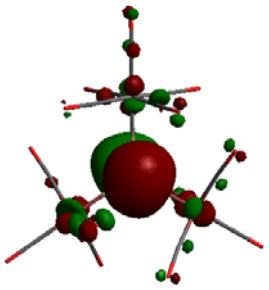
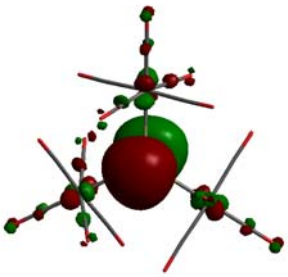
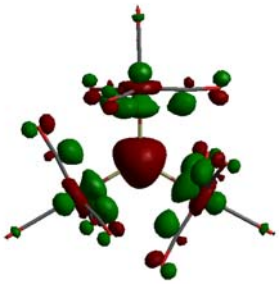
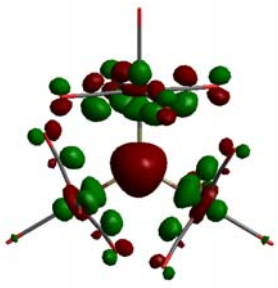
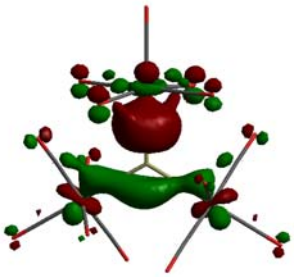
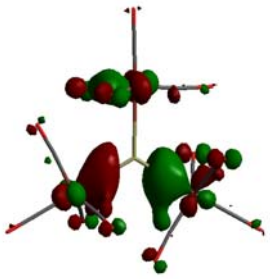
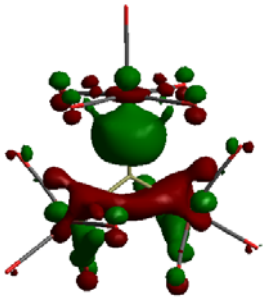
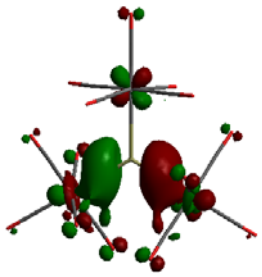
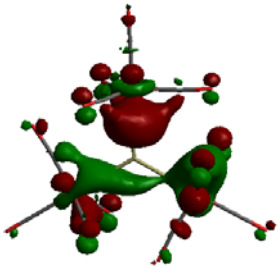
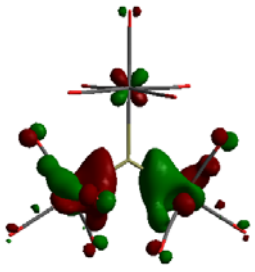
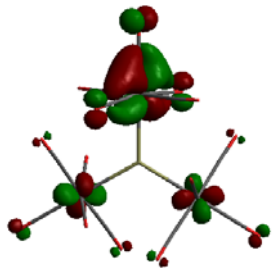
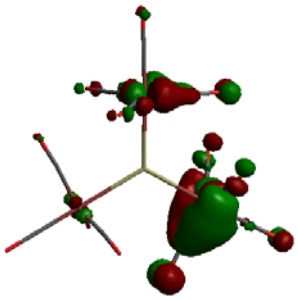
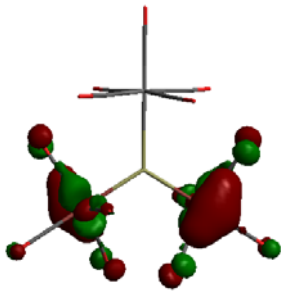
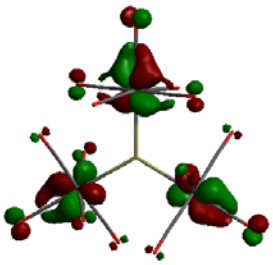
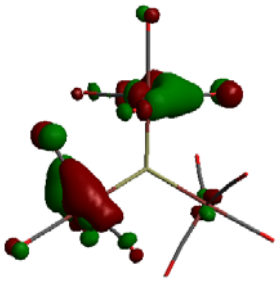
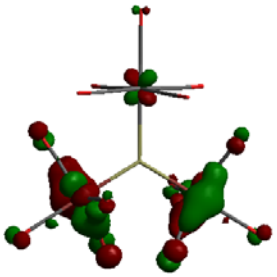
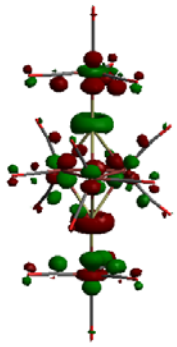
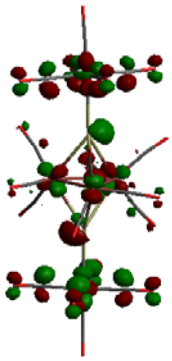
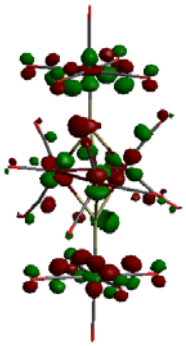
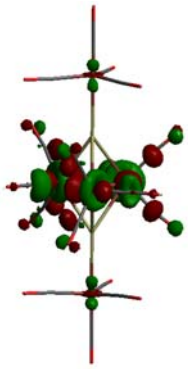
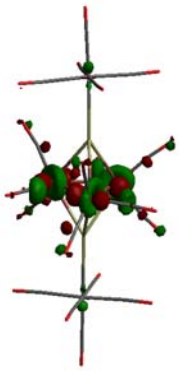
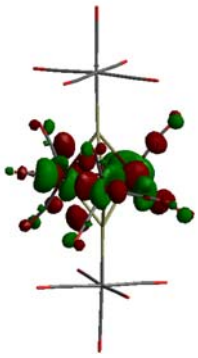
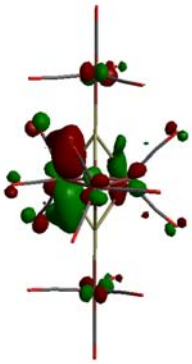
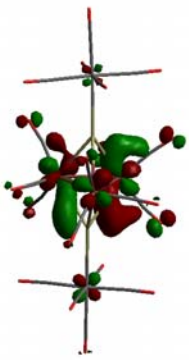
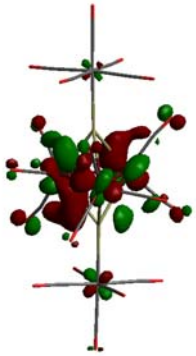
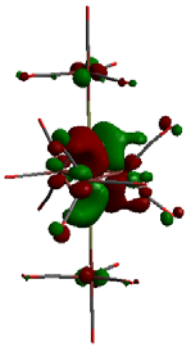
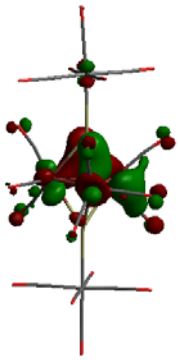
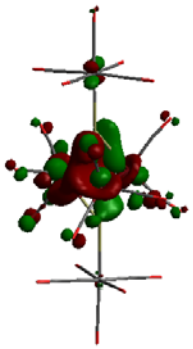
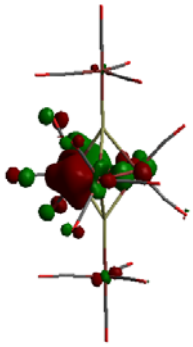
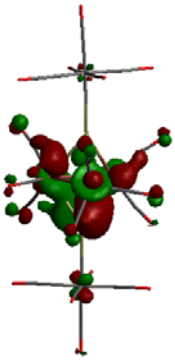
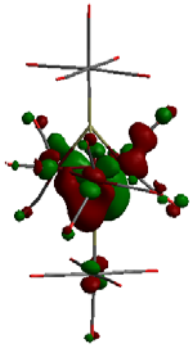
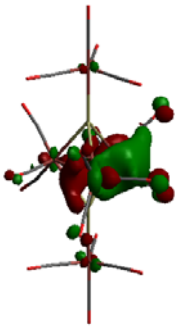
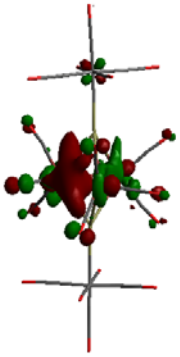
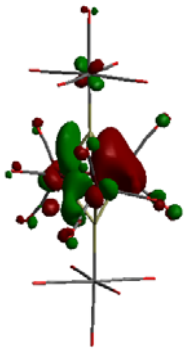


Figure S2. The spatial graphs (isovalue = 0.04~0.05) of the selected frontier molecular orbitals of complexes **1—3** and **5—7**.

1	2	3
		
LUMO+1, 3.57 eV	LUMO+1, 3.75 eV	LUMO+1, 3.62 eV
		
LUMO, 3.38 eV	LUMO, 3.63 eV	LUMO, 3.61 eV
		
HOMO, 0.36 eV	HOMO, 0.14 eV	HOMO, 0.32 eV
		
HOMO−1, 0.35 eV	HOMO−1, 0.13 eV	HOMO−1, 0.11 eV

 HOMO−2, −0.43 eV	 HOMO−2, 0.00 eV	 HOMO−2, 0.01 eV
 HOMO−3, −0.43 eV	 HOMO−3, −0.03 eV	 HOMO−3, −0.12 eV

5	6	7
		
LUMO+1, 3.02 eV	LUMO+1, 2.97 eV	LUMO+1, 2.89 eV
		
LUMO, 2.61 eV	LUMO, 2.75 eV	LUMO, 2.69 eV
		
HOMO, −0.69 eV	HOMO, −0.60 eV	HOMO, −0.68 eV
		
HOMO−1, −0.70 eV	HOMO−1, −0.62 eV	HOMO−1, −0.71 eV

 HOMO−2, −0.74 eV	 HOMO−2, −0.67 eV	 HOMO−2, −0.82 eV
 HOMO−3, −0.75 eV	 HOMO−3, −0.68 eV	 HOMO−3, −0.84 eV

Computational Details:

All calculations were performed via the density functional theory (DFT) with Becke's three-parameter (B3) exchange functional and the Lee-Yang-Parr (LYP) correlation functional (B3LYP) with LanL2DZ/6-31G(d) basis sets using the Gaussian 03 series of packages.

$[Pb\{Cr(CO)_5\}_3]^{2-}$ (**1**) (the optimized geometry)
G = −1962.649799 a.u.

	x	y	z
Pb	-0.001145	-0.000631	0.000996
Cr	2.724634	-0.768805	-0.000395
Cr	-0.696000	2.744097	0.000403
Cr	-2.029457	-1.974525	0.000213
C	2.212177	-2.411315	0.772596
C	2.346905	-1.436522	-1.720735
C	4.480813	-1.262353	-0.001183
C	3.145733	0.899714	-0.772979
C	2.753117	-0.005046	1.721689
C	0.071936	2.750376	-1.720181
C	0.982733	3.118404	0.774418
C	-1.142836	4.513079	-0.002609
C	-1.375878	2.388394	1.720846
C	-2.351050	2.273185	-0.773066
C	-3.195219	-0.708428	0.772487
C	-1.382518	-2.382983	1.721774
C	-3.330811	-3.251382	-0.001182
C	-0.788891	-3.165855	-0.773982
C	-2.422049	-1.315665	-1.720571
O	1.950232	-3.431674	1.263250
O	2.136794	-1.836901	-2.794086
O	5.608271	-1.579044	-0.001769
O	3.456277	1.906533	-1.263152
O	2.784287	0.442922	2.796362
O	0.522911	2.768405	-2.793829
O	1.998146	3.399517	1.264814
O	-1.429152	5.648622	-0.005220

O	-1.782879	2.191971	2.794354
O	-3.378358	2.036592	-1.261995
O	-3.947103	0.031179	1.260496
O	-1.009206	-2.636147	2.795588
O	-4.166043	-4.072394	-0.002728
O	-0.067440	-3.932202	-1.266635
O	-2.665656	-0.935919	-2.794313

$[Pb\{Fe(CO)_4\}_3]^{2-}$ (**2**) (the optimized geometry)
G = −1734.028340 a.u.

	x	y	z
Pb	-0.001406	-0.001179	0.002219
Fe	2.085452	-1.697252	0.002688
Fe	-2.512629	-0.960916	0.001690
Fe	0.431643	2.652471	-0.001940
O	4.404457	-3.461469	-0.022960
O	0.220690	-3.971483	0.025472
C	3.473979	-2.755326	-0.012423
C	2.489648	-0.882902	-1.514315
C	0.910300	-3.032216	0.016668
C	2.510709	-0.880533	1.512801
C	-4.140085	-1.592416	-0.021992
C	-2.012627	-1.735954	-1.507662
C	-2.032559	-1.744821	1.512815
C	-3.060727	0.730998	0.014681
O	0.795398	5.543587	-0.004586
C	0.651782	4.384333	-0.003583
C	-0.470715	2.605311	1.518215
C	-0.487292	2.604403	-1.512319
C	2.175058	2.300594	-0.011225
O	2.822717	-0.400595	-2.525045
O	2.856995	-0.395450	2.517645
O	-5.229834	-2.012710	-0.040218
O	-1.764277	-2.275225	-2.513820
O	-1.797564	-2.285392	2.521244
O	-3.519167	1.802245	0.022946
O	-1.050439	2.657262	2.531303

O	-1.077901	2.656070	-2.519072
O	3.333217	2.172661	-0.017322

$[Pb\{Cr(CO)_5\}\{Fe(CO)_4\}_2]^{2-}$ (**3**) (the optimized geometry)
G = −1810.236008 a.u.

	x	y	z
C	-4.528323	-0.034510	-0.003652
O	-5.699151	-0.042145	-0.006238
O	-2.576505	1.120081	2.825752
Cr	-2.704505	-0.021296	0.000200
C	-2.620614	-1.747201	0.765636
C	-2.645750	1.706336	-0.763262
C	-2.598001	0.704598	1.740485
C	-2.580625	-0.746189	-1.739607
Pb	0.123115	-0.000351	0.003229
O	-2.622645	-2.796089	1.262543
O	-2.664146	2.756188	-1.257732
O	-2.548814	-1.162029	-2.824460
Fe	1.525744	-2.305011	-0.015176
Fe	1.483792	2.329884	0.013916
C	0.132100	-3.008142	-0.852448
C	2.437369	-3.793383	0.036758
C	2.762782	-1.408296	-0.918213
C	1.424850	-2.087617	1.731631
C	1.360786	2.111380	-1.731969
C	2.376022	3.829460	-0.051230
C	0.086121	3.010324	0.862962
C	2.742587	1.454581	0.908119
O	1.307564	2.042225	-2.899500
O	-0.743272	-3.546996	-1.406801
O	3.047734	-4.788946	0.073786
O	3.624386	-0.907163	-1.523936
O	1.387168	-2.016134	2.899410
O	2.973349	4.832831	-0.094686
O	-0.794154	3.532580	1.425353
O	3.617101	0.968742	1.508002

The proposed structure $[BrPb\{Cr(CO)_5\}_2]^-$ (the optimized geometry)
G = −1322.868885 a.u.

	x	y	z
Pb	0.000000	0.282441	-0.000150
Br	-0.000461	3.049779	-0.000017
Cr	2.553480	-0.576020	0.006674
C	3.120125	1.013595	-0.870912
C	2.774988	0.287759	1.680811
C	4.273358	-1.238268	0.043194
C	1.901146	-2.124015	0.869602
C	2.219792	-1.360069	-1.682671
C	-2.217926	-1.363958	1.680638
C	-1.901635	-2.122081	-0.873864
C	-4.273170	-1.238607	-0.042554
C	-3.118972	1.011471	0.875012
O	3.508246	1.956140	-1.414011
O	2.938329	0.801904	2.705272
O	5.357645	-1.654352	0.068019
O	1.526159	-3.085480	1.397740
O	2.046665	-1.842156	-2.722639
O	-2.043885	-1.848227	2.719441
O	-1.526978	-3.082147	-1.404780
O	-5.357453	-1.654732	-0.066862
O	-3.506338	1.952927	1.420551
Cr	-2.553324	-0.576240	-0.006593
C	-2.776884	0.291160	-1.678624
O	-2.941460	0.807362	-2.701838

$[Pb_2Br_2Cr_4(CO)_{18}]^{2-}$ (**4**) (the optimized geometry)
G = −2418.956404 a.u.

	x	y	z
Pb	-2.443181	0.411096	-0.000063
Br	-2.920015	3.154988	-0.000282
Cr	-4.920366	-0.714108	0.000112
Cr	-0.000010	-0.000149	-1.482560
Cr	-0.000020	0.000090	1.482497
C	-5.443591	0.528274	1.336993

C	-5.443453	0.527682	-1.337366
C	-6.580560	-1.498271	0.000233
C	-4.315657	-1.895711	-1.349174
C	-4.315733	-1.895052	1.350011
Pb	2.443171	-0.411044	0.000011
C	-1.200058	0.325206	-2.844177
C	-0.455191	-1.843877	-1.478215
C	1.200077	-0.325822	-2.844069
C	0.455147	1.843578	-1.478606
C	1.200038	-0.325284	2.844099
C	0.455176	1.843810	1.478136
C	-1.200074	0.325784	2.844027
C	-0.455203	-1.843631	1.478531
O	-5.812835	1.257625	2.155556
O	-5.812600	1.256696	-2.156274
O	-7.635852	-1.992339	0.000307
O	-3.997271	-2.630816	-2.185902
O	-3.997394	-2.629728	2.187131
Br	2.920014	-3.154942	0.000060
Cr	4.920384	0.714102	0.000040
O	-1.912528	0.518650	-3.746341
O	-0.741977	-2.959444	-1.577886
O	1.912572	-0.519472	-3.746168
O	0.741911	2.959132	-1.578520
O	1.912512	-0.518737	3.746258
O	0.741968	2.959381	1.577776
O	-1.912540	0.519474	3.746143
O	-0.741967	-2.959186	1.578427
C	5.443600	-0.528110	-1.337000
C	5.443428	-0.527885	1.337354
C	6.580595	1.498223	0.000064
C	4.315684	1.895504	1.349507
C	4.315806	1.895264	-1.349695
O	5.812842	-1.257363	-2.155650
O	5.812558	-1.257007	2.156171
O	7.635894	1.992278	0.000067
O	3.997335	2.630475	2.186366

O	3.997494	2.630074	-2.186708

$[Fe_3(CO)_9\{PbFe(CO)_4\}_2]^{2-}$ (**5**) (the optimized geometry)
G = −2551.186765 a.u.

	x	y	z
Pb	-2.053561	-0.000585	0.004343
Fe	0.001688	-1.317887	-0.993519
Fe	0.002867	-0.218850	1.642198
Fe	0.001767	1.517312	-0.629188
Pb	2.054486	-0.000644	-0.001188
C	-1.287288	-1.778202	-2.096525
C	1.287711	-1.795799	-2.090956
C	-0.003498	-2.688439	0.098667
C	-1.281649	-0.968217	2.579208
C	1.295904	-0.914642	2.606184
C	-0.022781	1.409366	2.291648
C	1.280136	2.712142	-0.475268
C	-1.288090	2.701853	-0.488951
C	0.014348	1.254061	-2.362640
C	-4.544266	0.751402	-1.620480
C	-4.558388	-1.760295	0.158247
C	-6.418046	0.009039	-0.017956
C	-4.562259	1.041838	1.436550
O	-2.020327	-2.208422	-2.894394
O	2.020077	-2.242369	-2.880427
O	-0.007034	-3.697570	0.680325
O	-2.019859	-1.461918	3.334325
O	2.029464	-1.370415	3.389391
O	-0.041463	2.414463	2.880357
O	2.006894	3.623085	-0.445856
O	-2.021689	3.607893	-0.474895
O	0.023676	1.254092	-3.527560
O	-4.529935	1.240577	-2.675705
O	-4.555065	-2.918708	0.264566
O	-7.581452	0.009359	-0.023254
O	-4.563452	1.719328	2.382229
C	4.561024	-1.756299	0.192330

C	6.419463	0.013161	-0.014142
C	4.557957	1.063503	1.420726
C	4.546354	0.717958	-1.634691
O	4.558616	-2.912426	0.321898
O	7.582920	0.016513	-0.018442
O	4.553884	1.754040	2.356882
O	4.533748	1.183925	-2.700630
Fe	4.669569	0.008493	-0.007598
Fe	-4.668497	0.008419	-0.008083

$[Fe_3(CO)_9\{PbCr(CO)_5\}_2]^{2-}$ (**6**) (the optimized geometry)
G = −2703.606615 a.u.

	x	y	z
Pb	2.086131	0.070404	0.038254
Fe	0.028989	-1.100436	-1.166763
Fe	-0.013747	1.627919	-0.389835
Fe	-0.010811	-0.408452	1.566766
Cr	4.845872	-0.070132	-0.017642
Pb	-2.084622	0.032596	-0.060945
C	1.362992	-2.178716	-1.533398
C	-1.201468	-2.323555	-1.433143
C	-0.023935	-0.189910	-2.662274
C	1.311394	2.582217	-1.029404
C	-1.219251	2.468559	-1.347356
C	-0.213327	2.406219	1.164843
C	-1.389861	-0.325574	2.648541
C	1.164306	0.017804	2.797167
C	0.180540	-2.147304	1.485589
C	4.915782	0.247783	1.849596
C	4.660135	-1.926800	0.321898
C	6.666515	-0.228463	-0.112998
C	4.669257	-0.350733	-1.883856
C	4.955467	1.801448	-0.297257
Cr	-4.841647	-0.078261	0.012563
O	2.127661	-2.981432	-1.899508
O	-1.896338	-3.224547	-1.691820
O	-0.053552	0.262610	-3.736772

O	2.053291	3.398318	-1.414350
O	-1.911761	3.161100	-1.980842
O	-0.348015	3.094964	2.097685
O	-2.181719	-0.351742	3.507214
O	1.828987	0.277795	3.719428
O	0.301477	-3.299417	1.624011
O	5.028103	0.445999	2.984936
O	4.603744	-3.059720	0.553897
O	7.827281	-0.330975	-0.177104
O	4.606132	-0.509254	-3.029543
O	5.098344	2.940636	-0.447247
C	-4.787091	-1.078505	-1.595605
C	-4.928028	1.518019	-1.005605
C	-6.669858	-0.153218	0.059320
C	-4.781809	0.965471	1.595219
C	-4.672975	-1.669258	1.030670
O	-4.811421	-1.671924	-2.590035
O	-5.060035	2.488717	-1.622907
O	-7.836025	-0.192780	0.081124
O	-4.802439	1.623643	2.547575
O	-4.615351	-2.646023	1.650075

The proposed structure $[Cr(CO)_5]^{2-}$ (the optimized geometry)
G = −652.959964 a.u.

	x	y	z
Cr	-0.000305	-0.000430	-0.000679
O	0.007723	-1.796068	-2.434779
C	0.003123	-1.088083	-1.476173
O	-0.002622	3.009270	-0.318527
C	-0.001470	1.823921	-0.194184
O	3.053263	0.015891	0.002490
C	1.867715	0.007836	0.001448
O	-3.053736	0.010179	-0.005424
C	-1.868338	0.004917	-0.004084
O	-0.002953	-1.237089	2.759244
C	-0.002041	-0.749782	1.671703

The proposed structure $[Fe(CO)_4]^{2-}$ (the optimized geometry)
G = −576.754423 a.u.

	x	y	z
C	-0.753879	-0.254259	1.554045
C	-0.528223	-1.237911	-1.112166
C	-0.453851	1.568952	-0.617144
C	1.736086	-0.076569	0.175081
Fe	0.000534	0.000091	-0.000120
O	-1.269658	-0.427794	2.616352
O	-0.889669	-2.084448	-1.871796
O	-0.764784	2.641179	-1.039006
O	2.922278	-0.129392	0.294979

$[Ru_3(CO)_9\{PbCr(CO)_5\}_2]^{2-}$ (**7**) (the optimized geometry)
G = −2615.105906 a.u.

	x	y	z
Pb	-2.181913	-0.035544	0.013857
Ru	-0.016563	1.602230	-0.771567
Ru	-0.025595	-1.463975	-0.966979
Ru	0.044720	-0.102383	1.772615
Cr	-4.944660	-0.004276	-0.012350
Pb	2.180818	0.066225	-0.011366
C	0.169978	1.421376	-2.651053
C	-1.545594	2.765282	-0.689618
C	1.300777	2.957784	-0.441378
C	-1.195374	-1.718062	-2.464202
C	-0.491739	-2.947311	0.119455
C	1.562960	-2.183032	-1.784967
C	-1.486789	-0.593520	2.828768
C	0.377883	1.594286	2.550775
C	1.338752	-1.173710	2.697078
C	-4.893820	-1.530700	-1.129267
C	-4.818222	1.113574	-1.536480
C	-6.772641	0.066600	-0.062885
C	-4.836927	1.493321	1.143769
C	-4.986383	-1.163847	1.486045
Cr	4.938718	-0.044110	-0.025667

O	0.286449	1.417286	-3.807884
O	-2.341553	3.615774	-0.714228
O	1.984202	3.890695	-0.315044
O	-1.832885	-1.958965	-3.405811
O	-0.766315	-3.922019	0.691860
O	2.372178	-2.795052	-2.359428
O	-2.259256	-0.867353	3.657625
O	0.579298	2.586094	3.123554
O	2.045623	-1.812844	3.363829
O	-4.907364	-2.475827	-1.800034
O	-4.790609	1.782566	-2.482089
O	-7.938240	0.115012	-0.096875
O	-4.809329	2.401065	1.863264
O	-5.079695	-1.890429	2.383146
C	5.021393	1.811523	-0.390905
C	4.868422	0.333978	1.827588
C	6.764559	-0.169482	-0.006408
C	4.757862	-1.898204	0.325640
C	4.858017	-0.369346	-1.890757
O	5.134651	2.940892	-0.623823
O	4.863804	0.577658	2.960783
O	7.928707	-0.250936	0.007579
O	4.694755	-3.034272	0.542306
O	4.855697	-0.543844	-3.035991

The proposed structure $[Pb\{Cr(CO)_5\}\{Ru(CO)_4\}_2]^{2-}$ (the optimized geometry)
G = −1751.201078 a.u.

	x	y	z
C	0.000000	0.000000	0.000000
O	1.170856	0.000000	0.000000
O	-1.965550	3.047099	0.000000
Cr	-1.823869	0.000332	0.001291
C	-1.898195	0.062904	-1.886099
C	-1.892203	-0.060404	1.888797
C	-1.938948	1.885325	0.021591
C	-1.939177	-1.884879	-0.019463
Pb	-4.651566	-0.001711	0.004819

O	-1.890422	0.130584	-3.044738
O	-1.879561	-0.125372	3.047524
O	-1.965880	-3.046642	0.001364
C	-4.639047	-1.922122	-2.463163
C	-6.941105	-1.402301	-3.536416
C	-7.279954	-1.395434	-0.968998
C	-5.943476	0.812782	-2.584801
C	-5.899145	-0.824744	2.606417
C	-6.929273	1.372742	3.564164
C	-4.636104	1.923666	2.474102
C	-7.282462	1.370652	1.000958
O	-5.842895	-1.932873	2.980088
O	-3.758958	-2.634062	-2.750446
O	-7.545045	-1.743758	-4.476483
O	-8.143468	-1.773110	-0.281901
O	-5.908841	1.922422	-2.955932
O	-7.533032	1.705742	4.507577
O	-3.760497	2.644724	2.752145
O	-8.155112	1.740847	0.321171
Ru	-6.027429	0.875244	2.154121
Ru	-6.039092	-0.888650	-2.132299

$Ru_3(CO)_{12}$ (the optimized geometry)
G = −1641.861724 a.u.

	x	y	z
Ru	-1.405596	-0.954423	-0.000403
Ru	1.527902	-0.740707	-0.000972
Ru	-0.124282	1.690677	0.001462
C	-1.318896	-0.987142	1.966029
O	-1.401692	-1.094639	3.107669
C	-1.406890	-0.863881	-1.966862
O	-1.542455	-0.896667	-3.107976
C	-3.253600	-0.360463	0.054282
O	-4.355344	-0.033718	0.091391
C	-1.553456	-2.890001	-0.051657
O	-1.669169	-4.033478	-0.085162
C	1.517153	-0.654515	1.965788

O	1.658318	-0.668906	3.106602
C	1.446994	-0.788985	-1.967676
O	1.547138	-0.880849	-3.109291
C	1.959572	-2.633764	0.051979
O	2.242321	-3.747762	0.088697
C	3.268747	0.118068	-0.056346
O	4.311620	0.600929	-0.093223
C	-0.190480	1.632962	1.967993
O	-0.228900	1.757233	3.110332
C	-0.049619	1.641621	-1.965284
O	0.000506	1.774728	-3.106171
C	1.302862	3.006745	0.049069
O	2.127941	3.806794	0.081720
C	-1.733817	2.777092	-0.048995
O	-2.670842	3.442525	-0.083804