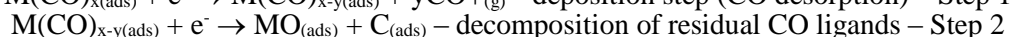
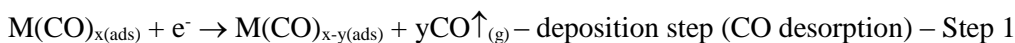


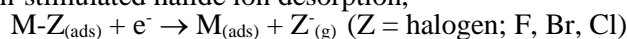
## Focused Electron Beam Induced Deposition of Nanostructures: Insights from Surface Science

Focused electron beam induced deposition (FEBID) is capable of creating a wide variety of size and shape selected metal-containing nanostructures using organometallic precursors. The need to develop organometallic precursors specifically for FEBID that can create deposits with higher metal contents than are currently possible with existing chemical vapor deposition (CVD) precursors has provided the motivation for surface science studies designed to better understand the elementary bond breaking processes that accompany FEBID.

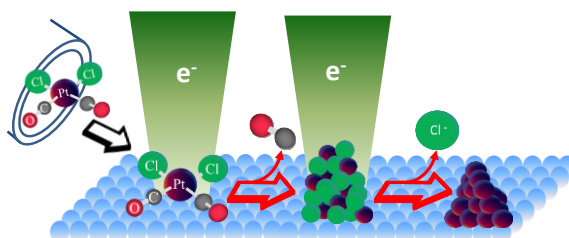
Results from these experiments have shown that the electron-stimulated reactions of organometallic precursors during the FEBID process can be broken down into two sequential steps. In the first step, the electron induced deposition of surface bound organometallic precursor's proceeds through **desorption** of one or more of the ligands present in the parent compound. In situations where different types of ligands are attached to the central metal atom, certain ligands (e.g. CO) are "preferred" leaving groups. Following the initial deposition step, however, subsequent electron-stimulated reactions of the remaining ligands typically lead to ligand **decomposition** and this is responsible for the organic contamination in FEBID nanostructures. For example, in the case of metal carbonyls:



One exception to the ligand decomposition process involves metal-halogen bonds which are susceptible to electron-stimulated halide ion desorption,

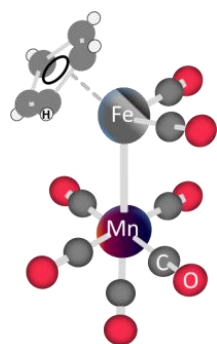


Thus, halogen atoms directly attached to the central metal atom in organometallic complexes can be scrubbed by electron processing. Based on this information we have evaluated the potential of  $Pt(CO)_2Cl_2$  to serve as FEBID precursor. Results from these studies have shown that CO groups are ejected during the initial deposition step and that halogen atoms can subsequently be removed by post-deposition electron beam processing. This provides a potential route to create pure Pt nanostructures using FEBID, as shown in Figure 1 and also supports the idea that understanding how different ligands and ligand architectures behave during FEBID can be used as the basis to design precursors specifically for FEBID applications.



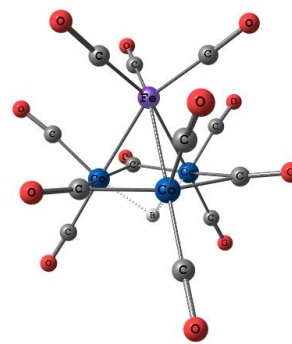
**Figure 1:** Electron stimulated deposition of Pt nanostructures from  $Pt(CO)_2Cl_2$

An emerging aspect of FEBID involves the use of bimetallic organometallic complexes to create



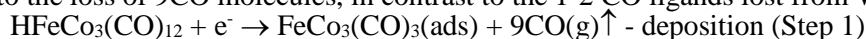
$CpFe(CO)_2Mn(CO)_5$

mixed metal nanostructures. I will present findings on the electron stimulated reactions of two bimetallic complexes,  $CpFe(CO)_2Mn(CO)_5$  and  $HFeCo_3(CO)_{12}$ . Several of the important mechanistic details observed for organometallics that contain a single metal atom (e.g.  $W(CO)_6$  and  $Pt(PF_3)_4$ ) are retained in bimetallic complexes, such as (i) the two-step sequential electron stimulated process of ligand desorption followed by ligand decomposition, (ii) the existence of ligands that are preferentially desorbed during the first ligand



$HFeCo_3(CO)_{12}$

desorption step (e.g. CO) and those that are retained and undergo decomposition (e.g. Cp). New findings include the observation that the fate of each metal atom appears to be determined by the nature of the surrounding ligands (i.e. electron stimulated reactions are localized). For example, in the case of  $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$ , extensive Mn oxidation is observed in the absence of any Fe oxidation even though the Fe-O and Mn-O bond energies are nearly identical. Perhaps more significantly, the reason for the greater metal content often observed for bimetallic precursors appears to be a consequence of both the large fraction of volatile ligands ejected in the first step, often combined with the relatively inefficient electron-stimulated decomposition of the residual ligands. For example, in the case of  $\text{HFeCo}_3(\text{CO})_{12}$  electron stimulated deposition leads on average to the loss of 9CO molecules, in contrast to the 1-2 CO ligands lost from  $\text{W}(\text{CO})_6$ , thus:



Moreover, the relative inefficiency of CO decomposition from the partially decarbonylated species formed in the deposition step provides an opportunity for thermal desorption process to contribute to the overall sequence of reactions, leading to a more efficient and complete loss of organic contaminants as the deposit is growing, thus:

