

## Electron Transfer Reactions of Polynuclear Species

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Literature Seminar

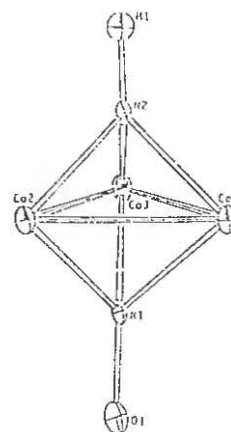
November 10, 1988

Organometallic reactions are almost exclusively viewed in terms of two-electron processes involving 16 or 18 valence electron intermediates. This viewpoint has been increasingly challenged over the last decade as examples of radical ions, transient radicals, and electron transfer catalyzed (ETC) reactions have appeared [1,2]. Radical chain processes are easily inhibited (i.e., by self decomposition or reaction with a contaminant such as  $O_2$ ), and it is possible that some two-electron processes are actually inhibited reactions of radical chain processes [3].

The first investigations of one electron processes involved the electrochemical oxidation or reduction of mononuclear complexes. Later work explored chemical reactions catalyzed either electrochemically or by electron-transfer reagents. Unfortunately, electrochemical studies of metal cluster compounds have lagged behind those of mononuclear species. Although some cluster species readily undergo reversible redox processes, most notably a series of Fe-S clusters and ruthenium clusters [4], addition or subtraction of one or more electrons usually leads to structural changes resulting in increased reactivity or structural fragmentation.

Early investigations of the electrochemistry of metal clusters compared the redox properties of series of related clusters such as trinuclear nickel or cobalt clusters [5]. Stable radical species were isolated and their crystal structures were determined. From structural changes occurring upon reduction or oxidation, it was determined that the highest occupied molecular orbital (HOMO) is usually a metal-metal  $\sigma$ -bonding MO, and the lowest unoccupied molecular orbital (LUMO) is a metal-metal anti-bonding orbital [1,2]. Figure 1 below shows structural changes that occur upon reduction of the  $48e^-$  species  $Co_3(\eta^5-C_5H_4Me)_3(\mu_2-NO)(\mu_3-NH)$  to the  $49e^-$  monoanion [5]. Recent EPR studies of  $[Fe_4(CO)_{12}CC(O)R]^{2-}$ ,  $R = CH_3$ ,  $CH_2C_6H_5$  have confirmed this assignment by showing that the odd electron is localized on the iron core [6].

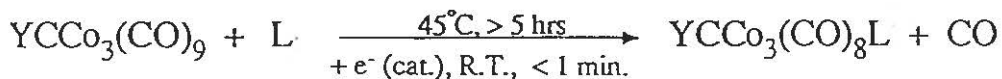
	$48e^-$	$49e^-$
Co-Co' (Å)	2.391	2.426
	2.399	2.414
	2.428	2.554
mean Co-Co' (Å)	2.406	2.465



Interconversion of structural units has been shown to occur upon reduction of some metal clusters.  $Os_6(CC)_{18}$  undergoes two one-electron reductions to the

corresponding dianion  $[\text{Os}_6(\text{CO})_{18}]^{2-}$ . The neutral species has a bicapped tetrahedral structure while the dianion has an octahedral structure, and this interconversion is consistent with the structural change predicted by the polyhedral skeletal electron-pair (PSEP) theory. Other examples of such reactions exist in the literature [2,7]. Isomerization of metal clusters has been shown to occur through electron transfer catalysis. The  $\text{Cp}_3\text{Rh}_3(\text{CO})_3$  cluster isomerizes from the  $\text{C}_5\text{-Cp}_3\text{Rh}_3(\mu_2\text{-CO})_2(\text{CO})$  isomer to the  $\text{C}_{3v}\text{-Cp}_3\text{Rh}(\mu_2\text{-CO})_3$  isomer through oxidative electron transfer catalysis at a rate more than  $10^6$  faster than the thermal isomerization [8].

The rates of nucleophilic substitutions of metal carbonyl clusters can sometimes be greatly accelerated electrochemically. Metal carbonyl clusters often require elevated temperatures for simple substitutions with donor ligands. These reaction conditions often result in a decrease in selectivity so that polysubstitution is common. The first example of an electron-induced nucleophilic substitution reaction was the selective replacement of one, two, or three CO groups in  $\text{YCCo}_3(\text{CO})_9$  ( $\text{Y} = \text{Ph}, \text{Cl}$ ) by either a phosphine or phosphite. Reaction times were lowered from several hours for the thermal reaction to less than a minute for the electrochemical reaction as shown in the Scheme below [9]. Several metal clusters have since been determined to undergo similar electron-induced substitution processes. The most favorable conditions for this reaction involve formation of a stable radical anion, the presence of a good leaving group such as CO, and the presence of a chelating ligand in order to stabilize the metal core [2b]. A recent reaction involving  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-PPh})_2$  was discovered to involve the scission of an Fe-P bond to give a stable  $17e^-$  coordinatively unsaturated intermediate [10].



Similar reactions are found for other  $\text{M}_3(\mu_3\text{-E})_x\text{L}_n$  ( $x=0,1,2$ )

$\text{M} = \text{Co}, \text{Fe}, \text{Ru}, \text{Os} \quad \text{E} = \text{Ph}, \text{CR}, \text{PR}, \text{S}, \text{Se}, \text{NMe}$ .

ETC reactions characteristic of mononuclear species [11] will probably be increasingly applied to metal cluster systems in the future. Odd-electron metal clusters may also serve as models of intermediates formed during electron transfer reactions on metal surfaces.

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