Published in final edited form as:

Organometallics. 2014 September 9; 34(1): 3–12. doi:10.1021/om500838z.

Synthesis, Spectroscopy, and Electrochemistry of (α -Diimine)M(CO)₃Br, M = Mn, Re, Complexes: Ligands Isoelectronic to Bipyridyl Show Differences in CO₂ Reduction

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Abstract

The synthesis and characterization of new Mn(I)- and Re(I)-centered organometallic complexes fashioned with 1,4-diazabutadiene (DAB) ligands is reported. Ten compounds of the type *fac*-(α -diimine)M(CO)₃Br (M = Mn, Re) were obtained in moderate to excellent yield (35–80%) and high purity from the coordination of the five ligands with M(CO)₅Br in refluxing ethanol. Despite the electronic similarity of DAB to 2,2'-bipyridyl, the complexes described herein were poor mediators of electrochemical CO₂ conversion to CO, but provide insight into the role of redox-active ligands in catalysis. Additional characterization of the one-electron reduced rhenium compounds, relevant intermediates in CO₂ reduction, by EPR and single-crystal X-ray analysis is described.

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ASSOCIATED CONTENT

Supporting Information

Crystallographic and electrochemical details as well as computed geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.

INTRODUCTION

The utilization of CO₂ as a potential feedstock for liquid fuels has attracted much attention for its synchronous application in mitigating global warming and producing sustainable energy.¹ Various approaches have been applied to mediate this process using modern electrochemical techniques, including heterogeneous photovoltaics, metal oxide surfaces, and homogeneous catalysis.^{2–6} Generally, catalysis has focused on either the production of CO for use in syngas (a feedstock for Fischer-Tropsch processes) or the direct production of liquid fuels such as formic acid or methanol.^{7,8} In many cases the rate of CO₂ conversion suffers from several slow proton transfers (in acidic media) and the formation of multiple products as a result of low selectivity for a singular reaction trajectory.⁹ Thus, methodologies that yield high selectivity (e.g., the sole production of CO) show the greatest promise for application. Mitigating competing side reactions is a challenge, but homogeneous electrocatalysts, which are amenable to tuning at the molecular level, may provide a solution.

Organometallic electrocatalysts consisting of Mn(I) and Re(I) carbonyl complexes supported by 2,2'-bipyridyl (bpy)-derived ligands have demonstrated the ability of producing CO through the electrochemical reduction of CO₂.^{10–12} Mechanistically, conversion involves two sequential single-electron reductions of the complex, a concerted reaction with the substrate (CO₂), and subsequent release of the product (CO) to complete the catalytic cycle. As such, the stabilization of transient ligand-centered or metal-centered reduced species and the redox activity of the supporting ligands are central to successful catalytic activity.^{13,14} Our interest in 1,4-diazabutadiene (DAB) ligands arose from the ease of manipulating their steric and electronic properties and their similarity to popular bpy derivatives: both provide a redox couple in which one- and two-electron reduced species are isolable, Figure 1.^{15,16} To our knowledge, and despite known complexes of Mn(I)^{10,17} and Re(I) with DAB or α -diimine ligands,^{18–21} only recently has their application to CO₂ reduction been explored.²² Herein we report the synthesis and characterization of new Mn(I) and Re(I) organometallic complexes with supporting DAB ligands and their reactivity with respect to the electrochemical reduction of CO₂. Significantly, and unlike the Re or Mn bpy-based systems

that have been previously reported, these complexes catalyze the disproportionation reaction of 2 equiv of CO₂ to CO and CO₃²⁻.

EXPERIMENTAL SECTION

General Considerations

All syntheses and manipulations were conducted under dry nitrogen unless otherwise noted. Metal carbonyls (Acros) and bromine (Aldrich) were used as received. M(CO)₅Br (M = Mn, Re) and α -diimine ligands were synthesized in accordance to literature procedures.^{23–25} All solvents were dried over activated molecular sieves before use. FTIR measurements were made on a Thermo-Nicolet instrument using spectroscopic grade KBr. UV-vis spectrophotometry measurements were performed on a Varian UV-50 Bio instrument. All NMR data was acquired using a Bruker Advance II 300 or 500 MHz spectrometer (¹H, ¹³C, ¹⁹F). Elemental analysis was performed by Atlantic Microlab, Inc. (Norcross, GA) on the Re complexes.

Electrochemical Studies

For all electrochemical studies, acetonitrile (MeCN, HPLC grade) was dried on a custom solvent purification system under Ar atmosphere. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was obtained from Aldrich (98%), recrystallized from methanol, and dried under vacuum at 90 °C overnight before use. Ferrocene (Fc, Aldrich, 98%) was recrystallized from ethanol (EtOH) and dried under vacuum overnight before use.²⁶ The working electrode (WE) was glassy carbon (GC; 3 mm diameter), the counter electrode (CE) was a Pt wire, and the reference electrode (RE) was a Ag/AgCl wire behind a Vycor tip. Electrochemical experiments were performed with a BAS Epsilon Potentiostat. Cyclic voltammograms were performed at room temperature in the dark under N₂ or CO₂ saturation conditions. All experiments used an MeCN solution of 1 mM complex and 0.1 M TBAPF₆ as the supporting electrolyte. The solution was purged with N₂ or CO₂ before each experiment and experiments with CO₂ were performed at gas saturation (~0.28 M in MeCN).^{12,27} Fc was used as the internal reference.

Infrared Spectroelectrochemical (IR-SEC) Studies

Solvent and electrolyte were prepared identically to the electrochemical studies. The experimental setup and design of the IR-SEC cell has been published previously.^{28,29} A Pine Instrument Company model AFCBP1 bipotentiostat was employed to control the cell potential. As the potential was changed stepwise, thin layer bulk electrolysis was monitored by reflectance IR off the electrode. All experiments were conducted in 0.1 M TBAPF₆/MeCN solutions with known catalyst loadings prepared under N₂ atmosphere. In catalytic tests, the electrolyte was additionally sparged for 20 s with ¹²CO₂ or ¹³CO₂. As noted in figure captions, the cell used (WE/RE/CE) was either Pt/ Ag/Pt or GC/Ag/Pt, making the pseudo-RE Ag/Ag⁺.

EPR Studies

EPR spectra at 110 K were obtained with a Bruker EMX spectrometer located at the National Biomedical EPR Center at the Medical College of Wisconsin. Instrument settings are indicated in the figure caption. Spectra were simulated with EasySpin.³⁰

General Synthesis of (DAB)M(CO)₃Br

The synthesis was carried out as a modification of previous work.¹² A 25 mL round-bottom flask was charged with M(CO)₅Br, M = Mn, Re (1 mmol), and the corresponding α-diimine (1.1 mmol) in EtOH (10 mL; M = Mn) or toluene (10 mL; M = Re). The mixture was allowed to reflux for 2 h in which time the solution color changed from yellow to deep red or purple. Subsequently, the solution was allowed to cool to room temperature then submerged in a dry ice/acetone bath to precipitate the microcrystalline product. For (DAB)Mn(CO)₃Br compounds, upon completion of 2 h reflux, the solution was filtered hot to avoid decomposition. The powder was then collected on a fritted filter and washed with 10 mL of cold hexanes. Crystals suitable for single-crystal X-ray diffraction analyses were grown by slow evaporation from a saturated CH₂Cl₂/MeCN (1:2) solution.

(2-CF₃DABMe)Re(CO)₃Br, 1—Purple solid (81% yield). ¹H NMR (CDCl₃, 25 °C): 7.92 (d, Ph, 2H, ³J_{H-H} = 8 Hz), 7.79 (d, Ph, 2H, ³J_{H-H} = 8 Hz), 7.74 (t, Ph, 2H, ³J_{H-H} = 8 Hz), 7.52 (t, Ph, 2H, ³J_{H-H} = 8 Hz), 2.30 (s, CH₃, 3H), 2.28 (s, CH₃, 3H). ¹³C{¹H} NMR (CDCl₃, 25 °C): 195.3 (CO), 177.5 (CO), 146.9 (Ph), 146.8 (Ph), 133.8 (Ph, q, ³J_{F-C} = 85 Hz), 128.4 (Ph-CF₃ q, ²J_{F-H} = 134 Hz), 123.6 (Ph), 123.5 (CF₃, q, ¹J_{C-F} = 262 Hz), 122.1 (Ph), 119.9 (Ph-CF₃, q, ³J_{C-F} = 126 Hz), 22.0 (CH₃), 21.6 (CH₃). ¹⁹F NMR (CDCl₃, 25 °C): -58.03 (s, 3F, CF₃), -58.66 (s, 3F, CF₃). IR (KBr, cm⁻¹): 3111 (m), 2958 (m), 2918 (m), 2028 (s), 1940 (s), 1925 (s), 1319 (s), 1177 (m), 1142 (m), 1117 (w), 768 (w). Anal. Found (Calcd): C, 34.89 (34.91); H, 2.05 (1.95); N, 3.52 (3.88).

(MesDABMe)Re(CO)₃Br, 2—Red solid (80% yield). ¹H NMR (CDCl₃, 25 °C): 7.01 (s, Ph, 2H), 6.96 (s, Ph, 2H), 2.52 (s, CH₃, 3H), 2.36 (s, CH₃, 3H), 2.21 (s, CH₃, 3H), 2.17 (s, CH₃, 3H). ¹³C{¹H} NMR (CDCl₃, 25 °C): 199.5 (CO), 176.0 (CO), 145.7 (Ph), 136.8 (Ph), 130.2 (Ph), 129.6 (Ph), 129.5 (Ph), 126.1 (Ph), 21.4 (CH₃), 20.6 (CH₃), 18.2 (CH₃). IR (KBr, cm⁻¹): 2955 (m), 2924 (m), 2855 (m), 2019 (s), 1934 (s), 1895 (s), 1383 (s), 866 (w), 835 (w). Anal. Found (Calcd): C, 43.64 (44.78); H, 4.15 (4.21); N, 3.94 (4.18).

(2,6-iPr₂DABMe)Re(CO)₃Br, 3—Red solid (70% yield). ¹H NMR (CDCl₃, 25 °C): 7.36 (d, Ph, 2H, ³J_{H-H} = 8 Hz), 7.34 (t, Ph, 2H, ³J_{H-H} = 8 Hz), 7.27 (d, Ph, 2H, ³J_{H-H} = 8 Hz), 3.81 (sept, H-ⁱPr, 2H, ³J_{H-H} = 7 Hz), 2.91 (sept, H-ⁱPr, 2H, ³J_{H-H} = 7 Hz), 2.24 (s, CH₃, 6H), 2.00 (s, CH₃, 6H), 1.39 (d, CH₃, 6H, ³J_{H-H} = 7 Hz), 1.35 (d, CH₃, 6H, ³J_{H-H} = 7 Hz), 1.16 (d, CH₃, 6H, ³J_{H-H} = 7 Hz), 1.08 (d, CH₃, 6H, ³J_{H-H} = 7 Hz). ¹³C{¹H} NMR (CDCl₃, 25 °C): 194.7 (CO), 177.4 (CO), 145.4 (Ph), 140.8 (Ph), 138.1 (Ph), 128.5 (Ph), 125.6 (Ph), 124.5 (Ph), 28.6 (CH₃), 28.3 (CH₃), 25.6 (CH₃), 25.0 (CH₃), 24.7 (CH₃), 24.0 (CH₃), 23.0 (CH₃). IR (KBr, cm⁻¹): 3064 (w), 2967 (m), 2929 (m), 2869 (m), 2021 (s), 1931 (s), 1909 (s), 1384 (s), 834 (w), 798 (w). Anal. Found (Calcd): C, 49.13 (49.33); H, 5.25 (5.34); N, 3.71 (3.71).

(4-BrDABMe)Re(CO)₃Br, 4—Red solid (77% yield). ¹H NMR (CDCl₃, 25 °C): 7.66 (d, Ph, 4H, ³J_{H-H} = 1 Hz), 7.64 (d, Ph, 4H, ³J_{H-H} = 1 Hz), 2.34 (s, CH₃, 6H). ¹³C{¹H} NMR (CDCl₃, 25 °C): 195.1 (CO), 175.0 (CO), 148.5 (Ph), 133.2 (Ph), 121.8 (Ph), 20.8 (CH₃). IR (KBr, cm⁻¹): 2955 (s), 2922 (s), 2855 (s), 2025 (s), 1924 (s), 1901 (s), 1463 (m), 1382 (s), 1011 (w). Anal. Found (Calcd): C, 30.66 (30.66); H, 1.94 (1.90); N, 3.77 (3.76).

(2-CF₃DABMe)Mn(CO)₃Br, 5—Purple solid (35% yield). ¹H NMR (CDCl₃, 25 °C): 8.13 (d, Ph, 2H, ³J_{H-H} = 8 Hz), 7.82 (d, Ph, 2H, ³J_{H-H} = 8 Hz), 7.77 (t, Ph, 2H, ³J_{H-H} = 7.5 Hz), 7.56 (t, Ph, 2H, ³J_{H-H} = 7.5 Hz), 2.29 (s, CH₃, 6H). ¹³C{¹H} NMR (CDCl₃, 25 °C): 176.1 (s, CO), 148.1 (s, CO), 133.8 (s, Ph), 128.1 (s, Ph), 127.7 (q, Ph, ³J_{C-F} = 10 Hz), 123.5 (q, CF₃, ¹J_{C-F} = 272 Hz), 123.5 (s, Ph), 119.9 (q, Ph, ²J_{C-F} = 31.37), 21.4 (s, CH₃). ¹⁹F NMR: -58.12 (s, CF₃, 6F). IR (KBr, cm⁻¹): 2929 (w), 2851 (w), 2761 (m), 2032 (s), 1964 (s), 1937 (s), 1384 (s), 1320 (s). Anal. Found (Calcd): C, 42.74 (42.66); H, 2.33 (2.39); N, 4.79 (4.74).

(MesDABMe)Mn(CO)₃Br, 6—Purple solid (70% yield). ¹H NMR (CDCl₃, 25 °C): 6.97 (s, Ph, 2H), 6.92 (s, Ph, 2H), 2.55 (s, CH₃, 6H), 2.36 (s, CH₃, 6H), 2.22 (s, CH₃, 6H), 2.15 (s, CH₃, 6H). ¹³C{¹H} NMR (CDCl₃, 25 °C): 174.6 (CO), 147.0 (CO), 136.6 (Ph), 130.4 (Ph), 129.7 (Ph), 128.7 (Ph), 126.5 (Ph), 21.9 (CH₃), 20.8 (CH₃), 20.7 (CH₃), 18.7 (CH₃). IR (KBr, cm⁻¹): 2967 (m), 2918 (m), 2857 (m), 2022 (s), 1949 (s), 1910 (s), 1383 (m), 1221 (w). Anal. Found (Calcd): C, 54.01 (53.64); H, 5.40 (5.22); N, 4.85 (5.00).

(2,6-iPr₂DABMe)Mn(CO)₃Br, 7—Purple solid (35% yield). ¹H NMR (CDCl₃, 25 °C): 7.35 (m, Ph, 4H), 7.27 (m, Ph, 2H), 3.89 (sept, ⁱPr, 2H, ³J_{H-H} = 3 Hz), 2.94 (sept, H-ⁱPr, 2H, ³J_{H-H} = 3 Hz), 2.28 (s, CH₃, 6H), 1.39 (m, ⁱPr, 12H), 1.19 (d, ⁱPr, 6H, ³J_{H-H} = 3 Hz), 1.10 (d, ⁱPr, 6H, ³J_{H-H} = 3 Hz). ¹³C{¹H} NMR (CDCl₃, 25 °C): 175.5 (CO), 146.4 (CO), 140.5 (Ph), 138.2 (Ph), 128.1 (Ph), 125.7 (Ph), 124.4 (Ph), 28.6 (ⁱPr), 28.5 (ⁱPr), 25.9 (ⁱPr), 25.2 (ⁱPr), 24.9 (ⁱPr), 23.9 (ⁱPr), 22.7 (CH₃). IR (KBr, cm⁻¹): 2961 (m), 2930 (m), 2869 (w), 2764 (w), 2024 (s), 1947 (s), 1922 (s), 1384 (s), 834 (m). Anal. Found (Calcd): C, 48.22 (48.31); H, 5.18 (5.37); N, 4.87 (4.97).

(4-BrDABMe)Mn(CO)₃Br, 8—Purple solid (62% yield). ¹H NMR (CDCl₃, 25 °C): 7.41 (s, Ph, 2H), 6.91 (s, Ph, 2H), 2.32 (s, CH₃, 6H). ¹³C{¹H} NMR (CDCl₃, 25 °C): 173.6 (CO), 149.9 (CO), 133.3 (Ph), 132.9 (Ph), 122.8 (Ph), 121.3 (Ph), 121.1 (Ph), 20.4 (CH₃). IR (KBr, cm⁻¹): 3086 (w), 3054 (m), 3022 (m), 2961 (w), 2029 (s), 1944 (s), 1922 (s), 1383 (s), 1247 (m), 1010 (m). Anal. Found (Calcd): C, 37.15 (37.23); H, 2.44 (2.30); N, 4.53 (4.57).

(•MesDABMe)Re(CO)₃(NCCH₃), 9

To a stirred suspension of potassium graphite (18 mg, 13 mmol) in THF (10 mL) was added 2 (100 mg, 15 mmol). Over the course of 2 h a precipitate formed (C₈, KBr). The solution was then reduced to 3 mL, and hexane was added to precipitate a portion of pure product (33 mg, 37% yield). The solid was then filtered, dissolved in a minimum amount of MeCN, and cooled to -35 °C. Light red crystals formed over the course of several days. Consistent with a single unpaired spin, the ¹H NMR spectrum was indicative of a paramagnetic species. IR (KBr, cm⁻¹): 2950 (m), 2912 (s), 2855 (m), 1985 (vs), 1826 (vs), 1791 (vs), 1471 (m), 1246 (m).

In electrochemical *and* photochemical reduction reactions, the reduced metal complex is an important reactive intermediate. As such, we sought to isolate select one-electron reduced rhenium compounds for characterization. Similar work with the manganese complexes was not attempted due to their relative instability.⁴³ Upon addition of **1** equiv of KC_8 to a stirred solution of complexes **2** and **3** in THF no immediate color change was noted. However, after 2 h a deep brown-red color was observed. Subsequent recrystallization from acetonitrile yielded air- and moisture-sensitive radical anions $(\bullet^{\text{Me s DAB}^{\text{Me}}})\text{Re}(\text{CO})_3(\text{NCCH}_3)$, **9**, and $(\bullet^{2,6\text{-}i\text{Pr}_2\text{DAB}^{\text{Me}}})\text{Re}(\text{CO})_3(\text{NCCH}_3)$, **10**, eq 2.

(2)

Complexes **1–8** were found to create rigid chelates with hindered rotation. A decrease in symmetry was observed in the ^1H NMR spectrum of these complexes compared to the free ligand, consistent with complexation. With the exception of **1**, all complexes exhibited a dihedral plane of symmetry through the metal center and diimine core. For example, the ^1H NMR spectrum of complex **3** indicated the presence of two chemically inequivalent isopropyl methine protons. This trend is additionally reflected in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, in which six resonances arise from distinct isopropyl carbon atoms.

Based on carbonyl resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, we can conclude that the reported complexes contain a *fac*- $\text{M}(\text{CO})_3$ fragment. Typically, for the $\text{Re}(\text{I})$ complexes, the lone axial carbonyl perpendicular to the DAB plane displayed a resonance in a narrow window between 199.5 and 194.7 ppm while the equatorial carbonyl resonances occurred between 177.5 and 175.0 ppm. These signals integrated approximately to 2:1 (equatorial to axial) as expected. In contrast, the carbonyl groups on the $\text{Mn}(\text{I})$ complexes resonate within ranges shifted upfield relative to corresponding $\text{Re}(\text{I})$ signals; the axial and equatorial carbonyls were observed between 173.6 and 176.1 ppm and between 147.0 and 151.8 ppm, respectively. We note that these shifts agree well with previous reports of both known $\text{Re}(\text{I})$ and $\text{Mn}(\text{I})$ complexes containing DAB or bpy derivatives.^{12,34}

The decreased symmetry in molecules **1–8** relative to the metal precursor is evidenced by the number of observed CO stretching frequencies, Table 1. $\text{Re}(\text{CO})_5\text{Br}$, a C_{4v} molecule, displays four bands at 2154, 2048, 2018, and 1987 cm^{-1} .²³ After refluxing for 2 h in toluene, complexes **2–8** displayed only the $\nu(\text{CO})$ resonances associated with a *fac*- $\text{M}(\text{CO})_3^+$ fragment. Upon the reduction of **2** and **3** with KC_8 , the products (**9** and **10**) show a shift in the CO stretching frequencies to lower wavenumbers. For **2** specifically, the carbonyl stretches at 2019, 1934, and 1895 cm^{-1} shift to 1985, 1826, and 1791 cm^{-1} in **9**. This shift may be rationalized by considering the increased backbonding after ligand-based reduction and the resulting increase in π^* donation to the carbonyl carbon, which increases the CO bond distance and lowers the stretching frequency.

The singly reduced Re complex ($\bullet^{\text{MesDAB}^{\text{Me}}}\text{Re}(\text{CO})_3(\text{NCCH}_3)$, **9**), was studied by EPR spectroscopy since it was observed to be paramagnetic by ^1H NMR. Six lines out of the expected 12 lines for an immobilized radical are resolved in the X-band EPR spectrum at 110 K, Figure 2. A simulation with a narrow line width shows the expected lines. After the lines are broadened, six lines are resolved. The simulations are consistent with the experimental spectrum except for one line. This deviation may be attributed to more complicated M_I dependent line width parameters, Euler angles that shift the g and A tensors, inclusion of nitrogen hyperfine, and inclusion of a quadruple interaction.³⁵ Nevertheless, it is clear that the g -values from the experimental spectra ($g_{\text{iso}} = 2.0055 \pm 0.0005$, $g_{x,y} = 2.008$, $g_z = 2.00$) are typical for a ligand-centered radical. A^{Re} values ($A^{\text{Re}}_{x,y,z} = 28, 28, 48$ G) from the simulations also indicate that much of the unpaired electron is delocalized onto the ligand.

X-ray Crystallographic Analysis

Complexes **1–6** and **8–10** were structurally characterized using single-crystal X-ray crystallography. Each compound was structurally characterized as a six-coordinate, octahedral complex with two metal-nitrogen bonds to the bidentate ligand (α -diimine), three metal-carbon bonds to carbonyls, and a metal-bromide bond. To condense the discussion of all structurally characterized complexes, we only present **2**, Figure 3, **6**, Figure 4, and **9**, Figure 5, as examples of a Re, Mn, and reduced Re complex with a $\text{MesDAB}^{\text{Me}}$ ligand, respectively. Selected bond distances and angles are provided for all complexes in Table S3 in the Supporting Information, but those for **2**, **6**, and **9** are shown in Table 2.

For each of the neutral complexes, **1–8**, the metal-ligand bonds are similar to those previously described.^{36–38} The reduced species, **9**, is characterized by a decrease in the bond length of the C–C backbone of 0.07 Å from 1.4799(4) Å in **2** to 1.41(1) Å in **9**. Complexes **9** and **10** are solvent adducts, with an acetonitrile molecule coordinated in the axial position. Limited solubility of the reduced complex in non-coordinating solvents prevented isolation of the five-coordinate structure. Recrystallization from MeCN or THF yielded the respective solvent adducts. In **9** and **10**, the MeCN adduct was crystallographically characterized but solvation (MeCN or THF) depends on the solvent in which the complex is dissolved.

Electrochemistry

A standard electrochemical survey under inert (N_2) atmosphere showed that both the Re(I) and Mn(I) complexes exhibited redox behavior at negative potentials with some similarity to previously reported bpy-based complexes.^{11,12,14} The observed redox features under N_2 saturation are summarized below, Table 3, and in Figures S9–S14 in the Supporting Information. In order to better compare our results with the chemically reduced species, we decided to focus on complexes **2** and **7** for study under CO_2 -saturation conditions. Complex **2** is observed to undergo an initial reversible ligand-based reduction at -1.23 vs Fc/Fc^+ .³⁹ This is followed by an additional less chemically reversible redox feature at -1.77 V vs Fc/Fc^+ .¹ Under CO_2 -saturation conditions, complex **2** exhibited a modest increase in current as compared to voltammograms under N_2 . This increase did not correspond to a pre-existing redox feature (-2.17 V vs Fc/Fc^+), which suggests that product dissociation is rate-limiting, Figure 6.⁴⁰ The addition of 2,2,2-trifluoroethanol (TFE) as a proton source showed a further

increase in the observed current under CO₂, although returning to N₂ saturation showed a new irreversible redox feature at -2.79 V vs Fc/Fc⁺, indicative of proton reduction under these conditions.⁵⁴

In the case of the Mn(I) complex **6**, a standard electrochemical survey showed a single, quasi-reversible 2e⁻ reductive response at anodic potentials under N₂ atmosphere. This is assigned to a combined ligand and metal-based process on the basis of its similarity to literature reports of bpy-based Mn(I) catalysts.¹² Under CO₂-saturation conditions with added TFE (795 mM), a very slight increase of current after the initial redox feature was observed, Figure 7.^{12,41} In the absence of added TFE the current response under CO₂ was almost identical to that taken under N₂. The CVs of **6** with TFE under N₂ did not show an increased redox response in comparison to those taken before its addition until very reducing potentials. We conjecture that the role of TFE in this reaction is to stabilize the Mn-CO₂ adduct through protonation before the disproportionation reaction.^{42,55} This is similar to the case of bipyridine, where an added proton source is required to form a stable Mn-CO₂H species before further reactions can occur.⁴³

Based on these experiments and previous determinations of the mechanism for the related bpy-based complexes, it is likely that the rate of product dissociation limits the catalytic response. Unlike the highly active bpy-based catalysts, the α-diimine catalysts also do not appear to be as selective for CO₂ reduction over the thermodynamically preferred proton reduction under similar experimental conditions. Bulk electrolyses of **2** and **7** were observed to have a rapid decrease in current and showed low Faradaic efficiencies for CO by GC-MS (<10%). We sought to elucidate this proposed mechanism for **2** and **7** with IR-SEC.

Infrared Spectroelectrochemistry

To correlate the electrochemical surveys with the data obtained from characterizing the chemically reduced species (**9** and **10**), we examined **2** by IR-SEC, Figure 8. When the potential of the first reduction was reached, the principal IR stretches at 2027, 1937, and 1898 cm⁻¹ begin to slowly diminish in intensity with the concomitant appearance of a new species with IR stretches at 2010, 1896, and 1884 cm⁻¹. These frequencies are consistent with a single reduction of the parent complex, [(^{Mes}DAB^{Me})-Re^I(CO)₃Br]⁻. An increase in potential to that of the second reduction causes the bands corresponding to [(^{Mes}DAB^{Me})-Re^I(CO)₃Br] and [(^{Mes}DAB^{Me})-Re^I(CO)₃Br]⁻ to disappear with the appearance of six new IR stretches, assigned to two isomers of the doubly reduced complex. The first has bands at 1984, 1875, and 1865 cm⁻¹ which are assigned to an MeCN adduct of the doubly reduced complex where the bromide ligand has dissociated, [(^{Mes}DAB^{Me})-Re^I(CO)₃-(MeCN)]⁻.^{13,38} The second species has bands at 1951, 1840, and 1829 cm⁻¹, which are comparable to previously characterized five-coordinate, doubly reduced *Re fac*-tricarbonyl complexes, [(^{Mes}DAB^{Me})-Re⁰(CO)₃]⁻.¹⁴ This behavior is consistent with the solvent coordination observed in the crystallographically derived molecular structures.

Repeating these experiments under partially saturated ¹²CO₂ and ¹³CO₂ atmospheres and with the CO capture agent nickelocene (NiCp₂) provided some mechanistic insight, Figure 9. The addition of NiCp₂ into the cell allows for the visualization of CO product in conditions where its low solubility and reduced dipole moment would otherwise make this

impossible.²⁸ In a model experiment, the cell was charged with **2** (4.2 mM) dissolved in 0.1 M TBAPF₆/MeCN which was sparged briefly with ¹²CO₂. A spectrum was obtained at resting potential, and then the cell set to -2.1 V vs Ag/Ag⁺ pseudo-RE (values are ~0.18 V less negative than versus Fc/ Fc⁺). Consistent with the IR-SEC data obtained under inert atmosphere, the species observed in solution change from the parent state to the mixture containing the doubly reduced five-coordinate [(^{Mes}DAB^{Me})Re⁰(CO)₃]⁻ complex, with IR stretches observed at 1950, 1840, and 1830 cm⁻¹. This species begins to slowly disappear and new metal carbonyl stretches are observed at 2003 and 1870 (broad) cm⁻¹, Figure 9. These carbonyl bands indicate the presence of a species similar to either a Re^I-CO₂ or Re^I-CO₃²⁻, although the presence of free CO₃²⁻ precludes definitive assignment.^{44,45} There is also an appearance of two new stretches at 1682 and 1633 cm⁻¹. These new stretches are assigned to carbonate (CO₃²⁻).⁴³ Consumption of CO₂ stops after several minutes, which is indicative of product inhibition. With ¹³CO₂ as the substrate for this reaction (4.0 mM **2**), an identical series of species are observed in the Re carbonyl region of the spectrum. The two distinct stretching modes observed at 1682 and 1633 cm⁻¹ are replaced, however, with a single broad stretch centered at 1626 cm⁻¹, Figure 9A. The lack of resolution for this CO₃²⁻ band arises in part from the increasingly strong absorbance of MeCN in this portion of the IR window.⁴⁶

When the previous experiment was repeated with ¹²CO₂ (1.9 mM) and NiCp₂ (26.5 mM), a new band appeared at 1848 cm⁻¹, corresponding to the presence of a [Ni^I(μ₁-CO)Cp]₂ dimer, Figure S15 in the Supporting Information. This Ni(I) dimer species is known to form at negative potentials under CO atmosphere.⁴⁷ CO is the expected co-product of CO₃²⁻ during the reduction and disproportionation of CO₂.⁴⁸ When ¹³CO₂ was used as the substrate under identical conditions (3.8 mM **2**, 53 mM NiCp₂), this band shifted to 1803 cm⁻¹, consistent with ¹³CO incorporation into the [Ni^I(μ₁-CO)Cp]₂ dimer, Figure 9B. These experiments indicate that the reaction catalyzed is the reduction of 2 equiv of CO₂ to CO and CO₃²⁻.

The IR-SEC experiments detailed above were also repeated for the corresponding Mn-based complex **6**. Under inert atmosphere, this complex behaved in a similar manner to Mn(bpy)-based complexes, although no Mn⁰-Mn⁰ dimer is observed. At resting potentials three IR bands are observed for **6**, [(^{Mes}DAB^{Me})Mn^I(CO)₃Br], at 2027, 1951, and 1913 cm⁻¹, Figure 10. As the potential of the cell is increased stepwise to that corresponding to the first reduction observed electrochemically (-1.26 V vs Fc/Fc⁺), these stretches begin to diminish in intensity and a single electron reduced species, [(^{Mes}DAB^{Me})Mn^I(CO)₃Br]⁻, is observed briefly with stretches at 2011, 1923, and 1905 cm⁻¹. Interestingly, this species is not observed for Mn(bpy)-based complexes.²⁸ Over the course of several minutes at this potential, these two species rapidly disappear with the concomitant appearance of two bands at 1924 and 1815 cm⁻¹. These bands are assigned to the presumptive active state [(^{Mes}DAB^{Me})Mn⁰(CO)₃]⁻ on the basis of literature precedent.^{12,28,43}

When samples of **6** were prepared with 0.5 M TFE and sparged with ¹²CO₂ or ¹³CO₂ before being set to catalytic potentials, CO₃²⁻ was observed, similar to the experiments conducted with complex **2** (bands consistent with [(^{Mes}DAB^{Me})Mn^I(CO)₃(MeCN)]⁺ are observed at 2049 and 1970 cm⁻¹ under these conditions, indicative of Br⁻ displacement). In the case

of $^{12}\text{CO}_2$, when the cell was set to -2.1 V (vs Ag/Ag^+), the bands associated with the parent complex began to slowly disappear, Figure 11. A new broad stretch assigned to $^{12}\text{CO}_3^{2-}$ was observed at 1650 cm^{-1} . Over the course of several minutes, the growth of this peak slowed and an additional three stretches were observed at 1983 , 1903 , and 1866 cm^{-1} , assigned to Mn carbonyl species. After several minutes the current diminished significantly, although a static CO_2 band was still observed by IR, Figure 11A. When the cell was set again to the resting potential, these IR bands disappeared, replaced by stretches at 2047 , 2033 , 2012 , 1978 , and 1916 cm^{-1} . This suggests that as the reaction proceeds, the $^{12}\text{CO}_3^{2-}$ product inhibits turnover. The band observed at 1650 cm^{-1} does not diminish when the cell is set to resting potential, which is indicative of $^{12}\text{CO}_3^{2-}$ formation. Consistent with this interpretation, when the experiment is repeated with $^{13}\text{CO}_2$, the band assigned to carbonate grows in at 1609 cm^{-1} , meaning that the source of carbon in the observed CO_3^{2-} is CO_2 (41 cm^{-1} shift). At catalytic potentials bands assigned to Mn carbonyl species are observed at 1983 , 1903 , and 1866 cm^{-1} , similar to the experiment conducted with $^{12}\text{CO}_2$. Returning the cell to resting potential (vs Ag/Ag^+) had no effect on the intensity of the $^{13}\text{CO}_3^{2-}$ stretch at 1609 cm^{-1} .

CONCLUSION

On the basis of these data, we are able to propose a mechanism for the reduction of CO_2 by Re and Mn DAB complexes. In the case of **2**, two sequential one-electron reduction steps result in the formation of the active state $[(^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Re}^0(\text{CO})_3]^-$, **A**. A subsequent reaction with 1 equiv of CO_2 generates a $\text{Re}^{\text{I}}\text{-CO}_2$ species, **B**. In the presence of a second equivalent of CO_2 , a disproportionation reaction occurs, which yields 1 equiv each of CO and CO_3^{2-} . Although bulk electrolysis experiments show a dramatic loss of current, the IR-SEC experiments under catalytic conditions indicate that CO_3^{2-} is generated during the course of this reaction. We propose the limiting step to be CO_3^{2-} loss from a Re-CO_3^{2-} species, **C**. In the case of **6**, a proton source is required before an increase in current may be observed under CO_2 -saturation conditions. It is likely that the addition of TFE stabilizes a $\text{Mn-CO}_2\text{H}$ species, similar to the case of Mn bipyridine complexes.^{43,55} In the proposed mechanism, the anionic $[(^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Mn}^0(\text{CO})_3]^-$, **D**, reacts with CO_2 and 1 equiv of H^+ to generate **E**. In the presence of a second equivalent of CO_2 , a disproportionation reaction occurs, resulting in the formation of **F**. We note that the difference between our study and one recently published with $(\alpha\text{-diimine})\text{Mn}(\text{CO})_3\text{Br}$ complexes is their observation as $[\text{Mn}(\text{CO})_5]^-$ as a degradation product which we do not in our system. This is presumably due to the methyl substituents on the diimine backbone which prevent ligand dimerization.

Ten new complexes of Re(I) and Mn(I) with α -diimine ligands have been characterized using FTIR, UV-vis, ^1H NMR, and ^{13}C NMR spectroscopy, as well as nine structurally determined by single-crystal X-ray diffraction. The one-electron ligand-based radical complexes were isolated from reduction with KC_8 and EPR spectroscopy showed a ligand-centered radical on the DAB ligand. Isolation of these free radical species motivated an investigation into the electrochemistry of the neutral complexes, and their reactivity with CO_2 was explored. These results indicate that transient stabilization of reactive intermediates can be accomplished by the use of redox active ligands, similar to bpy-based systems. Unlike bpy-based systems under identical conditions, however, a reductive disproportionation reaction is observed: the conversion of 2 equiv of CO_2 into CO and CO_3^{2-} . Although EPR^{13,18,49–52} and IR-SEC data indicate that the mechanism of reduction under inert conditions is similar in many respects to that of the bpy-based compounds, the CV response in the presence of CO_2 shows an increase in current only after two redox equivalents have been added to the starting complex. This indicates that in order to complete the catalytic cycle for the disproportionation reaction, the dissociation of CO_3^{2-} product requires an additional reduction.

We propose that this product inhibition is the consequence of the DAB ligand framework donating less electron density to the metal center in the reduced state. Indeed, the observation by of the equilibrium achieved between $[(\bullet^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Re}^0(\text{CO})_3(\text{MeCN})]^-$ and $[(\bullet^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Re}^0(\text{CO})_3]^-$ via IR-SEC is indicative that a metal center appended to the DAB framework is electron-poor relative to analogous bipyridine ligands. Furthermore, the carbonyl stretches of $[(\bullet^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Re}(\text{CO})_3]^-$ and $[(\bullet^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Mn}(\text{CO})_3]^-$ have higher frequencies than those of analogous bipyridine-based anionic species, which is consistent with less back-bonding from the metal center to the CO ligand.^{53,45,28,43,48} In the case of Re, $[\text{Re}(4,4'\text{-dimethyl-2,2'-bipyridine})(\text{CO})_3]^-$ has bands at 1940 and 1832 cm^{-1} , whereas $[(\bullet^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Re}^0(\text{CO})_3]^-$ has observable bands at 1951, 1840, and 1829 cm^{-1} .⁴⁵ Likewise, $[\text{Mn}(6,6'\text{-dimesityl-2,2'-bipyridine})(\text{CO})_3]^-$ shows bands at 1909 and 1808 cm^{-1} , while $[(\bullet^{\text{Mes}}\text{DAB}^{\text{Me}})\text{Mn}^0(\text{CO})_3]^-$ exhibits bands at 1924 and 1815 cm^{-1} .⁴³ Higher frequency carbonyl stretches are indicative of decreased back-bonding from the metal center to the CO ligand. As a consequence, the metal centers of the Re and Mn DAB complexes are less nucleophilic than their bipyridine analogues, which is directly observed in both the decreased current response for CO_2 reduction and alternate catalytic mechanism.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

We gratefully acknowledge the University of Missouri College of Arts & Science Alumni Faculty Incentive Grant for funding (J.R.W.) as well as the Undergraduate Research Mentor Program (URMP) to M.V.V. C.P.K. acknowledges support for this work from the AFOSR through a Basic Research Initiative grant (FA9550-12-1-0414). Research at the University of Georgia was supported by the National Science Foundation (Grant No. CHE-1361178).

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Figure 1.
Comparison of neutral, radical anion, and dianionic forms of 2,2'-bipyridyl and α -diimine ligands.

Figure 2.

Experimental (black) and simulated (red) spectra for 9 are shown. Experimental parameters: microwave frequency 9.268 GHz, 110 K, 5 G mod., power 16 dB, time constant 31.2 ms, sweep time 33.4 s, nine scans. Simulation parameters: $g = 2.008, 2.008, 2.00$; $A = 28.6$ G, 28.6 G, 47.5 G; $lwpp = 5$ G; $H_{strain} = 0$ (top red); $H_{strain} = 80, 80, 60$ MHz (bottom red).

Figure 3.
Thermal ellipsoid plot of **2** shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Figure 4.
Thermal ellipsoid plot of 6 shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Figure 5. Thermal ellipsoid plot of 9 shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Figure 6.

Cyclic voltammogram of **2** in MeCN under N_2 (black) and CO_2 (red) atmospheres (left).

The effect of TFE addition is shown on the right. Conditions: 1 mM **2** in 0.1 M $\text{TBAPF}_6/\text{MeCN}$; GC WE, Pt wire CE, Ag/AgCl pseudo-RE; scan rate 100 mV/s.

Figure 7.

Cyclic voltammogram of 6 in MeCN under N_2 (black) and CO_2 (red) saturation. The effect of TFE addition is shown in blue. Conditions: 1 mM 6 in 0.1 M TBAPF₆/MeCN; GC WE, Pt wire CE, Ag/AgCl pseudo-RE; scan rate 100 mV/s.

Figure 8.

IR-SEC of complex 2 showing the parent species being reduced by one electron to the anionic $[(\text{MesDAB}^{\text{Me}})\text{Re}^{\text{I}}(\text{CO})_3\text{Br}]^-$, red, and then again to an equilibrium distribution between $[(\text{MesDAB}^{\text{Me}})\text{Re}^{\text{I}}(\text{CO})_3(\text{MeCN})]^-$ and $[(\text{MesDAB}^{\text{Me}})\text{Re}^0(\text{CO})_3]^-$, blue. Pt WE, Ag pseudo-RE, Pt CE, 0.1 M TBAPF₆/MeCN; 2.2 mM 2 in 0.1 M TBAPF₆/MeCN.

Figure 9.

(A) IR-SEC of complex **2** with ¹²CO₂ at resting potential (black) and catalytic potential after several minutes (−2.1 V vs Ag/Ag⁺ pseudo-RE, red) showing the growth of bands consistent with CO₃^{2−} formation and a persistent ¹²CO₂ band. (B) IR-SEC of complex **2** with ¹²CO₂ (black) and ¹³CO₂ (red) demonstrating the C source for CO₃^{2−} formation is CO₂. GC WE, Ag pseudo-RE, Pt CE, 0.1 M TBAPF₆/MeCN, sparge with ¹²CO₂ or ¹³CO₂ for 20 s; A, 4.2 mM **2**; B, 4.2 mM (black) and 4.0 mM (red) **2**.

Figure 10.

IR-SEC of complex **6** showing the parent species being reduced by one electron to an equilibrium with the short-lived anionic [([•]MesDAB^{Me})Mn(CO)₃Br]⁻, red, and then again to an [([•]MesDAB^{Me})Mn⁰(CO)₃]⁻, blue, at the same potential. Pt WE, Ag pseudo-RE, Pt CE, 0.1 M TBAPF₆/MeCN; 3.9 mM **6** in 0.1 M TBAPF₆/MeCN.

Figure 11.

(A) IR-SEC of complex **6** with $^{12}\text{CO}_2$ in 0.1 M TBAPF₆/MeCN with 0.5 M TFE at resting potentials (black), catalytic potentials after several minutes (-2.1 V vs Ag/Ag⁺, red) and resting (blue) potentials after catalytic potential. (B) IR-SEC of complex **7** with $^{12}\text{CO}_2$ (black) and with $^{13}\text{CO}_2$ (red) in 0.1 M TBAPF₆/MeCN with 0.5 M TFE showing a shift consistent with isotopic labeling in the stretch assigned to CO_3^{2-} (1650 to 1609 cm⁻¹). GC WE, Ag pseudo-RE, Pt CE, 0.1 M TBAPF₆/MeCN with 0.5 M TFE, sparge with $^{12}\text{CO}_2$ or $^{13}\text{CO}_2$ for 20 s; A, 5.8 mM **7**; B, 5.8 mM **7** (black) or 4.7 mM **2** (red).

Table 1

Infrared Stretching Frequencies for Complexes 1–10

complex	$\nu(\text{CO})$ (cm^{-1})	$\nu(\text{C}=\text{N})$ (cm^{-1})
1	2028, 1940, 1925	1319
2	2019, 1934, 1895	1383
3	2021, 1931, 1909	1384
4	2025, 1924, 1901	1382
5	2032, 1964, 1937	1384
6	2022, 1949, 1910	1383
7	2024, 1947, 1922	1384
8	2027, 1944, 1930	1383
9	1985, 1826, 1791	-
10	1936, 1838, 1802	-

Table 2

Selected Bond Distances (Å) and Angles (deg) for 2, 6, and 9

bond distance (Å)/angle (deg)	(^{Mes} DAB ^{Me})Re(CO) ₃ Br, 2 (E = Br)	(^{Mes} DAB ^{Me})Mn(CO) ₃ Br, 6 (E = Br)	(^{Mes} DAB ^{Me})Re(CO) ₃ (NCMe), 9 (E = N)
M1–N1, M1–N2	2.1576(8), 2.1600(8)	2.037(3), 2.046(3)	2.158(6), 2.138(6)
M1–C1, M1–C2, M1–C3	1.9234(5), 1.9243(7), 1.9294(5)	1.818(4), 1.832(4), 1.818(4)	1.903(9), 1.914(8), 1.930(9)
M1–E	2.6206(6)	2.5401(8)	2.178(7)
N1–C4, N2–C5	1.3013(4), 1.2955(4)	1.296(4), 1.301(4)	1.34(1), 1.33(1)
C4–C5	1.4799(4)	1.483(5)	1.41(1)
N1–M1–N2	74.12(1)	77.93(11)	74.8(2)
N1–M1–E, N2–M1–E	86.42(1), 86.35(1)	88.73(8), 88.74(8)	82.4(2), 83.4(2)

Table 3Electrochemical Data Obtained for Complexes 1–8^a

complex	E_1 (V)	E_2 (V)
1	–1.17	–1.52
2	–1.23 (r)	–1.77
3	–1.28	–1.72 (r)
4	–1.23 (r)	–1.52
5	–1.11	–1.24
6	–1.26	
7	–1.14	
8	–1.23	

^aFeatures denoted (r) are reported as $E_{1/2}$; others are reported at the i_p . All potentials are referenced to the Fc/Fc⁺ couple using an internal ferrocene standard.