

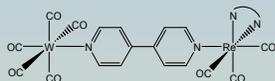
# Electrochemical Investigations of $W(CO)_5(L)$ and $W(CO)_4(L)_2$ Complexes: Reaction Pathways of Electrogenerated $[W(CO)_5(L)]^+$ and $[W(CO)_4(L)_2]^+$ Radical Cations (L = pyridine or substituted derivatives)

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## Introduction.

The goal of this work was to evaluate the viability of the  $W(CO)_5$  moiety toward the synthesis of redox active multinuclear transition metal complexes, such as that shown below. Ideally, a highly luminescent moiety, such as  $Re(CO)_3(LL)$ , where LL = a polypyridyl ligand such as 2,2'-bipyridine (bpy), 1,10-phenanthroline or related ligands, would be bridged to a non-emissive second metal center,  $W(CO)_5$  in this example, that undergoes reversible redox processes. Such compounds could potentially have "redox-tunable" luminescent properties making them promising candidates for sensing and other applications.<sup>1</sup>



Complexes such as that shown above, in which the bridging ligand is 4,4'-bpy, will show redox-tunable properties only if the non-emissive fragment can undergo one or more chemically reversible electron-transfer processes. We therefore undertook a systematic study of the oxidative electrochemistry of  $W(CO)_5L$ , where L is a pyridine or similar ligand, to develop a better understanding of the stability of the electrogenerated species than is available in the literature.

## Electrochemistry of $W(CO)_5(py)$ .

$W(CO)_5(py)$  undergoes a quasi-reversible metal-centered one-electron oxidation in  $CH_2Cl_2/TBAH$ , a relatively non-coordinating solvent, to yield the corresponding radical cation,  $[W(CO)_5(py)]^+$ . Figure 1a shows the cyclic voltammogram obtained at 250 mV/s. The return reduction is discernable ( $i_p/i_a = 0.43$ ;  $E_{1/2} = 1,176$  mV vs. Ag/AgCl) and increases at higher scan rates ( $i_p/i_a = 0.67$  at 1000 mV/s). There is also a second coupled reduction peak observable at slightly lower potentials (988 mV) that we attribute to a short-lived decomposition product. The radical cation is highly susceptible to attack by coordinating ligands, as Figures 1b-1e illustrate. These show the cyclic voltammograms obtained when the radical cation is generated in the presence of free pyridine. Three trends are observed as the level of pyridine is increased:

- The current of the two coupled reductions decrease.
- The bulk oxidation peak potential shifts to lower potentials
- A reversible redox couple assigned to  $[W(CO)_4(py)_2]^{2+}$  emerges (see Figure 2).<sup>2</sup>

The results shown in Figure 1 indicate that the seventeen electron radical cation undergoes a rapid ligand exchange in which a carbon monoxide is replaced by a pyridine. In addition, the shift in the oxidation peak potential (over 120 mV) upon addition of pyridine is strong evidence that the ligand exchange is preceded by an equilibrium between the radical cation and the free pyridine with a nineteen electron intermediate (Scheme 1). Loss of CO from the intermediate leads to the observed substitution product.<sup>3</sup>

In addition to the ligand exchange reaction,  $[W(CO)_5(py)]^+$  also undergoes an apparent

disproportionation in the presence of low levels of pyridine. Specifically, under such conditions the rapid ligand substitution depletes the available pyridine, allowing  $[W(CO)_5(py)]^+$  to persist long enough to oxidize  $[W(CO)_5(py)]^+$ , forming the parent pentacarbonyl and a tungsten (II) tetracarbonyl; the latter species would be expected to coordinate with additional ligand to form an eighteen-electron complex.<sup>4</sup>

## Electrochemistry of $cis-W(CO)_4(py)_2$ .

The oxidation of  $cis-W(CO)_4(py)_2$ , shown in Figure 2, is characterized by markedly enhanced chemical reversibility ( $E_{1/2} = 562$  mV,  $i_p/i_a = 0.94$  at 250 mV/s) compared to the pentacarbonyl analog. In addition, the corresponding radical cation,  $[W(CO)_4(py)_2]^+$  is much less prone to attack by coordinating ligands as is indicated by the reversibility of the redox couple in the presence of excess pyridine (Figure 2, top trace). The enhanced stability of the bis-pyridine complex is likely due to the increased electron density of the metal center. Nevertheless, the resistance  $cis-W(CO)_4(py)_2^+$  toward attack by nucleophiles is surprising, however, based on the susceptibility of the structurally similar  $[W(CO)_4(bpy)]^+$ . Figure 3 presents a side-by-side comparison of the cyclic voltammetry response of  $cis-W(CO)_4(py)_2$  and  $W(CO)_4(bpy)$  in the presence of various levels of pyridine. Both complexes show quasi-reversible oxidations in non-coordinating solvents (for the bpy complex,  $E_{1/2} = 673$  mV,  $i_p/i_a = 0.78$  at 250 mV/s), but oxidation of the bipyridine derivative becomes virtually irreversible in the presence of sub-equivalent levels of pyridine. The bis-pyridine complex, however, shows reversible behavior in the presence of 10 equivalents of pyridine ( $i_p/i_a = 0.87$ ). The basis for the unusual stability of the bis-pyridine compound is unclear; we speculate that it is related to the difference in geometry between the planar bidentate bipyridine ligand and the twisted geometry adopted by two separate pyridine rings.<sup>5</sup> The planar geometry may cause a labilization of the axial carbon monoxide ligands, which are trans to each other upon oxidation; the twisted pyridine rings of the bis complex may allow for greater delocalization of the positive charge and, as a result, decrease the affinity of the radical cation toward coordinating ligands.

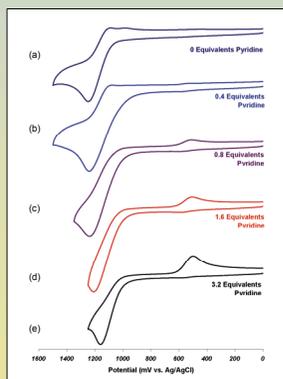


Figure 1: Cyclic Voltammogram of  $W(CO)_5(py)$  in  $CH_2Cl_2/TBAH$  in the presence of various levels pyridine; scan rates are 250 mV/s.

Figure 2: Cyclic Voltammogram of  $W(CO)_4(py)_2$  in  $CH_2Cl_2/TBAH$  in the presence of 10 equivalents pyridine (blue trace) and  $W(CO)_4(py)_2$  (red trace); scan rates are 250 mV/s.

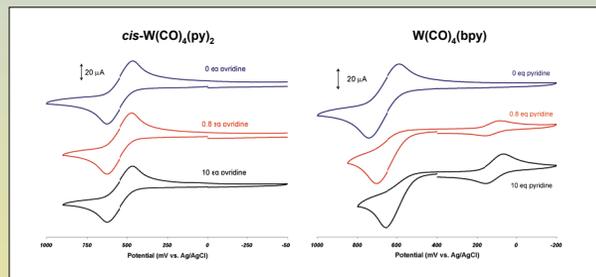
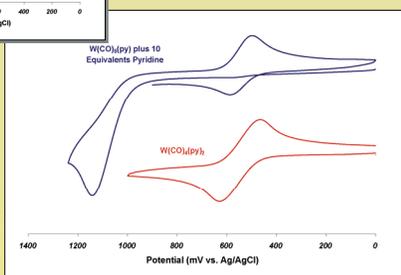


Figure 3: Cyclic voltammogram of  $cis-W(CO)_4(py)_2$  and  $W(CO)_4(bpy)$  in  $CH_2Cl_2/TBAH$  in the presence of pyridine; scan rates are 250 mV/s.

Given the exceptional stability of the bis pyridine radical cation, we synthesized other bis pyridyl complexes using picoline (4-methylpyridine) and 3,5-lutidine (lut, 3,5-dimethylpyridine) and have begun to spectroscopically characterize the corresponding cations using infrared spectroelectrochemistry. Bulk oxidation of the bis 3,5-lutidine complex yielded the spectral changes shown in Figure 4. Here, peaks due to  $[W(CO)_4(lut)_2]^{2+}$  are seen to grow in isospectrally as those of the parent complex fall. The peak positions are consistent with those expected for a tungsten (I) carbonyl species and the broadening of the lower frequency peaks is similar to that seen in the chromium and molybdenum complexes,  $[M(CO)_4(LL)]^+$ .<sup>4,6</sup>

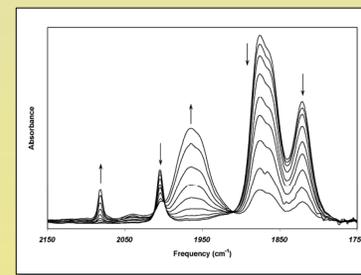
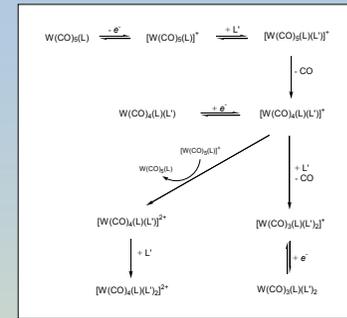
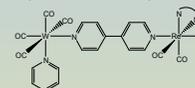


Figure 4: Infrared spectral changes observed upon oxidation of  $cis-W(CO)_4(lut)_2$  in  $CH_2Cl_2/TBAH$ . The set of peaks growing during the electrolysis correspond to  $[W(CO)_4(lut)_2]^{2+}$  (lut = 3,5-lutidine, or 3,5-dimethylpyridine)

At higher concentrations of added pyridine, the bis-pyridine complexes begin to undergo measurable ligand exchange, resulting in formation of the corresponding tris complexes.

## Conclusions and Future Work.

The reactions undergone by the electrogenerated complexes,  $[W(CO)_5(py)]^+$  and  $[W(CO)_4(py)_2]^+$  are summarized in Scheme 1, at right. The exceptional stability of  $[W(CO)_4(L)_2]^+$  radical cations, combined with the relatively accessible oxidation potentials of the parent complexes, make these compounds attractive candidates for the design of the redox-tunable complexes described in the introduction. One possible class of compounds, shown below,



Scheme 1: Electrochemical oxidation of  $W(CO)_5L$  and  $W(CO)_4(L)_2$  and coupled chemical reactions.

bridges the luminescent rhenium tricarbonyl moiety to a tungsten tetracarbonyl pyridine fragment with 4,4'-bipyridine. The tungsten complex in such a compound is structurally very similar to the  $W(CO)_4(L)_2$  species examined in this study and would be expected to have similar redox properties. Another possibility would be to use  $W(CO)_4(4,4'-bpy)_2$  to bridge two rhenium fragments forming  $[(Re(CO)_3(4,4'-bpy))_2(\mu-W(CO)_4)]^{2+}$ . We will be pursuing the syntheses of such compounds and examining their electrochemical, spectroscopic, and luminescent properties in the near future.

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## References.

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