Supporting Information For:

Carbon Monoxide Release Catalysed by Electron Transfer: Electrochemical and Spectroscopic Investigations of [Re(bpy-R)(CO)$_4$](OTf) Complexes Relevant to CO_2 Reduction.

Kyle A. Grice, Nina X. Gu, Matthew D. Sampson and Clifford P. Kubiak*

Department of Chemistry and Biochemistry, University of California
San Diego, 9500 Gilman Drive MC 0358, La Jolla, California 92093, USA.
E-mail: ckubiak@ucsd.edu;
Fax: 01 858 534 5383;
Tel: 01 858 822 2665

Contents **Page**

Table S1. Crystal data and structure refinement for **1**.

Identification code	ms_120423_0m	
Empirical formula	C23 H24 F3 N2 O7 Re S	
Formula weight	715.70	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.9153(4) Å	α= 90°.
	b = 11.3329(4) Å	β= 103.586(2)°.
	c = 21.3969(7) Å	γ = 90°.
Volume	2572.78(16) $Å^3$	
Z	4	
Density (calculated)	1.848 Mg/m^3	
Absorption coefficient	4.871 mm^{-1}	
F(000)	1400	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.92 to 25.48°.	
Index ranges	-13<=h<=13, -13<=k<=13, -25<=l<=25	
Reflections collected	17077	
Independent reflections	4769 [R(int) = 0.0365]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.7927 and 0.4425	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4769 / 0 / 340	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0221, wR2 = 0.0515	
R indices (all data)	R1 = 0.0305, wR2 = 0.0559	
Largest diff. peak and hole	0.786 and -0.551 $e.Å^{-3}$	

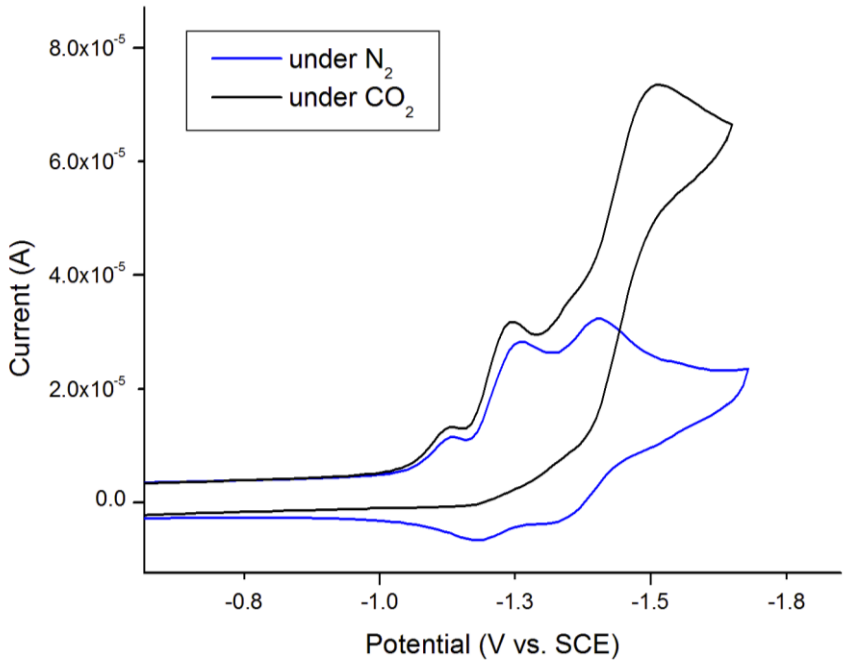

Figure S1. Cyclic voltammograms of **2** (1 mM) under nitrogen and carbon dioxide (i_{cat}/i_p = 2.3). Electrochemical experiments were performed at 100 mV/s in 0.1 M TBAH in acetonitrile with a glassy carbon working electrode, Ag wire pseudo-reference and Pt counter electrode. Ferrocene was added as an internal reference.

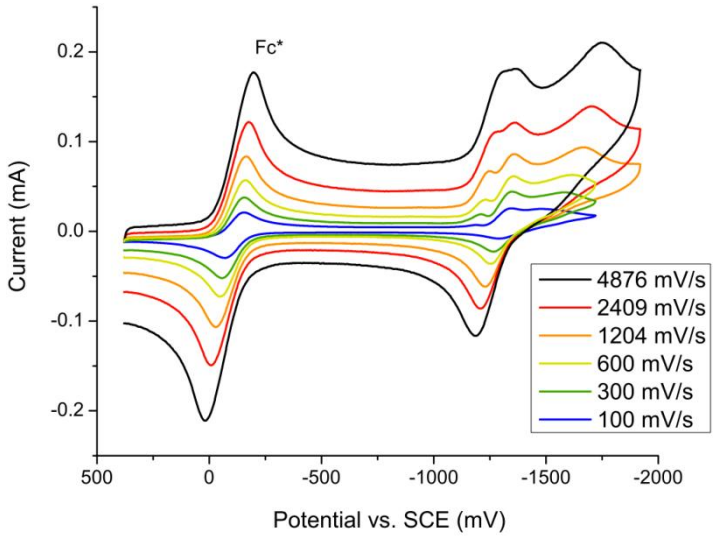

Figure S2. Scan rate studies of **1** (1 mM) under nitrogen with 1 mM decamethylferrocene (Fc*) added as an internal standard.

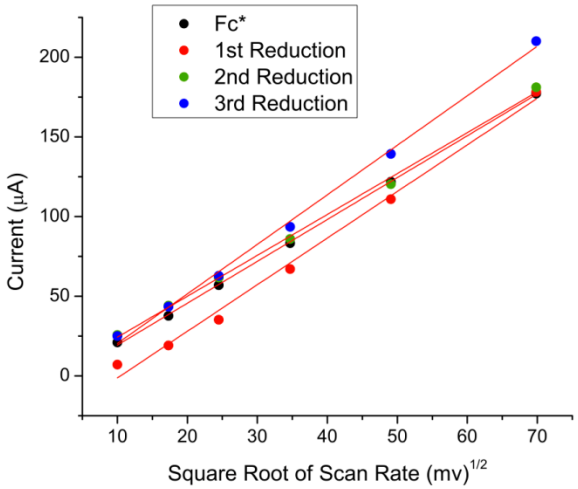

Figure S3. Plot of the peak height of each wave in figure **S2** (decamethylferrocene (Fc*), and the three reductions of **1**) versus square root of scan rate, illustrating that the waves are all $1e^-$ events associated with freely-diffusing species.

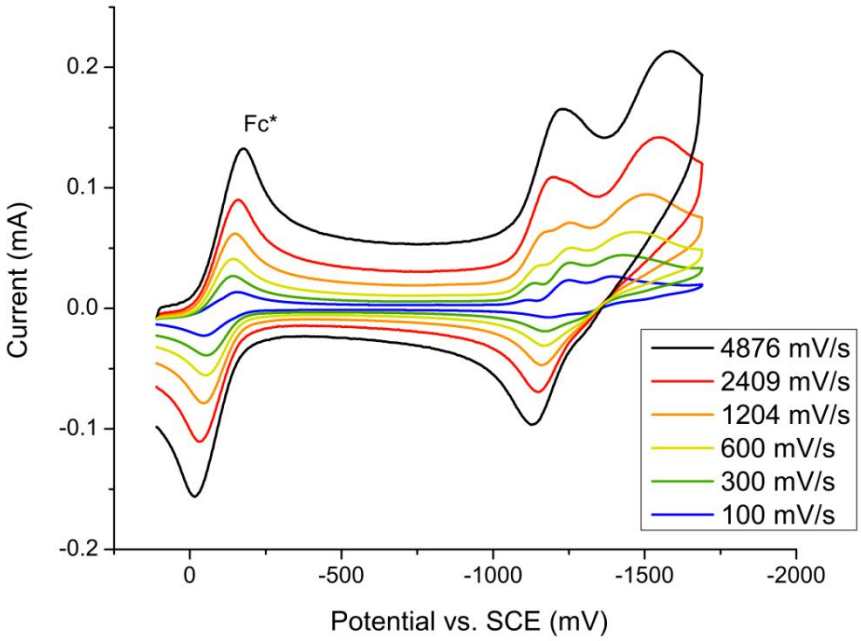

Figure S4. Scan rate studies of **2** (1 mM) under nitrogen with 1 mM decamethylferrocene (Fc*) added as an internal standard.

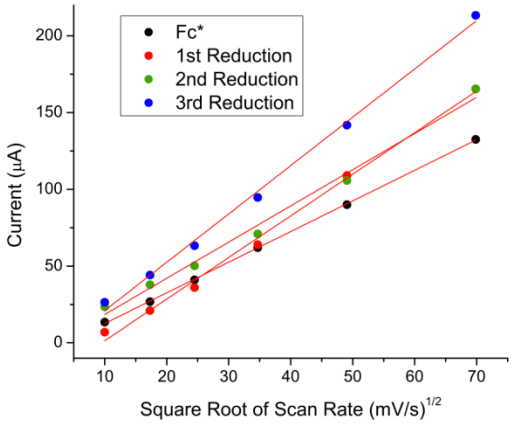

Figure S5. Plot of the peak height of each wave in figure **S4** (decamethylferrocene (Fc*), and the three reductions of **2**) versus square root of scan rate, illustrating that the waves are all $1e^-$ events associated with freely-diffusing species.

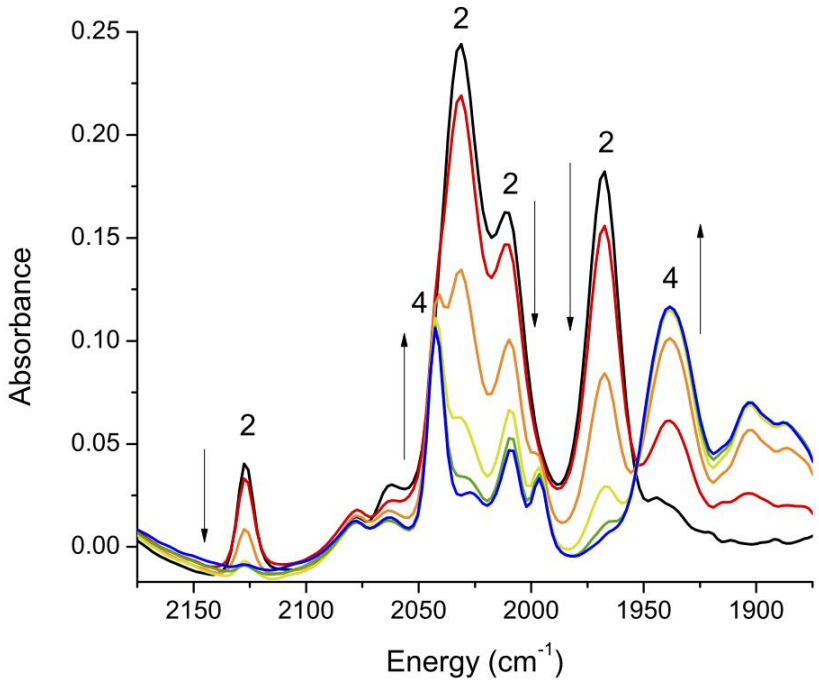

Figure S6. First reduction of **2** (2 mM) by IR-SEC in 0.1 M TBAH in acetonitrile to yield $Re(bpy)(CO)_3(CH_3CN)$ (**4**) by electrode-catalyzed substitution.

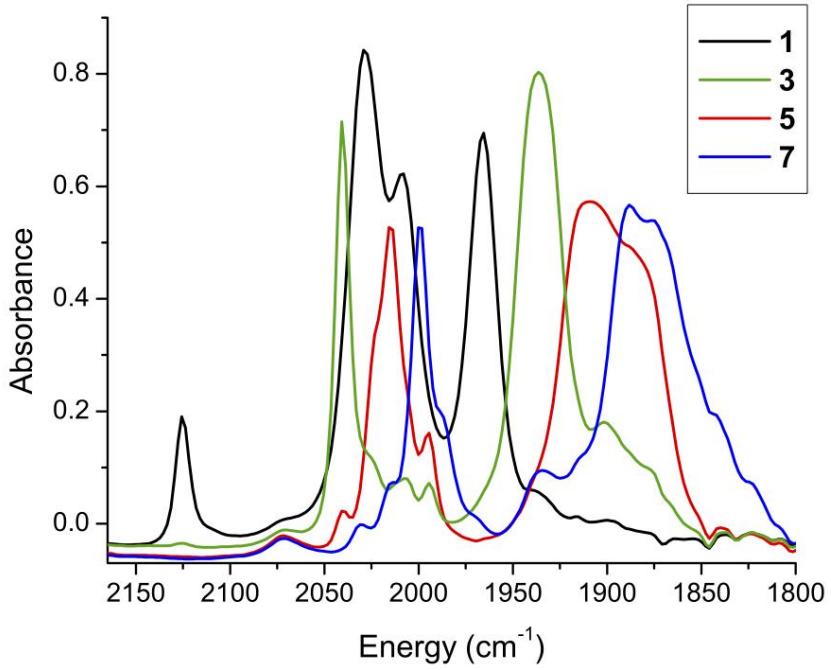

Figure S7. IR-SEC spectra of **1** and the resulting three reduction species (**3**, **5**, **7**).

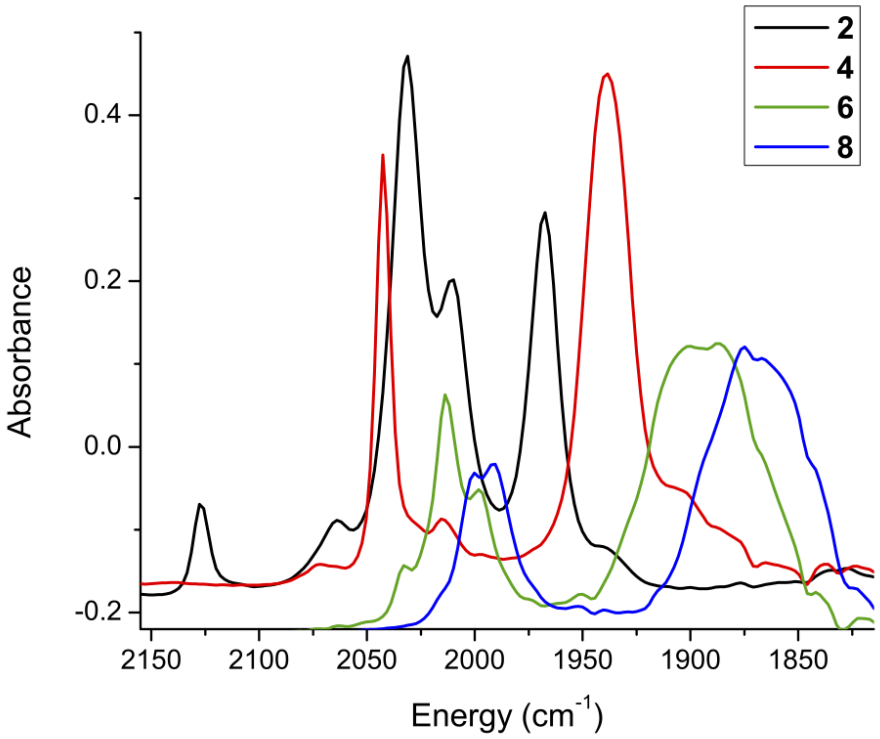

Figure S8. IR-SEC spectra of **2** and the resulting three reduction species (**4**, **6**, **8**).

Table S2. IR-SEC data for **1** in 0.1 M TBAH in acetonitrile.

Complex	ν(CO)/cm^{-1}
[Re(bpy–*t*Bu)(CO)$_4$](OTf) (**1**)	2126, 2029, 2008, 1965
[Re(bpy-*t*Bu)(CO)$_3$(CH$_3$CN)]$^+$ (**3**)	2041, 1936
[Re(bpy-*t*Bu)(CO)$_3$(CH$_3$CN)]^0 (**5**)	2014, 1908, 1885
[Re(bpy-*t*Bu)(CO)$_3$(CH$_3$CN)]$^-$ (**7**)	1999, 1888, 1875

Table S3. IR-SEC data for **2** in 0.1 M TBAH in acetonitrile.

Complex	ν(CO)/cm^{-1}
[Re(bpy)(CO)$_4$](OTf) (**2**)	2128, 2031, 2011, 1968
[Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ (**4**)	2043, 1939
[Re(bpy)(CO)$_3$(CH$_3$CN)]^0 (**6**)	2016, 1913, 1899
[Re(bpy)(CO)$_3$(CH$_3$CN)]$^-$ (**8**)	1992, 1875, 1867

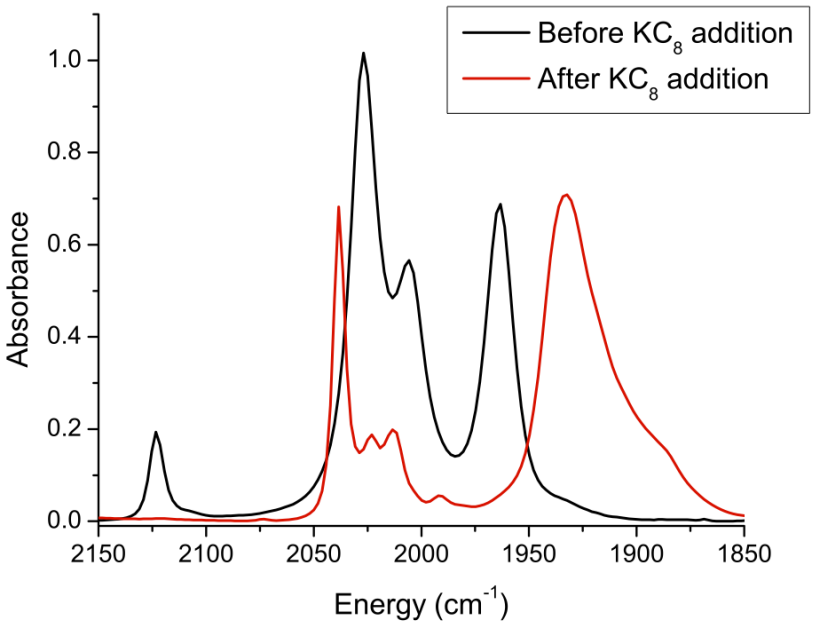

Figure S9. IR spectra of [Re(bpy–*t*Bu)(CO)$_4$](OTf) (**1**) before and after addition of 12 mol % of KC_8 in the presence of 0.1 M TBAH in acetonitrile. The spectra indicate complete conversion of **1** to [Re(bpy–tBu)(CO)$_3$(CH$_3$CN)]$^+$ (**3**) within minutes after addition of KC_8.

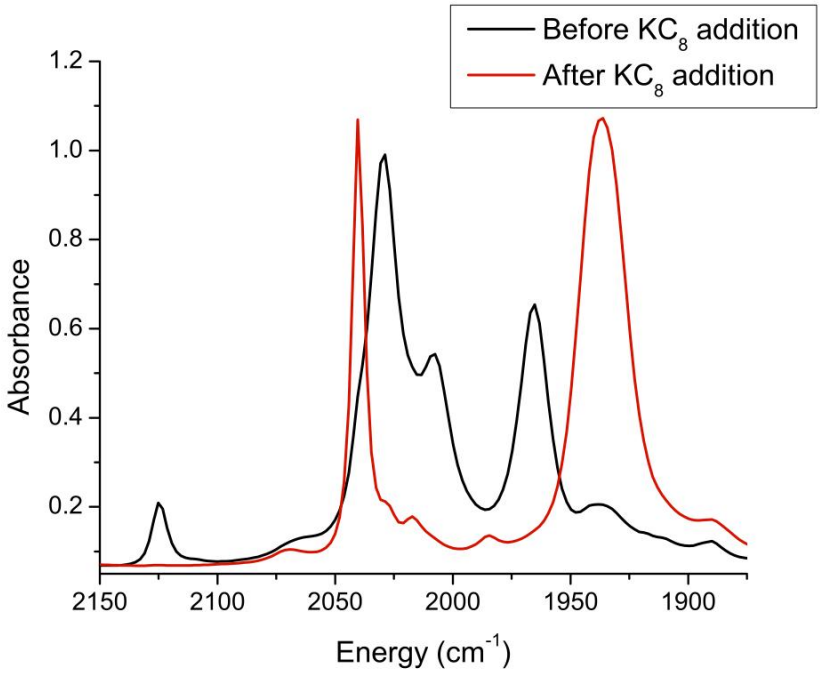

Figure S10. IR spectra of [Re(bpy)(CO)$_4$](OTf) (**2**) before and after addition of 11 mol % of KC_8 in the presence of 0.1 M TBAH in acetonitrile. The spectra indicate complete conversion of **2** to [Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ (**4**) within minutes after addition of KC_8.

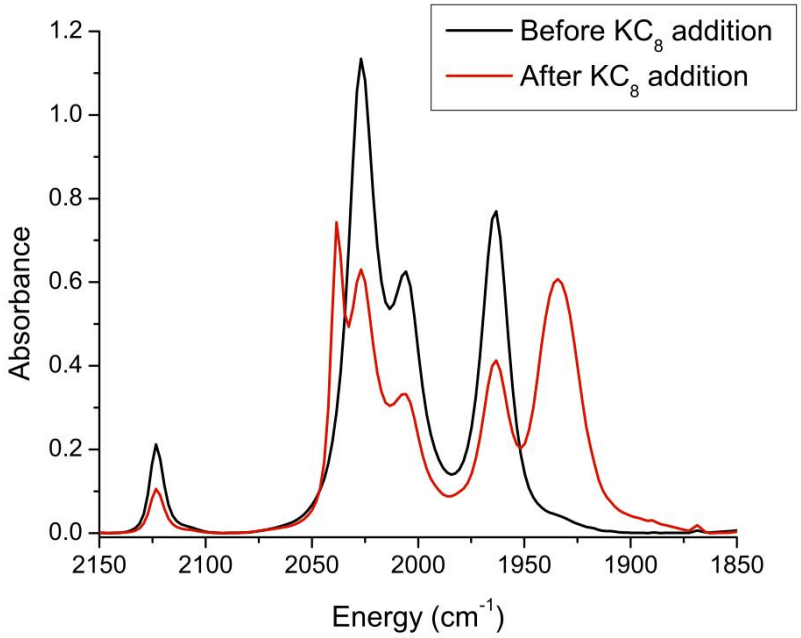

Figure S11. IR spectra of [Re(bpy–*t*Bu)(CO)$_4$](OTf) (**1**) before and after addition of 10 mol % of KC_8 in acetonitrile without TBAH in solution. The spectra indicate ca. 50% conversion of **1** to [Re(bpy–tBu)(CO)$_3$(CH$_3$CN)]$^+$ (**3**) within minutes after addition of KC_8.

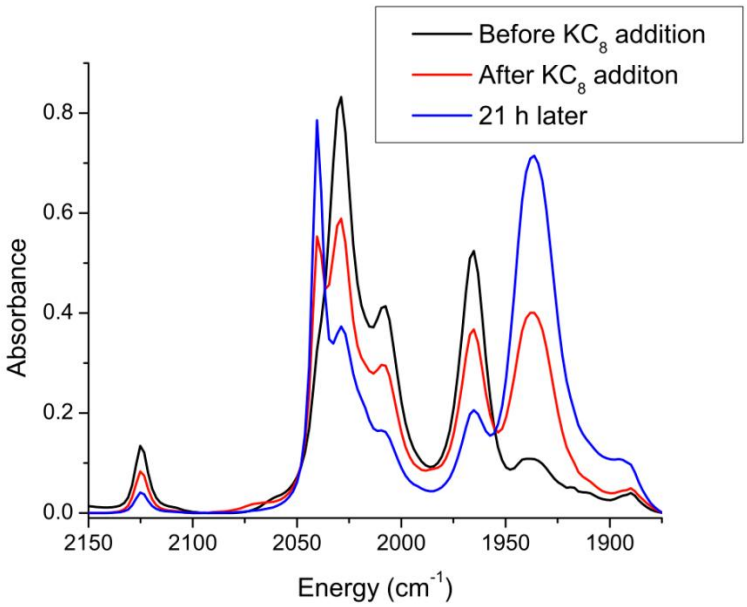

Figure S12. IR spectra of [Re(bpy)(CO)$_4$](OTf) (**2**) before and after addition of 16 mol % of KC_8 in acetonitrile without TBAH. The spectra indicate ca. 40% conversion of **2** to [Re(bpy)(CO)$_3$(CH$_3$CN)]$^+$ (**4**) within minutes after addition of KC_8. Even after sitting for 21 hours, the IR spectra indicate only ca. 70% conversion of **2**.

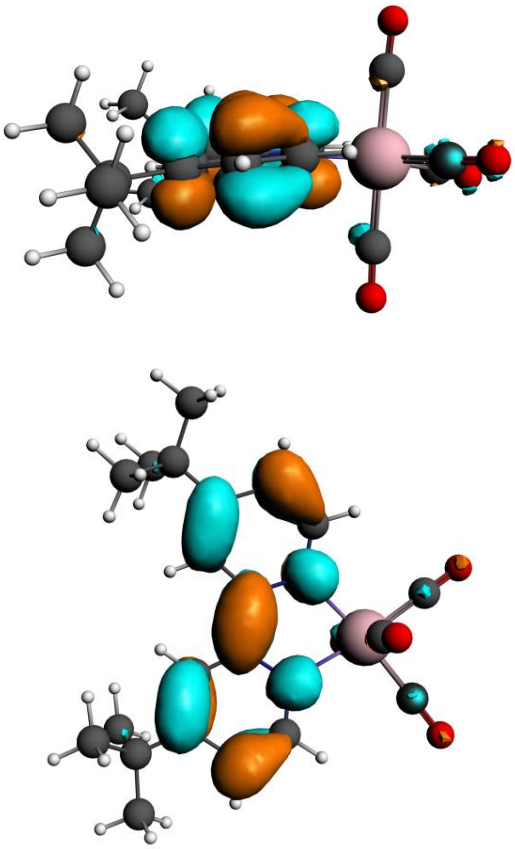

Figure S13. Side and top view of the Lowest Unoccupied Molecular Orbital (LUMO) of [Re(bpy-*t*Bu)(CO)$_4$]$^+$ calculated with ADF 2007.1.

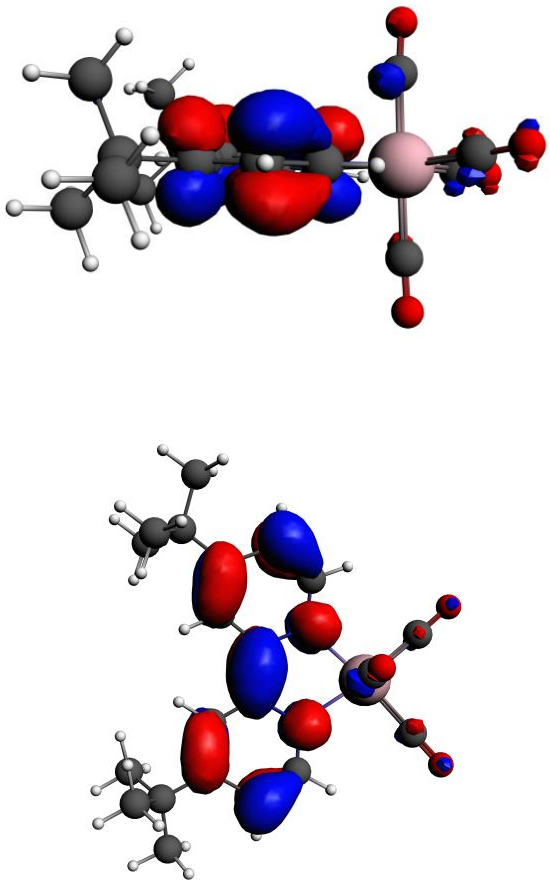

Figure S14. Side and top view of the Singly Occupied Molecular Orbital (SOMO) of [Re(bpy-*t*Bu)(CO)$_4$]^0 calculated with ADF 2007.1.

Geometry optimized xyz coordinates for [Re(bpy-*t*Bu)(CO)$_4$]$^+$

Re	7.436215	7.199012	2.238354
O	6.245465	8.477245	-0.395629
O	4.643639	6.030838	2.951763
O	7.935698	4.648714	0.525119
O	8.463274	5.865601	4.921645
N	9.370602	8.210484	1.983057
N	7.203320	9.167284	3.196601
C	6.696725	8.031444	0.560372
C	5.676702	6.462826	2.667310
C	7.772185	5.575504	1.194922
C	8.120137	6.359990	3.945479
C	10.467614	7.649477	1.438070
H	10.361824	6.622569	1.099757
C	11.673584	8.321490	1.307687
H	12.512365	7.789431	0.866753

C	11.796679	9.649899	1.741294
C	10.642419	10.220884	2.297752
H	10.675157	11.245153	2.659099
C	9.452550	9.502859	2.413387
C	8.232242	10.050420	3.031791
C	8.102921	11.379234	3.429658
H	8.924993	12.067044	3.247928
C	6.930497	11.855835	4.034585
C	5.921953	10.906304	4.250164
H	4.987826	11.171408	4.738496
C	6.088965	9.597736	3.818648
H	5.301200	8.862050	3.955657
C	13.090077	10.454580	1.593913
C	14.289613	9.545068	1.277120
H	14.180476	9.034767	0.311098
H	14.444347	8.789101	2.058683
H	15.200758	10.153579	1.217670
C	13.393230	11.237842	2.889668
H	13.507363	10.566112	3.750741
H	12.614765	11.975283	3.126075
H	14.332821	11.792337	2.765084
C	12.893974	11.457743	0.427896
H	13.810949	12.048242	0.299036
H	12.067439	12.152702	0.629024
H	12.685731	10.937785	-0.516718
C	6.789054	13.333755	4.403389
C	6.941202	14.178063	3.115197
H	6.165474	13.927267	2.379051
H	7.922371	14.033867	2.643387
H	6.844973	15.243327	3.363723
C	7.901429	13.724576	5.404089
H	7.801168	14.787834	5.660746
H	8.905001	13.579093	4.982505
H	7.829489	13.142053	6.332244
C	5.420014	13.634456	5.034424
H	5.352021	14.705871	5.261246
H	5.273092	13.088759	5.976317
H	4.593082	13.390801	4.353550

Geometry optimized xyz coordinates for $[Re(bpy\text{-}t\text{Bu})(CO)_4]^0$

Re	7.434114	7.200159	2.237238
O	6.208014	8.442829	-0.402957
O	4.613674	6.086478	2.936944
O	8.035281	4.628311	0.588074
O	8.476791	5.874398	4.909244
N	9.356961	8.184251	1.978395
N	7.180891	9.150072	3.177955
C	6.694394	8.031344	0.555774

C	5.663430	6.500908	2.659240
C	7.819634	5.579416	1.221209
C	8.122066	6.370099	3.932484
C	10.463196	7.639337	1.423408
H	10.363057	6.611327	1.082232
C	11.662296	8.305772	1.280682
H	12.494095	7.778104	0.823363
C	11.783724	9.650917	1.741482
C	10.650837	10.212390	2.301009
H	10.683422	11.232375	2.677577
C	9.428736	9.503458	2.425736
C	8.247002	10.036339	3.017114
C	8.096474	11.381630	3.436371
H	8.922360	12.066728	3.252059
C	6.940760	11.849407	4.033565
C	5.901247	10.895179	4.240139
H	4.966441	11.159695	4.726784
C	6.065669	9.599387	3.795620
H	5.269720	8.869321	3.925344
C	13.083735	10.457426	1.590879
C	14.284533	9.548169	1.268779
H	14.166509	9.039281	0.303151
H	14.433161	8.785698	2.045821
H	15.199566	10.154048	1.210354
C	13.404464	11.230313	2.888251
H	13.518931	10.546083	3.740069
H	12.621861	11.957549	3.140843
H	14.343631	11.789852	2.767037
C	12.908196	11.469658	0.434323
H	13.828190	12.058810	0.299975
H	12.082354	12.164567	0.639782
H	12.688577	10.954117	-0.511021
C	6.800199	13.331987	4.414510
C	6.943686	14.199337	3.142315
H	6.171812	13.943611	2.403135
H	7.923679	14.059188	2.667215
H	6.839441	15.265185	3.395322
C	7.906495	13.725879	5.419037
H	7.814770	14.790354	5.682741
H	8.908614	13.569100	4.998183
H	7.831194	13.134811	6.342184
C	5.433738	13.632540	5.053022
H	5.369531	14.701617	5.298973
H	5.285398	13.066418	5.982809
H	4.606246	13.397955	4.369511

Input file for ADF calculations of complex [Re(bpy-*t*Bu)(CO)$_4$]$^+$

```
#$ -S /bin/bash
#$ -cwd

#$ -o output
#$ -e $JOB_ID.err
#$ -j y
#$ -M kgrice@ucsd.edu
#$ -m beas
#$ -N RetbuCO4OTfGOFC
#$ -q all.q
#$ -pe mpi 8

export cur_dir="`pwd`"
echo Running as user `whoami` on `hostname` at `date` in dir `pwd`
export temp_dir="/state/partition1/`whoami`.$JOB_ID"
mkdir $temp_dir
cd $temp_dir
echo With temp dir $temp_dir


# ADF enviroment variables, change as you need

export ADFHOME=/share/apps/adf2007.01/
export ADFBIN=/share/apps/adf2007.01/bin
export ADFRESOURCES=/share/apps/adf2007.01/atomicdata
export SCMLICENSE=/share/apps/adf2007.01/license
export SCM_TMPDIR=$temp_dir
export SCM_USETMPDIR=yes
export NSCM=8
export SCM_IOBUFFERSIZE=512


 #Put main code here ****************************************

$ADFBIN/adf -n8 \
 <<< "
TITLE RetbuCO4OTfGOFC

MAXMEMORYUSAGE 22000

RELATIVISTIC ZORA

UNRESTRICTED

CHARGE 1 0

SCF
```

```
DIIS
END

XCq
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
Re      7.447693    7.228203    2.246328
O       6.247090    8.494009   -0.339842
O       4.691517    6.071035    2.926304
O       7.870978    4.739419    0.492501
O       8.495321    5.895375    4.896308
N       9.362544    8.202753    1.994338
N       7.234803    9.147917    3.206248
C       6.712236    8.055425    0.598988
C       5.714805    6.509618    2.662167
C       7.765305    5.639251    1.191736
C       8.165338    6.382689    3.953734
C      10.448702    7.645174    1.456497
H      10.390161    6.746475    1.152219
C      11.648671    8.303616    1.319437
H      12.391231    7.859366    0.929679
C      11.776032    9.613699    1.749959
C      10.639894   10.199610    2.309430
H      10.676956   11.099442    2.612252
C       9.458689    9.484504    2.427564
C       8.239136   10.040949    3.038614
C       8.095459   11.360099    3.402790
H       8.802730   11.973209    3.240357
C       6.921225   11.804349    4.006978
C       5.947127   10.859185    4.248236
H       5.149102   11.108509    4.700389
C       6.124533    9.558168    3.839344
H       5.435538    8.925792    4.011969
C      13.064859   10.414935    1.597508
C      14.257025    9.515103    1.289487
H      14.123878    9.081053    0.422203
H      14.339195    8.831729    1.988306
H      15.074063   10.054549    1.264529
C      13.361646   11.211638    2.876180
H      13.441700   10.595128    3.633442
H      12.629945   11.841747    3.044854
H      14.200333   11.705752    2.766158
C      12.858077   11.388431    0.429690
H      13.680555   11.901812    0.282855
```

```
H      12.123813   12.001541    0.640584
H      12.639117   10.884117   -0.380607
C       6.767552   13.271959    4.362834
C       6.913596   14.113994    3.094561
H       6.197572   13.885069    2.466664
H       7.782005   13.932667    2.680886
H       6.853389   15.064824    3.325629
C       7.847482   13.655011    5.363851
H       7.739729   14.595642    5.615509
H       8.730304   13.525816    4.958286
H       7.769085   13.091766    6.162501
C       5.404168   13.568881    4.972845
H       5.325338   14.531044    5.145470
H       5.309256   13.079300    5.817251
H       4.699282   13.290092    4.353059
END

GEOMETRY
 GO
END

AnalyticalFreq
END

BASIS
 type TZ2P
END

END INPUT
"
# end main code **********************************************

cp * $cur_dir/

# Optional, have to manually clean up otherwise
rm -r -f $temp_dir
```