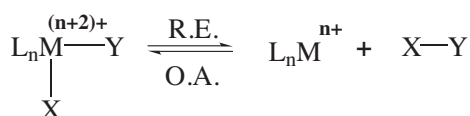


Reductive Elimination Reactions

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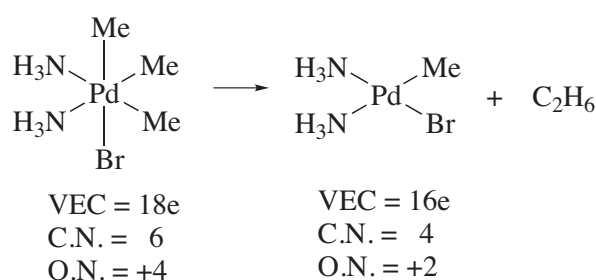
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Reductive elimination (R.E.) is the opposite or the reverse of oxidative addition (O.A.), in which X–Y oxidatively adds on to L_nM^{n+} to give $L_n(X)(Y)M^{(n+2)+}$.

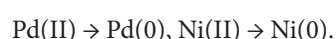
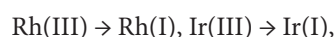


X and Y groups are combined to form X–Y, just before they are eliminated from the metal. Some reactions are reversible, e.g., addition and elimination of H_2 and O_2 . R.E. is the last step in catalytic cycles.

During this process, the oxidation number (O.N.), coordination number (C.N.) and valence electron count (VEC) of the metal get reduced by **two units** as shown below.



During this process, Pd(IV) is reduced to Pd(II), octahedral \rightarrow square-planar, and $d^6 \rightarrow d^8$. Some of the common conversions are given below: e.g.,



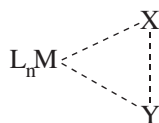
The groups that are easily combined (and then eliminated) include R–H, R–R' to give **alkanes**; $H-C(=O)R$ to give **aldehydes**; $R^2-C(=O)R$ to give

ketones; and $X-C(=O)R$ to give **acid halides**, etc.

The driving-force for these elimination processes could be the formation of stable organic molecules and/or metal complexes.

Importance of *cis* arrangement

The two groups (to be eliminated) must be in the ***cis* positions** before elimination can take place. Because, only the *cis* arrangement of ligands can form a **3 centred** transition state with the metal.



Creation of this **transition state** is crucial: as reductive elimination occurs *via* a **concerted** process, hence, all bond breaking and bond-forming occur simultaneously in a single step.

In square-planar complexes, **trans groups** must rearrange to *cis* positions before the elimination step to take place; e.g., *trans*-[PtH(CH₂CN)(PPh₃)₂] reductive eliminates MeCN, after **isomerising** it into the *cis*-isomer, *cis*-[PtH(CH₂CN)(PPh₃)₂].

Reductive elimination is facilitated:

- (i) when the positive charge on the metal centre is increased due to the formation of a cationic complex.
- (ii) when electron density (or π -basicity) of the metal centre is reduced by dissociating a good σ -donor ligand/s.

Sometimes, reductive elimination process is accelerated by prior coordination of another ligand/s; for example, in the presence of 2 equivalents of PPh₃, $[(\eta^5-C_5Me_5)ZrMe_2]$ eliminates an ethane molecule.

Problems

1. Suggest the metal complex and the organic product(s) formed from the following reactions.

(dppe = Ph₂PCH₂CH₂PPh₂)

 - (i) $[(\eta^5-C_5Me_5)ZrMe_2] + 2 PPh_3 \rightarrow$
 - (ii) $[(\eta^5-C_5Me_5)Zr(H)Me] + dppe \rightarrow$
 - (iii) *fac*-[PdI Me₃(dppe)] \rightarrow (heat)
 - (iv) *fac*-[RhI₃(COMe)(CO)₂]⁻ \rightarrow (heat)
 - (v) *trans*-[PtI₂(Ph)₂(PEt₃)₂] \rightarrow (heat)
2. [TiMe₄] decomposes above -50 °C, but [TiMe₄(Me₂PCH₂CH₂PMe₂)] is stable at room temperature. Explain.