CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Electrochemical Conversion of $[FeIr_5(CO)_{16}]^-$ to $[FeIr_5(CO)_{15}]^{3-}$

Purpose

$[FeIr_5(CO)_{15}]^{3-}$ (I) readily reacts with excess acid at room temperature to give $[FeIr_5(CO)_{16}]^-$ (II). Both these clusters are based an octahedral metal geometry (F1), and both have the required number of valence electrons (86) (1). Since CO dissociation is often observed following cluster reduction (2), it may be possible to convert II to I by electrochemical reduction.

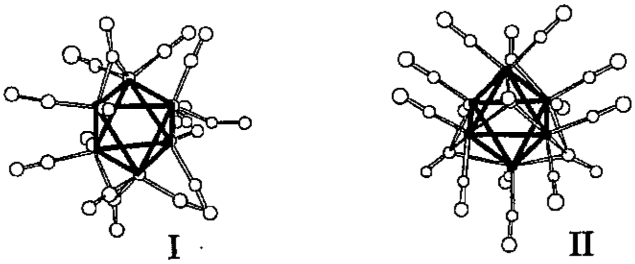

Figure 1. Molecular Structures of $[FeIr_5(CO)_{15}]^{3-}$ (I) and $[FeIr_5(CO)_{16}]^-$ (II).

Reference

Iron-Iridium Mixed-Metal Carbonyl Clusters. 3. Synthesis, Chemical Characterization, Electrochemical Behavior, and Solid-State Structures of $[NEt_4]_3[FeIr_5(CO)_{15}]$, $[NMe_3(CH_2Ph)]_2[HFeIr_5(CO)_{15}]$ and $[NMe_3(CH_2Ph)][FeIr_5(CO)_{16}]$. Spectroscopic and Chemical Evidence for the Existence of $[HFe_3Ir(CO)_{12}]^{2-}$, $[H_2Fe_3Ir(CO)_{12}]^-$ and $[H_2FeIr_5(CO)_{15}]^-$, A. Ceriotti, R. D. Pergola, L. Garlaschelli, F. Laschi, M. Manassero, N. Masciocchi, M. Sansoni and P. Zanello, Inorg. Chem. 30 (1991) 3349-3357.

Method

The postulated interconversion requires a chemical reaction to follow electron transfer. The easiest way of looking for such a reaction is to use cyclic voltammetry, since the reactive dianion can be generated on the forward scan, and the product of the chemical reaction can be detected on the reverse and subsequent scans.

Results

The cyclic voltammograms of I are shown in F2. The first oxidation (A) is reversible at scan rates greater than 100 mV/s. Controlled potential coulometry at this potential showed n=1. The second oxidation (B) is irreversible. The chemical reactions following both oxidations involve cluster decomposition.

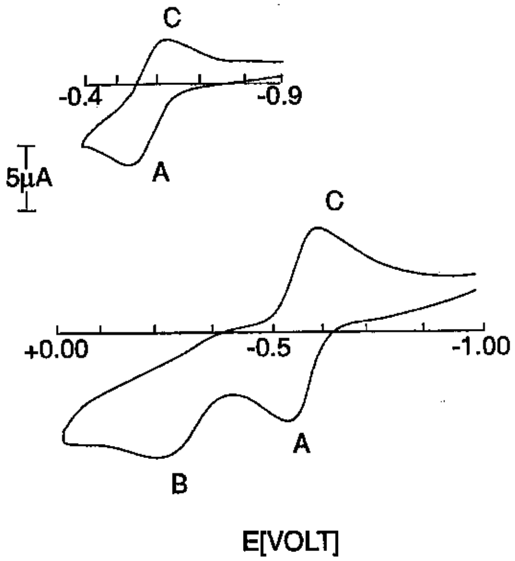

Figure 2. Cyclic voltammograms of $[FeIr_5(CO)_{15}]^{3-}$ (I). All potentials were measured with reference to Ag/AgCl.

In contrast, the cyclic voltammograms of II show an irreversible reduction (D), which leads to the formation of I (F3) (observable on the reverse scan and the second scan). Coulometry at D showed n=1.5. This is consistent with a two electron reduction to give an unstable product, which is oxidized at E. This product was thought to be $[FeIr_5(CO)_{16}]^{3-}$, which is apparently unstable and loses a carbonyl ligand to produce I. Increasing the scan rate from 200 to 1000 mV/s causes an increase in the peak current of E relative to the other peaks currents (F3), which is consistent with its assignment to the oxidation of an unstable intermediate.

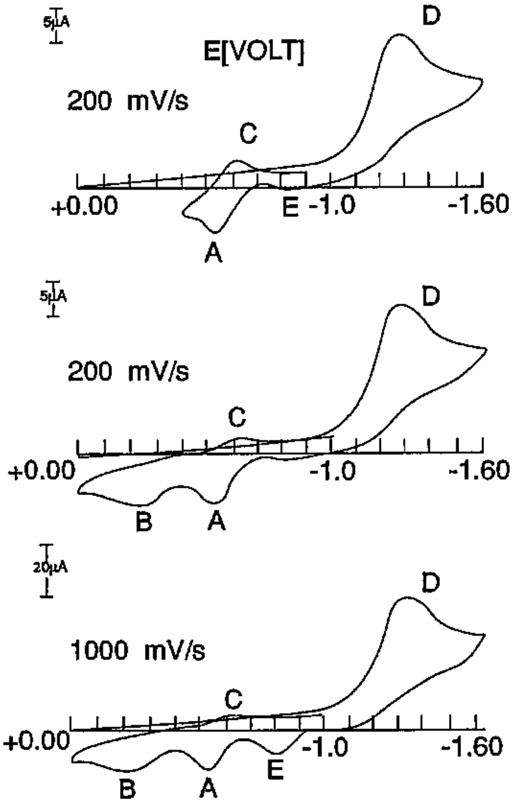

Figure 3. Cyclic voltammograms of $[FeIr_5(CO)_{16}]^-$ (II).

Discussion

It is interesting to speculate on the structure of the unstable trianionic intermediate. Although the reduction apparently involves two electrons, it is important to realize that it in fact consists of two sequential one electron transfers, the second reduction being more favorable than the first. Therefore, there must be some structural change that is concerted with or sequential to the first reduction, since electron-electron repulsion would otherwise make the second reduction more difficult than the first. Generally, there are two possibilities for such a structural change in a carbonyl cluster: a) dissociation of a carbonyl ligand b) rearrangement of the metal geometry to a geometry that is suitable for two additional electrons. Both rearrangements have been reported for hexanuclear carbonyl clusters (1,2), and would produce electron deficient complexes which would be readily reduced at the potential of the first reduction (this fulfils the condition for an apparent two electron reduction). However, the first possibility can be discounted, since the product of the second reduction would be $[FeIr_5(CO)_{15}]^{3-}$, whereas the data require an unstable intermediate which converts to this trianion. Therefore, the second possibility appears to be more likely, particularly as there does not appear to be a stable geometry for hexanuclear carbonyl clusters with 88 valence electrons (1). In addition, the activation energy for the second process is probably lower than for the first process i.e. the product with the different metal geometry is the kinetic product, whereas the product of ligand dissociation is the thermodynamic product.

Additional References

1) B. Tulyathan and W. E. Geiger, J. Am. Chem. Soc. 107 (1985) 5960-5967.

2) S. R. Drake, B. F. G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans. (1989) 243-248.