S1. Isomers and energies of $Rh(TFA)_3(CO)_2$

The nuclear Cartesian coordinates for the three isomers of $Rh(TFA)_3(CO)_2$ are shown below. The three isomers are described by the positions of the two carbonyl ligands relative to the plane defined by the bidentate acetate ligand. Energies are given relative to the mixed isomer (one axial, and one equatorial carbonyl), which is lowest in Energy. HOMO-LUMO gaps are also given for each species

Mixed Isomer (primary isomer); E = 0.00 kcal/mol; HOMO-LUMO: 4.93 eV

O	-0.426499	2.167328	-1.283176
C	0.058297	2.337961	-0.086249
O	0.464485	1.435072	0.649096
C	0.093648	3.811556	0.371492
Rh	0.161012	-0.430924	-0.307580
F	0.587234	3.896786	1.602590
F	-1.149522	4.302555	0.352105
F	0.861982	4.514728	-0.467811
F	-4.788153	-2.026797	0.458512
C	-3.917205	-1.093832	0.844285
C	-2.546438	-1.288807	0.146482
F	-3.764779	-1.167946	2.176465
F	-4.418095	0.115904	0.538332
O	-2.349142	-2.246670	-0.590109
O	-1.718526	-0.345073	0.462084
O	1.611061	-1.497684	1.155864
C	2.499532	-1.122669	0.363358
O	2.216885	-0.496322	-0.720899
C	3.986084	-1.418050	0.631219
F	4.159736	-1.877045	1.871283
F	4.716559	-0.305267	0.468286
F	4.416251	-2.345111	-0.241499
O	-0.885555	0.574226	-2.862332
C	-0.488703	0.715315	-1.765505
C	-0.125647	-2.061745	-1.293805
O	-0.016436	-2.981728	-1.955416

Equatorial Isomer; E = 0.36 kcal/mol; HOMO-LUMO: 4.87 eV

O	-2.452738	-1.748744	1.157040
C	-2.773568	-0.959982	0.262024
O	-1.998708	-0.222401	-0.445460
C	-4.267427	-0.800696	-0.120484
Rh	-0.005184	-0.334222	0.014184
F	-4.631673	0.485620	-0.017661
F	-5.044189	-1.536443	0.674651
F	-4.446505	-1.199528	-1.390169
F	4.475074	-1.497918	1.245527

C	4.254430	-0.836545	0.096629
C	2.754773	-0.962441	-0.274831
F	4.587710	0.448930	0.268247
F	5.025725	-1.359349	-0.857337
O	1.991581	-0.252009	0.470532
O	2.418411	-1.720549	-1.191577
O	-0.233037	1.487145	1.095261
C	0.013273	2.119865	0.025260
O	0.249154	1.487341	-1.048835
C	0.033829	3.655939	0.009481
F	-0.277170	4.145264	1.210727
F	-0.849714	4.104643	-0.892005
F	1.258067	4.078388	-0.337554
O	0.036475	-2.425176	-2.203622
C	0.280373	-1.698120	-1.357832
C	-0.305320	-1.713143	1.369202
O	-0.077554	-2.448874	2.211610

Axial Isomer; E = 3.84 kcal/mol; HOMO-LUMO: 4.41 eV

O	1.270653	2.141687	-1.458726
C	1.565844	2.024023	-0.274463
O	1.042239	1.236994	0.606670
C	2.713304	2.873307	0.333486
Rh	-0.443982	0.008996	-0.016146
F	3.128966	3.795042	-0.535653
F	3.745115	2.069565	0.640576
F	2.299281	3.486823	1.452168
F	3.256500	-3.621664	0.672891
C	2.633346	-2.948073	-0.294371
C	1.525676	-2.036880	0.297886
F	2.080554	-3.826247	-1.147774
F	3.534590	-2.211881	-0.960992
O	1.223162	-2.121783	1.482990
O	1.015450	-1.265408	-0.604739
O	-2.307732	-0.982398	-0.441685
C	-2.931589	0.045998	-0.040329
O	-2.285548	1.059273	0.364742
C	-4.468230	0.046750	0.009001
F	-4.963368	-0.806619	-0.889613
F	-4.937582	1.272901	-0.236607
F	-4.857607	-0.334538	1.236172
O	-0.628166	0.879959	-3.005026
C	-0.404710	0.709887	-1.902866
C	-0.465818	-0.690594	1.872538
O	-0.722685	-0.858080	2.967750

S2. Nuclear coordinates for the distorted $Rh(TFA)_3(CO)_2$ complex shown in figure 4b.

O	-0.448885	2.296663	-1.302059
C	0.070721	2.605348	-0.140934
O	0.381148	1.810822	0.741487
C	0.235818	4.126816	0.062702
Rh	0.013354	-0.233275	-0.059717
F	0.937049	4.366737	1.168300
F	-0.980286	4.680461	0.180817
F	0.861095	4.668614	-0.987200
F	-4.217746	-3.074532	0.098639
C	-3.826731	-1.959418	0.709804
C	-2.406939	-1.546552	0.269210
F	-3.819213	-2.154030	2.033485
F	-4.674050	-0.968353	0.415116
O	-1.783669	-2.373225	-0.512081
O	-1.938686	-0.477585	0.686769
O	1.561238	-1.246251	1.311884
C	2.380247	-0.870834	0.445980
O	2.002920	-0.244231	-0.607460
C	3.885381	-1.153802	0.588768
F	4.161629	-1.634264	1.803266
F	4.586670	-0.025659	0.396726
F	4.263634	-2.054942	-0.331394
O	-1.300364	0.586496	-2.553930
C	-0.722392	0.810094	-1.550700
C	-0.394312	-1.962781	-0.900957
O	0.165049	-2.732303	-1.595863

S3. Nuclear coordinates, HOMO-LUMO gaps, and raw thermochemical data (at 353K) for Rh(I) species

$[Rh(CO)_2(TFA)]_2$:
HOMO-LUMO: 3.92 eV
E_{tot} = -1082601.79 kcal/mol
G_{tot} = -1082669.76 kcal/mol
Coordinates:

O	-0.688320	1.456827	-1.169593
C	-1.099074	1.800645	-0.034105
O	-0.706391	1.451678	1.107184
C	-2.305617	2.773056	-0.022901
F	-2.157899	3.700799	0.934271
F	-3.424660	2.071126	0.231867
F	-2.451585	3.393839	-1.198119
Rh	0.755883	-0.008566	-1.623144
Rh	0.763899	0.026976	1.607063

C	1.983118	-1.280607	2.156063
O	2.712803	-2.105549	2.474893
C	1.925676	1.403248	2.113918
O	2.617267	2.270034	2.405228
C	1.959040	-1.357459	-2.111015
O	2.676510	-2.206852	-2.390506
C	1.957125	1.330988	-2.141896
O	2.674091	2.174608	-2.439674
O	-0.682272	-1.465762	-1.127084
C	-1.055713	-1.825849	0.017500
O	-0.642439	-1.474927	1.149768
C	-2.239925	-2.825489	0.017474
F	-2.363590	-3.445286	1.195721
F	-2.077866	-3.753086	-0.937607
F	-3.375912	-2.149449	-0.231810

$[Rh(CO)_2Cl]_2$:
HOMO-LUMO: 4.33 eV
E_{tot} = -999679.74 kcal/mol
G_{tot} = -999728.39 kcal/mol

Rh	1.642265	0.000386	-0.137762
Cl	0.000448	1.653508	-0.904210
Rh	-1.642105	0.001130	-0.137716
Cl	-0.000299	-1.650933	-0.904920
C	-2.807861	1.344685	0.442973
O	-3.504516	2.183597	0.797414
C	-2.805438	-1.342882	0.444266
O	-3.500940	-2.182591	0.799212
C	2.808642	1.343451	0.442823
O	3.505809	2.182024	0.797058
C	2.805045	-1.344108	0.444217
O	3.500176	-2.184082	0.799264

$Rh(CO)_2(TFA)$:
HOMO-LUMO: 4.52 eV
E_{tot} = -541285.39 kcal/mol
G_{tot} = -541327.40 kcal/mol

Rh	1.086988	-0.001317	0.001862
C	2.396510	1.336685	-0.015774
O	3.168043	2.184609	-0.027779
C	2.405567	-1.330207	0.009139
O	3.181162	-2.174514	0.015042
O	-0.754712	1.091963	-0.002431
C	-1.369993	-0.016326	0.005948
O	-0.742738	-1.116917	0.017927
C	-2.907125	-0.006080	-0.004832

F	-3.396636	-1.248511	-0.000872
F	-3.346120	0.630615	-1.102922
F	-3.364532	0.644320	1.077316

S4. Nuclear Coordinates, HOMO-LUMO gaps, and raw thermochemical data (at 353K) for Vanadium Species

$[VO_2(TFA)]_2$:
HOMO-LUMO: 4.33 eV
E_{tot} = -939053.61 kcal/mol
G_{tot} = -939111.51 kcal/mol

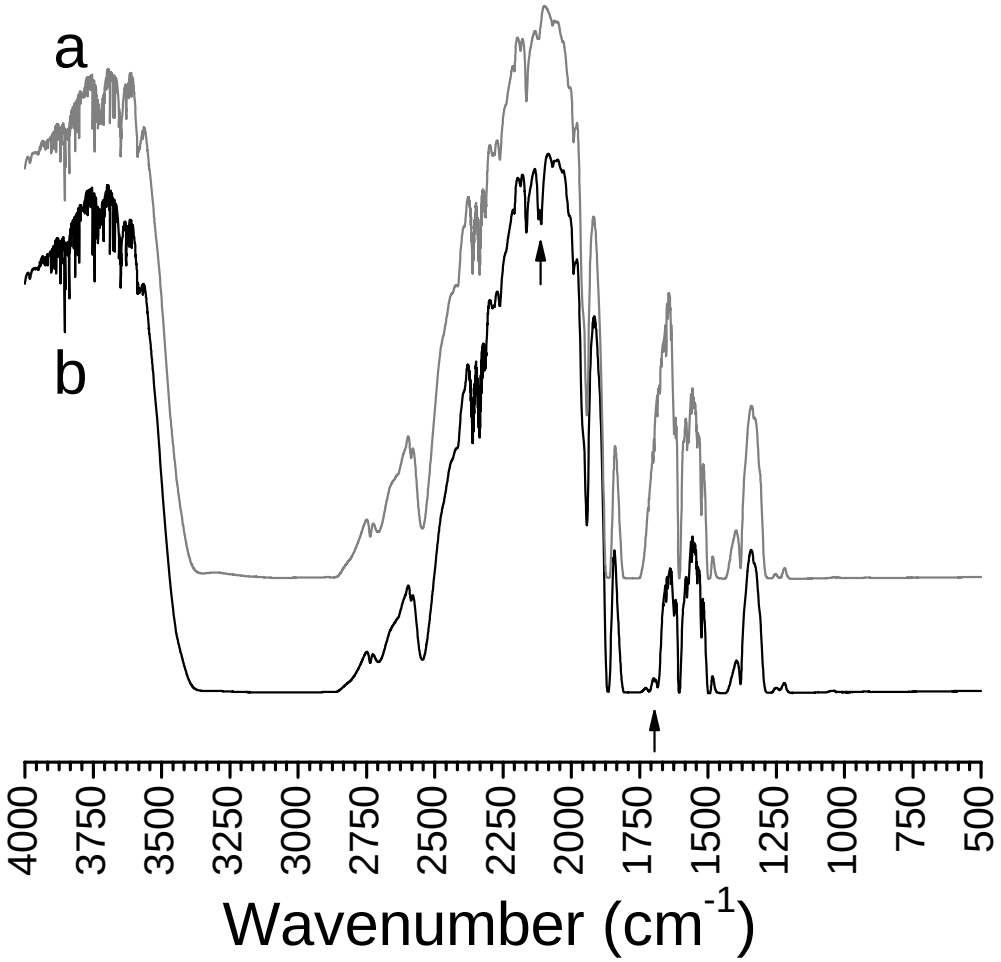
V	1.326491	1.239512	0.010115
O	-0.006080	1.253531	1.199791
V	-1.326264	1.235184	-0.013170
O	0.006473	1.140405	-1.201505
O	-2.535592	0.005039	1.062082
C	-3.015618	-0.448628	-0.022830
O	-2.551889	-0.012290	-1.113753
C	-4.156352	-1.477386	0.009646
F	-4.276625	-2.080748	-1.172872
F	-5.298339	-0.836516	0.297683
F	-3.916040	-2.392187	0.954717
O	2.549384	0.019885	1.065746
C	3.020631	-0.440955	-0.021908
O	2.548652	-0.011816	-1.110177
C	4.158628	-1.472651	0.011853
F	4.285860	-2.068845	-1.173336
F	3.907710	-2.393036	0.949212
F	5.300577	-0.837940	0.313296
O	1.991881	2.656669	-0.042404
O	-1.996005	2.650104	-0.071347

$VO(TFA)_2$:
HOMO-LUMO: 6.83 eV
E_{tot} = -752585.56 kcal/mol
G_{tot} = -752634.87 kcal/mol

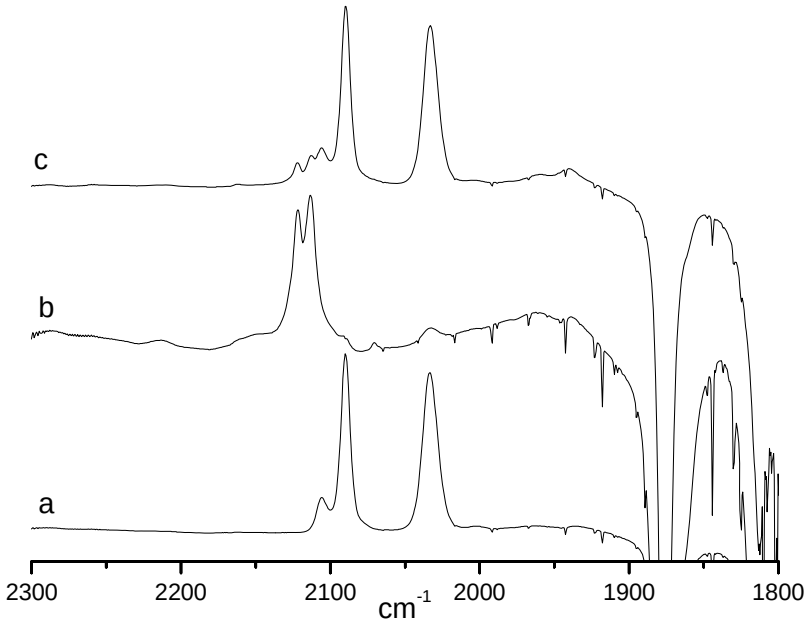
V	-0.000287	-1.013838	-0.024986
O	-1.533957	-0.222233	-1.087879
C	-2.119654	0.008573	0.015060
O	-1.542650	-0.310350	1.098771
C	-3.520202	0.643243	0.017452
F	-3.830550	1.103659	1.229490
F	-4.413260	-0.291007	-0.341885
F	-3.562432	1.647779	-0.864506
O	1.544387	-0.237062	-1.084961
C	2.131951	-0.017736	0.019413

O	1.547806	-0.329131	1.101399
C	3.526169	0.631603	0.024560
F	4.024576	0.672683	1.259858
F	3.430501	1.880281	-0.455768
F	4.345807	-0.076018	-0.762108
O	-0.008465	-2.577502	-0.089549

2. Infrared Spectra



S2: Infrared spectra of the solution after ½ hour reaction. Arrows indicate peaks peaks associated with carbonyl groups. a) Background. Toluene (12.4 mmol), trifluoroacetic acid (4.2 mmol), and trifluoroacetic anhydride (1.3 mmol) b) Reaction solution after ½ hour. Toluene (12.4 mmol), trifluoroacetic acid (4.2 mmol), and trifluoroacetic anhydride (1.3 mmol), $[Rh(CO)_2Cl]_2$ (5 μmol), NH_4VO_3 (170 μmol), 0.345 MPA O_2, 0.345 MPa CO, T = 353K, t = ½ h.



S1: a) IR absorbances in the carbonyl reagion. a) Reaction solution before reaction. Toluene (12.4 mmol), trifluoroacetic acid (4.2 mmol), and trifluoroacetic anhydride (1.3 mmol), $[Rh(CO)_2Cl]_2$ (5 μmol) b) Reaction solution after ½ hour. Toluene (12.4 mmol), trifluoroacetic acid (4.2 mmol), and trifluoroacetic anhydride (1.3 mmol), $[Rh(CO)_2Cl]_2$ (5 μmol), NH_4VO_3 (170 μmol), 0.345 MPA O_2, 0.345 MPa CO, T = 353K, t = ½ h. c) Reaction solution after exposure to CO for 3 hours. 0.345 MPa CO, T = 353K, t = 3 h.