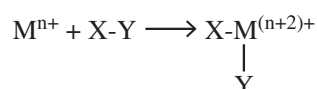


Oxidative Addition Reactions

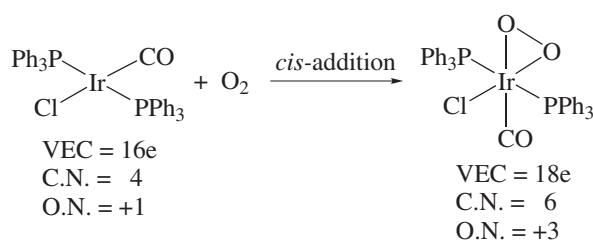
K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

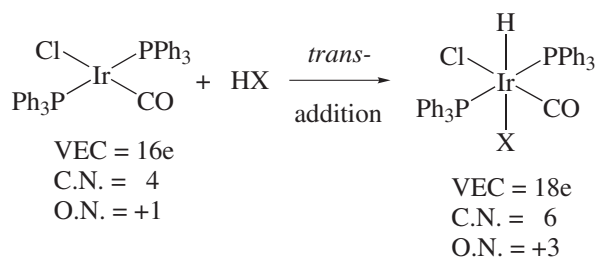
Coordinatively unsaturated metal centres (M^{n+}) (valence electron count, $VEC < 18$) may undergo oxidative addition reactions to form saturated metal complexes by cleaving the X-Y bond of a molecule (e.g. H_2 , O_2 , Br_2 , I_2 , Cl_2 , organic halides (RX), HX , RCO_2H , alkenes and alkynes with electron withdrawing groups).



During this process, VEC, oxidation number (O.N.) and coordination number (C.N.) may be increased by either one or two units. Generally, the oxidative addition of non-polar molecules such as H_2 , O_2 , halogens, alkenes and alkynes is *cis*.



But oxidative addition of polar molecules such as HX , MeI and $ArSO_2Cl$ to Vaska's complex *trans*- $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ is *trans*.



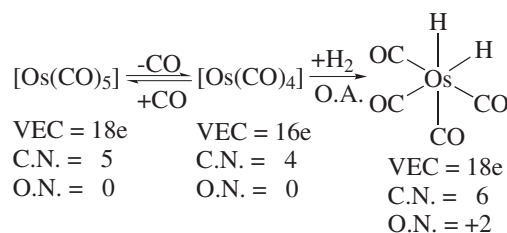
Let us consider the factors which influence the oxidative addition reactions.

- Oxidative addition is facile if the metal centre is coordinatively unsaturated.
- Oxidative addition is facile if the metal centre M^{n+} has an accessible oxidation state $M^{(n+1)+}$ or $M^{(n+2)+}$, e.g.

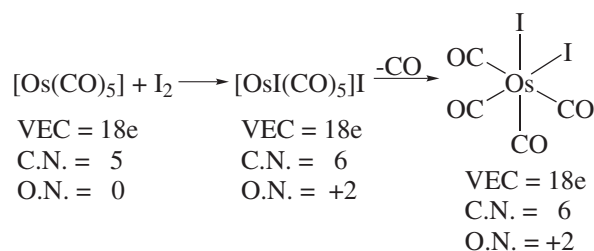


- The nature of other coordinated ligands also influences oxidative addition, for example, electron withdrawing ligands (e.g. $C \equiv O$) deactivate the metal centre whilst electron donors (e.g. PMe_3) increase the basicity of the metal centre, thus, promotes oxidative addition. Similarly, anionic complexes with more basic metal centres are more activated towards oxidative addition than neutral complexes.

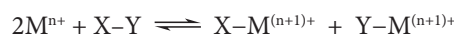
Some coordinatively saturated compounds can also undergo oxidative addition reactions by prior dissociation of a ligand. e.g. formation of *cis*- $[\text{OsH}_2(\text{CO})_4]$ by oxidative addition of H_2 to $[\text{Os}(\text{CO})_5]$ via the intermediate $[\text{Os}(\text{CO})_4]$.



In some cases, a coordinatively saturated metal centre can cleave a X-Y bond via a labile, salt-like intermediate as shown below.



1e-Oxidative addition reactions are also known, where two metal centres ($2M^{n+}$) are involved with one molecule (X-Y).



This type of reaction particularly occurs with 17e-complexes. e.g.



Problems

1. Draw the structure of the product formed due to oxidative addition reaction of H_2 to *trans*-[IrCl(CO)(PPh₃)₂].
2. What structural changes would you expect for a 2e-oxidative addition process of a d⁸ metal centre? Explain giving an example
3. The d¹⁰-complex [Pd(PPh₃)₄] undergoes 2e-oxidative addition reaction with Br₂ to give a four coordinate neutral complex **A**. Draw the possible structures of **A**.
4. [(η⁵-Cp)Ir(PMe₃)₂] (VEC=18e) undergoes oxidative addition with MeI to give a saturated salt **B**. Draw the structure of **B**.