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Electrochemical Oxidation of $W(CO)_4(LL)$: Generation, Characterization and Reactivity of $[W(CO)_4(LL)]^+$; (LL = α-diimine ligands)

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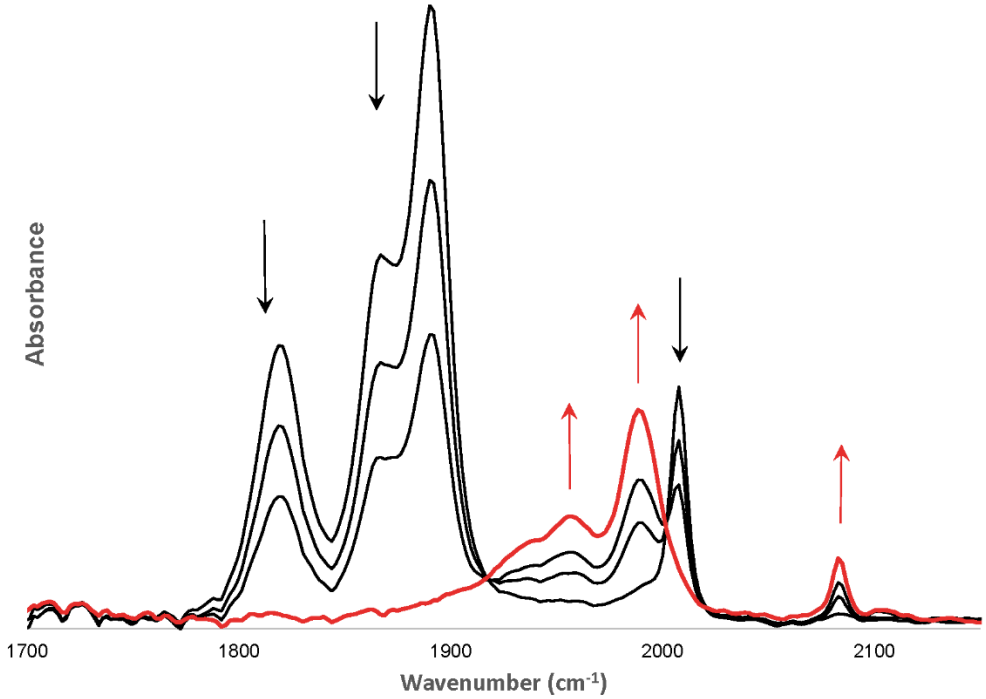

Figure SI-1: Changes in infrared spectra of the carbonyl region during room temperature thin-layer bulk electrolysis of $W(CO)_4$(bcp), **1g**; arrows indicate the direction of change for the peaks heights. Black traces are experimental data collected while isosbestic behavior was followed; the red trace is the infrared spectrum of 1g+ as calculated from the spectral changes observed before isosbestic behavior was lost.

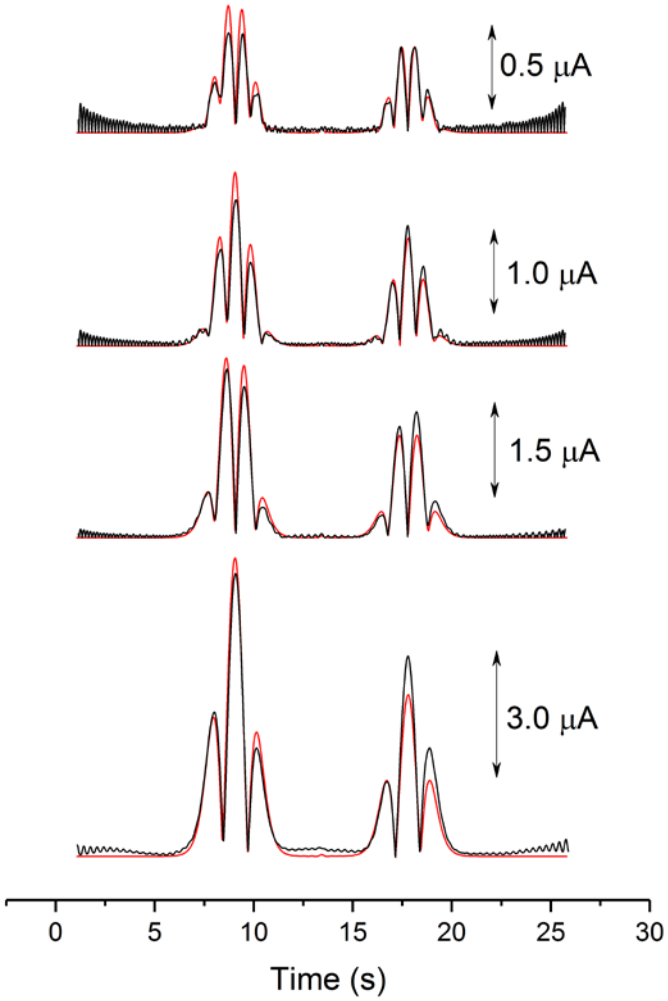

Figure SI-2. Optimized fit of ac voltammetric response for the oxidation of 1a coupled to simultaneous disproportionation and first-order decarbonylation. Third (bottom row) through sixth (top row) harmonics of large amplitude ac voltammetry results of 0.28 mM **1a** (black traces); red traces show optimized fits. The switching time in each experiment was 13.4 s; peaks observed at earlier times correspond to those occurring during the anodic sweep, those at longer time are from the cathodic sweep. Experimental parameters are: scan rate = 0.0894 V s^{-1}, electrode area = 0.071 cm^2, ac amplitude, ΔE = 0.1 V, frequency = 13.49 Hz. Simulation parameters: diffusion coefficient = 1.2×10^{-5} cm^2 s^{-1}, k° = 0.25 cm s^{-1}, and the homogeneous rate constants (see Scheme 1) k_{disp} = 400 M^{-1} s^{-1}, $k_{first\ order}$ = 0.2 s^{-1}, uncompensated resistance = 210 Ω. We attribute the deviations from the observed data to be a result of the exclusion of any equilibrium reactions involving electrogenerated **1a**$^+$.

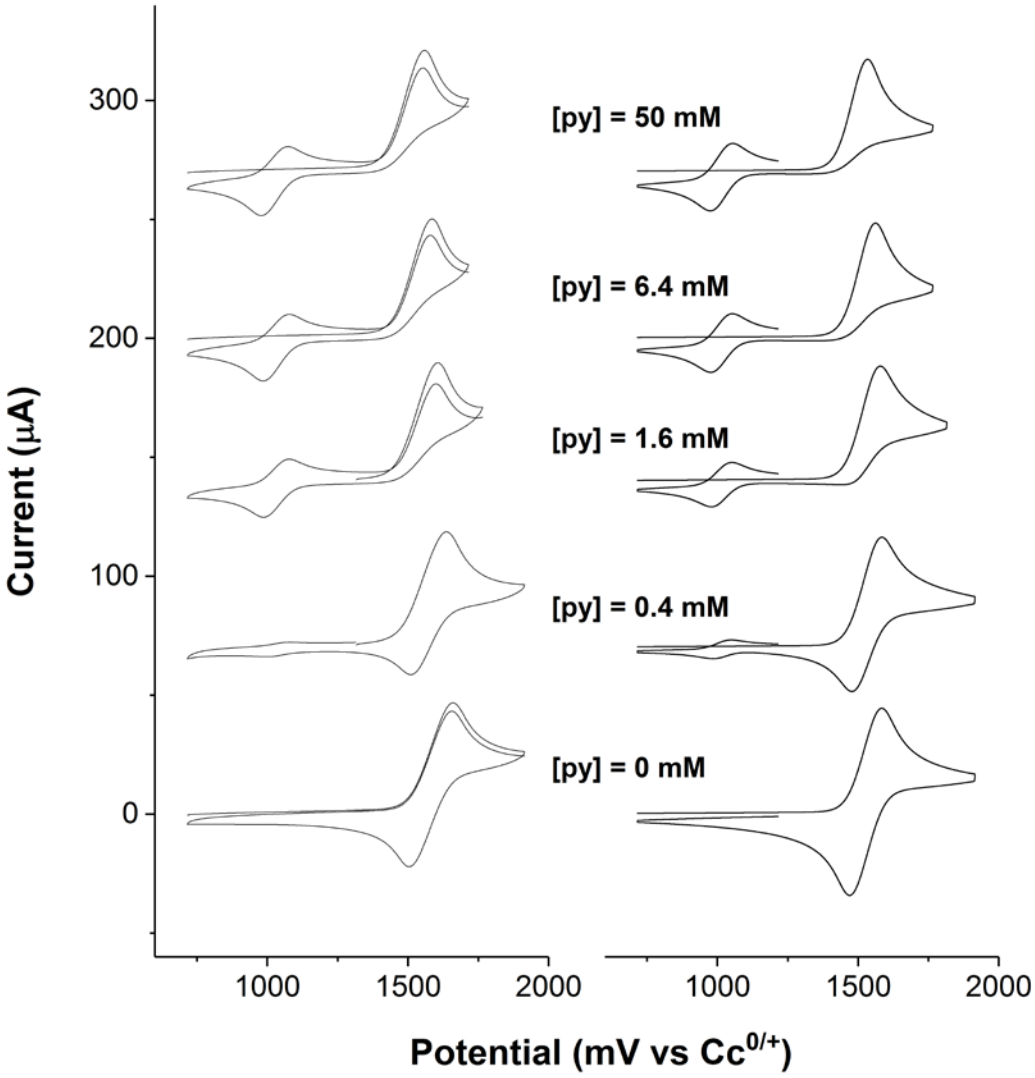

Figure SI-3. Left: Cyclic voltammograms of 1.4 mM **1b** at 0.25 V s^{-1} in the presence of pyridine at the concentrations indicated. Right: Simulations of the voltammograms obtained using the mechanism shown in Scheme 1 with the following rate constants: $k_1 = 2 \times 10^4$ M^{-1} s^{-1}, $k_{-1} = 1 \times 10^5$ M^{-1} s^{-1}, $k_2 = 0.10$ s^{-1}, $k_3 = 0.20$ s^{-1}, $k_4 = 5 \times 10^3$ M^{-1} s^{-1}, $k_{-4} = 0.1$ s^{-1}, $k_5 = 0.35$ s^{-}, $k_6 = 3 \times 10^3$ M^{-1} s^{-1}. Potentials are in mV relative to $Cc^{0/+}$.

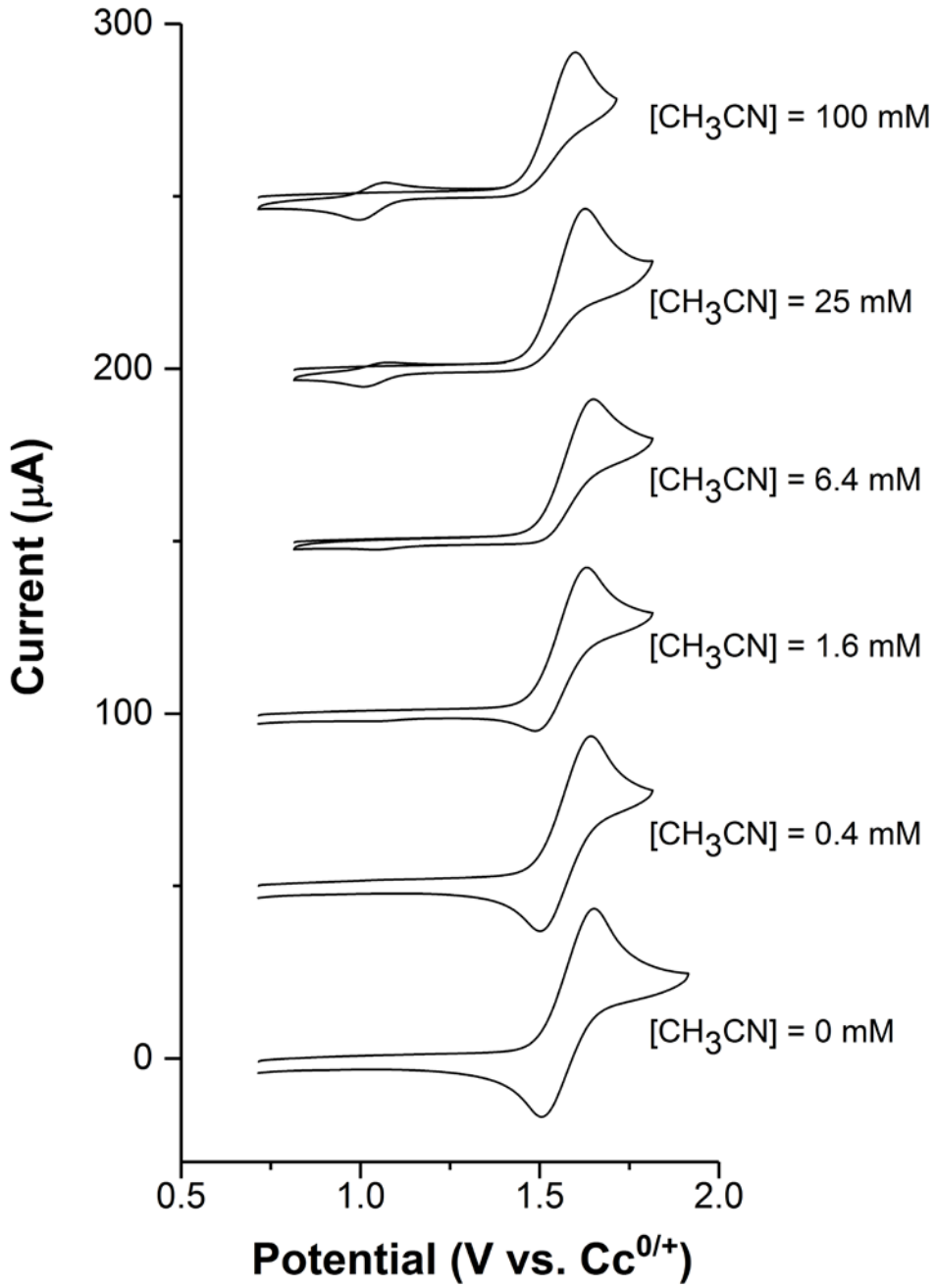

Figure SI-4. Cyclic voltammograms of 1.4 mM **1b** at 0.25 V s^{-1} in the presence of acetonitrile at the concentrations indicated. Potentials are in mV relative to $Cc^{0/+}$.