“Hydrogenation of two-electron mixed-valence iridium alkyl complexes”

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The presentation focuses on the two electron chemistry of hydrogen and how it is relevant to mixed valence di-iridium complexes. The paper investigates the complexes by first starting with a precursor ((tfepma)$_3$Ir$_2^{0,II}$Cl$_2$) and synthesizing (tfepma)$_3$Ir$_2^{0,II}$CH$_3$Br (2), (tfepma)$_3$Ir$_2^{0,II}$NpBr (3) (Np= neopentyl). Complexes 2 and 3 were investigated with respect to their reactivity with hydrogen and were also structurally characterized. Hydrogenation proceeds in a cascade reaction when complexes 2 and 3 were reacted with hydrogen to form an alkyl complex then upon a second hydrogen atom, the di-iridium trihydride complex (tfepma)$_3$Ir$_2^{I,III}$H$_3$Br (4) was formed. The mechanism of how hydrogen attacks the mixed valence di-iridium bond was examined. The mechanism is based on the notion that in the mixed valence bond the Ir$^0$ is an 18 electron complex and has a different geometry than the octahedral Ir$^{II}$ end which is a 16 electron complex. Hydrogen reactivity was calculated using nonlocal density-functional theory. The bonding was examined to produce a $\eta^2$ H$_2$ complex. The movement of the hydrogen atom was examined and found that it can move intact between the Ir-Ir bond.

References:

Veige, A, Gray, T and Daniel Nocera “Hydrogenation of Two-Electron Mixed-Valence Iridium Alkyl Complexes
