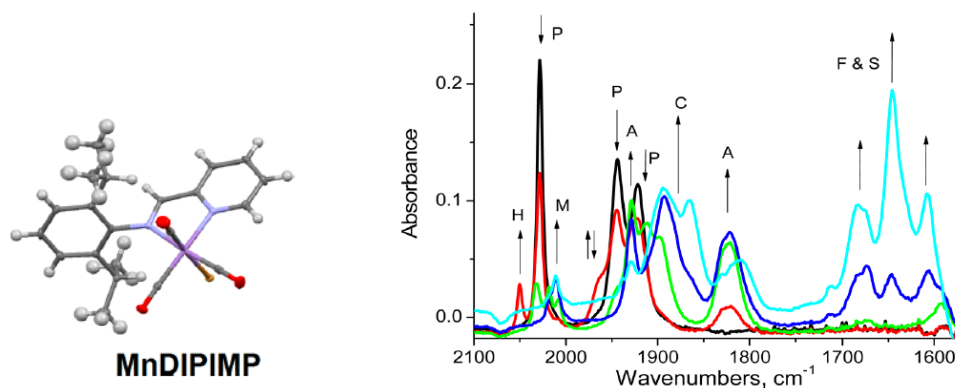


Assignment A04: Electrochemical $[\text{Mn}(\text{CO})_3(\text{DIPIMP})]^+$ -Catalyzed CO_2 Reduction

As we begin to work on research-based assignments and to deal with nature's complexity, it is worthwhile to reflect on a quote from Melville's *Moby Dick*: "As for me, I am tormented with an everlasting itch for things remote. I love to sail forbidden seas, and land on barbarous coasts."



This assignment is based on the following recently published research article: *Manganese Tricarbonyl Complexes with Asymmetric 2-Iminopyridine Ligands: Toward Decoupling Steric and Electronic Factors in Electrocatalytic CO_2 Reduction*. S. J. P. Spall, T. Keane, J. Tory, D. C. Cocker, H. Adams, H. Fowler, A. J. H. M. Meijer, F. Hartl, J. A. Weinstein. *Inorg. Chem.*, **2016**, 55, 12568–12582 (10.1021/acs.inorgchem.6b01477). The article is linked to the assignment section of the course web site (direct link and link to local PDF).

The goals of assignment A04 include (i) to review your knowledge of the electrolysis of water, (ii) to learn about electrolysis of manganese tricarbonyl complexes with 2-iminopyridine ligands $\text{Mn}(\text{CO})_3(\text{IMP})$ in (not entirely) dry acetonitrile/0.2 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ in the presence of CO_2 and to create Scheme 1 (based on and improving on Figure 14 of the Source) to describe this redox chemistry, (iii) to create your Figure 1 by simulation of the bottom half of Figure 9 of the Source, (iv) to create your Figure 2 by importing the plot of Figure 12 of the Source, and (v) to write some text to summarize the chemistry incorporating these items.

The simulations in (iii) are at the core of A04, they require the generation and manipulation of large arrays of data, and you need to be well organized from the start. Use the “examples” and

“samples” posted on the assignments section of the course web site for guidance, and (try to) enjoy the challenge.

Read the Source and try to understand what the paper is about; this will take some time. Here are some thoughts to guide your studies. Review your knowledge of the electrochemistry of water (i.e., visit https://en.wikipedia.org/wiki/Electrolysis_of_water). Application of an electrical current leads to the anodic oxidation of water ($2 \text{ OH}^- \rightarrow \frac{1}{2} \text{ O}_2 + \text{ H}_2\text{O} + 2 \text{ e}^-$; $2 \text{ H}_2\text{O} \rightarrow \frac{1}{2} \text{ O}_2 + \text{ H}_2\text{O} + 2 \text{ H}^+ + 2 \text{ e}^-$) and to the cathodic reduction of water ($2 \text{ H}^+ + 2 \text{ e}^- \rightarrow \text{ H}_2$; $2 \text{ H}_2\text{O} + 2 \text{ e}^- \rightarrow \text{ H}_2 + 2 \text{ OH}^-$). The usual formulation invokes the oxidation of hydroxide ions and the reduction of protons; i.e., reflects the autoionization of water ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$). The electrolysis reactions described in the Source are performed in dry acetonitrile that contains 0.2 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$; tetrabutylammonium hexafluorophosphate serves as electrolyte. Note the “ H^+ ” in Figure 12 of the Source; where does it come from? “Dry” acetonitrile is not *entirely* dry to begin with and, as the catalytic CO_2 reduction proceeds, more water is generated (see below).

(a) Create Scheme 1 to Describe the Redox Chemistry. Your Scheme 1 should improve on Figure 14 of the Source and contain at least 11 structures (DIPIMP, **P**, **A**, **D**, **I1**, **I2**, **I3**, **H**, **M**, $[\text{Mn}(\text{CO})_3(\text{DIPIMP})]^+$, $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^+$). Create your Scheme 1 for the specific ligand DIPIMP. Show the structure of DIPIMP in Scheme 1 (i.e., specify R, R₁, and R₂ in the “box” that defines the ligand abbreviated as “N—N”). Show complete structures including all lone pairs, lone electrons and formal charges. **P** contains Mn^+ coordinated by bromide, 3 CO and 2 N-atoms of DIPIMP; show dashed lines between the central metal and each one of its ligands. **A** contains Mn^- (show the lone pair at Mn^- explicitly) and remains coordinated by 3 CO and 2 N-atoms of DIPIMP. **A** is formed by 2e[−]-reduction of **P** with concomitant bromide loss: $\text{P} + 2\text{e}^- \rightarrow \text{A} + \text{Br}^-$. **A** also can be formed stepwise from **P** with catalysis by **A**. Step 1 (bromide elimination): **D** is formed by the reaction $\text{P} + \text{A} \rightarrow \text{D} + \text{Br}^-$. Step 2 (2e[−]-reduction): $\text{D} + 2\text{e}^- \rightarrow 2 \text{ A}$; regenerate catalyst **A** and one new **A**.

In the presence of CO_2 , another reaction channel opens because the nucleophile **A** can add to

CO₂. And here we want to draw three structures: (a) the structure of intermediate **I1** (an anion) formed by addition of CO₂ to **A**, (b) the structure of intermediate **I2** (a neutral species) formed by protonation of **I1**, and (c) the structure of intermediate **I3** (a cation) formed by another protonation of **I2** (at the same O). Loss of water and CO from **I2** generates the *cation* [Mn(CO)₃(DIPIMP)]⁺; not anion [Mn(CO)₃(DIPIMP)]⁻ (**A**)! The cation [Mn(CO)₃(DIPIMP)]⁺ may add ligand water to form [Mn(CO)₃(OH₂)(DIPIMP)]⁺ (**H**), or it may add acetonitrile to form [Mn(CO)₃(MeCN)(DIPIMP)]⁺, or it may re-add bromide to re-form neutral **P**.

The **A**-catalyzed CO₂ reduction thus may include the chain reactions $\mathbf{A} + \text{CO}_2 + 2 \text{H}^+ + \text{Br}^- \rightarrow \mathbf{P} + \text{CO} + \text{H}_2\text{O}$ and $\mathbf{P} + 2\text{e}^- \rightarrow \mathbf{A} + \text{Br}^-$, or it may include the chain reactions $\mathbf{A} + \text{CO}_2 + 2 \text{H}^+ + \text{L} \rightarrow [\text{Mn}(\text{CO})_3(\text{L})(\text{DIPIMP})]^+ + \text{CO} + \text{H}_2\text{O}$ and $[\text{Mn}(\text{CO})_3(\text{L})(\text{DIPIMP})]^+ + 2\text{e}^- \rightarrow \mathbf{A} + \text{L}$ (with L = water, acetonitrile). No matter which paths are travelled, the overall process is $\text{CO}_2 + 2 \text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$.

Almost done, one more thing. As we generate more and more water, the reaction rate increases for the addition of water to CO₂ and bicarbonate HCO₃⁻ can form. In Scheme 1, add the reaction of **I1** with HCO₃⁻ to form the bicarbonate complex by substitution of HCO₂⁻. (How could the bicarbonate complex possibly be made by oxidation of **I1** with CO₂ as suggested by the authors?)

Use color to enhance the message. Pay attention to alignment and spacing. Import the scheme into a Word file and add a Scheme legend.

(b) Create Figure 1 by Simulation of the Spectra in the Bottom of Figure 9 of the Source.

The bottom half of Figure 9 of the Source shows IR spectral changes accompanying in situ reduction of the complex [MnBr(CO)₃(DIPIMP)] (**P**) in argon-saturated acetonitrile containing 0.2 M [Bu₄N]⁺[PF₆]⁻ within an optically transparent thin-layer electrochemical (OTTLE) cell.

Colors indicate various times in the course of the reduction. **Black** line, before the reduction: Spectrum of the parent complex [MnBr(CO)₃(DIPIMP)] (**P**). **Blue** line, after the reduction:

Spectrum of the product of 2e-reduction, the five-coordinate anion $[\text{Mn}(\text{CO})_3(\text{DIPIMP})]^-$ (**A**). **Red** line, early in the reaction: Lots of **P** still present, not much product **A** formed as yet. Additional bands due to the aquo cation $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DIPIMP})]^+$ (**H**). **Green** line, later in the reaction: Some **P** left, lots of product **A** already formed. Additional bands due to the product of 1e-reduction of $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^+$ to $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^\bullet$ (**M**).

Your Figure 1 should be a complete re-creation of the bottom part of Figure 9 of the Source in every way (same sizes, same labels, same tick marks, same colors, same everything) using the program EXCEL. (Obviously, there is no need to simulate the experimental noise in the experimental spectra.)

Each spectral curve $f(\bar{\nu})$ can be approximated as the sum of a number of Gaussian functions $f_i(\bar{\nu})$ which are determined by the positions of their maxima $\bar{\nu}_{\text{max},i}$ and their extinction coefficients ε_i which determine the absorbance; $f(\bar{\nu}) = \sum f_i(\bar{\nu})$. At least three Gaussians are needed for the simulation of the black curve ($i = 4$). At least seven Gaussians are needed for the simulation of the red curve ($i = 7$). Start with reasonable initial guesses for $\bar{\nu}_{\text{max},i}$ and ε_i and adjust the parameters to obtain a good fit. You may choose a fitting procedure of any sophistication; i.e., from visual inspection to mathematical regression. Refer to the posted examples to get an idea about the organization of your excel sheet to generate Figure 1.

Generation of Spectrum $f(\bar{\nu})$: For each Gaussian $f_i(\bar{\nu})$, list the parameters for $\bar{\nu}_{\text{max},i}$, h_i and width σ_i on top of the sheet, i.e., in the posted example in rows 3, 4 and 5, respectively. List discrete values of $\bar{\nu}$ in column B, i.e., 1700 - 2100 cm^{-1} in steps of 20 cm^{-1} (or better) starting in row 8 in the example. Then compute the values of the Gaussian function and place the values in a column to the right of the wavenumbers (i.e., column D in the example); this default Gaussian is normed such that its integral equals unity. Once you have the Gaussian values computed, determine the maximum value n_i of your Gaussian (i.e., D50 in the example). You can now compute the value of the height-normed and intensity-weighted Gaussian and place it in a new column (i.e., Column E in the example) by dividing the value of the default Gaussian by the maximum values

of the Gaussian (height normation) and multiplication by h_i (intensity-weighted). Proceed in the same fashion for the other Gaussians $f_i(\bar{\nu})$. Finally, compute the $f(\bar{\nu})$ values in a new column and plot the spectrum as an unmarked XY scatter plot.

Generation of Spectra $f_m(\bar{\nu})$: Apply the procedure for the spectrum simulation to each one of the four spectra ($m = 1 - 4$), i.e., simulate all of them as sums of Gaussian functions $f_{i,m}(\bar{\nu})$ which are determined by the positions of their maxima $\bar{\nu}_{\max,i,m}$ and their heights $h_{i,m}$; $f_m(\bar{\nu}) = \sum f_{i,m}(\bar{\nu})$. Plot all the simulated spectra $f_m(\bar{\nu})$ in their respective colors in one graph. Do not plot the individual Gaussians $f_{i,m}(\bar{\nu})$; only plot the spectra $f_m(\bar{\nu})$.

Import the plot as Figure 1 into your Word file and add a Figure legend. Report the parameters used for the Gaussians of the four spectra in the legend to this Figure 1. For each one of the four spectra (m), list the values ($\bar{\nu}_{\max,i,m}$ [1/cm], $h_{i,m}$, $\sigma_{i,m}$ [1/cm], $n_{i,m}$) for all i Gaussians.

(c) Create Figure 2 by Importing the Plot of Figure 12 from the Source. Figure 12 of the Source shows IR spectral changes accompanying in situ reduction of the complex $[\text{MnBr}(\text{CO})_3(\text{DIPIMP})]$ (**P**) in CO_2 -saturated acetonitrile containing 0.2 M $[\text{Bu}_4\text{N}]^+[\text{PF}_6]^-$ within an OTTLE cell. Import the plot as Figure 2 into your Word file and add a Figure legend.

Colors indicate various times in the course of the reduction and, in contrast to your Figure 1, there now are five spectra. **Black** line, before the reduction: Spectrum of the parent complex $[\text{MnBr}(\text{CO})_3(\text{DIPIMP})]$ (**P**). **Red** line, early in the reaction: Lots of **P** still present, not much product **A** formed as yet. Additional bands due to the aquo cation $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DIPIMP})]^+$ (**H**). **Green** line, later in the reaction: Some **P** left, lots of product **A** already formed. Additional bands due to the product of 1e-reduction of $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^+$ to $[\text{Mn}(\text{CO})_3(\text{MeCN})(\text{DIPIMP})]^\bullet$ (**M**). So far, all looks pretty much the way it looked in the absence of CO_2 . But the CO_2 -related features do show in the subsequent spectra (**blue** line, **light blue** line) and you need to describe and explain these features.

(d) Write Text with Proper Bridges to Scheme 1 and Figures 1 and 2. Write a brief and concise description of the context (no more than 2 pages of text, double-spaced, Times New Roman, 12 pt, 1 inch margins, your names in the header, page numbers centered in the footer) at the beginning of a Word file. Cite the schemes and the figures in your text using appropriate bridges at the most suitable places. Scheme 1 and Figures 1 and 2 follow the text, each with its own legend and on separate pages. Cite references in the text where needed and have them appear as numbered footnotes.

Your text should include four paragraphs. Begin with a brief introduction of overall purpose of the study, that is, the electrochemical, transition-metal complex catalyzed CO₂ reduction to CO. In the next paragraph and using Scheme 1, you then explain which pro-catalyst (**P**) was used and how the active catalyst (**A**) was made *in situ*. In the third paragraph and using Figure 1, you then provide evidence in support of the mechanism of the electrochemical formation of the catalyst outlined in Scheme 1. Finally, in the fourth paragraph and using Figure 2, you discuss the electrochemistry in the presence of CO₂. Feel free to dig into the literature and cite some literature to clarify the chemistry reported in the Source.

The assignment must be completed with MS WORD and MS EXCEL. Create one WORD file with the name “A04_‘your_last_names’.docx” and one EXCEL file with the name “A04_‘your_last_names’.xlsx”. Organize the XL file as clearly as you can so that it will be easily accessible (as in “understandable”) to the peer reviewers! Label your sheets. Perhaps show the graph in a separate sheet (you can “Move Chart” to a new sheet).

Deadlines: Instructor and/or GTA will provide feedback and an opportunity to update before the peer review starts. Here is how it works: Submit drafts both electronic files on Tuesday, 02/28/17 by midnight. Instructor will review submissions and comment in class on Wednesday, 03/01/17. Submit updates of both electronic files on Thursday, 03/02/17 by midnight. Bring one hardcopy (stapled) of the Word file only to class on Friday, 03/03/17. Peer reviewers will receive the associated EXCEL file via email once peer review assignments will have been made.

Importing Graphs from Excel: (cf. A02 about importing ChemDraw schemes.)

There are many ways to import an Excel Graph into a WORD file. One way to import a graph from Excel into Word involves the following steps: select the graph in Excel, copy the graph to the clipboard (click “Copy” in the Edit menu, or type Command-C), go to the Word file, and paste the clipboard (click “Paste” in the Home menu, or type Command-V).

This import method inserts the graph as a Microsoft Excel Chart Object and such an object can be edited after it was inserted in the Word file. Double-clicking the chart in the Word file will open a Excel window where you can edit the graph and the respective XLSX file.

For other ways to import a graph from Excel into Word use “Paste Special”. Click the small triangle under “Paste” in the Home menu to see the “Paste Options” and then select “Paste Special”. A menu comes up and you can chose among various formats including Microsoft Excel Chart Object, Bitmap, several Picture formats (Enhanced Metafile, GIF, PNG, JPEG), and Microsoft Office Graphic Object.

Embedding a Microsoft Excel Chart Object can be advantageous and it is straightforward if the WORD file and the associated CDX files are in the same file system. However, in collaborations that involve several people working on several computer systems, there are advantages to using alternatives. As a general rule, we want to paste schemes and graphs as “Picture (Enhanced Metafile)”. Even if the assignment only requests the submission of embedded figures, keep the associated XLSX files because you might be asked for their submission during review.