Supporting Information

Molecular Au(I) Complexes in the Photosensitized Photocatalytic CO_2 Reduction Reaction

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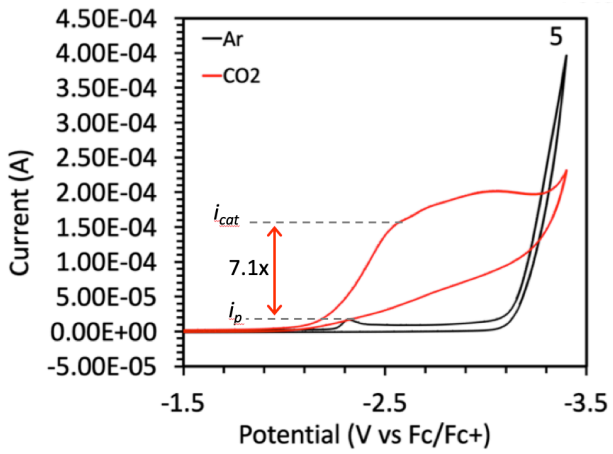
Table S1. CV data of complexes **1**-**5**.

Cat.	CO_2 $E_{(S/S^-)}$ peak [onset] (V)	argon $E_{(S/S^-)}$ peak [onset] (V)	η (mV)	i_{cat}/i_p
1	-2.73 [-2.6]	-3.00 [-2.9]	530	32
2	-2.40 (sh) [-2.2]	-3.04 (sh) [-2.8]	740	1.2
3	-2.70 (sh) [-2.4]	-2.99 [-2.7]	590	---
4	-1.80 [-1.7]	-1.80 [-1.7]	600	3.2[a]
5	-2.58 (sh) [-2.2]	-2.33 [-2.3]	690	7.1

"sh" is shoulder. An example illustrating how i_{cat}/i_p was determined is shown below. [a] indicates this value was measured at a later reduction potential than the first reduction potential.



Data File C:\CHEM32\2\DATA\TEST\04281.D
Sample Name: Agilent_Standard_valve_syringe

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Sample Operator : SYSTEM
Acq. Instrument : Agilent                       Location : Vial 1
Injection Date  : 9/13/2017 4:30:39 PM
                                                Inj Volume : Manually
Acq. Method     : C:\CHEM32\2\METHODS\START.M
Last changed    : 3/13/2017 3:12:26 PM by SYSTEM
Analysis Method : C:\CHEM32\2\METHODS\START.M
Last changed    : 9/13/2017 1:11:51 PM by SYSTEM
                  (modified after loading)
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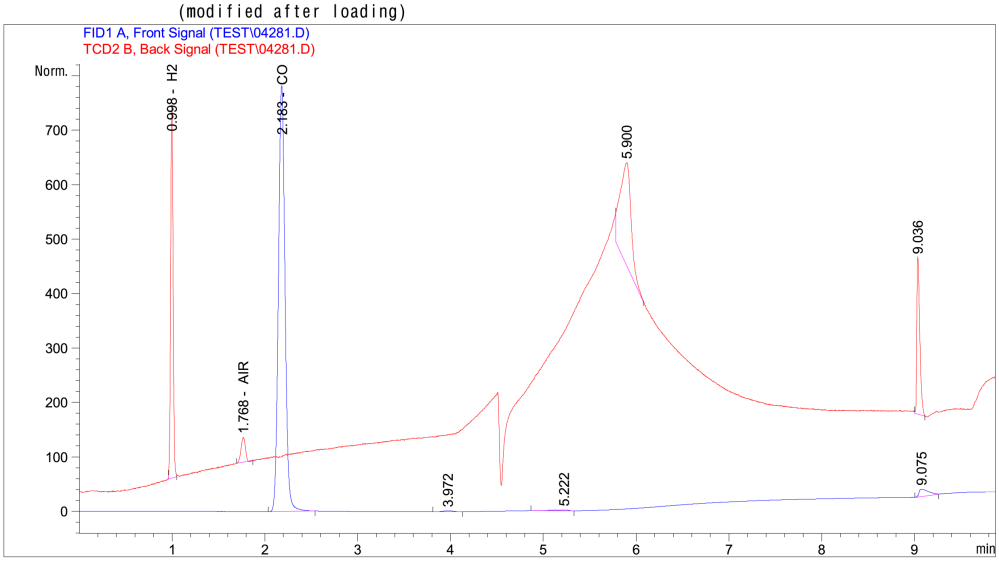


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                    External Standard Report
======================================================================

Sorted By             :      Signal
Calib. Data Modified  :      9/13/2017 1:11:51 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

RetTime  Type     Area     Amt/Area    Amount   Grp   Name
 [min]          [pA*s]                [ng/ul]
-------|------|----------|----------|----------|--|------------------
  2.183 BB     3863.32617 1.15369e-1  445.70937    CO
  4.159            -          -          -         CH4

Totals :                              445.70937
```


Figure S1. Example GC trace for a photoreaction with complex **1**. The blue trace is the FID trace after a methanizer which analyzes for CO and CH_4. The red trace is a TCD trace which analyzes for H_2. The TCD trace is zoomed in substantially so that peaks in the baseline can be observed. A backflush occurs at approximately 5 minutes and any peaks after this are from the oven bake. The peaks are calibrated manually via Excel due to software limitations. The second page of the report is below.

Data File C:\CHEM32\2\DATA\TEST\04281.D
Sample Name: Agilent_Standard_valve_syringe

Signal 2: TCD2 B, Back Signal

RetTime [min]	Type	Area [25 µV*s]	Amt/Area	Amount [ng/ul]	Grp	Name
0.998	BB	29.75568	2.65015e-4	7.88571e-3		H2
1.768	BB	3.50677	6.02348e-2	2.11230e-1		AIR

Totals : 2.19115e-1

1 Warnings or Errors :

Warning : Calibrated compound(s) not found

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*** End of Report ***

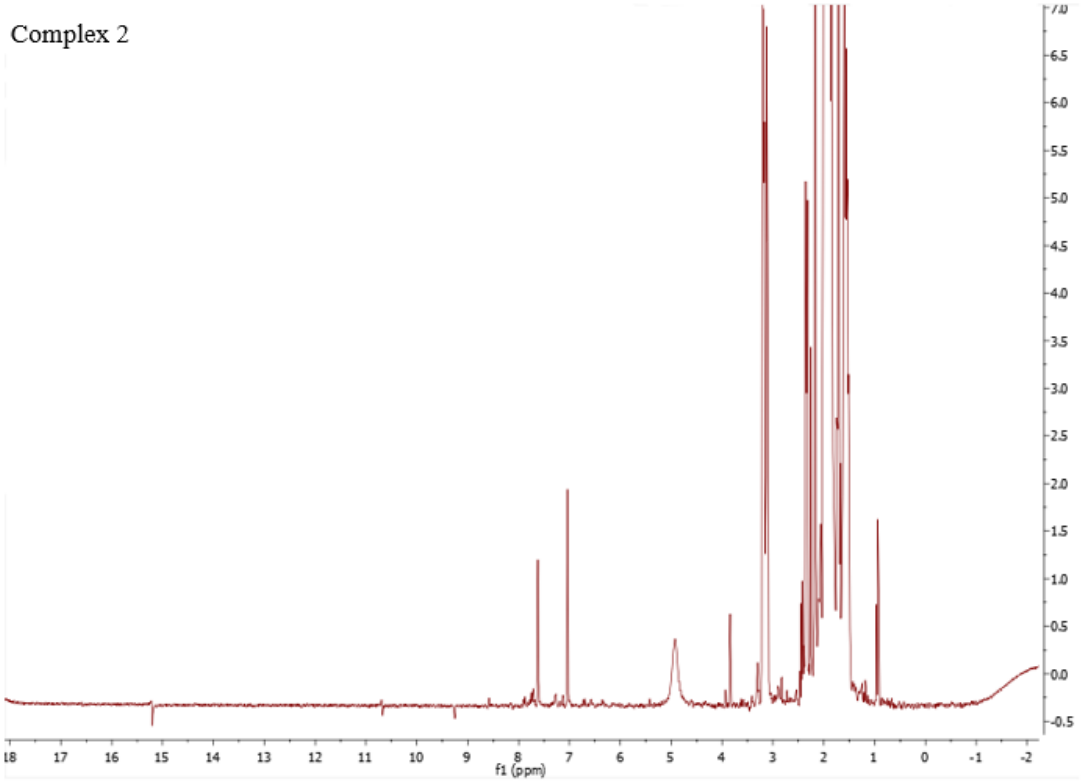

Figure S2. Formate and methanol ^{1}H NMR analysis spectrum in d3-MeCN for a photoreaction with complex **1**. Formate would appear as a singlet at ~8.7 ppm and methanol would appear as a singlet at ~3.3 ppm. Trace formate and MeOH may be observed; however, significantly larger quantities would be necessary to observe a turnover. The peak at ~7.0 ppm is the internal standard, *p*-xylene.

Table S2. Quantum yields for CO production at 1 hour for each Au complex.

Entry	Complex	Average mmol CO	Molecules CO	QY (%)
1	1	0.00063254	3.80916×10^{17}	0.103
2	2	0.00015826	9.53042×10^{16}	0.026
3	3	0.00000751	4.52252×10^{15}	0.001
4	4	0.00015006	9.03661×10^{16}	0.025
5	5	0.00017379	1.04656×10^{17}	0.028