

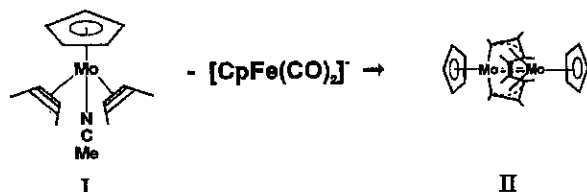


CAPSULES

notes and applications from Bioanalytical Systems, Inc.

Investigation of the Metal-Initiated Oligomerization of Alkynes**Purpose**

Reaction of $[\text{CpMo}(\text{C}_2\text{Me}_2)_2(\text{NCMe})]^+$ (I) with $[\text{CpFe}(\text{CO})_2]^+$ gives a product in which the alkyne ligands have been linked to form a dimeric complex with a longer hydrocarbon chain (II) (F1) (1). Since this transformation can also be achieved using reducing agents such as Na/Hg amalgam, it was proposed that the first step involves the reduction of I to give a 19⁻ electron radical. This proposal can be tested by electrochemical methods.

**Figure 1.** Conversion of I to II.**Reference**

Confirmation of a Radical Mechanism in the Alkyne-Linkage Reduction Reaction of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{C}_2\text{Me}_2)_2(\text{NCMe})]^+$ Cation, D. Pufahl, W. E. Geiger and N. G. Connelly, *Organometallics* 8 (1989) 412 - 415.

Method

The proposed mechanism involves a reduction followed by a chemical reaction (an irreversible EC process). Cyclic voltammetry is the method of choice, since the reduction can occur on the forward scan, and the reactivity of the radical can be examined on the reverse and subsequent scans.

Results

One characteristic of the cyclic voltammogram of an EC reduction is a decrease in the peak current ratio (i_{pa}/i_{pc}), since the chemical reaction decreases the number of reduced species that can be oxidized during the associated oxidation process. When the chemical reaction is fast, the oxidation peak may be absent, and this was found for the reduction of I at 25 °C using a scan rate of 0.3 V/s. Reversibility can often be restored by eliminating the effect of the chemical reaction, by either increasing the scan rate (which decreases the time available for the reaction) or lowering the

temperature (which lowers the reaction rate). However, the reduction of I remains irreversible even using a scan rate of several volts/second at 253 K, which shows that the reaction of the reduced species is very rapid. Since the products of the chemical reaction may also be electroactive, their redox processes may be identified on the reverse and subsequent scans. F2 shows part of the positive (reverse) scan and the second negative scan of I, from which the products of the chemical reaction can be identified by comparison with cyclic voltammograms of known compounds. Peaks O_2 and O_3 are due to the oxidation of II, and peak O_1 is due to the oxidation of another dimeric complex $[\text{CpMo}(\text{C}_2\text{Me}_2)_2]_2$ (III) (F3). The products suggest that the reduction is followed by rapid dissociation of MeCN to give the 17-electron complex $[\text{CpMo}(\text{C}_2\text{Me}_2)]^+$, which dimerizes to give either II or III.

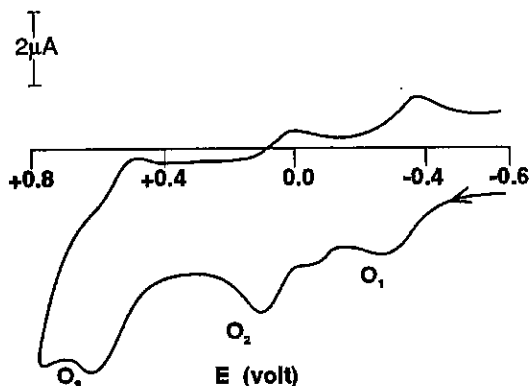
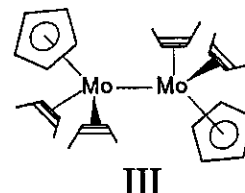


Figure 2. Cyclic voltammogram of I in THF (0.5 mM), showing the redox processes of the products of the chemical reaction. Scan rate = 0.3 V/s, temperature = 27 °C, supporting electrolyte 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$. All potentials measured with reference to the SCE. Figure adapted from Reference.

**Figure 3.** Structure of III.

Although it is apparent that the irreversibility of the reduction of I is due to a following chemical reaction, very slow charge transfer kinetics can also produce a cyclic voltammogram which shows only one peak (i.e., the reverse electron transfer is very slow). These two cases can be distinguished by two methods:

a) Peak width - For a reversible one-electron reduction, the difference between the cathodic peak potential (E_{pc}) and the half peak current potential ($E_{pc/2}$) is 57 mV (2). For reduction that is irreversible due to very slow electron transfer, this difference is $48/\alpha$ mV (2). α is the charge transfer coefficient, and is often about 0.5 (i.e., the peak for this latter case is much broader).

b) Variation of E_{pc} with scan rate (ν) - When a reduction is followed by a chemical reaction, the equilibrium between the surface concentrations of the oxidized and reduced species is disturbed, and E_{pc} is shifted to more positive values. Increasing the scan rate decreases the effect of the chemical reaction, so the potential shifts to more negative values, ca. 30 mV per tenfold increase in ν (3). A decrease in the rate of electron transfer also produces a negative shift in E_{pc} , since a more negative potential is required to activate the charge transfer. However, in this case, the shift per tenfold increase in ν is $30/\alpha$ mV (3).

In this study, the value of ($E_{pc} - E_{pc/2}$) was 58 mV, and a plot of E_{pc} vs. $\log \nu$ gave a straight line plot with a slope of -32 mV. These data are consistent with a rapid electron transfer followed by a rapid chemical reaction.

One potential problem with these methods is that peak broadening and shifts in peak potentials can be caused by uncompensated solution resistance. However, the effect of solution resistance can be estimated by performing the above measurements on a system which has a known reversible redox process.

Additional References

- 1) M. Green, N. C. Norman, A. G. Open and C. J. Schaverien, *J. Chem. Soc., Dalton Trans.* (1984) 2455 - 2461.
- 2) A. J. Bard and L. R. Faulkner, *Electrochemical Methods*; Wiley, New York, 1980; Chap. 6.
- 3) R. S. Nicholson and I. Shain, *Anal. Chem.* 36 (1964) 706 - 721.

