Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

A Computational Study of the CO Dissociation in Cyclopentadienyl Ruthenium Complexes Relevant to the Racemization of Alcohols

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Computational details: general considerations

DFT-method

Calculations were carried out at the density functional theory (DFT) level using the so-called global hybrid meta density functional M06-2X,[1] which has been shown to provide broad accuracy for main group and organometallic chemistry. For comparison, limited calculations have been also performed with the classical hybrid functional, B3LYP.[2, 3] The computational workflow employed M06-2X and B3LYP functionals as implemented in Jaguar computational package (v. 7.7), which has been employed for all calculations in this work.[4] The molecular orbital visualization only has been performed with Gaussian.[5]

The strength of the Minnesota 2006 family of density functionals, to which M06-2X belongs, is accurate description of organic and inorganic bonding as well as noncovalent interactions.[1b] The B3LYP functional, still one of the most popular functional in chemistry, has an estimated averaged error of 3.29 kcal/mol, while M06-2X error is only about a half of that or even better.[6,1] This is fully acceptable for our purpose. Combined with medium size basis sets, these density functionals allow to draw reliable mechanistic conclusions based on the relative energies.[7, 8, 9]

Basis sets

All calculations were performed using, first, lacvp* basis for geometry optimizations and comparison of conformers, and thereafter, lacvp*+ basis sets was used for a more accurate geometry optimizations.[10,11] These basis sets are based on the 6-31G basis set with polarization (and diffuse) functions, including an effective core potential (ECP) for the Ru atom thus reducing computational costs.[10] Cationic and neutral species should be well represented by this basis set considering the presence of a double set of polarization functions.

Self consistent reaction field (bulk solvent)

The solvated molecular systems was described with a self consistent reaction field (SCRF) method based on the solution of the Poisson-Boltzmann (field) equation; the method makes possible to compute minimum- energy solvated structures of complex systems at relatively

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[1] a) Y. Zhao, D. G. Truhlar, J. Chem. Phys. 2006, 125, 194101; b) Y. Zhao, D. G. Truhlar, Chem. Phys. Lett. 2011, 502, 1-13, and references therein; c) Y. Zhao, D. G. Truhlar, Acc. chem. Res. 2008, 41, 157.
[2] a) A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648-5652; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785-789.
[3] Lundberg, M.; Blomberg, M. R. A.; Siegbahn, P. E. M., Inorg. Chem. 2004, 43, 264, and references therein.
[4] Jaguar, version 7.7, Schrodinger, LLC, New York, NY, 2010.
[5] Gaussian, M. J. Frisch et al., see full reference at the end of SI.
[6] Curtis, L. A:; Raghavachari, K.; Redfern, R. C.; Pople, J. A. J. Chem. Phys. 2000, 112, 7374-7383.
[7] S. Ling, W. Yu, Z. Huang, Z. Lin, M. Haranczyk, M. Gutowski, *J. Phys. Chem. A* **2006**, *110*, 12282.
[8] B. M. Rice, S. V. Pai, C. F. Chabalowski, *J. Phys. Chem. A* **1998**, *102*, 6950.
[9] W.-R- Zheng, Y. Fu, Q.-X. Guo, *J. Chem. Theory Comput.* **2008**, *4*, 1324.
[10] P. J. Hay, W. R. Wadt, *J. Chem. Phys*. **1985**, *82*, 299-310.
[11] a) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys*. **1972**, *56,* 2257-2261; b) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys*. **1982**, *77*, 3654-3665; c) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213-222.

low computational cost.[12] Solvent effect were calculated using the single point energy calculations with toluene as a solvent (dielectric constant 2.38 at 297K, molecular weight 92.14 g mol^{-1}, density 0.8996 g cm^{-3}).

XYZ Information

Due to quite a large number of the fully stationary and transient structures that we have calculated only selected XYZ data is included herein - an additional XYZ data of all calculated structures are available upon request from authors.

[12] (a) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A., III; Honig, B. *J. Am. Chem. Soc.* **1994,** *116,* 11875. (b) Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitkoff, D.; Honig, B. *J. Phys. Chem.* **1996,** *100,* 11775; (c) Cramer, C.J.; Truhlar, D., G.; *Chem .Rev.*, **1999**, *99*, 2161-2200.

Ref. Gaussian: Gaussian 03, Revision B.02:

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,
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O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari,
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J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,
I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,
C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill,
B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople,
Gaussian, Inc., Pittsburgh PA, 2003.

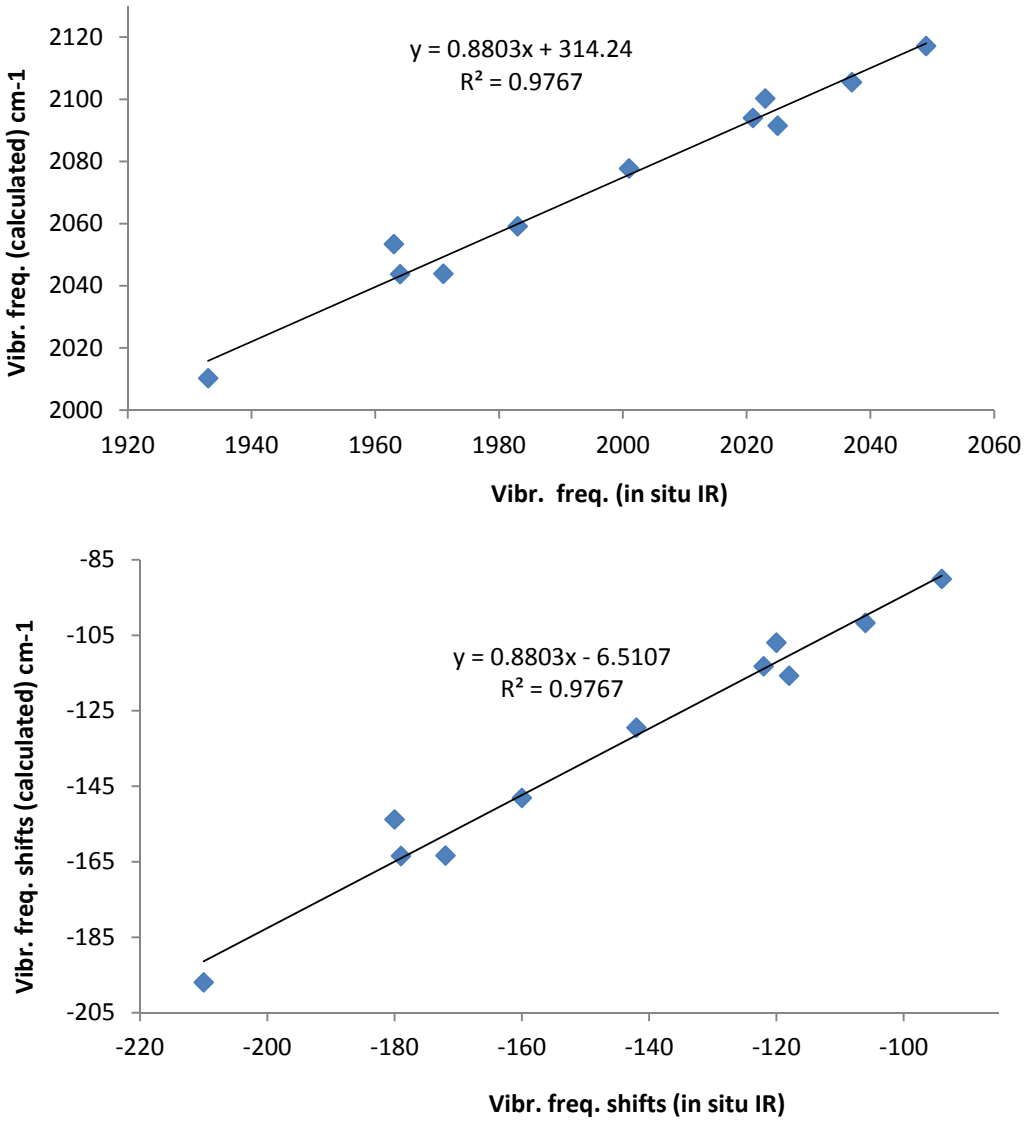


Figure S1. The relationship (correlation) between the absolute values, as well as the shifts with respect to free CO, of calculated and measured vibrational frequencies. The trend line is the best fit with the parameters shown in the figure.

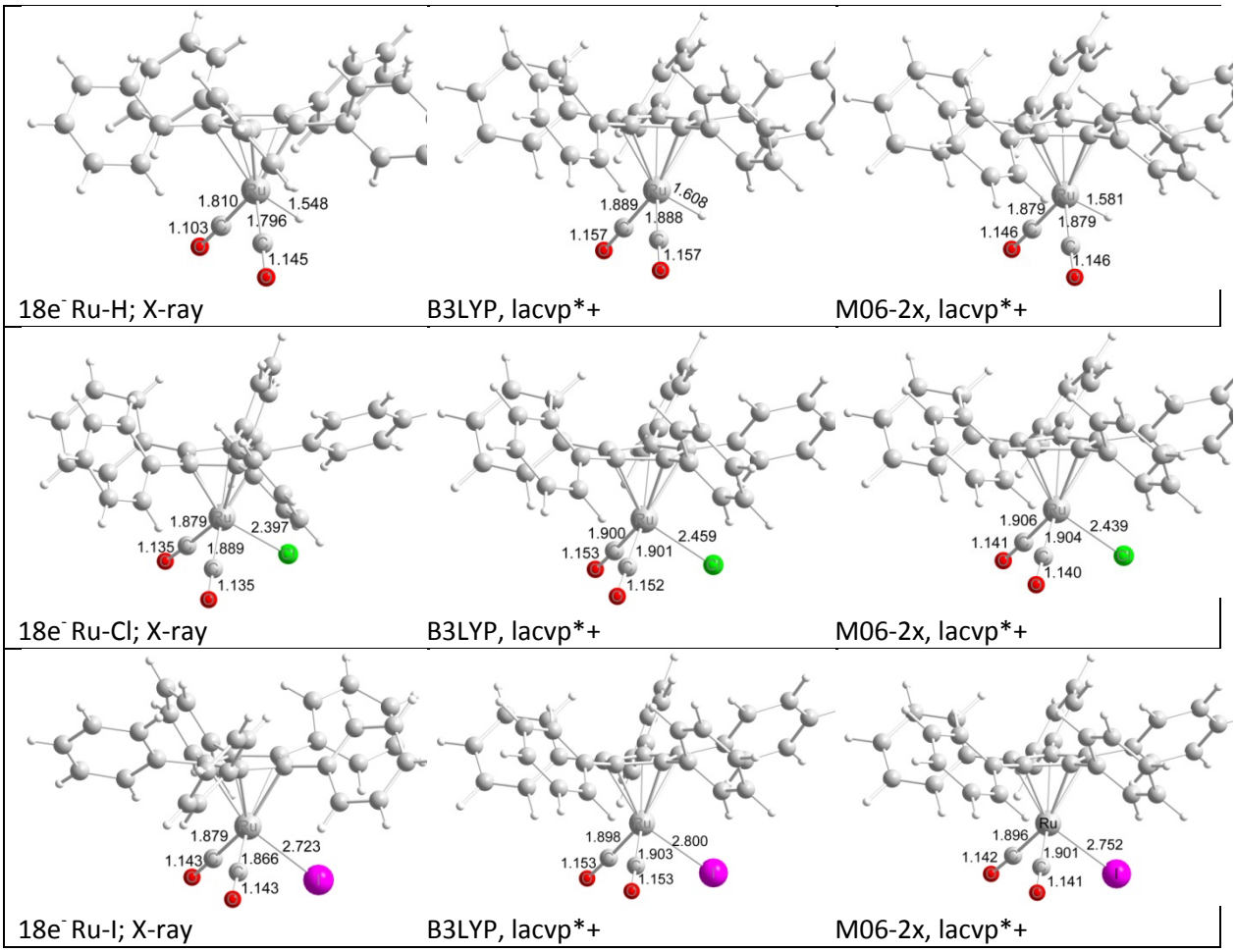


Figure S2. Structural comparison- 18-electron $CpRu(CO)_2X$ complexes with X=H, Cl and I. X-ray structures: see details in B. Martín-Matute, M. Edin, K. Bogár, B. Kaynak, J.-E. Bäckvall, *J. Am. Chem. Soc.*, 2005, **127**, 8817

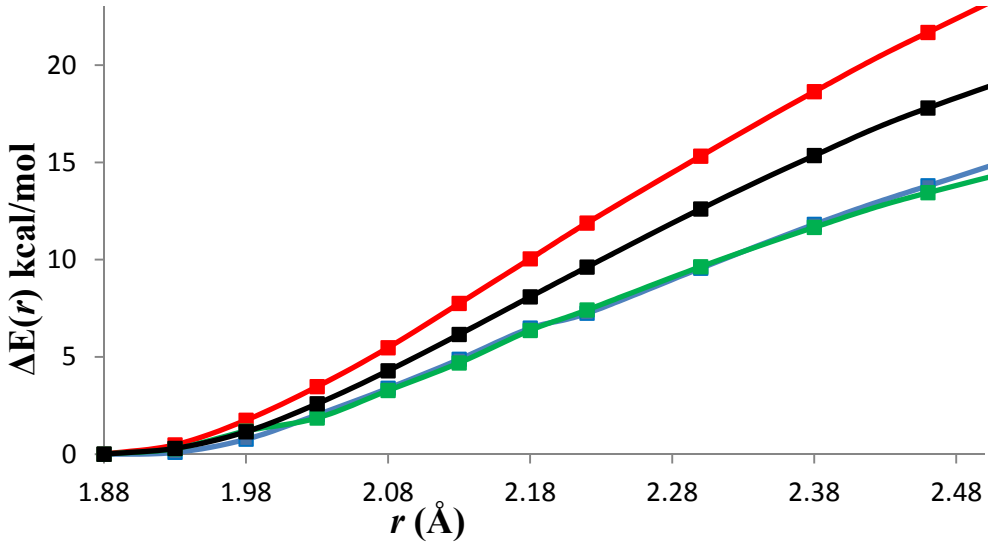


Figure S3A. From Figure 1 in the article - an enlarged the range of the Ru─C_{CO} distance from the equilibrium till 2.5 Å. The change of the potential energy versus r, $\Delta E(r)$, is in kcal/mol. The distance between ruthenium and C_{CO}, $\boldsymbol{r}$ = Ru─C_{CO}, is in Å.

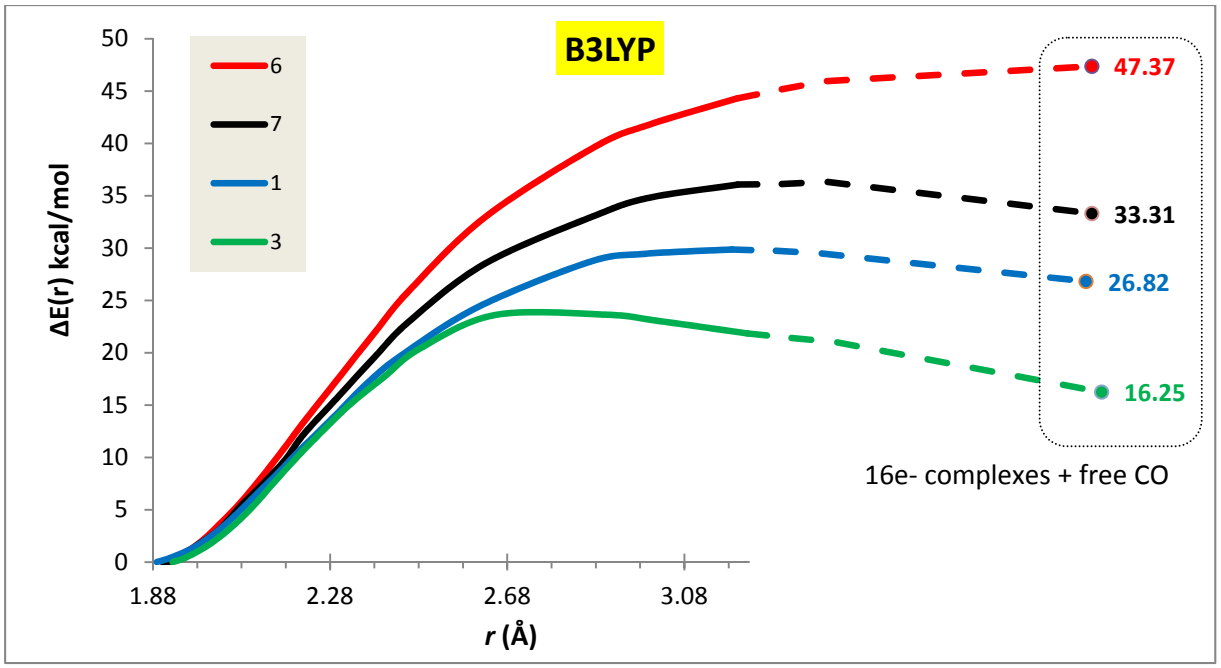
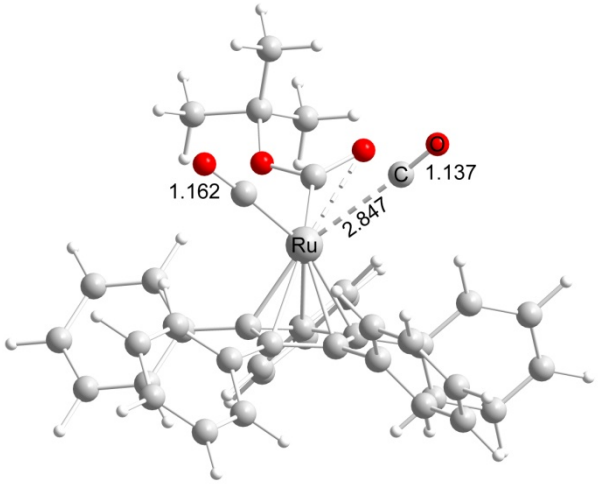


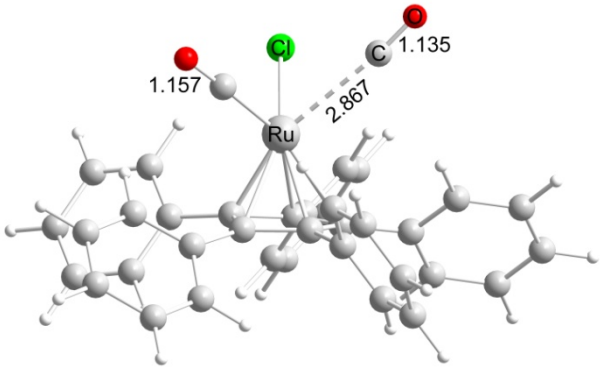
Figure S3B. Same as Figure 1 in the article but calculated with B3LYP density functional. The change of the potential energy versus r, $\Delta E(r)$, is in kcal/mol. The distance between ruthenium and C_{CO}, $\boldsymbol{r}$ = Ru─C_{CO}, is in Å.

(a)



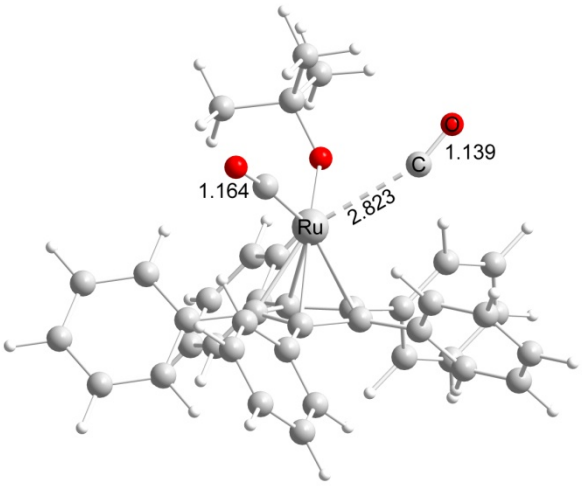
ν_0 = -159.65 cm^{-1}

(b)



ν_0 = -150.8 cm^{-1}

(c)



ν_0 = -167.7 cm^{-1}

Figure S4. Transition states of CO dissociation in complexes **7** (a), **1** (b) and **3** (c). All distances are in Å.

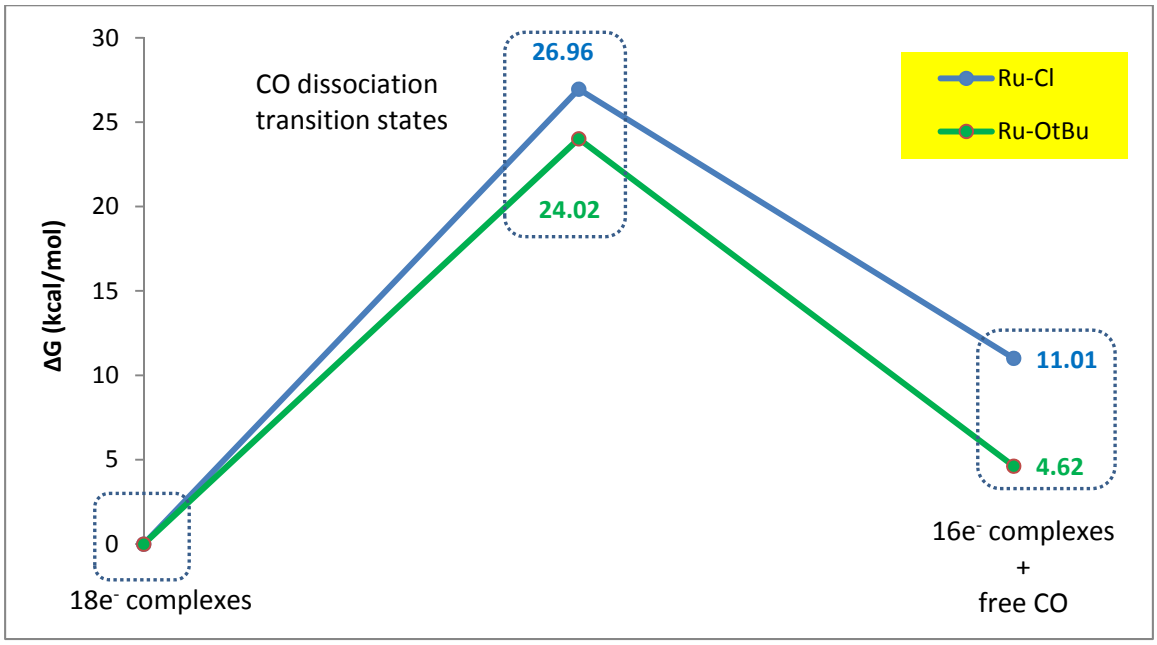


Figure S5. The Gibbs free energy changes (in kcal/mol) upon CO dissociation in Ru-Cl and Ru-O^{t}Bu complexes.

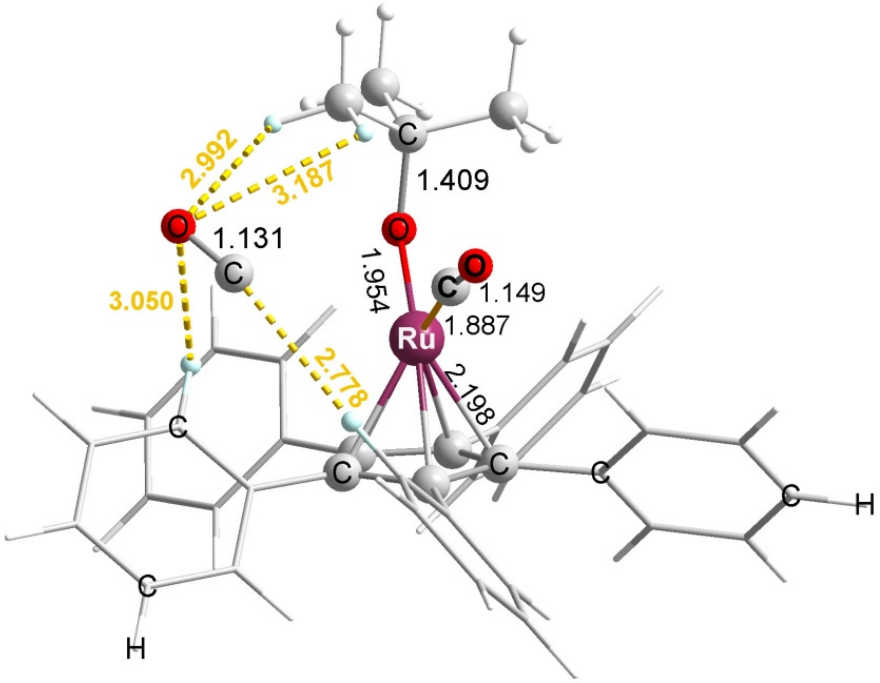
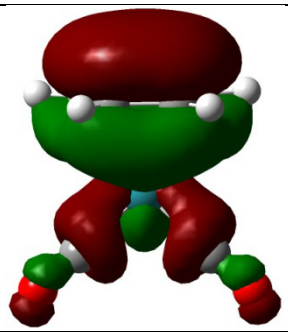
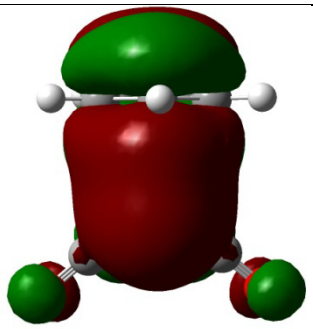
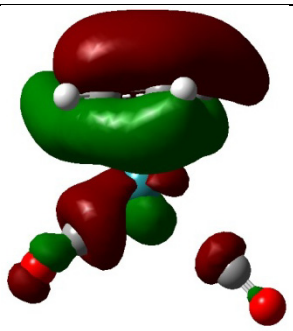


Figure S6. Due to the non-covalent interactions between the dissociating CO molecule and C-H groups of O^{t}Bu and Ph groups a stable but weakly bound complex has been computationally found. All distances are in Å.

The digest of molecular orbital analysis for the selected Cp-ruthenium complexes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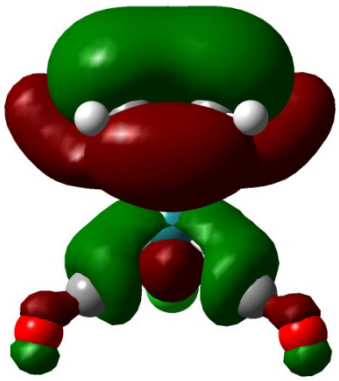	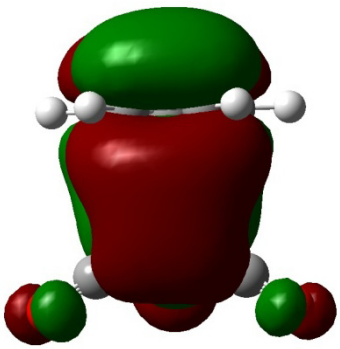	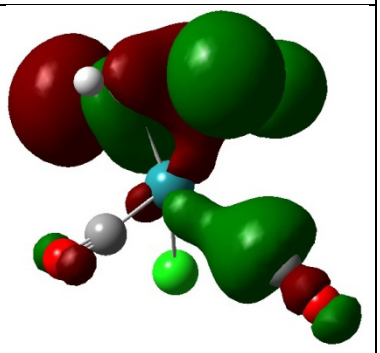
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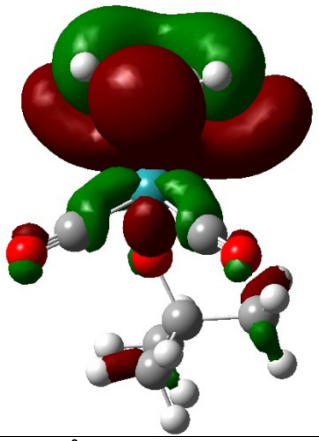	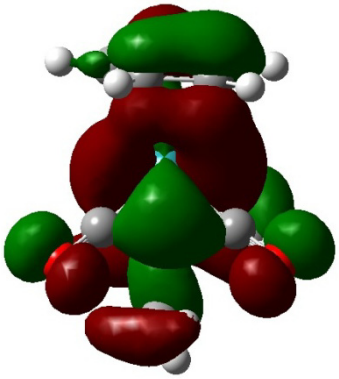	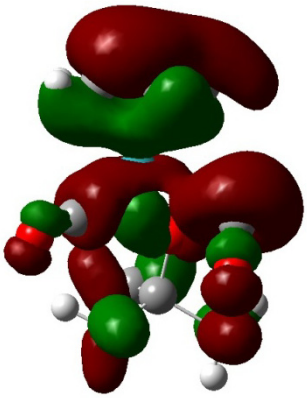
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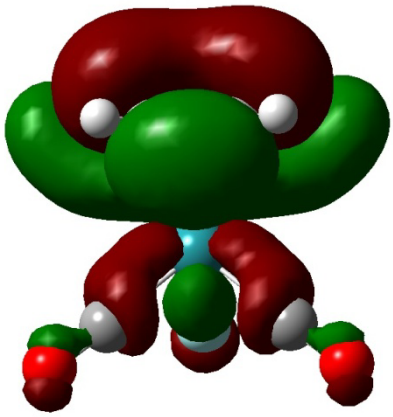	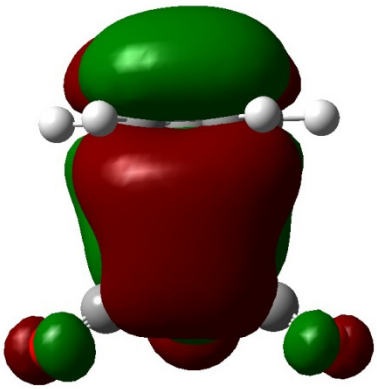	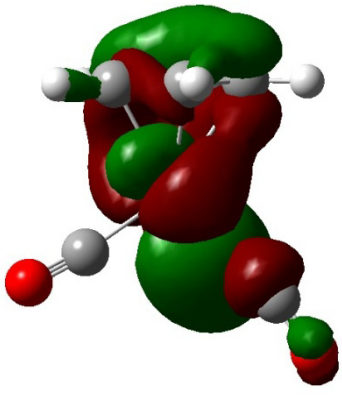
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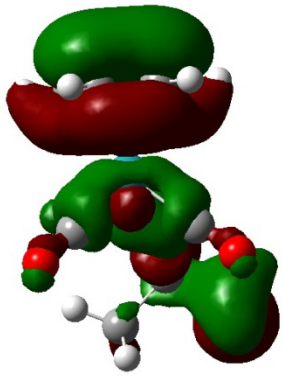	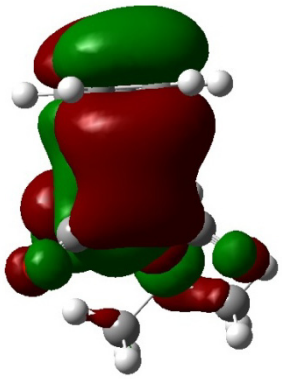	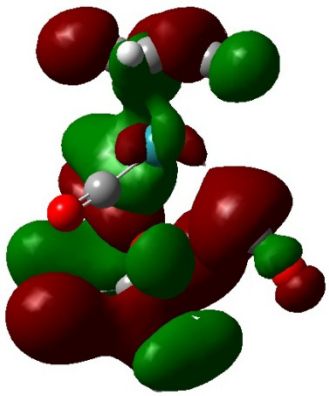
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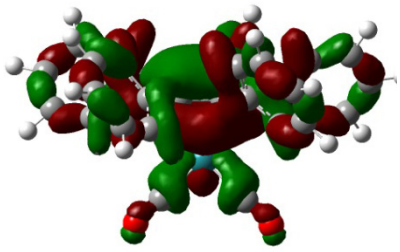	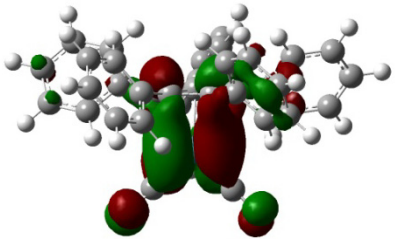	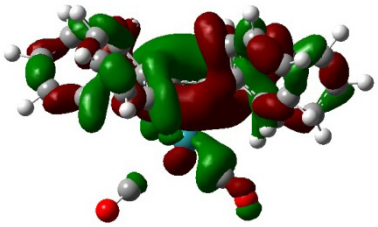
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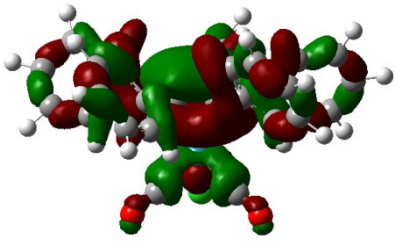	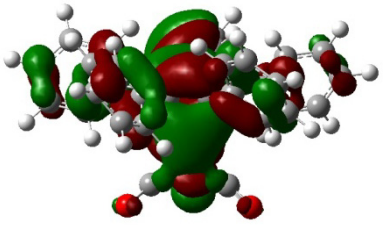	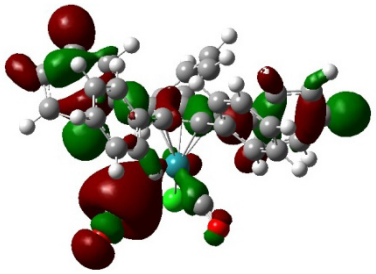
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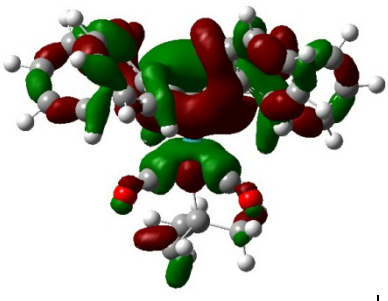	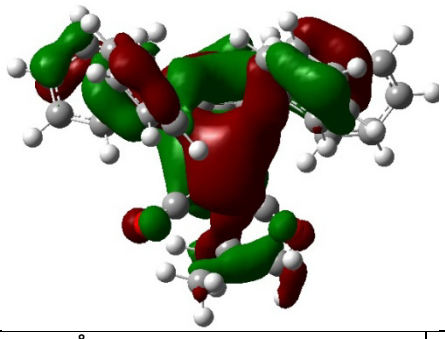	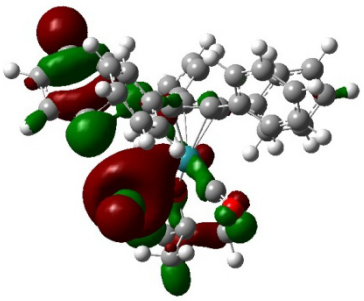
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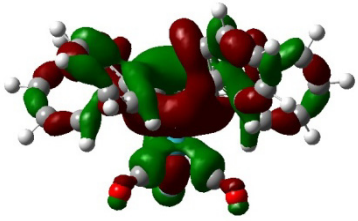	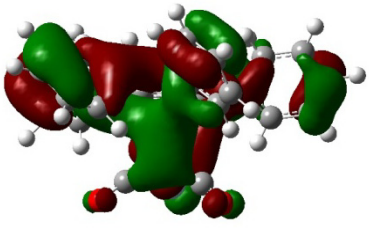	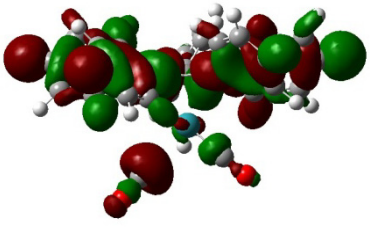
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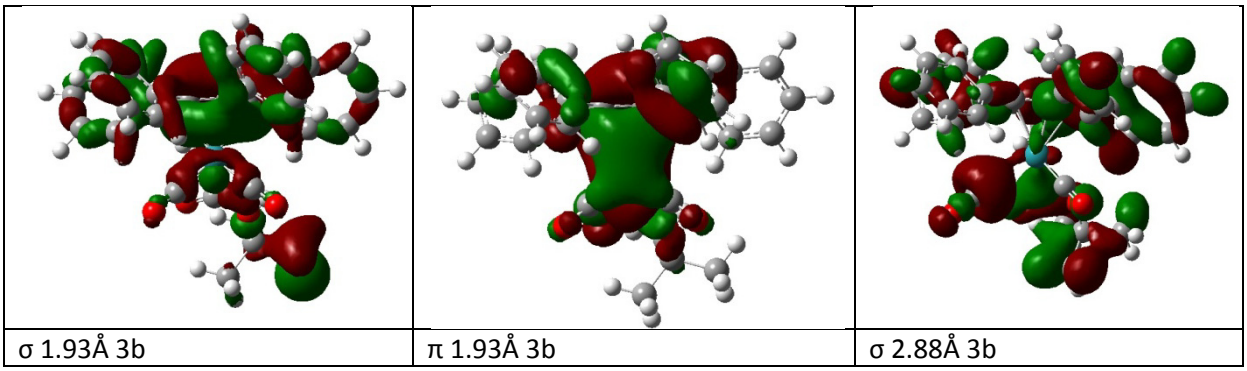
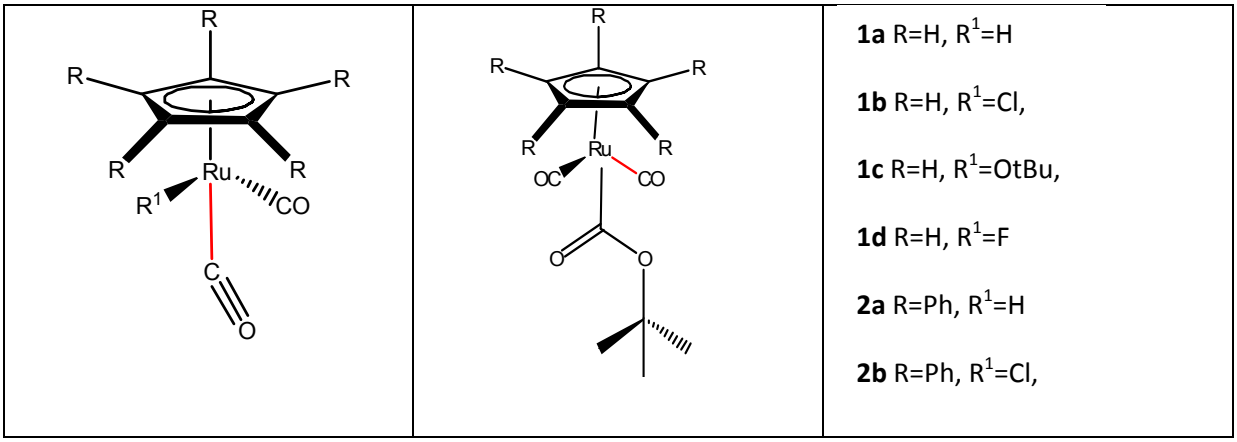


σ 1.93Å 3b	π 1.93Å 3b	σ 2.88Å 3b

Molecular orbital diagram for the hydrogen substituted species. (l) σ interaction, (c) π-interaction at x = 193Å. (r) the only interaction at x=288Å which is interpreted to be σ-type bonding. Labelling of complexes is a s follows (different from the text):



1a R=H, R^1=H

1b R=H, R^1=Cl,

1c R=H, R^1=OtBu,

1d R=H, R^1=F

2a R=Ph, R^1=H

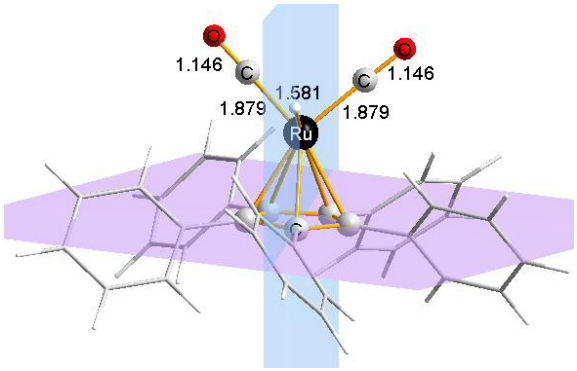
2b R=Ph, R^1=Cl,

$CpRu(CO)_2H$: (the highest barrier to CO dissociation) the molecular orbital interactions at equilibrium revealed that within the HOMO manifold there is both notable π and σ interactions. As dissociation continues along the potential energy surface, the π interaction, which could be attributed to a back-donation type interaction between a ruthenium d orbital and a carbon p orbital disappears yet what seems to be a very significant σ-type donation persists and becomes dominant at greater Ru-CO distances.

$CpRu(CO)_2OtBu$: (the lowest barrier for CO loss) the π bonding is comparable with that in other complexes but accompanied by a smaller degree of σ bonding. This suggest that the bonding between the ruthenium centre and the CO ligand is in fact made up of π and σ-interactions at shorter values of X; approximately equilibrium to 2.40Å and at distances beyond this the bonding is dominated only by σ-type interactions.

For species which have higher dissociation barriers the amount of σ-type bonding seems greater than for 1c and 2c which have the lowest barriers for CO ligand loss. This finding is in support of the earlier proposed conjecture that bonding between the metal centre and the CO ligand consists of donor and acceptor interactions of both σ and π orbitals, where up to a certain value for Ru-CO distance this bonding consists of both types of interactions and at distances beyond this value is attributed mainly to σ interactions.

Selected XYZ data followed by Table S1 with the thermochemical corrections, Table S2 and Table S3 with the "raw" electronic energies



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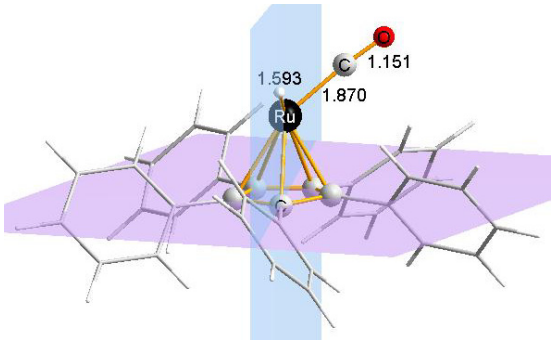

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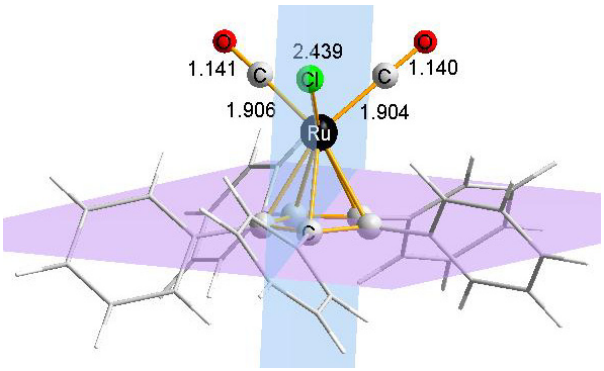

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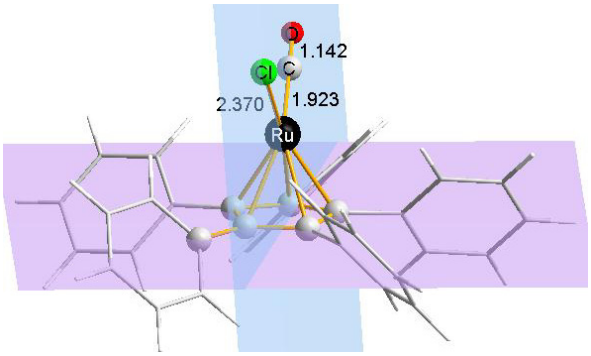

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C	-0.9734565645	-0.4318109668	-1.2406175487
C	-2.1922139286	-1.0925985113	-1.0457111771
C	-3.1907333865	-1.0399583859	-2.0138646021
C	-2.9883451435	-0.3235659097	-3.1926320841
C	-1.7826698252	0.3457918192	-3.3922992234
C	-0.7835116053	0.2948374085	-2.4234394189
C	1.4065997148	-3.0141299890	2.7353059122
O	1.6718018507	-3.4442154225	3.7631228434
C	-0.6741353356	-3.3009896615	1.1152902768
O	-1.6560386373	-3.8865518229	1.1458436385
C	2.7605186261	-5.2548557724	-1.3848112151
C	3.5785157800	-4.8679041498	0.9457380764
H	-0.0064440279	1.9940749705	3.1494096114
H	0.5048253087	2.8213605038	5.4173454888
H	2.2765620112	1.7286388212	6.7762567362
H	3.5387926497	-0.1946391697	5.8319223384
H	3.0387425567	-1.0124389111	3.5636042009
H	-1.1935236668	-1.2173176808	3.4626855493
H	-3.3290018825	-0.5832625872	4.5480676732
H	-4.7639270521	1.1770857073	3.5404236782
H	-4.0462010048	2.3009674720	1.4426116349
H	-1.9081659896	1.6699066012	0.3671647461
H	-2.3689822157	-1.6427965538	-0.1265434514
H	-4.1279627538	-1.5617156390	-1.8456633988
H	-3.7665407007	-0.2854704113	-3.9489465232
H	-1.6162945145	0.9114234542	-4.3041664781
H	0.1522036900	0.8226178380	-2.5836974293
H	3.6403106765	1.7174322909	1.8981336363
H	6.1083076218	1.8524208084	2.0589842205
H	7.5153740154	-0.0081285453	1.2059198081
H	6.4396883278	-2.0044580717	0.1891724150
H	3.9509228128	-2.1311022452	0.0276039172
H	3.4800964590	0.9089853285	-1.5494194579
H	4.5098573999	0.5779934197	-3.7751136142
H	3.7598864927	-1.2957080481	-5.2257021926
H	1.9795845565	-2.8351924130	-4.4311587467
H	0.9599888783	-2.5073953220	-2.1944181037
H	3.1851937487	-6.2655603721	-1.3685061161
H	1.8872939793	-5.2480507467	-2.0463066323
H	3.5031315448	-4.5631216443	-1.7968582773
H	3.9092776257	-5.9047042671	1.0798409531
H	4.4111561443	-4.2963933848	0.5221987426
H	3.3584114671	-4.4569308843	1.9367748216
H	1.5573564802	-6.7515737205	0.5403962875
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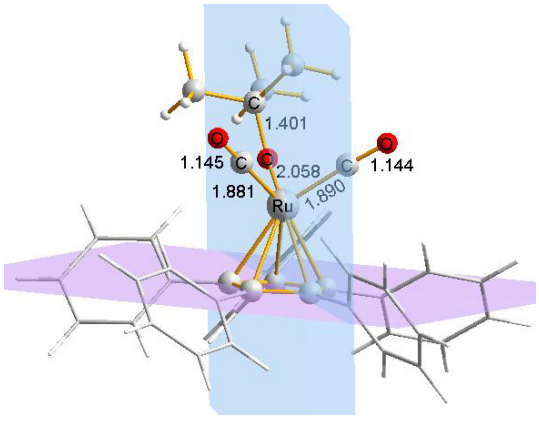

3:

80

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C	1.7206132747	-1.8231708984	-2.5556402985
C	2.3047102240	-2.0092048065	-3.8053461673
C	3.3068885097	-1.1472575134	-4.2497202186
C	3.7289443831	-0.0962752259	-3.4364966020
C	1.4888892194	-0.5101161275	-0.4346022640
C	2.1747442422	-0.2915251090	0.8087268336
C	1.1796833735	-0.0239085993	1.8155403093
C	-0.1101423247	-0.1363090879	1.2050973980
C	0.0880412881	-0.4213229992	-0.2042792298
C	3.6466190136	-0.2228629649	0.9587890169
C	4.4418019398	-1.2680422399	0.4748265096
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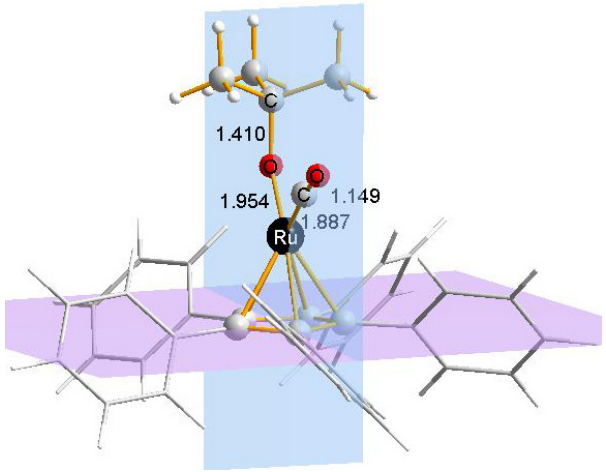
C	6.4331636112	-0.0686111935	1.1371883084



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78

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C	-2.7190498865	-1.8005691538	-2.0656272102
C	-2.7291860342	-1.0161878071	-3.2190222097
C	-1.7518591808	-0.0394832812	-3.4022851013
C	0.2762367725	-0.3893189052	-0.2437418018
C	1.6644685291	-0.3306520664	-0.4593293113
C	2.3145161218	-0.1304135639	0.8338465215
C	1.2934072506	0.0266476877	1.8231868130
C	0.0325567629	-0.2359159715	1.1880061323
C	2.3592142078	-0.5092570532	-1.7538699633
C	3.2855578437	0.4467121705	-2.1859274315
C	3.9098474058	0.3070590535	-3.4233187854
C	3.6189340580	-0.7907409196	-4.2320410694
C	2.7056217821	-1.7519821109	-3.7982404912
C	2.0755058007	-1.6162947524	-2.5639177959
Ru	1.2471444164	-2.0597839161	0.9960170875
C	3.7671631551	0.0960076096	1.0101638716
C	4.6969720785	-0.8487848819	0.5643878112
C	6.0614445049	-0.5984949852	0.6826611988
C	6.5086126254	0.5960494250	1.2470322004
C	5.5858272786	1.5408637078	1.6932346958
C	4.2202006521	1.2933294673	1.5743421165
C	1.5021581123	0.4284304517	3.2350885948
C	2.5375336809	-0.1112615324	4.0074668550
C	2.7480841587	0.3279024726	5.3111178455
C	1.9280357736	1.3119334166	5.8625645460
C	0.8982984007	1.8581276281	5.0990262244
C	0.6878303261	1.4219018895	3.7928997012
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C	-1.6084846792	-0.8207674149	2.9976953990
C	-2.8554416763	-0.6710702734	3.5974805901
C	-3.8155153085	0.1616094626	3.0227295636
C	-3.5206736941	0.8467388487	1.8456856851
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O	1.1055048168	-3.5994846080	-0.1982996753
C	1.1582521050	-4.9940712118	-0.0001423680
C	2.5065933834	-5.3961131384	0.6047185834
C	1.4578932575	-2.8705075995	2.6868612657
O	1.5639691747	-3.2168984407	3.7774895571
C	0.0053089743	-5.4452227634	0.9008473933
C	1.0063345181	-5.6223174973	-1.3906235061
H	-0.1127399433	1.8548589474	3.1996293635
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H	2.0915350097	1.6507379184	6.8811581470
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H	-4.2629287460	1.4955363485	1.3904740028
H	-2.0440791791	1.2358784344	0.3280124359
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H	-3.4739936899	-2.5676753366	-1.9224645563
H	-3.4944542902	-1.1685087016	-3.9742862556
H	-1.7517030704	0.5717356558	-4.2997707558
H	-0.0023771365	0.9111650335	-2.5776790689
H	3.4985392387	2.0279859360	1.9224515336
H	5.9277894097	2.4722808158	2.1344613706
H	7.5731149348	0.7897128772	1.3393245451
H	6.7762589594	-1.3372300818	0.3332022488
H	4.3414679387	-1.7780357106	0.1244527627
H	3.5154303938	1.2992709236	-1.5518661062
H	4.6247883445	1.0547661178	-3.7534319642
H	4.1072663890	-0.8993985354	-5.1960649846
H	2.4848131695	-2.6139654421	-4.4208608298
H	1.3845205324	-2.3754801952	-2.2036343791
H	1.0277421971	-6.7170641481	-1.3444608937
H	0.0572873259	-5.3059707645	-1.8365143539
H	1.8199359519	-5.2824212712	-2.0406673683
H	2.5994781374	-6.4855976174	0.6803447905
H	3.3190340793	-5.0171044589	-0.0249174114
H	2.6253873767	-4.9740422028	1.6086687406
H	-0.0174530871	-6.5364642472	1.0006479692
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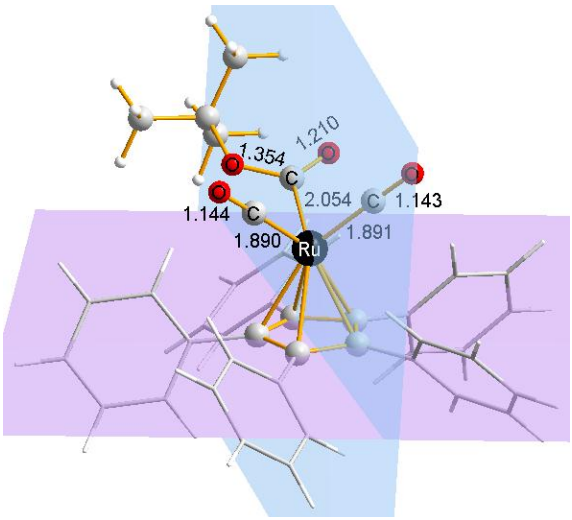

7 (not shown in Figure 4):

82

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C	3.1432053207	0.1002115887	-2.2231638726
C	3.6426972780	0.0119306239	-3.5204248552
C	3.1026766109	-0.9056685102	-4.4203228068
C	2.0625289852	-1.7380579275	-4.0105832634
C	1.5131770259	-0.5659565956	-0.4482907411
C	0.1129839261	-0.6405996325	-0.1478017185
C	-0.0714173820	-0.2196354945	1.2231645506
C	1.2041777149	0.0731766915	1.7741757728
C	2.1973430846	-0.1838977106	0.7504262884
Ru	1.1674414725	-2.2376130775	1.2157873245
C	1.7814641531	-3.6724489196	-0.1191764220
O	1.0674770965	-4.2476090226	-0.9082666911
C	-1.3780168724	-0.0415719895	1.9034529897
C	-1.6040975762	-0.5571319157	3.1852925041
C	-2.8123893361	-0.3278493549	3.8364222732
C	-3.8136359589	0.4180045416	3.2141579148
C	-3.5985687327	0.9331342002	1.9374685236
C	-2.3883021047	0.7055941177	1.2854004070
C	-0.9909005389	-0.8253145751	-1.1211126080
C	-1.9722253029	-1.8052547212	-0.9557455792
C	-3.0399690437	-1.8921208456	-1.8465981127
C	-3.1354160117	-1.0039396772	-2.9162370405
C	-2.1555421159	-0.0270323395	-3.0930918310
C	-1.0913822811	0.0621262589	-2.2003972875
C	3.6478694633	0.0981605661	0.8920552876
C	4.0626851016	1.3758661980	1.2865342716
C	5.4188736624	1.6763841717	1.3900886570
C	6.3746901236	0.7038324854	1.1000173974
C	5.9666214901	-0.5715085621	0.7095526942
C	4.6110372509	-0.8755844674	0.6075580856
C	1.4725947035	0.6650081733	3.1072527902
C	0.7068111914	1.7551190531	3.5414203430
C	0.9660820531	2.3604448338	4.7688858525
C	1.9991967937	1.8910150021	5.5776197668
C	2.7737601438	0.8134231552	5.1491827983

C	2.5127898634	0.2054042495	3.9246668258
C	2.3940057689	-2.9882684839	2.4416317358
O	3.1572860829	-3.4249060823	3.1731044668
C	-0.1796375077	-3.4520393746	1.7508216663
O	-1.0106740105	-4.1650825011	2.0798797539
O	3.1219848667	-3.8531404263	-0.0586142711
C	3.8258952639	-4.7823429750	-0.9437783680
C	3.3122975127	-6.2027322649	-0.7281258299
C	3.6986332201	-4.3303223715	-2.3932200472
C	5.2710432911	-4.6566346642	-0.4716735814
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H	5.6385399494	-3.6377568025	-0.6327118143
H	5.3480433988	-4.8920181970	0.5946130332
H	3.9475585383	-6.9032002397	-1.2808207639
H	3.3593900967	-6.4632063094	0.3347392060
H	2.2841118570	-6.3115022809	-1.0765827593
H	4.3578952091	-4.9403433267	-3.0213631899
H	2.6734680499	-4.4344647694	-2.7540159686
H	4.0004815644	-3.2814243433	-2.4910344705
H	-0.0946621418	2.1306045522	2.9110651492
H	0.3605531335	3.2027210916	5.0901728502
H	2.2020301102	2.3629371037	6.5343496084
H	3.5841839215	0.4428169989	5.7695939651
H	3.1288349826	-0.6272033309	3.5968227068
H	-0.8214353055	-1.1334159157	3.6735732739
H	-2.9729362507	-0.7337580311	4.8306321947
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H	-4.3724592947	1.5144700425	1.4452160941
H	-2.2238084541	1.1131545948	0.2921187482
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H	-3.7949877386	-2.6595577926	-1.7060091316
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H	4.4487047686	0.6713621600	-3.8287875905
H	3.4886383932	-0.9689549409	-5.4335678750
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H	0.7729288357	-2.3304245795	-2.4017781532
C	2.1940902483	1.2657772421	5.6942546105
C	1.1776362798	1.8895329348	4.9732833499
C	0.8452500873	1.4380493474	3.6979422822
Ru	1.1473839899	-2.1510054550	0.9721979972
C	1.1598684285	-3.0153296404	2.6423696299
O	1.1791280858	-3.4577335980	3.7028705054
C	-1.4008313915	0.0294101332	1.8684668793
C	-1.6605926780	-0.5718204017	3.1064292590
C	-2.8549989117	-0.3250164231	3.7767544374
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C	-1.0335083233	-0.6570084385	-1.1934331437
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C	-3.1023085880	-1.7405675726	-1.8291275659
C	-3.1344948525	-0.9986652975	-3.0096410140
C	-2.1156026044	-0.0874154072	-3.2839723426
C	-1.0679048522	0.0808371720	-2.3822698396
C	2.0523425614	-0.6077379274	-1.8843612892
C	1.6818694770	-1.6931501253	-2.6890413442
C	2.2061826576	-1.8327017969	-3.9716681105
C	3.1154432242	-0.8967066667	-4.4636161041
C	3.4940348445	0.1830391197	-3.6663196667
C	2.9631576678	0.3300049195	-2.3869687374
C	2.2776472274	-3.5553259742	0.2175991864
O	1.3460687094	-4.2021554568	-0.2660777224
O	3.5613718336	-3.8000124226	0.1023302804
C	4.0698346591	-4.9050269874	-0.7295935766
C	3.6600553332	-4.6740450231	-2.1791034029
C	5.5780968676	-4.7738228914	-0.5640183904
C	3.5684130054	-6.2351347085	-0.1806285258
H	6.0859793686	-5.5538009880	-1.1394896612
H	5.9178095622	-3.7976782900	-0.9247490304
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H	4.0649949018	-7.0524294361	-0.7139974034
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H	2.5787976188	-4.7636632025	-2.3079136060
H	3.9722142229	-3.6769136137	-2.5076855272
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H	0.6407030774	2.7305250584	5.4019951091
H	2.4519105140	1.6166538320	6.6891467520
H	3.6737860904	-0.3013267128	5.6859016821
H	3.0866167281	-1.0989443774	3.4175581471
H	-0.9195274155	-1.2349896609	3.5449994717
H	-3.0391791332	-0.7981780126	4.7366721575
H	-4.7476375420	0.7074804824	3.7384313608
H	-4.3063019614	1.7784748125	1.5388560928
H	-2.1742405996	1.3568721088	0.3592920183
H	-2.0318780597	-2.1454292342	-0.0013623246
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H	3.2506518347	2.0151618005	1.7927953714
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H	4.3192879370	-1.6505694201	-0.1680816271
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H	3.5270822109	-1.0076814843	-5.4624652090
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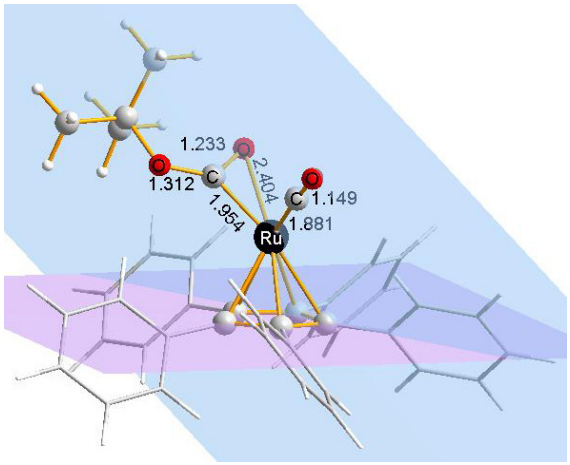
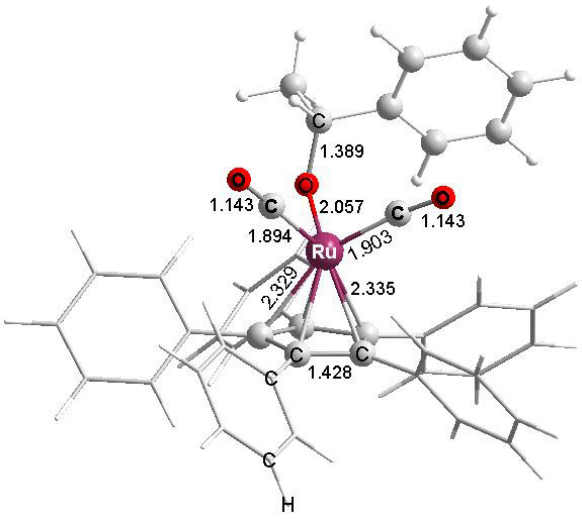


7' (not shown in Figure 4)**:**

81

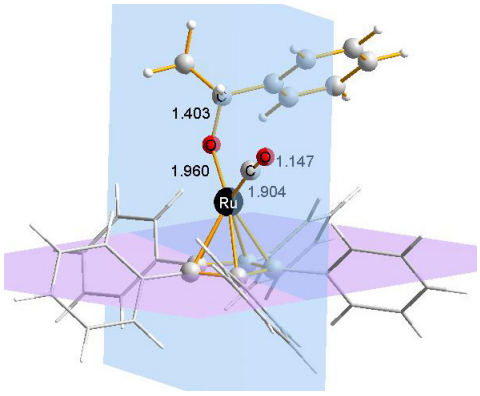
C	4.6102561199	-0.7055490934	0.2786385112
C	3.6252399109	0.1398139020	0.7992373344
C	4.0099193065	1.3515402122	1.3877381042
C	5.3541030471	1.7095992761	1.4573060386
C	6.3303058192	0.8618041285	0.9368921448
C	5.9535658690	-0.3448130762	0.3478208767
C	2.1803650076	-0.1703363791	0.6794612521
C	1.2063511679	-0.0627267967	1.7416848584
C	-0.1148718098	-0.1712629390	1.1644040046
C	0.0605778295	-0.4339253812	-0.2213323696
C	1.4661410291	-0.4300534251	-0.5350627766
C	1.5241847930	0.3533288748	3.1304407547
C	2.5467174191	-0.2647249559	3.8586231709
C	2.8788161269	0.1886797374	5.1319111345



4 (not the part of PES-scan in Figure 1)**:**

84

C	4.556339	-0.992454	0.489977
C	3.672561	-0.023762	0.982699
C	4.181610	1.121982	1.602570
C	5.558407	1.297292	1.729492
C	6.434965	0.332785	1.235483
C	5.930674	-0.811062	0.615424
C	2.212064	-0.194012	0.797898
C	1.187384	-0.080652	1.818565
C	-0.076392	-0.285105	1.186070
C	0.153075	-0.515765	-0.226064
C	1.562489	-0.414430	-0.452778
C	1.409285	0.358316	3.218869
C	2.421649	-0.191375	4.014393
C	2.643457	0.280137	5.305085
C	1.858415	1.310690	5.821448
C	0.855667	1.871945	5.033385
C	0.634556	1.402205	3.740597
Ru	1.129734	-2.245813	1.000819
C	2.205794	-3.123982	2.288943
O	2.870304	-3.630297	3.069476
C	-1.404448	-0.146553	1.831464
C	-1.702006	-0.787681	3.039071
C	-2.934368	-0.593524	3.655607
C	-3.885837	0.243237	3.072641
C	-3.596739	0.886626	1.870868
C	-2.363298	0.693953	1.252962
C	-0.894721	-0.619680	-1.270184
C	-1.964676	-1.514693	-1.156094
C	-2.967841	-1.544603	-2.121597
C	-2.912784	-0.687021	-3.219627
C	-1.849095	0.205239	-3.343746
C	-0.849725	0.241455	-2.374619
C	2.234313	-0.488454	-1.768499
C	1.903727	-1.472780	-2.706156
C	2.501050	-1.473705	-3.963474
C	3.431612	-0.491405	-4.299948
C	3.766582	0.492712	-3.370721
C	3.174093	0.492768	-2.110842
C	-0.343797	-3.379771	1.407717
O	-1.286299	-3.932994	1.742467
O	1.990693	-3.398678	-0.468601
H	-0.144067	1.849301	3.129271
H	0.243069	2.679970	5.421884
H	2.030529	1.675838	6.829441
H	3.432369	-0.159817	5.907490
H	3.050768	-0.982629	3.618264
H	-0.958264	-1.435024	3.497689
H	-3.152761	-1.099230	4.591152
H	-4.848677	0.391363	3.552304
H	-4.331389	1.540599	1.410682
H	-2.139932	1.200018	0.317873
H	-2.016305	-2.191121	-0.307184
H	-3.794456	-2.240978	-2.013890
H	-3.693969	-0.713754	-3.973460
H	-1.796493	0.877868	-4.194691
H	-0.025502	0.942759	-2.471872
H	3.497845	1.876060	1.984048
H	5.944760	2.189613	2.213055
H	7.507583	0.471292	1.333490
H	6.609488	-1.565369	0.228841
H	4.151483	-1.879871	0.003915
H	3.435174	1.262508	-1.389695
H	4.489332	1.262185	-3.625168
H	3.894633	-0.492228	-5.282483
H	2.239328	-2.245934	-4.680898
H	1.196776	-2.245412	-2.431238
C	1.964154	-4.787284	-0.461865
C	2.825232	-5.263964	-1.637065
H	2.401115	-5.198918	0.470561
C	0.554452	-5.347869	-0.586190
H	2.863786	-6.357490	-1.684811
H	2.401059	-4.885443	-2.573675
H	3.840140	-4.868648	-1.532502
C	0.167451	-6.505620	0.090037
C	-1.133591	-6.996234	-0.023633
C	-2.064043	-6.330385	-0.819762
C	-1.683902	-5.176484	-1.506326
C	-0.384454	-4.691407	-1.388876
H	0.887900	-7.018564	0.725050
H	-1.424490	-7.891912	0.517773
H	-3.079926	-6.705637	-0.902324
H	-2.402027	-4.648231	-2.128409
H	-0.094197	-3.775909	-1.898460

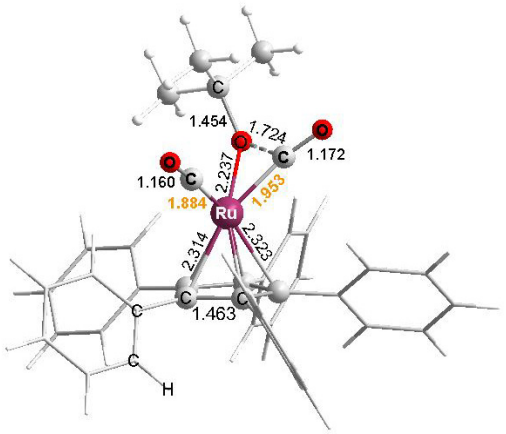


4' (not the part of PES-scan in Figure 1)**:**

82

C	4.311342	-1.272954	0.207900
C	3.555632	-0.205612	0.706578
C	4.204064	0.904056	1.260516
C	5.595352	0.955778	1.298308
C	6.346465	-0.102733	0.788912
C	5.702213	-1.216113	0.249515
C	2.078543	-0.225242	0.626196
C	1.163527	-0.050465	1.749833
C	-0.173447	-0.078810	1.245677
C	-0.103287	-0.411084	-0.149794
C	1.302270	-0.445367	-0.530786
C	1.590911	0.273401	3.129265
C	2.523961	-0.533606	3.789453
C	2.964725	-0.193946	5.065248
C	2.478973	0.953574	5.691986
C	1.549079	1.760660	5.038398
C	1.106218	1.423230	3.761335
Ru	0.800139	-2.083294	0.969882
C	-1.404410	0.215256	2.017291
C	-1.625726	-0.337725	3.283418
C	-2.762528	0.000049	4.011377
C	-3.694048	0.893372	3.483107
C	-3.480110	1.450118	2.223754
C	-2.341067	1.115168	1.495201
C	-1.247176	-0.460391	-1.089894
C	-2.378799	-1.239337	-0.827469
C	-3.464868	-1.219275	-1.697886
C	-3.432667	-0.423669	-2.842773
C	-2.308444	0.354728	-3.111717
C	-1.222205	0.337668	-2.240054
C	1.812487	-0.705863	-1.895169

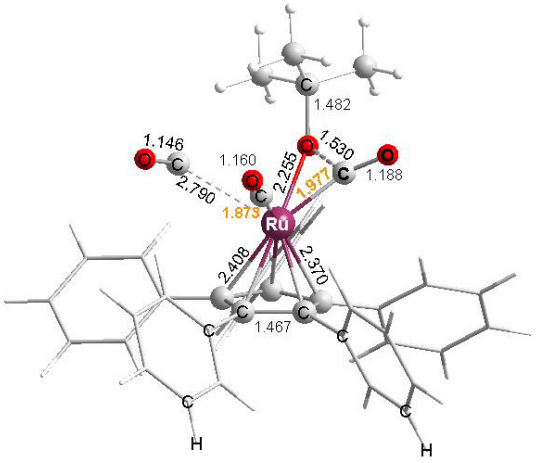
C	1.297573	-1.753441	-2.667340
C	1.760067	-1.958084	-3.964383
C	2.737256	-1.120546	-4.502023
C	3.256157	-0.078388	-3.734941
C	2.797898	0.128185	-2.436259
C	-0.651934	-3.058845	1.722574
O	-1.611229	-3.499837	2.171840
O	2.048961	-3.559753	0.650629
H	0.380485	2.050670	3.250441
H	1.167087	2.654710	5.522011
H	2.824584	1.217825	6.686980
H	3.689574	-0.825480	5.569804
H	2.900858	-1.426520	3.295642
H	-0.900280	-1.032077	3.699458
H	-2.922104	-0.438762	4.991548
H	-4.582711	1.153234	4.050436
H	-4.199740	2.147456	1.805494
H	-2.175133	1.552770	0.514615
H	-2.408911	-1.860359	0.062918
H	-4.336357	-1.829851	-1.482428
H	-4.279122	-0.412213	-3.522837
H	-2.274278	0.976552	-4.001283
H	-0.347057	0.946686	-2.451190
H	3.615470	1.725969	1.660502
H	6.091473	1.821604	1.726613
H	7.431404	-0.062392	0.818055
H	6.284807	-2.047498	-0.136066
H	3.799872	-2.150491	-0.181490
H	3.203257	0.939053	-1.836985
H	4.019091	0.575546	-4.146435
H	3.094286	-1.280002	-5.515188
H	1.351958	-2.772964	-4.554704
H	0.544599	-2.415478	-2.246011
C	1.777626	-4.933132	0.739808
C	3.084438	-5.669616	1.034041
H	1.068583	-5.138337	1.560260
C	1.149271	-5.424339	-0.552434
H	2.920787	-6.749873	1.109112
H	3.802601	-5.480552	0.228853
H	3.511736	-5.303761	1.972675
C	0.001916	-6.217123	-0.549661
C	-0.557938	-6.663230	-1.748732
C	0.030252	-6.318855	-2.962992
C	1.176261	-5.520459	-2.973443
C	1.727902	-5.072457	-1.777020
H	-0.462751	-6.483409	0.397916
H	-1.454634	-7.276143	-1.732592
H	-0.402081	-6.665605	-3.897161
H	1.640879	-5.249381	-3.917875
H	2.603630	-4.427188	-1.782046



TS1:

79

C	1.87993	-0.24837	4.33880
C	1.07522	0.44623	3.42185
C	0.53097	1.68337	3.80503
C	0.77632	2.20751	5.07524
C	1.57295	1.50479	5.98310
C	2.12491	0.27575	5.60832
C	0.83425	-0.07654	2.05445
C	-0.41542	-0.13955	1.37453
C	-0.17067	-0.60316	0.00887
C	1.26264	-0.75193	-0.15086
C	1.87695	-0.47413	1.11104
C	1.94987	-1.09573	-1.42394
C	1.45836	-2.10742	-2.26659
C	2.08205	-2.38891	-3.48104
C	3.20986	-1.66423	-3.87958
C	3.70543	-0.65437	-3.05138
C	3.08093	-0.37122	-1.83432
Ru	0.43069	-2.29314	1.37450
C	-1.21328	-3.13630	1.74134
O	-2.27381	-3.57537	1.90618
C	-1.15784	-0.54000	-1.10439
C	-2.34176	-1.29073	-1.11929
C	-3.26999	-1.13671	-2.15162
C	-3.03004	-0.23089	-3.18853
C	-1.85180	0.52100	-3.18569
C	-0.92624	0.36781	-2.15268
C	-1.73112	0.30416	1.90985
C	-2.28037	-0.23360	3.08422
C	-3.49505	0.23687	3.58326
C	-4.17995	1.25955	2.92019
C	-3.63939	1.80700	1.75359
C	-2.42684	1.33103	1.25095
C	3.33682	-0.38818	1.38870
C	3.90599	0.88270	1.57475
C	5.27617	1.02385	1.79563
C	6.09685	-0.10754	1.84588
C	5.53543	-1.37548	1.67513
C	4.16431	-1.51758	1.44489
C	1.18366	-3.96131	0.69400
O	1.86663	-3.75921	2.26412
C	1.80935	-4.81338	3.26340
C	2.01997	-4.13719	4.62234
O	1.47714	-4.88880	0.04092
C	0.47466	-5.56832	3.25146
C	2.97190	-5.76856	2.94713
H	2.02300	-4.88368	5.42601
H	2.97839	-3.60707	4.64348
H	1.21927	-3.41786	4.82437
H	0.50067	-6.37902	3.98883
H	-0.35501	-4.90634	3.51615
H	0.27208	-6.01582	2.27334
H	3.03003	-6.56657	3.69759
H	2.84084	-6.22611	1.96192
H	3.92139	-5.22208	2.95005
H	-0.08773	2.23730	3.10589
H	0.34309	3.16484	5.35317
H	1.76348	1.91170	6.97254
H	2.74709	-0.27830	6.30619
H	2.30527	-1.20529	4.05582
H	-1.75424	-1.02710	3.60535
H	-3.90838	-0.20053	4.48836
H	-5.12771	1.62340	3.30766
H	-4.16150	2.60291	1.22936
H	-2.01616	1.76069	0.34222
H	-2.53968	-2.00031	-0.32374
H	-4.18160	-1.72824	-2.14385
H	-3.75264	-0.11281	-3.99172
H	-1.64987	1.22673	-3.98732
H	-0.01338	0.95681	-2.15770
H	3.26974	1.76374	1.53988
H	5.70047	2.01549	1.92983
H	7.16401	-0.00052	2.02203
H	6.16421	-2.26096	1.72416
H	3.72916	-2.50556	1.33958
H	3.47615	0.41712	-1.20229
H	4.58242	-0.08478	-3.34783
H	3.69825	-1.88746	-4.82458
H	1.68849	-3.18089	-4.11275
H	0.59171	-2.68468	-1.96279



TS2:

81

C	1.87474	0.21007	4.37875
C	0.98669	0.72636	3.41689
C	0.32759	1.93575	3.70407
C	0.53057	2.59224	4.91882
C	1.40314	2.05927	5.87219
C	2.07792	0.86783	5.59241
C	0.78221	0.05352	2.11234
C	-0.44814	-0.07976	1.39135
C	-0.15783	-0.68539	0.08754
C	1.28174	-0.83883	-0.00580
C	1.84155	-0.46170	1.24876
C	2.03138	-1.19810	-1.23924
C	1.66107	-2.28279	-2.05143
C	2.34775	-2.55004	-3.23655
C	3.41036	-1.73531	-3.63835
C	3.78081	-0.64739	-2.84351
C	3.09782	-0.38205	-1.65541
Ru	0.26411	-2.24322	1.60966
C	-1.40290	-2.95661	2.07912
O	-2.46518	-3.36110	2.30991
C	-1.08912	-0.75287	-1.07548
C	-2.20687	-1.59745	-1.11105
C	-3.06560	-1.59850	-2.21288
C	-2.81952	-0.75729	-3.30089
C	-1.70685	0.08889	-3.27768
C	-0.85131	0.09061	-2.17524
C	-1.78458	0.44644	1.78938
C	-2.40557	0.09351	2.99714
C	-3.64400	0.63227	3.34634
C	-4.28347	1.54064	2.49727
C	-3.67066	1.90753	1.29669
C	-2.43298	1.36414	0.94561
C	3.29705	-0.45673	1.55192
C	3.93399	0.74502	1.90356
C	5.31133	0.78019	2.12642
C	6.07310	-0.38641	2.00768
C	5.44630	-1.58680	1.66100
C	4.06962	-1.62218	1.43190
C	0.65104	-3.97887	0.74651
O	1.63906	-4.00504	1.91408
C	1.99873	-5.27073	2.59620
C	2.87012	-4.84679	3.78071
O	0.49516	-4.86094	-0.03413
C	0.73161	-5.99169	3.06478
C	2.80907	-6.12982	1.61653
H	3.22513	-5.73591	4.31601
H	3.74267	-4.28281	3.43504
H	2.31044	-4.21903	4.47776
H	1.00431	-6.89703	3.61993
H	0.13967	-5.35427	3.72977
H	0.10593	-6.29310	2.21913
H	3.17005	-7.02966	2.12993
H	2.20793	-6.43625	0.75796
H	3.67943	-5.57416	1.25044
H	-0.34494	2.36839	2.97083
H	0.00614	3.52350	5.11708
H	1.55890	2.56900	6.81938
H	2.76427	0.44404	6.32110
H	2.40871	-0.71114	4.17678
H	-1.92266	-0.60875	3.66681
H	-4.11138	0.33530	4.28143
H	-5.25152	1.95463	2.76725
H	-4.15641	2.61147	0.62593
H	-1.96979	1.65320	0.00770
H	-2.40045	-2.26776	-0.28157
H	-3.92348	-2.26578	-2.22117
H	-3.48425	-0.76459	-4.16092
H	-1.49963	0.74432	-4.11981
H	0.01442	0.74728	-2.16913
H	3.34909	1.65536	1.99853
H	5.78798	1.71951	2.39456
H	7.14544	-0.35951	2.18313
H	6.02995	-2.49891	1.56464
H	3.58529	-2.55691	1.16987
H	3.39219	0.46852	-1.04878
H	4.60228	-0.00279	-3.14559
H	3.94341	-1.94589	-4.56204
H	2.04960	-3.39961	-3.84541
H	0.84160	-2.92712	-1.75457
C	0.34176	-2.44790	4.39106
O	-0.58841	-2.34801	5.05286

Complex in Figure S6:

80

C	-2.224726	0.627401	1.248122
C	-1.248610	-0.186922	1.834663
C	-1.541113	-0.839512	3.037341
C	-2.785273	-0.681046	3.640376
C	-3.754885	0.127976	3.047996
C	-3.471098	0.782042	1.850829
C	0.084545	-0.298782	1.198614
C	0.321561	-0.450881	-0.232742
C	1.708649	-0.388344	-0.456720
C	2.365714	-0.185385	0.833066
C	1.351216	-0.040313	1.828923
C	-0.713974	-0.703790	-1.258882
C	-0.731149	0.062635	-2.429185
C	-1.711570	-0.152625	-3.394759
C	-2.678869	-1.137086	-3.200591
C	-2.662525	-1.906386	-2.036993
C	-1.686169	-1.691964	-1.068636
Ru	1.288332	-2.126133	0.995461
C	1.347227	-2.943587	2.695224
O	1.342512	-3.292453	3.790135
C	2.389383	-0.548529	-1.761533
C	3.270116	0.441130	-2.212321
C	3.882318	0.318809	-3.457409
C	3.623843	-0.795066	-4.255673
C	2.755196	-1.788593	-3.803618
C	2.137237	-1.670263	-2.560958
C	3.820795	0.030950	0.996659
C	4.738362	-0.857183	0.424318
C	6.106123	-0.622872	0.533015
C	6.571758	0.503244	1.211472
C	5.662764	1.395869	1.777705
C	4.293609	1.163384	1.669268
C	1.560888	0.345860	3.245183
C	2.556884	-0.247504	4.029248
C	2.769029	0.178933	5.337054
C	1.989660	1.200718	5.879381
C	0.997274	1.797306	5.103716
C	0.784887	1.374152	3.793506
O	1.157270	-3.661857	-0.205968
C	1.090104	-5.055424	-0.006109
C	1.044025	-5.678483	-1.406389
C	2.329757	-5.554574	0.740784
C	-0.184164	-5.413749	0.763731
H	0.012843	1.843501	3.189791
H	0.385923	2.594264	5.516392
H	2.154626	1.529044	6.901261
H	3.543562	-0.292207	5.934610
H	3.169196	-1.042530	3.611941
H	-0.789231	-1.470839	3.502021
H	-2.998478	-1.194100	4.573191
H	-4.727273	0.246083	3.516641
H	-4.220044	1.413268	1.382039
H	-2.006599	1.139386	0.314777
H	-1.661149	-2.299076	-0.167224
H	-3.409961	-2.679139	-1.884618
H	-3.441156	-1.307319	-3.955078

H	-1.716512	0.447100	-4.299943
H	0.028115	0.825131	-2.582016
H	3.586108	1.861555	2.108293
H	6.018199	2.276637	2.304062
H	7.638908	0.685519	1.296592
H	6.808116	-1.322176	0.088545
H	4.372480	-1.733266	-0.107335
H	3.474795	1.305376	-1.585144
H	4.562283	1.092174	-3.802190
H	4.102702	-0.890363	-5.225885
H	2.559703	-2.662276	-4.418417
H	1.480019	-2.452779	-2.186935
H	0.977144	-6.771371	-1.360703
H	0.175650	-5.293899	-1.952009
H	1.947209	-5.405065	-1.962690
H	2.337236	-6.648278	0.811056
H	3.233896	-5.230540	0.214107
H	2.361218	-5.151600	1.759347
H	-0.291221	-6.499173	0.871987
H	-0.168647	-4.969265	1.765372
H	-1.059616	-5.027128	0.230594
C	4.627423	-3.170820	2.582654
O	5.258738	-3.834451	1.918413

Transition States in Figure S4:

(a)

82

C	4.681108	-0.878810	0.623160
C	3.682894	0.058805	0.926225
C	4.063258	1.365081	1.281327
C	5.411360	1.725587	1.329097
C	6.400132	0.785046	1.026548
C	6.029141	-0.516007	0.674975
C	2.234937	-0.276022	0.823242
C	1.219849	0.067633	1.832813
C	-0.050652	-0.190928	1.265708
C	0.140688	-0.577837	-0.141276
C	1.532878	-0.546578	-0.427115
C	1.490150	0.653398	3.170993
C	2.529885	0.200435	4.001530
C	2.783962	0.816189	5.227904
C	2.013478	1.904678	5.646967
C	0.986526	2.374571	4.824417
C	0.729485	1.757354	3.598893
Ru	1.207766	-2.201931	1.174808
C	2.255880	-2.951998	2.545246
O	2.945257	-3.364246	3.384487
C	-1.368592	-0.043225	1.936867
C	-1.611158	-0.612251	3.199671
C	-2.839897	-0.438767	3.836949
C	-3.852330	0.309175	3.226466
C	-3.623024	0.882852	1.973828
C	-2.392964	0.708489	1.334486
C	-0.944623	-0.712103	-1.152582
C	-1.836350	-1.793328	-1.175371
C	-2.855860	-1.855537	-2.128847
C	-2.999111	-0.838130	-3.075592
C	-2.111779	0.242256	-3.066685
C	-1.093821	0.303517	-2.113982
C	2.128056	-0.639779	-1.784862
C	1.718185	-1.615097	-2.709677
C	2.215548	-1.613530	-4.013345
C	3.134266	-0.640344	-4.418277
C	3.551065	0.333165	-3.507210
C	3.052449	0.334653	-2.202709
C	-0.887755	-4.046703	1.730734
O	-1.681293	-4.815094	1.998226
C	1.849116	-3.751958	-0.020632
O	1.037676	-4.547172	-0.481878
O	3.186062	-3.850061	-0.235438
C	3.812825	-4.999406	-0.939698
C	3.330068	-5.098419	-2.390396
C	5.300826	-4.639367	-0.897037
C	3.547390	-6.285744	-0.150650
H	5.893676	-5.432362	-1.367645
H	5.488834	-3.703466	-1.434873
H	5.642157	-4.521391	0.137386
H	4.115152	-7.112281	-0.595260
H	3.870894	-6.171324	0.890418
H	2.487263	-6.548220	-0.165003
H	3.917183	-5.863416	-2.914449
H	2.274050	-5.369909	-2.444221
H	3.477856	-4.145173	-2.907747
H	-0.064319	2.139484	2.964128
H	0.384789	3.226161	5.132401
H	2.213910	2.383051	6.602400
H	3.588230	0.441921	5.856300
H	3.139729	-0.641292	3.695523
H	-0.829885	-1.194458	3.679220
H	-3.007345	-0.889680	4.811957
H	-4.810331	0.441846	3.722925
H	-4.399973	1.469664	1.490028
H	-2.226334	1.166875	0.365135
H	-1.718615	-2.600958	-0.459846
H	-3.533474	-2.705485	-2.134566
H	-3.791092	-0.889176	-3.818559
H	-2.208736	1.036598	-3.802799
H	-0.404101	1.143627	-2.113953
H	3.301605	2.103056	1.518042
H	5.687343	2.740013	1.606747
H	7.450338	1.063515	1.068156
H	6.792023	-1.255122	0.442487
H	4.392958	-1.889885	0.354010
H	3.376612	1.103474	-1.509262
H	4.264643	1.096033	-3.808873
H	3.521864	-0.641433	-5.434132
H	1.884840	-2.376785	-4.713279
H	1.013618	-2.381607	-2.405384
XX	0.990847	-0.281696	0.643438

(b)

67

C	-0.894831	0.090005	-2.357831
C	-0.940460	-0.689044	-1.188468
C	-2.041067	-1.538994	-0.992336
C	-3.053742	-1.628893	-1.947820
C	-2.994059	-0.855740	-3.110874
C	-1.913734	0.008388	-3.308407
C	0.130302	-0.542004	-0.171850
C	1.519020	-0.535781	-0.433503
C	2.224552	-0.308874	0.836398
C	1.210775	-0.016214	1.847011
C	-0.076372	-0.275251	1.262559
C	2.170930	-0.680830	-1.758662
C	3.013040	0.349904	-2.212856
C	3.583499	0.291989	-3.485622
C	3.329828	-0.802031	-4.317963
C	2.502159	-1.835469	-3.869171
C	1.923030	-1.776307	-2.600337
Ru	1.144944	-2.145521	1.214638
C	-0.870622	-4.185120	1.207515
O	-1.560622	-5.085894	1.170150
C	3.679858	-0.027089	0.944238
C	4.642886	-0.989450	0.602973
C	6.001327	-0.665802	0.638902
C	6.415636	0.616682	1.010575
C	5.461843	1.579895	1.352353
C	4.103146	1.259920	1.321305
C	1.471290	0.549117	3.198741
C	2.547805	0.124081	3.997160
C	2.804411	0.726066	5.229142
C	2.002388	1.777386	5.682751
C	0.942906	2.223543	4.889671
C	0.681756	1.618142	3.658392
C	-1.397800	-0.061197	1.910787
C	-1.761301	-0.759770	3.073234

C	-2.991093	-0.526750	3.690950
C	-3.882565	0.407282	3.154308
C	-3.531187	1.108926	1.997891
C	-2.300123	0.876298	1.380097
Cl	2.323813	-3.958189	0.101570
C	1.699282	-2.863806	2.879323
O	2.071887	-3.272144	3.895526
H	-0.137432	1.985521	3.049209
H	0.317055	3.046937	5.224665
H	2.203238	2.244602	6.643540
H	3.634119	0.370960	5.834807
H	3.184703	-0.685285	3.661041
H	-1.073255	-1.489803	3.489349
H	-3.253595	-1.078181	4.590358
H	-4.842928	0.584737	3.631772
H	-4.216178	1.837977	1.572161
H	-2.037385	1.430895	0.483881
H	-2.101256	-2.136640	-0.089266
H	-3.891343	-2.301356	-1.781293
H	-3.784113	-0.923664	-3.854318
H	-1.859804	0.620716	-4.204933
H	-0.060159	0.764246	-2.522812
H	3.367386	2.014469	1.586529
H	5.773019	2.579703	1.645442
H	7.474012	0.864369	1.036080
H	6.737402	-1.420585	0.374304
H	4.321687	-1.987288	0.318440
H	3.214999	1.204015	-1.572747
H	4.228141	1.100002	-3.822582
H	3.779120	-0.851369	-5.306850
H	2.311970	-2.696661	-4.504437
H	1.301910	-2.591778	-2.248599
XX	0.980014	-0.316742	0.663670

(c)

80

C	-1.989626	1.426849	1.503215
C	-1.293445	0.321592	2.028197
C	-1.732510	-0.226729	3.243733
C	-2.840588	0.306373	3.906048
C	-3.528149	1.399355	3.371557
C	-3.096139	1.960082	2.166489
C	-0.074924	-0.146528	1.312772
C	0.036019	-0.371142	-0.095659
C	1.458109	-0.493463	-0.435824
C	2.203954	-0.384518	0.772175
C	1.261898	-0.254940	1.877914
C	-1.088981	-0.333976	-1.063948
C	-0.995082	0.440389	-2.233475
C	-2.072845	0.529080	-3.118153
C	-3.260131	-0.156755	-2.853186
C	-3.363662	-0.931660	-1.693099
C	-2.289762	-1.019041	-0.807614
Ru	0.844994	-2.236668	0.967857
C	0.014755	-3.092821	2.426702
O	-0.532745	-3.500092	3.369325
C	2.036987	-0.547915	-1.805631
C	2.773912	0.553641	-2.275309
C	3.300313	0.560856	-3.568404
C	3.099526	-0.534611	-4.413646
C	2.377970	-1.638983	-3.952408
C	1.854127	-1.646677	-2.657630
C	3.681418	-0.326561	0.875738
C	4.498353	-1.281752	0.248755
C	5.888003	-1.158620	0.296945
C	6.481602	-0.082114	0.964109
C	5.675438	0.871921	1.591638
C	4.285033	0.748999	1.551716
C	1.641833	0.056091	3.282715
C	2.442960	-0.814472	4.036944
C	2.839799	-0.473586	5.330995
C	2.443273	0.743831	5.892537
C	1.646093	1.618474	5.149472
C	1.247675	1.277661	3.854888
C	-0.548635	-3.884802	-0.852073
O	-0.802547	-4.833314	-1.428752
O	2.142779	-3.658804	0.395428
C	2.655455	-4.832951	1.013073
C	3.711686	-5.386727	0.033524
C	3.327714	-4.490055	2.354918
C	1.560035	-5.895240	1.226266
H	0.629032	1.964980	3.285345
H	1.330434	2.567485	5.575958
H	2.750988	1.007548	6.901357
H	3.458318	-1.162027	5.901315
H	2.749626	-1.761100	3.604084
H	-1.212589	-1.072444	3.677635
H	-3.165336	-0.136814	4.844095
H	-4.390171	1.811611	3.890173
H	-3.617802	2.813697	1.740556
H	-1.658580	1.874498	0.570636
H	-2.376144	-1.621628	0.090973
H	-4.283183	-1.469831	-1.476832
H	-4.097497	-0.089401	-3.543232
H	-1.980284	1.135979	-4.015384
H	-0.081368	0.983207	-2.451069
H	3.665982	1.495643	2.040001
H	6.126118	1.712026	2.114274
H	7.564406	0.011512	0.996254
H	6.509562	-1.907446	-0.187969
H	4.034149	-2.127838	-0.246924
H	2.932772	1.408185	-1.622323
H	3.867554	1.421758	-3.913850
H	3.508689	-0.529880	-5.420883
H	2.228460	-2.501350	-4.597230
H	1.324829	-2.519435	-2.290947
H	4.152825	-6.319399	0.408039
H	3.252855	-5.587798	-0.941398
H	4.516854	-4.658104	-0.112977
H	3.828473	-5.368840	2.781054
H	4.075087	-3.701174	2.214459
H	2.586104	-4.138595	3.081167
H	1.979075	-6.805756	1.673633
H	0.774255	-5.529770	1.895185
H	1.099590	-6.171020	0.270878
XX	0.963039	-0.331997	0.672430

Table S1. Thermochemical corrections (A) for the CO dissociation in Figure 1, and (B) relative to complex 3 in Scheme 2.

	ΔZPE (kcal/mol)	ΔG (kcal/mol)
(A)		
$CpRu(CO)_2H$: 16e complex + CO	-2.389	-12.3957
$CpRu(CO)_2OtBu$: 16e + CO	-2.194	-11.6192
$CpRu(CO)_2Cl$: 16e + CO	-2.292	-12.3021
Complex **7**: 16e + CO	-2.701	-12.0432
(B)		
TS1	-0.105	-1.2653
TS2	1.033	10.2713
complex 7'	1.116	-1.7395

Table S2. Additional "raw" electronic energies.

Complex	E (Hartrees) Method: DFT(m06-2x/lacvp*+)
4	-2053.994822
4'	-1940.68093
from Figure S6	-1901.593426
TS1	-1901.605257
TS2	-2014.871845
TS in Figure S4a	-2014.904483
TS in Figure S4b	-2128.828275
TS in Figure S4c	-1901.585202
CO isolated	-113.2770953

Table S3. "Raw" electronic energies - selected points of the potential energy scans as well as the optimized 18-electron and 16-electron initial and final complexes:

		DFT B3LYP/lacvp+*		DFT M06-2X/lacvp*+		SOLVENT	
RuCpPh5(CO)2H							
Complex	r	Opt E /Hartrees	Rel E	Opt E	Rel E	Sol E	Rel Sol E
6: 18e-CpPh5-H	1.879	-1670.02826848	0.0000	-1669.26262233	0	-5.3289	0
18e-CpPh5-H-193	1.9300	-1670.02755325	0.4488	-1669.26185628	0.480708126	-4.7097	1.068017366
18e-CpPh5-H-198	1.9800	-1670.02562563	1.6584	-1669.25983714	1.747731271	-4.7234	2.263915487
18e-CpPh5-H-203	2.0300	-1670.02254267	3.5930	-1669.25709294	3.469742868	-4.6457	4.276202108
18e-CpPh5-H-208	2.0800	-1670.01903819	5.7921	-1669.25389703	5.475205288	-4.6607	6.460290719
18e-CpPh5-H-213	2.1300	-1670.01498638	8.3346	-1669.25027501	7.748055969	-4.7114	8.952139115
18e-CpPh5-H-218	2.1800	-1670.01062054	11.0742	-1669.24661856	10.04251095	-4.5743	11.82884345
18e-CpPh5-H-222	2.2200	-1670.00700559	13.3427	-1669.24368736	11.88186497	-3.4233	15.24825781
18e-CpPh5-H-230	2.3000	-1670.00018231	17.6243	-1669.23821039	15.3187172	-4.4652	18.48802633
18e-CpPh5-H-238	2.3800	-1669.99338433	21.8901	-1669.23292866	18.63304885	-4.5038	22.71521954
18e-CpPh5-H-246	2.4600	-1669.98684673	25.9925	-1669.22807561	21.67838251	-4.6847	26.63672308
18e-CpPh5-H-263	2.6300	-1669.97575495	32.9527	-1669.21903912	27.34885612	-4.8054	33.47621817
18e-CpPh5-H-288	2.8800	-1669.96497082	39.7199	-1669.20875221	33.80399053	-4.6079	40.44085444
18e-CpPh5-H-300	3.0000	-1669.96168387	41.7824	-1669.20496413	36.18104416	-4.6328	42.47854636
18e-CpPh5-H-320	3.2000	-1669.95764583	44.3164	-1669.19996207	39.31987943	-4.5737	45.07155162
18e-CpPh5-H-330	3.3000	-1669.95627448	45.1769	-1669.19812267	40.47412091	-4.6091	45.89668292

18e-CpPh5-H-340	3.4000	-1669.95503590	45.9541	-1669.19652833	41.47458237	-4.6644	46.61860878
6': 16e-CpPh5-H		-1556.635441036		-1555.91202938			
16e-CpPh5-H + CO		-1669.952774	47.3735	-1669.189125	46.12052966	-5.2122	47.49020882
RuCpPh5(CO)2Cl							
Complex	X	Opt E /Hartrees	Rel E	Opt E	Rel E	Sol E	Rel Sol E
1: 18e-CpPh5-Cl	1.905	-2129.6562519	0.0000	-2128.86595972	0	-7.0607	0
18e-CpPh5-Cl-193	1.9300	-2129.6556648	0.3684	-2128.86580849	0.094895293	-6.4394	0.989700456
18e-CpPh5-Cl-198	1.9800	-2129.6542156	1.2778	-2128.86473122	0.770893118	-6.2279	2.110562936
18e-CpPh5-Cl-203	2.0300	-2129.6520179	2.6569	-2128.86273130	2.02585719	-6.4676	3.249954274
18e-CpPh5-Cl-208	2.0800	-2129.6490708	4.5062	-2128.86055560	3.391133717	-6.5359	5.030986538
18e-CpPh5-Cl-213	2.1300	-2129.64573310	6.6006	-2128.85818332	4.879759488	-6.4146	7.246711862
18e-CpPh5-Cl-218	2.1800	-2129.6423883	8.6995	-2128.85563259	6.480366975	-6.9	8.860213861
18e-CpPh5-Cl-222	2.2200	-2129.6395515	10.4796	-2128.85441347	7.245375051	-6.9658	10.57451641
18e-CpPh5-Cl-230	2.3000	-2129.6342583	13.8011	-2128.85072255	9.561460086	-6.4462	14.41562304
18e-CpPh5-Cl-238	2.3800	-2129.6288210	17.2131	-2128.84712860	11.81669332	-6.4126	17.86122811
18e-CpPh5-Cl-246	2.4600	-2129.6246567	19.8262	-2128.84397575	13.79513682	-6.0689	20.81804365
18e-CpPh5-Cl-263	2.6300	-2129.6173211	24.4294	-2128.83805329	17.51153347	-6.1127	25.37741508
18e-CpPh5-Cl-288	2.8800	-2129.6105317	28.6898	-2128.83180589	21.43183212	-6.5626	29.18788675
18e-CpPh5-Cl-300	3.0000	-2129.6093375	29.4392	-2128.82980350	22.68834784	-6.5983	29.90158395
18e-CpPh5-Cl-320	3.2000	-2129.6086606	29.8640	-2129.61003454	-466.9136492	-6.4836	30.44107119
18e-CpPh5-Cl-330	3.3000	-2129.6088352	29.7544	-2128.82791294	23.87469132	-6.2455	30.56960416
18e-CpPh5-Cl-340	3.4000	-2129.6092318	29.5055	-2128.82790866	23.87737734	-6.0035	30.56270011
1': 16e-CpPh5-Cl		-2016.29617740		-2015.54806785			
16e-CpPh5-Cl + CO		-2129.61351	26.8207	-2128.825163	25.60030448	-5.8723	28.00911325
RuCpPh5(CO)2OtBu							
Complex	X	Opt E /Hartrees	Rel E	Opt E	Rel E	Sol E	Rel Sol E
3: 18e-CpPh5-OtBu	1.886	-1902.4878634	0.0000	-1901.62046684	0.0000	-4.1328	0
18e-CpPh5-OtBu-193	1.9300	-1902.4872293	0.3979	-1901.62001704	0.2823	-3.2826	1.24805965
18e-CpPh5-OtBu-198	1.9800	-1902.4853969	1.5477	-1901.61857418	1.1877	-4.9531	0.727429732
18e-CpPh5-OtBu-203	2.0300	-1902.4828485	3.1469	-1901.61750587	1.8580	-3.4684	3.811290228
18e-CpPh5-OtBu-208	2.0800	-1902.4796303	5.1663	-1901.61525068	3.2732	-4.1586	5.140540006
18e-CpPh5-OtBu-213	2.1300	-1902.4758229	7.5555	-1901.61298704	4.6936	-3.3198	8.368506747
18e-CpPh5-OtBu-218	2.1800	-1902.4721039	9.8892	-1901.61032706	6.3628	-3.25	10.77203645
18e-CpPh5-OtBu-222	2.2200	-1902.4692948	11.6520	-1901.60865334	7.4131	-3.2858	12.49896626
18e-CpPh5-OtBu-230	2.3000	-1902.4640168	14.9640	-1901.60511058	9.6362	-3.8678	15.22896279
18e-CpPh5-OtBu-238	2.3800	-1902.4596390	17.7110	-1901.60188681	11.6591	-3.9093	17.93452108
18e-CpPh5-OtBu-246	2.4600	-1902.4550100	20.6158	-1901.59904720	13.4410	-3.352	21.39659483
18e-CpPh5-OtBu-263	2.6300	-1902.4502331	23.6133	-1901.59436173	16.3812	-4.1058	23.64031523
18e-CpPh5-OtBu-288	2.8800	-1902.4501784	23.6476	-1901.58877802	19.8850	-3.9335	23.84694538
18e-CpPh5-OtBu-300	3.0000	-1902.4516749	22.7086	-1901.58958285	19.3800	-4.0388	22.80257347
18e-CpPh5-OtBu-330	3.3000	-1902.4537438	21.4103	-1901.59186556	17.9476	-4.1313	21.4118184
18e-CpPh5-OtBu-340	3.4000	-1902.4540206	21.2367	-1901.59222318	17.7231	-3.788	21.58145438
3': 16e-CpPh5-OtBu		-1789.1446398		-1788.31286319			
16e-CpPh5-OtBu + CO		-1902.461973	16.2466	-1901.58995834	19.1444	-4.2765	16.10291348

RuCpPh5(CO)3OtBu							
Complex	X	Opt E /Hartrees	Rel E	Opt E	Rel E	Sol E	Rel Sol E
7: 18e-CpPh5-3CO-OtBu	1.890	-2015.85389973	0.0000	-2014.952558	0	-5.2896	0
18e-CpPh5-3CO-OtBu-193	1.9300	-2015.85349563	0.1323	-2014.952084	0.297074156	-4.9515	0.470444432
18e-CpPh5-3CO-OtBu-198	1.9800	-2015.85134287	1.6045	-2014.950719	1.15368464	-4.9766	1.917451777
18e-CpPh5-3CO-OtBu-203	2.0300	-2015.84895432	3.1033	-2014.948431	2.58926048	-4.8683	3.524587163
18e-CpPh5-3CO-OtBu-208	2.0800	-2015.84524794	5.4291	-2014.945722	4.289321843	-5.1684	5.550270638
18e-CpPh5-3CO-OtBu-213	2.1300	-2015.84189654	7.5321	-2014.942748	6.155661094	-4.5796	8.242109377
18e-CpPh5-3CO-OtBu-218	2.1800	-2015.83822327	9.8371	-2014.93967	8.087041232	-4.4413	10.68541888
18e-CpPh5-3CO-OtBu-222	2.2200	-2015.83448460	12.1832	-2014.937233	9.616151618	-4.8460	12.62676879
18e-CpPh5-3CO-OtBu-230	2.3000	-2015.82859975	15.8760	-2014.932471	12.60448454	-5.2688	15.89676443
18e-CpPh5-3CO-OtBu-238	2.3800	-2015.82273553	19.5558	-2014.928094	15.35096229	-4.9035	19.94191252
18e-CpPh5-3CO-OtBu-246	2.4600	-2015.81717120	23.0475	-2014.924199	17.79557215	-5.0502	23.28688233
18e-CpPh5-3CO-OtBu-263	2.6300	-2015.80844931	28.5205	-2014.917632	21.91584695	-4.6025	29.20764365
18e-CpPh5-3CO-OtBu-288	2.8800	-2015.80108434	33.1421	-2014.909444	27.0541051	-4.8605	33.57122841
18e-CpPh5-3CO-OtBu-300	3.0000	-2015.79842801	34.8090	-2014.906489	28.90864065	-5.1094	34.98920107
18e-CpPh5-3CO-OtBu-320	3.2000	-2015.79642388	36.0666	-2014.902828	31.20600523	-5.462	35.89421311
7': 16e-CpPh5-3CO-OtBu		-1902.483491707		-1901.619032			
16e-CpPh5-3CO-OtBu + CO		-2015.800825	33.3051	-2014.896128	35.41030156	-5.4548	33.13991426