Developing a Mechanistic Understanding of Molecular Electrocatalysts for CO_2 Reduction Using Infrared Spectroelectrochemistry

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Supporting Information

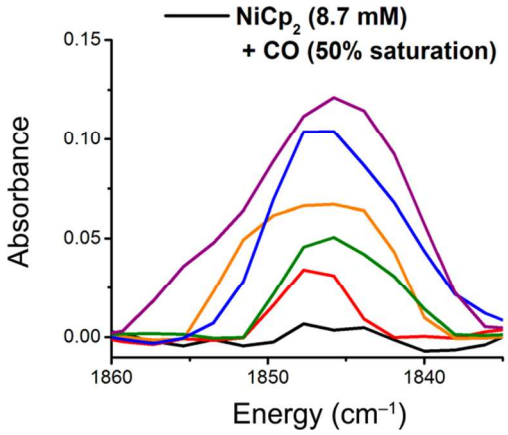

Figure S1. Growth of absorbance consistent with the formation of $[Ni(\mu_1\text{-}CO)Cp]_2$ dimer (**16**) at 1845 cm^{-1} under partially saturated CO atmosphere. Reflectance FTIR-SEC spectra obtained sequentially in 0.1 M $TBAPF_6$/MeCN (50% CO saturation) at -2.00 V (vs Ag/Ag^+). Conditions: $NiCp_2$ (**14**, 8.7 mM) with a glassy carbon WE, Pt CE, and Ag pseudo-RE.

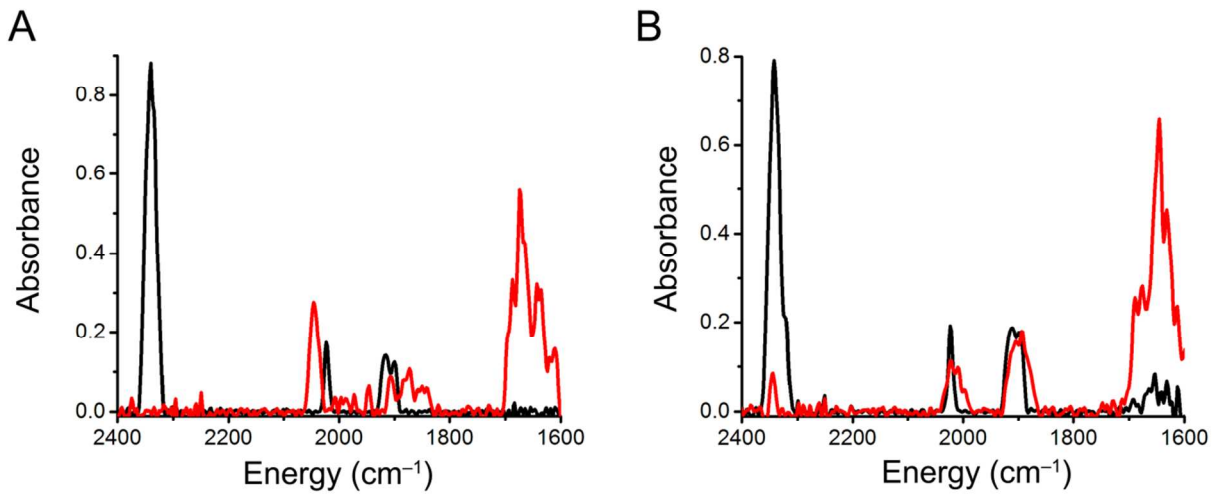

Figure S2. Resting potential (black) and final catalytic (red) reflectance IR-SEC spectra of $Re^{I}(dmb)(CO)_3Cl$ (**1B**) in the presence (**A**) and absence (**B**) of $Ni^{II}Cp_2$ (**14**). Growth of absorbances consistent with the formation of $[Ni^{I}(\mu_1\text{-}CO)Cp]_2$ dimer (**16**) at 1845 cm^{-1} and $Ni^{I}(CO)_4$ (**17**) at 2045 cm^{-1} observed for **A** and not **B**. Additional, unassigned features overlapping with Re carbonyl species are also observed. Reflectance IR-SEC spectra obtained in 0.1 M $TBAPF_6$/MeCN (50% CO_2 saturation, ~0.14 M) at resting potential and -2.00 V (vs Ag/Ag^+), respectively. **A**: $Re^{I}(dmb)(CO)_3Cl$ (**1B**, 2.5 mM), $Ni^{II}Cp_2$ (**14**, 7.8 mM). **B**: $Re^{I}(dmb)(CO)_3Cl$ (**1B**, 3.5 mM). Glassy carbon WE, Pt CE, and Ag pseudo-RE.

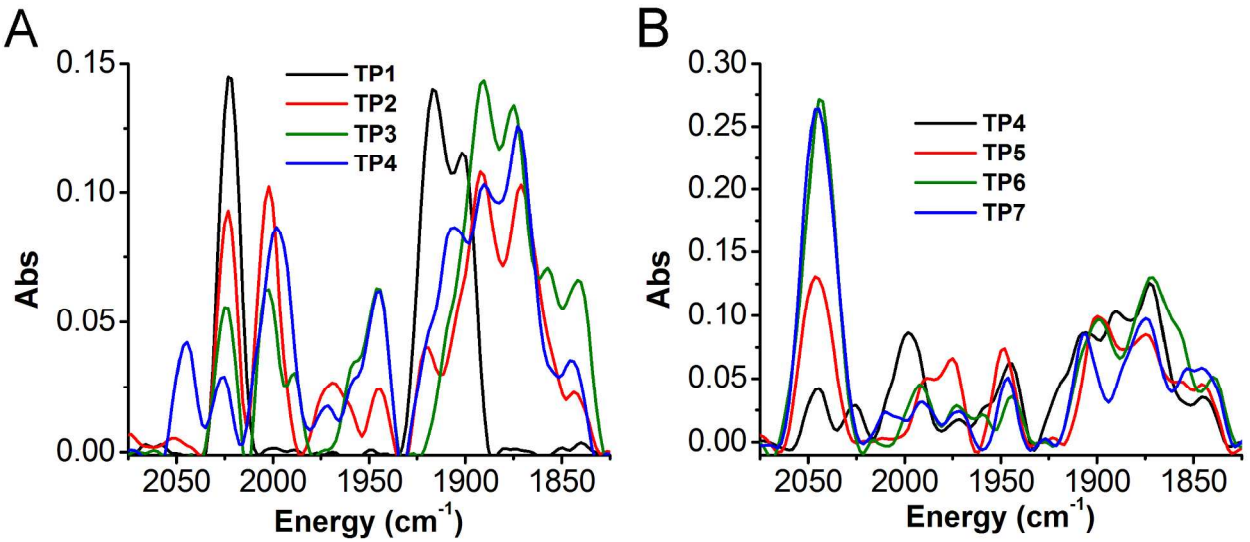

Figure S3. Sequentially obtained IR-SEC spectra of $Re^{I}(dmb)(CO)_3Cl$ (**1B**) under conditions catalytic for the reduction of CO_2 in the presence of $Ni^{II}Cp_2$ (**14**). Growth of absorbances consistent with the formation of $[Ni^{I}(\mu_1\text{-}CO)Cp]_2$ dimer (**16**) and $Ni(CO)_4$ (**17**) are observed at ~1840 cm^{-1} and 2045 cm^{-1}, respectively. Additional, unassigned features overlapping with Re carbonyl species are also observed between 2000 and 1900 cm^{-1}. Reflectance IR-SEC spectra obtained in 0.1 M $TBAPF_6$/MeCN (50% CO_2 saturation, ~0.14 M) at resting potential and -2.00 V (vs Ag/Ag^+), respectively. Conditions: $Re^{I}(dmb)(CO)_3Cl$ (**1B**, 2.5 mM), $NiCp_2$ (**14**, 7.8 mM); glassy carbon WE, Pt CE, and Ag pseudo-RE; TP = time point.

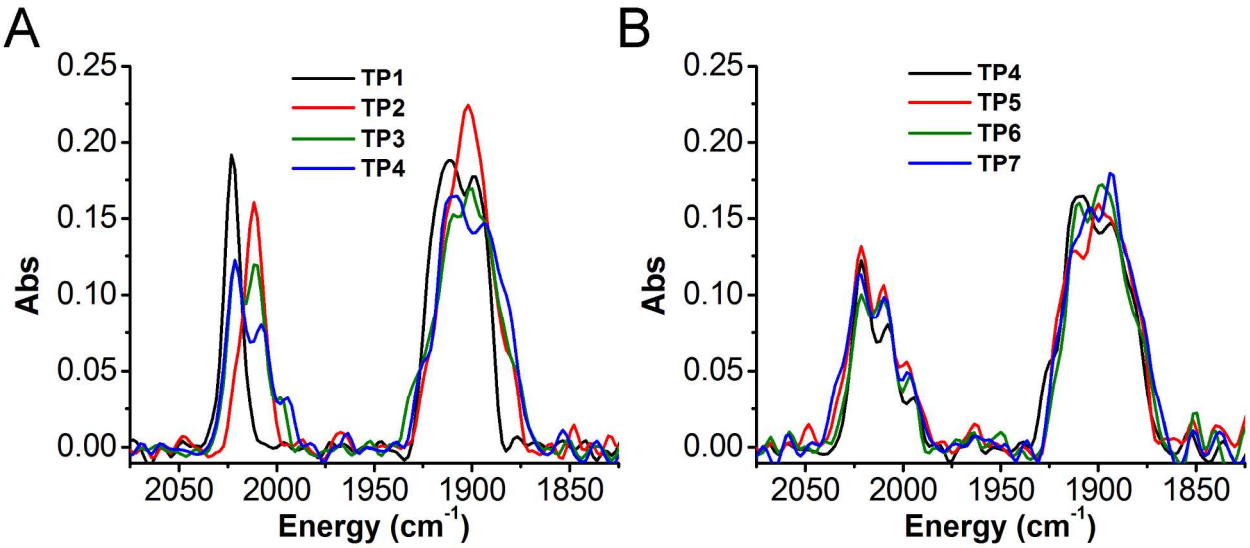

Figure S4. Sequentially obtained IR-SEC spectra of $Re^{I}(dmb)(CO)_3Cl$ (**1B**) under conditions catalytic for the reduction of CO_2. Growth of absorbances consistent with the formation of $[Ni^{I}(\mu_1\text{-}CO)Cp]_2$ dimer (**16**) at ~1840 cm^{-1} and $Ni(CO)_4$ (**17**) at 2045 cm^{-1} are not observed. Reflectance IR-SEC spectra obtained in 0.1 M $TBAPF_6$/MeCN (50% CO_2 saturation, ~0.14 M) at resting potential and -2.00 V (vs Ag/Ag^+), respectively. Conditions: $Re^{I}(dmb)(CO)_3Cl$ (**1B**, 3.5 mM); glassy carbon WE, Pt CE, and Ag pseudo-RE; TP = time point.

Table S1. Crystallographic Data for $Mn^{I}(bpy)(CO)_3Br$ (10A)

	$Mn^{I}(bpy)(CO)_3Br$ (**10A**)
Empirical formula	$C_{13}H_8BrMnN_2O_3$
Formula weight	375.06
Temperature (K)	100(2)
Wavlength (Å)	0.71073
Space group	P –1 (No. 2)
a (Å)	10.9342(10)
b (Å)	11.0264(10)
c (Å)	11.5050(11)
Alpha	85.763(3)
Beta	85.791(3)
Gamma	76.792(3)
Volume ($Å^3$)	1344.4(2)
Z	4
$Density_{calcd}$ (Mg/m^3)	1.853
Micro (mm^{-1})	3.960
R	0.0218
R_w	0.0521

Table S2. Crystallographic Data for $[Mn^{0}(bpy)(CO)_3]_2$ (12A)

	$[Mn^{0}(bpy)(CO)_3]_2$ **(12A)**
Empirical formula	$C_{26}H_{16}Mn_2N_4O_6$
Formula weight	590.31
Temperature (K)	100(2)
Wavlength (Å)	0.71073
Space group	C_2/c (No. 15)
a (Å)	9.5138(9)
b (Å)	19.278(2)
c (Å)	12.9529(11)
Alpha	90.00
Beta	104.443(4)
Gamma	90.00
Volume ($Å^3$)	2300.6(4)
Z	4
$Density_{calcd}$ (Mg/m^3)	1.704
Micro (mm^{-1})	1.151
R	0.0266
R_w	0.0628