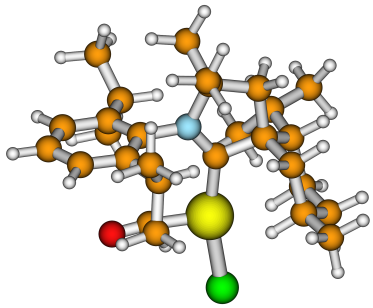
Electronic Supplementary Information
Cartesian Coordinates for **1-calc**



ATOM	CHARGE	X	Y	Z
C	6.0	2.7368524725	-1.0623068719	-0.7651738515
C	6.0	2.1926576151	0.1557751624	-0.2798645478
C	6.0	2.8176094947	0.8718476880	0.7719099046
C	6.0	4.0333720114	0.3822159269	1.2673649444
C	6.0	4.6102629343	-0.7777316598	0.7662209207
C	6.0	3.9558363532	-1.4944354174	-0.2277335165
N	7.0	0.9634957187	0.6708870082	-0.8712835672
C	6.0	-0.2571035880	0.3152493692	-0.4684287120
C	6.0	-1.3019856708	0.9587638517	-1.4133282874
C	6.0	-0.4730775809	1.9246230730	-2.3033463423
C	6.0	1.0218259571	1.6160722317	-2.0689464021
C	6.0	-2.4878256277	1.6919355306	-0.6922670566
C	6.0	-3.4201275110	0.6924800669	0.0163329325
C	6.0	-3.9720279763	-0.3981165578	-0.9060585026
C	6.0	-2.8482701664	-1.1538301465	-1.6252252781
C	6.0	-1.9081462446	-0.1608202501	-2.3217534770
RH	45.0	-0.9799144839	-0.8637739943	0.9227517774
C	6.0	0.5473372034	-1.3962894389	1.7282279901
O	8.0	1.4405258227	-1.8148458063	2.3343916696
C	6.0	1.6624403009	0.9414774535	-3.2918428426
C	6.0	1.8204423910	2.8889284134	-1.7614414225
C	6.0	-3.3867745481	-2.1966574902	-2.6116756620
C	6.0	-2.1138164012	2.9111854759	0.2148439923
C	6.0	-3.1843260694	4.0118663022	0.0917108915
C	6.0	2.2177018102	2.1010852545	1.4593429587
C	6.0	3.1771663610	3.3098888182	1.4546826300
C	6.0	2.0536910765	-1.9812370755	-1.7833055116
C	6.0	2.9549537046	-2.2977510769	-2.9955876738
CL	17.0	-2.3699051432	-2.1887373051	2.3190071342
C	6.0	-1.8738836777	2.5847254281	1.6994152235
C	6.0	1.8001014216	1.7839050552	2.9118675025
C	6.0	1.5939538176	-3.3033081600	-1.1303588057
H	1.0	-0.7270936888	1.7978935162	-3.3604025919
H	1.0	-0.6844162420	2.9677750566	-2.0550957245
H	1.0	-2.4702567297	0.3474777636	-3.1196730799
H	1.0	-1.0934448437	-0.7046113664	-2.8182560790
H	1.0	-4.6377709833	0.0599545850	-1.6541508467
H	1.0	-4.5792448387	-1.0994317633	-0.3219159875
H	1.0	-3.0687484152	2.1103754258	-1.5304457109
H	1.0	4.5265558105	0.9149132899	2.0750036482
H	1.0	5.5545741948	-1.1369196916	1.1669753667
H	1.0	4.3891470610	-2.4236534708	-0.5857078574
H	1.0	1.6784900691	1.6592313817	-4.1198882616
H	1.0	1.1029433102	0.0634597556	-3.6244472309
H	1.0	2.6950325650	0.6461874764	-3.0881969832
H	1.0	1.3912261894	3.4555474338	-0.9316445777
H	1.0	1.8012636194	3.5315259819	-2.6488571224

H	1.0	2.8666525833	2.6653705061	-1.5335896861
H	1.0	-3.9889249275	-1.7190926697	-3.3961897811
H	1.0	-4.0211528705	-2.9288421212	-2.0996682297
H	1.0	-2.5709694372	-2.7430298960	-3.1003845852
H	1.0	-1.1780411367	3.3419052397	-0.1673245861
H	1.0	-1.5123466390	3.4802241970	2.2197724437
H	1.0	-1.1780411367	3.3419052397	-0.1673245861
H	1.0	-1.5123466390	3.4802241970	2.2197724437
H	1.0	-1.1341827611	1.7898662910	1.8406834381
H	1.0	-2.7951850657	2.2677204301	2.2017232189
H	1.0	-4.1683326576	3.6497815155	0.4168127002
H	1.0	-3.2845198617	4.3647750460	-0.9422477036
H	1.0	-2.9308985010	4.8745868005	0.7189524566
H	1.0	1.3091775765	2.3906154660	0.9252851522
H	1.0	1.0391976032	1.0004812573	2.9544374457
H	1.0	1.3878788722	2.6827940374	3.3861179315
H	1.0	2.6577724323	1.4539734211	3.5096821886
H	1.0	4.0542680892	3.1265941246	2.0857381660
H	1.0	2.6674355292	4.1937230829	1.8567475479
H	1.0	3.5373544845	3.5535281744	0.4505825097
H	1.0	1.1537611156	-1.4827976197	-2.1506545410
H	1.0	2.4419440712	-3.8544603130	-0.7077839676
H	1.0	1.1202250284	-3.9445079476	-1.8841472559
H	1.0	0.8673003197	-3.1309828998	-0.3320876214
H	1.0	3.3345352368	-1.3959037942	-3.4853604357
H	1.0	2.3930125834	-2.8763271185	-3.7386421890
H	1.0	3.8203645902	-2.9033102753	-2.7030279492
H	1.0	-4.2493566921	1.2325309659	0.4908514613
H	1.0	-2.9051060876	0.2185578278	0.8795049155
H	1.0	-2.2659926392	-1.7071656989	-0.8593727998

NBO Analysis of **1-calc.**

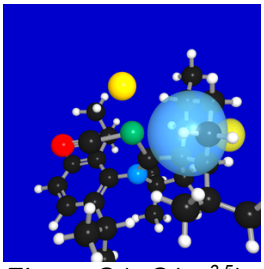


Figure S1: C($sp^{3.5}$)-H1(s) bond.

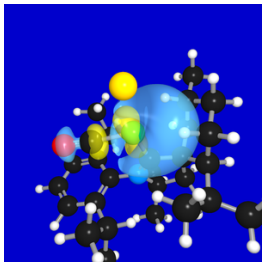


Figure S2: Rh(s)-C($sp^{0.57}$) antibonding orbital.

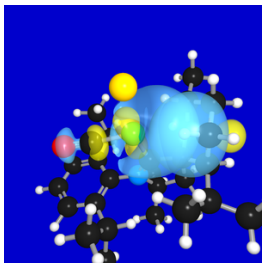


Figure S3: CH1 -> RhC. E_{2P} = 39.82 kJ/mol

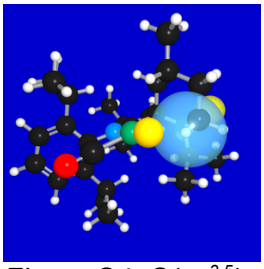


Figure S4: C($sp^{3.5}$)-H1(s) bond.

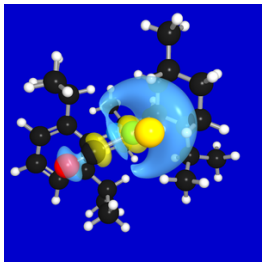


Figure S5: Rh(s)-C($sp^{0.57}$) antibonding orbital.

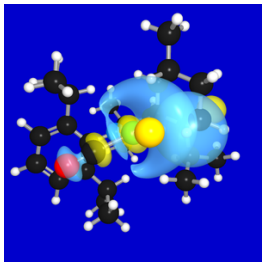


Figure S6: CH1 -> RhC. E_{2P} = 39.82 kJ/mol

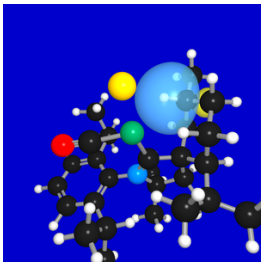


Figure S7: C($sp^{3.60}$)-H2(s) bond.

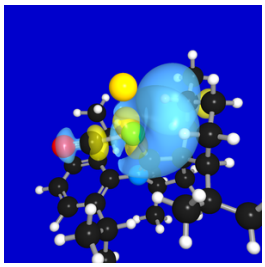


Figure S8: CH2 -> RhC. E_{2P} = 15.91 kJ/mol

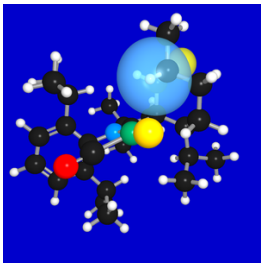


Figure S9: C($sp^{3.60}$)-H2(s) bond.

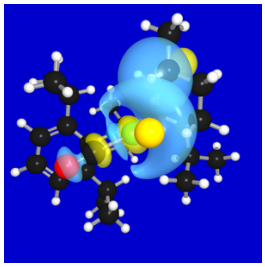


Figure S10: CH2 -> RhC. E_{2P} = 15.91 kJ/mol

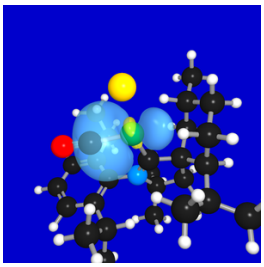


Figure S11: Rh(s)-C($sp^{0.57}$) bond.

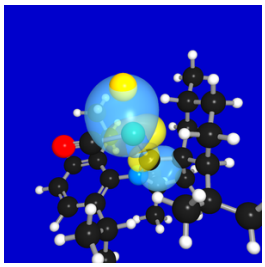


Figure S12: Rh($sd^{1.48}$)-C($sp^{1.85}$) antibonding orbital.

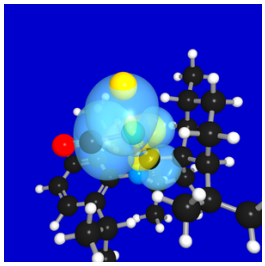
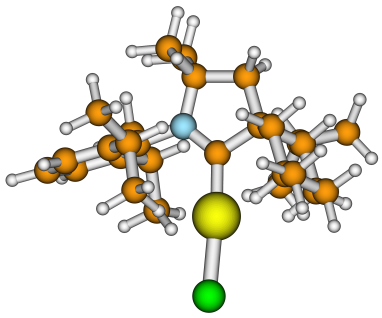


Figure S13: RhC -> RhC. E_{2P} = 69.97 kJ/mol

Cartesian Coordinates for **2**
COORDINATES OF SYMMETRY UNIQUE ATOMS (ANGS)



ATOM	CHARGE	X	Y	Z
C	6.0	1.8125829502	0.7197762911	-2.2576472866
C	6.0	1.1910213307	-0.5860185300	-1.6715287021
C	6.0	2.3675271644	-1.5198199047	-1.2162149269
C	6.0	3.3134041148	-0.7722194264	-0.2539272553
C	6.0	3.8795085730	0.5183996605	-0.8458420012
C	6.0	2.7570842079	1.4561949334	-1.2968084489
C	6.0	3.2789493411	2.7668792825	-1.8951835363
H	1.0	3.8524193512	2.5753745398	-2.8120991503
H	1.0	3.9369030662	3.2850432493	-1.1885967235
H	1.0	2.4558625347	3.4450145899	-2.1492877096
H	1.0	2.1665635684	1.7325717374	-0.3782847260
H	1.0	4.5147025017	0.2787727698	-1.7126135260
H	1.0	4.5195560490	1.0187438621	-0.1089238752
H	1.0	4.1291657598	-1.4355811107	0.0595156321
H	1.0	2.7685229580	-0.5194793291	0.6887983695
C	6.0	1.9699427204	-2.9321965947	-0.6780501711
C	6.0	1.7296402876	-3.0056963511	0.8397849060
H	1.0	1.2991564402	-3.9792582925	1.1042458450
H	1.0	1.0462351034	-2.2266215358	1.1915048836
H	1.0	2.6629748243	-2.8978534310	1.4042857652
C	6.0	3.0245975859	-3.9762822046	-1.0891627476
H	1.0	4.0122598551	-3.7253724994	-0.6813532401
H	1.0	3.1218988007	-4.0432230307	-2.1798829390
H	1.0	2.7586550574	-4.9712291428	-0.7130382771
H	1.0	1.0300207719	-3.2280409935	-1.1637679919
H	1.0	2.9367159763	-1.6976990575	-2.1430883186
C	6.0	0.2429433048	-1.2327343209	-2.7242425520
C	6.0	-1.2206162978	-1.0346935517	-2.2365146509
N	7.0	-1.0115520847	-0.4271059198	-0.8626835100
C	6.0	0.2580909224	-0.1731858645	-0.5257157136
RH	45.0	0.9335961425	0.6939312468	1.0158970922
CL	17.0	1.5837539039	1.6803080119	3.0907221776
C	6.0	-2.1172078212	0.0022794908	-0.0187467150
C	6.0	-2.5801331958	1.3405637716	-0.1126795139
C	6.0	-3.7101278909	1.7018329374	0.6318597474
C	6.0	-4.3535842663	0.7918994518	1.4630336883
C	6.0	-3.8388057887	-0.4912120644	1.6040033945
C	6.0	-2.7091983627	-0.9100980439	0.8889669636
C	6.0	-2.1137599740	-2.2756380108	1.2250939482
C	6.0	-1.5033147476	-2.2448632150	2.6439605916
H	1.0	-0.7489961368	-1.4554055585	2.7410426074
H	1.0	-1.0248288491	-3.2045539895	2.8736339033
H	1.0	-2.2739890956	-2.0626921346	3.4020578905
C	6.0	-3.1267135593	-3.4309304425	1.1059773090
H	1.0	-3.9335991544	-3.3419932023	1.8427030073
H	1.0	-2.6259345628	-4.3891495930	1.2891918345

H	1.0	-3.5874562698	-3.4744088860	0.1135599671
H	1.0	-1.2963468385	-2.4765229513	0.5285942030
H	1.0	-4.3082571231	-1.1796958386	2.3005926616
H	1.0	-5.2324833264	1.0931028137	2.0271791136
H	1.0	-4.0806745373	2.7208770451	0.5714812366
C	6.0	-1.8487504779	2.4354522218	-0.8867206702
C	6.0	-1.0806616814	3.3451936553	0.0959995135
H	1.0	-1.7582875858	3.8224707209	0.8134362595
H	1.0	-0.5440353366	4.1341299412	-0.4452313671
H	1.0	-0.3420383229	2.7700245533	0.6783211943
C	6.0	-2.7746225153	3.2739263551	-1.7889178932
H	1.0	-3.3737241490	2.6471716916	-2.4587392491
H	1.0	-2.1762473720	3.9555384281	-2.4048054862
H	1.0	-3.4639827984	3.8911126777	-1.2019333233
H	1.0	-1.1013264887	1.9657114547	-1.5294368849
C	6.0	-2.0042922382	-0.0825010244	-3.1558280267
H	1.0	-2.1384288504	-0.5594481472	-4.1333940219
H	1.0	-1.4765562743	0.8614869812	-3.3154554726
H	1.0	-2.9977257227	0.1365945181	-2.7512975596
C	6.0	-1.9823902177	-2.3650409075	-2.1550365118
H	1.0	-1.4483273124	-3.1045492260	-1.5520016044
H	1.0	-2.0995930940	-2.7755041559	-3.1645959777
H	1.0	-2.9828900272	-2.2257739284	-1.7338023787
H	1.0	0.3780855756	-0.7666900128	-3.7056636147
H	1.0	0.4552857777	-2.2973299907	-2.8532511264
H	1.0	2.3701558514	0.4485576694	-3.1669427151
H	1.0	1.0066083065	1.3934871837	-2.5773264309

NBO Analysis of **2**

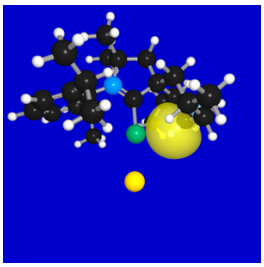


Figure S14: C($sp^{3.56}$)-H1(s) bond.

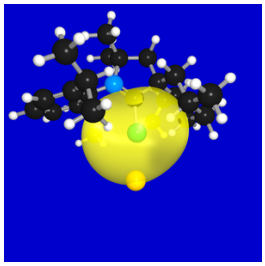


Figure S15: Rh(s) antibonding orbital.

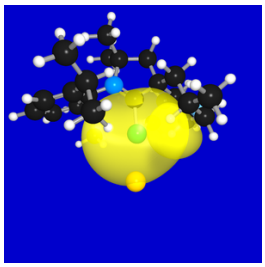


Figure S16: CH1 -> Rh. E_{2P} = 16.75 kJ/mol.

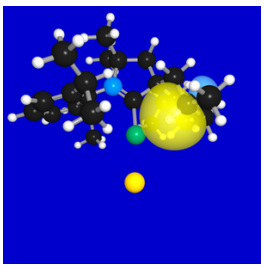


Figure S17: C($sp^{3.85}$)-H2(s) bond.

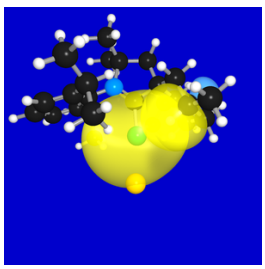


Figure S18: CH2 -> Rh. E_{2p} = 16.58 kJ/mol.

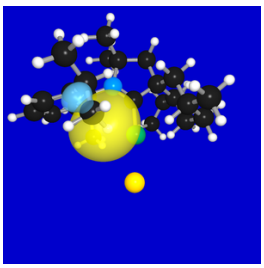


Figure S19: $C(sp^{3.11})$-H3(s) bond.

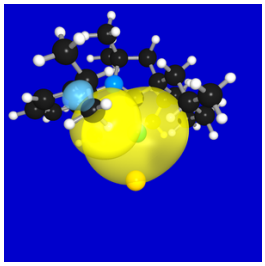


Figure S20: CH3 -> Rh. E_{2P} = 8.79 kJ/ mol.

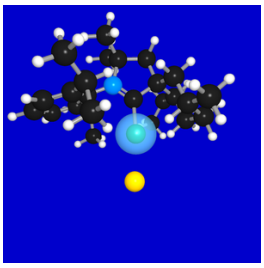


Figure S21: Rh(s) orbital.

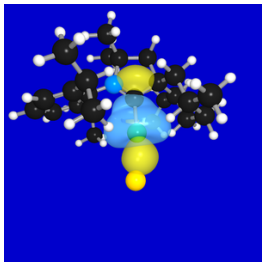


Figure S22: $Rh(sd^{54.30})$-$C(sp^{2.12})$ antibonding orbital.

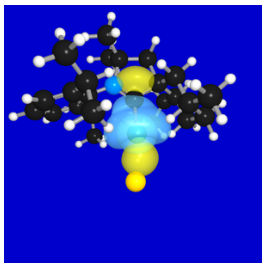
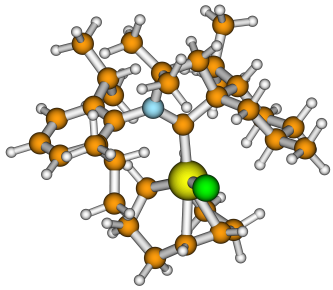


Figure S23: Rh -> RhC. E_{2P} = 86.62 kJ/mol.

Cartesian Coordinates for **3-calc**



COORDINATES OF SYMMETRY UNIQUE ATOMS (ANGS)

ATOM	CHARGE	X	Y	Z
C	6.0	2.9020745786	-1.0549460590	-0.6891052896
C	6.0	2.3576219831	0.1369953641	-0.1465580185
C	6.0	2.9468841444	0.7262583745	1.0097458600
C	6.0	4.0204404891	0.0734017620	1.6279631573
C	6.0	4.5447425712	-1.1081586986	1.1216614327
C	6.0	3.9912962915	-1.6474659996	-0.0294862298
N	7.0	1.2159449622	0.8399212337	-0.7574946487
C	6.0	-0.0717276887	0.6384240400	-0.4477871806
C	6.0	-0.9136706659	1.8302846099	-1.0485948797
C	6.0	0.1925783586	2.7496248574	-1.6456749303
C	6.0	1.4405569634	1.8887898050	-1.8537946144
C	6.0	-1.8049415739	2.6885170437	-0.0430972328
C	6.0	-3.0854007567	1.9556005458	0.4005784837
C	6.0	-3.9758348103	1.6081501027	-0.7928813078
C	6.0	-3.2147072543	0.7320621473	-1.7873894166
C	6.0	-1.8892057166	1.3935584465	-2.1985789925
RH	45.0	-0.8812996104	-1.1139891315	0.2258677740
C	6.0	-2.5870370001	-2.5095761951	0.7044904305
C	6.0	-3.3080195149	-1.9480649534	1.9155076275
C	6.0	-2.3664531987	-1.2868584117	2.9518947775
C	6.0	-1.1224714759	-0.6549291152	2.3249936129
C	6.0	0.1017718387	-1.3296879812	2.0993921331
C	6.0	0.3970537941	-2.7880252647	2.3981671856
C	6.0	-0.7452967185	-3.7478474642	1.9982873270
C	6.0	-1.4467551390	-3.2915895023	0.7309848579
C	6.0	2.7392422236	2.6831408327	-1.6975140575
C	6.0	1.4504729892	1.2169939771	-3.2414426359
C	6.0	-4.0496641821	0.3850790820	-3.0251567877
C	6.0	-1.0547787463	3.4379555426	1.1217074707
C	6.0	-1.6454714719	3.2607673222	2.5349447086
C	6.0	2.5166678018	2.0539838790	1.6380316705
C	6.0	3.6936606199	3.0507956943	1.7406869167
C	6.0	2.4253629250	-1.7601945109	-1.9556900999
C	6.0	2.0250219010	-3.2243350599	-1.6841349192
CL	17.0	-1.0322723587	-1.8274909947	-2.1340633227
C	6.0	-0.9813081222	4.9533354027	0.8395995940
C	6.0	1.8843389420	1.8758311037	3.0329347096
C	6.0	3.5145873530	-1.7259508423	-3.0514062939
H	1.0	-0.1271501550	3.2265190725	-2.5771585413
H	1.0	0.4448607013	3.5494809786	-0.9459866633
H	1.0	-2.1340855199	2.3152825250	-2.7486922734
H	1.0	-1.3757420112	0.7318180865	-2.8976942936
H	1.0	-2.9707439239	-0.2054778836	-1.2771229995
H	1.0	-4.8843294824	1.0919858892	-0.4507395182
H	1.0	-4.3124881077	2.5353825398	-1.2850050066
H	1.0	-2.8212784900	1.0362848084	0.9371193122
H	1.0	-3.6434633908	2.5888698970	1.0991781353

H	1.0	-2.1601443292	3.4878853483	-0.7139612267
H	1.0	4.4572094770	0.5119448051	2.5201590582
H	1.0	5.3828151008	-1.5960392216	1.6128235996
H	1.0	4.4074130758	-2.5618835524	-0.4398359202
H	1.0	2.8429813845	3.3504827364	-2.5607020128
H	1.0	3.6168469241	2.0288061632	-1.6787734523
H	1.0	2.7437395475	3.3051368624	-0.8010495155
H	1.0	0.6239017578	0.5160158700	-3.3717494735
H	1.0	2.3855577579	0.6828677382	-3.4199404921
H	1.0	1.3683709665	1.9981871567	-4.0065106864
H	1.0	-4.9942422506	-0.0931423399	-2.7365452772
H	1.0	-3.5082571744	-0.3073178796	-3.6789029699
H	1.0	-4.2975633067	1.2846193053	-3.6065643151
H	1.0	-0.0305307973	3.0563866460	1.1680270080
H	1.0	-1.9921003939	5.3819233347	0.8176067148
H	1.0	-0.5104307378	5.1824328648	-0.1223191452
H	1.0	-0.4179845874	5.4766892699	1.6224651041
H	1.0	-0.9685769510	3.7073018877	3.2732441510
H	1.0	-1.7921373976	2.2143222212	2.8133682007
H	1.0	-2.6121511820	3.7683440371	2.6370822650
H	1.0	1.7620237598	2.5058192430	0.9935097416
H	1.0	0.9820915154	1.2600146421	3.0009674983
H	1.0	1.6128943157	2.8529117632	3.4506495008
H	1.0	2.5880382026	1.4019783687	3.7275661397
H	1.0	4.4197430910	2.7393016720	2.5002068920
H	1.0	3.3222102519	4.0405700642	2.0330502677
H	1.0	4.2328770473	3.1527770469	0.7942925364
H	1.0	1.5314806720	-1.2597266463	-2.3250289521
H	1.0	3.8906512121	-0.7146138213	-3.2416503275
H	1.0	3.1141352753	-2.1230147342	-3.9917991503
H	1.0	4.3771562669	-2.3436712398	-2.7726293549
H	1.0	2.8851032363	-3.8312156993	-1.3736816132
H	1.0	1.6112605249	-3.6667093883	-2.5962895888
H	1.0	1.2531836814	-3.2838793139	-0.9134169711
H	1.0	-1.0470956831	0.4186499278	2.4686212117
H	1.0	0.9997553780	-0.7184691735	2.0790705032
H	1.0	0.6433015809	-2.9109416197	3.4665099780
H	1.0	1.3045443802	-3.0601934353	1.8457794511
H	1.0	-0.3348915795	-4.7524475512	1.8411331677
H	1.0	-1.4697304587	-3.8405482925	2.8146786545
H	1.0	-1.1683024182	-3.7945276559	-0.1912424517
H	1.0	-3.1463045025	-2.4847236351	-0.2291278499
H	1.0	-3.9096110716	-2.7358058645	2.3976621663
H	1.0	-4.0252041528	-1.2007059206	1.5568254636
H	1.0	-2.9277764533	-0.5119500593	3.4877287303
H	1.0	-2.0657328326	-2.0140412918	3.7164366227

NBO Analysis of **3-calc**

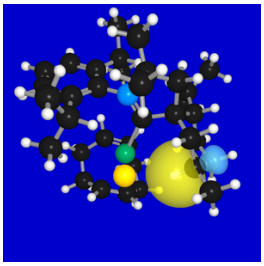


Figure S24: C($sp^{3.42}$)-H(s) bond

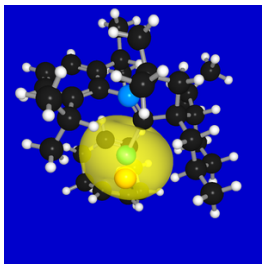


Figure S25: empty Rh($sd^{0.16}$) orbital

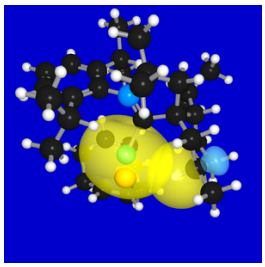


Figure S26: CH -> Rh. E_{2P} = 4.48 kJ/mol

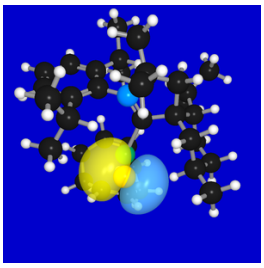


Figure S27: Cl(p) lone pair

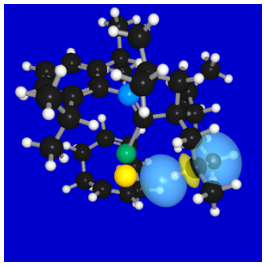


Figure S28: C($sp^{3.42}$)-H(s) antibonding orbital

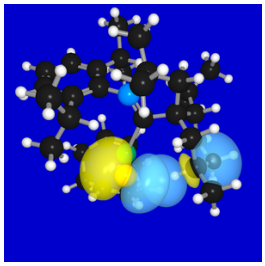


Figure S29: Cl -> CH. E_{2P} = 4.69 kJ/mol

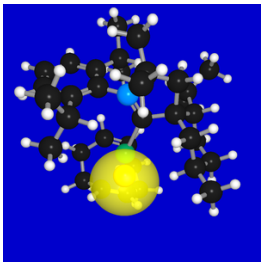


Figure S30: Cl($sp^{0.23}$) lone pair

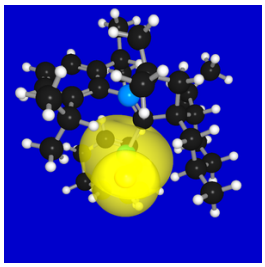


Figure S31: Cl -> Rh. E_{2p} = 92.07 kJ/mol

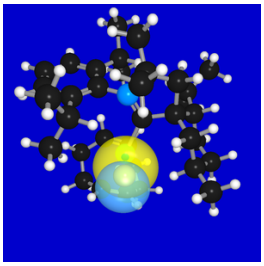


Figure S32: Cl($sp^{4.62}$) lone pair

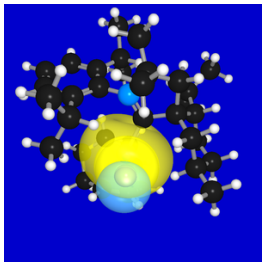


Figure S33: Cl -> Rh. E_{2P} = 376.52 kJ/mol