CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

## *Cis-Trans Isomerization of* $Ru(MeOCS_2)_2(PPh_3)_2$

### Purpose

There are two possible isomers for $Ru(MeOCS_2)_2(PPh_3)_2$, *cis* and *trans* (F1). For many mononuclear complexes, it is well known that different isomers are favored by different oxidation states (1), and that electron transfer is often followed by isomerization. The aim of this study was to investigate the effect of any isomerization on the electrochemical behavior.

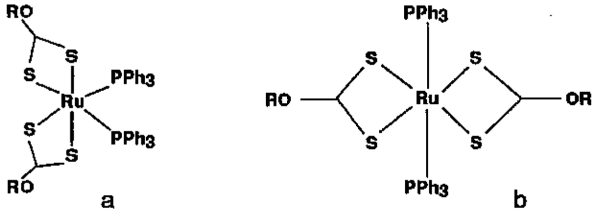

***Figure 1.*** *Cis* (a) and *trans* (b) isomers of $Ru(MeOCS_2)_2(PPh_3)_2$.

### Reference

Ruthenium in Isomeric $S_4P_2$ Coordination: Metal Redox and Geometrical Reorganisation, N. Bag, G. K. Lahiri and A. Chakravorty, J. Chem. Soc., Dalton Trans. (1990) 1557 - 1561.

### Method

Cyclic voltammetry is a powerful method for the qualitative investigation of chemical reactions (e.g. isomerization) that follow electron transfer (EC processes), as the reactive intermediate can be generated on the forward scan, and its fate can be monitored on the reverse and subsequent scans by looking for the redox processes of the products of the chemical reaction.

### Results

F2 shows the cyclic voltammograms of *cis* isomer at different temperatures. At room temperature, there are only two waves; the oxidation of the *cis* complex (A1) and reduction of the *trans*$^+$ complex (C2). Under these conditions the *cis*$^+$ complex rapidly isomerizes to the *trans*$^+$ isomer. The absence of the wave for the oxidation of the *trans* isomer indicates that it rapidly converts back to the *cis* configuration. Lowering the temperature slows this conversion, so the oxidation of the *trans* isomer (A2) appears. This shows that the isomerization is subsequent to the electron transfer (rather than concerted with it), since the *trans* to *cis* isomerization is inhibited, but the electron transfer still occurs. However, the rate of the isomerization of the *cis*$^+$ isomer to the *trans*$^+$ isomer is so fast that lowering the temperature has no effect.

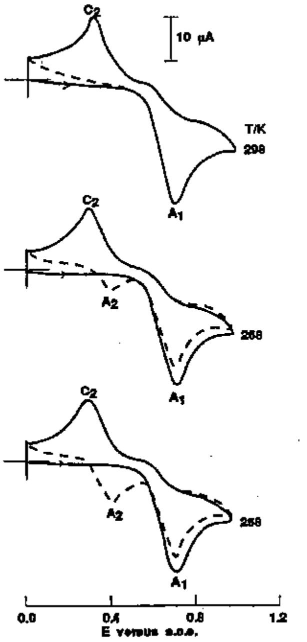

***Figure 2.*** Cyclic voltammograms of the *cis* isomer at different temperatures. Potentials were measured with reference to S.C.E.

The *trans*$^+$ complex was synthesized by controlled potential electrolysis, and its cyclic voltammograms are shown in F3. These confirm that the *trans* complex isomerizes to the *cis* complex as the temperature is increased. This is an example of a *chemically reversible* redox process, since the chemical reaction (i.e. isomerization) that accompanies the oxidation can be reversed by reduction of the product of the chemical reaction.

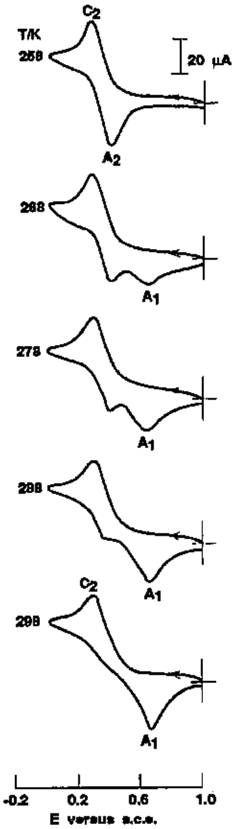

***Figure 3.*** Cyclic voltammograms of the coulometrically produced *trans*$^+$ isomer at different temperatures.

## Additional Reference

*1) W. E. Geiger, Prog. Inorg Chem. 33 (1985) 275 - 351.*