Supplementary Information

Table SI1 Frontier orbital energies and compositions for $Re(Cp)(CO)_2Xe$, bold marks the HOMO orbital.

Orbital	Energy /eV	Re *d* character /%	Xe character /%
63*a*'	-2.500	38.74	9.32
34*a*"	**-4.857**	**55.43**	**3.18**
62*a*'	-5.065	65.24	2.75
61*a*'	-5.400	56.6	0.71
33*a*"	-7.100	16.08	0.09
60*a*'	-7.359	17.85	3.37
32*a*"	-9.060	0.92	90.83
59*a*'	-9.087	2.16	88.02
58*a*'	-9.544	3.75	19.21
31*a*"	-9.579	2.32	0.40
57*a*'	-9.640	6.53	43.12
30*a*"	-9.807	0.70	98.37
56*a*'	-9.824	5.96	90.82
29*a*"	-9.861	5.02	91.43
55*a*'	-9.974	1.67	14.64
28*a*"	-10.006	7.83	0.27
54*a*'	-10.155	5.42	1.05
53*a*'	-10.579	7.65	5.81
27*a*"	-10.705	12.68	0.30
52*a*'	-11.043	0.55	5.61
26*a*"	-12.883	10.04	0.09
51*a*'	-13.386	2.96	0.78
47*a*'	-20.760	0.37	98.33

Table SI2 Frontier orbital energies and compositions for Re(Cp)(CO)(PF_3)Xe, bold marks the HOMO orbital.

Orbital	Energy /eV	Re *d* character /%	Xe character /%
111*a*	-2.628	40.69	9.51
110*a*	**-5.045**	**56.77**	**3.48**
109*a*	-5.272	66.90	3.07
108*a*	-5.653	59.23	0.71
107*a*	-7.274	16.75	0.24
106*a*	-7.523	18.12	3.45
105*a*	-8.976	15.80	7.57
104*a*	-9.173	1.43	90.15
103*a*	-9.218	1.98	83.33
102*a*	-9.598	0.11	1.26
101*a*	-9.717	4.76	50.17
100*a*	-9.832	2.66	7.73
99*a*	-9.885	3.58	1.51
98*a*	-9.947	2.70	4.30
97*a*	-9.964	0.54	0.66
96*a*	-9.992	4.76	5.82
95*a*	-10.079	1.74	11.50
94*a*	-10.171	2.85	3.43
93*a*	-10.597	3.94	0.17
92*a*	-10.747	7.94	4.83
91*a*	-10.983	0.11	0.43
90*a*	-11.005	0.23	0.14
89*a*	-11.043	3.25	5.94
88*a*	-12.363	4.31	0.69
87*a*	-12.992	0.39	0.15
86*a*	-13.025	0.36	0.00
85*a*	-13.352	5.11	0.66
78*a*	-20.866	0.38	98.23

Geometry Optimized Structures:

1. $Re(Cp)(CO)_3$

Atom	X	Y	Z (Angstrom)
1.Re	-0.131323	-0.075179	0.000000
2.C	1.211095	-0.206170	1.364285
3.C	0.037973	1.835946	0.000000
4.C	1.211095	-0.206170	-1.364285
5.O	0.058825	3.005644	0.000000
6.O	1.982374	-0.338451	2.233584
7.O	1.982374	-0.338451	-2.233584
8.H	-2.242433	-0.470573	2.192710
9.C	-2.056543	-0.752399	1.161727
10.C	-1.368208	-1.933532	0.712459
11.H	-3.015057	0.911493	0.000000
12.H	-0.932469	-2.697980	1.348530
13.C	-1.368208	-1.933532	-0.712459
14.H	-0.932469	-2.697980	-1.348530
15.C	-2.056543	-0.752399	-1.161727
16.H	-2.242433	-0.470573	-2.192710
17.C	-2.470062	-0.028056	0.000000

Energy: -4.40700640 a.u.

2. $Re(Cp)(CO)_2Xe$

Atom	X	Y	Z (Angstrom)
1.Re	-0.079951	-0.215701	0.000000
2.C	1.132458	0.352536	1.346332
3.C	1.132458	0.352536	-1.346332
4.Xe	-1.450945	2.351400	0.000000
5.O	1.895411	0.589493	-2.212605
6.O	1.895411	0.589493	2.212605
7.H	0.765442	-2.683791	1.354071
8.C	-0.037848	-2.321329	0.720378
9.C	-1.316903	-1.821595	1.166937
10.H	0.765442	-2.683791	-1.354071
11.H	-1.643097	-1.711497	2.196021
12.C	-2.071319	-1.492665	0.000000
13.H	-3.065987	-1.051532	0.000000
14.C	-1.316903	-1.821595	-1.166937
15.H	-1.643097	-1.711497	-2.196021
16.C	-0.037848	-2.321329	-0.720378

Energy: -3.77025225 a.u.

3. $Re(Cp)(CO)(PF_3)Xe$

Atom	X	Y	Z (Angstrom)
1.Re	0.002443	0.028391	0.025823
2.C	0.983614	0.937991	-1.327318

3.Xe	2.417406	-0.902920	1.335759
4.O	1.499116	1.486958	-2.233166
5.H	-1.792894	0.064375	-2.309892
6.C	-1.648968	-0.464433	-1.372598
7.C	-0.931337	-1.705859	-1.197097
8.H	-2.875611	0.750110	0.075077
9.H	-0.413116	-2.266162	-1.968828
10.C	-1.049016	-2.070212	0.181291
11.H	-0.590015	-2.943412	0.641011
12.C	-1.853851	-1.110638	0.861287
13.H	-2.143418	-1.138827	1.906535
14.C	-2.214833	-0.092992	-0.100552
15.P	-0.058106	1.895249	1.205192
16.F	-0.714427	3.206130	0.560867
17.F	1.238105	2.645033	1.786641
18.F	-0.916830	1.952269	2.562229

Energy: -3.93921439 a.u.