Insertion and deinsertion reactions

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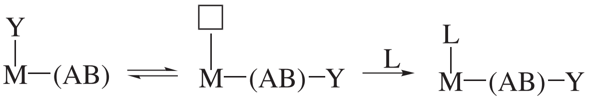
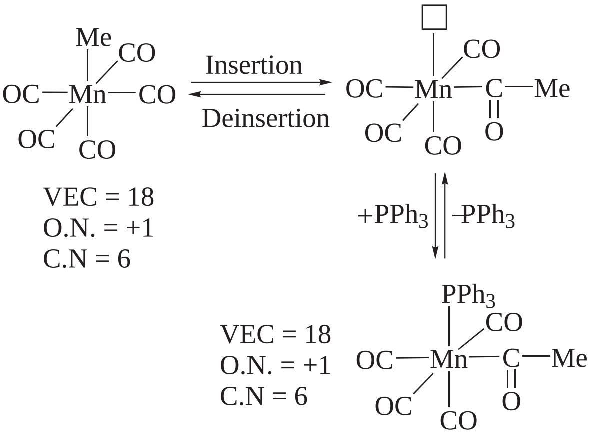
In an insertion reaction, Y gets transferred on to a ligand (AB). This can be considered as a **migration reaction** as shown below.



Hence, these types of reactions are also known as **migratory insertion reactions**. In almost all cases, Y is a **mono anionic ligand** while AB is a neutral ligand with a multiple bond between A and B. Often, the first step of the insertion or migration reaction can be reversible; coordination of a suitable incoming ligand (L) make the process irreversible. The reaction of $[MnMe(CO)_5]$ with 1 equiv. of PPh_3 gives cis-$[Mn(COMe)(PPh_3)(CO)_4]$.

Mechanism of this simple, two-step insertion reaction is as follows:

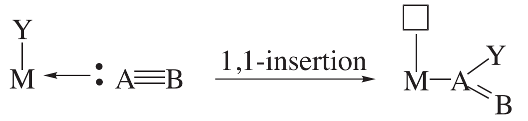


During this process, the oxidation number (O.N.), coordination number (C.N.), and VEC of the metal **remain unchanged.**

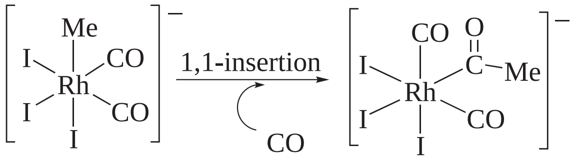
First, methyl group migrates on to CO ligand which is situated at ***cis* position** to form an acetyl group, and then PPh_3 group fills that vacant site. Therefore, PPh_3 group and acetyl group are ***cis* to each other**.

1,1-Insertion

Insertion can be either 1,1-insertion or 1,2-inserton. In 1,1-insertion, AB ligand is a neutral, **η^1-type** ligand with a multiple bond such as CO and isonitriles. Due to the migration of Y on to A, both M and Y are bonded to A atom to give anionic ligand -A(=B)Y, and a vacant site on the metal.

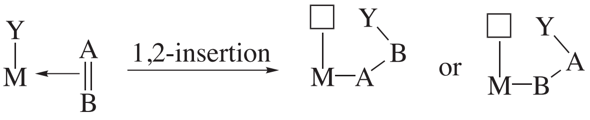


In the Monsanto process, before the final reductive elimination of MeCOI, the Me group migrates on to a CO ligand and the vacant site generated on Rh(III) is filled by another CO ligand.

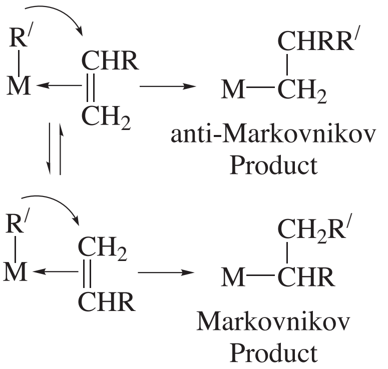


1,2-Insertion

In this case, ligands which are coordinated to a metal atom in the **η^2-fashion**, such as **alkenes** and **alkynes** undergo 1,2-insertion reaction as they contain double/triple bonds.



However, with unsymmetrical olefins, formation of two types of products (**Markovnikov** and **anti-Markovnikov**) is possible during this reaction.

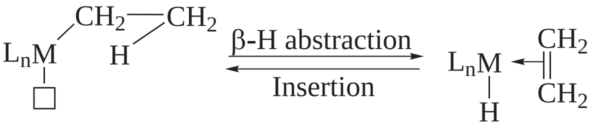


The product depends on the properties of the metal and ligands attached to it.

Deinsertion

Deinsertion can be simply known as the **reverse** or **opposite** reaction of the insertion reaction. To take place deinsertion reactions, there should be either a vacant site in the cis position of the metal centre, or coordinatively saturated metal should lose a ligand to generate a vacant site.

Deinsertion is somewhat similar to **β-hydride abstraction** by a metal centre: as the β-H of the alkyl group migrates to fill a vacant site in the metal centre.



Some examples for deinsertion of N_2, CO_2 or SO_2 are given below. These reactions take place by the action of heat or light. (L = PPh_3)

$$[PtPh(N{=}NPh)L_2] \rightarrow [PtPh_2L_2] + N_2$$

$$[Rh(CO_2Ph)L_3] \rightarrow [RhPhL_3] + CO_2$$

$$[(OC)_2CpFeSO_2Ph] \rightarrow [(OC)_2CpFePh] + SO_2$$

Problems

1. Suggest products for the following insertion and deinsertion reactions.
   (i) $[Cp^*{}_2ZrMe_2] + CO \rightarrow$
   (ii) $[Cp_2MoH(\eta^2\text{-}C_2H_4)]^+ + PMe_3 \rightarrow$
   (iii) $[CpCo(Et)PMe_3]^+ \rightarrow$ deinsertion
2. Suggest a suitable mechanism for the following reaction.
   $[MnMe(CO)_5] + CF_2{=}CF_2 \rightarrow [MnCF_2CF_2Me(CO)_5]$
3. Draw the structures of **A**, **B** and **C** of the following reaction scheme.

$$[Mn_2(CO)_{10}] \xrightarrow[\text{(i)}]{\text{Na}} \mathbf{A} \xrightarrow[\text{(ii)}]{\text{MeCOCl}} \mathbf{B} \xrightarrow[\text{(iii)}]{\triangle} \mathbf{C}$$

(**A**, **B** & **C** are 18e-complexes; (i) Reduction; (ii) Substitution; (iii) Deinsertion)

Student Corner

Reductive Elimination Reactions

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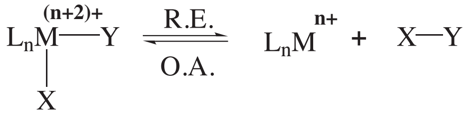
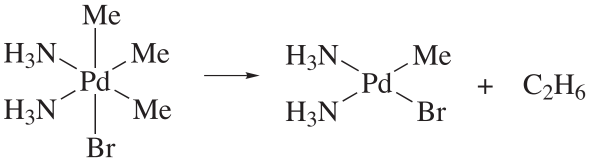
Reductive elimination (R.E.) is the opposite or the reverse of oxidative addition (O.A.), in which X—Y oxidatively adds on to L_nM^{n+} to give $L_n(X)(Y)M^{(n+2)+}$.



$$L_nM^{(n+2)+}(X){-}Y \underset{\text{O.A.}}{\overset{\text{R.E.}}{\rightleftharpoons}} L_nM^{n+} + X{-}Y$$

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 valance electron count (VEC) of the metal get reduced by **two units** as shown below.



VEC = 18e
C.N. = 6
O.N. = +4

VEC = 16e
C.N. = 4
O.N. = +2

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

Rh(III) → Rh(I), Ir(III) → Ir(I),

Co(III) → Co(I), Pt(IV) → Pt(II),

Pd(II) → Pd(0), Ni(II) → Ni(0).

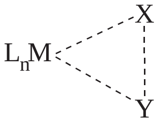
The groups that are easily combined (and then eliminated) include R—H, R—R' to give **alkanes**; H—C(=O)R to give **aldehydes**; R'—C(=O)R to give

ketones; and X—C(=O)R to give **acid halide**s, 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*-$[PtH(CH_2CN)(PPh_3)_2]$ reductive eliminates MeCN, after **isomerising** it into the *cis*-isomer, *cis*-$[PtH(CH_2CN)(PPh_3)_2]$.

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 PPh_3, $[(\eta^5\text{-}C_5Me_5)ZrMe_2]$ eliminates an ethane molecule.

Problems

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

   ($dppe = Ph_2PCH_2CH_2PPh_2$)

   (i) $[(\eta^5\text{-}C_5Me_5)ZrMe_2] + 2\ PPh_3 \rightarrow$

   (ii) $[(\eta^5\text{-}C_5Me_5)Zr(H)Me] + dppe \rightarrow$

   (iii) *fac*-$[PdIMe_3(dppe)] \rightarrow$ (heat)

   (iv) *fac*-$[RhI_3(COMe)(CO)_2]^- \rightarrow$ (heat)

   (v) *trans*-$[PtI_2(Ph)_2(PEt_3)_2] \rightarrow$ (heat)

2. $[TiMe_4]$ decomposes above −50 °C, but $[TiMe_4(Me_2PCH_2CH_2PMe_2)]$ is stable at room temperature. Explain.

Student Corner

Metal Carbonyls

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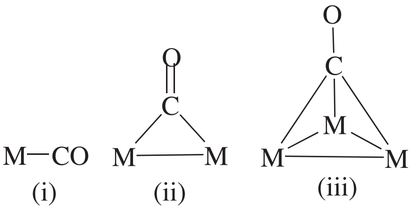
Carbon monoxide is a **good π-acceptor** and the M—C bond in metal carbonyls $[M(CO)_n]$ has a significant π character. Thus, the M—C bond is **strengthened** and the carbon oxygen bond is **weakened** with the **increase in back bonding**.

The common coordination modes of CO are; (i) **terminal**, (ii) **doubly** or edge **bridging** $M_2(\mu_2\text{-}CO)$, and (iii) **triply** or face **bridging** $M_3(\mu_3\text{-}CO)$.



The **carbonyl stretching frequency** ν(CO) decrease in the following order, M—CO > $M_2(\mu_2\text{-}CO)$ > $M_3(\mu_3\text{-}CO)$: as back donation increases with the increase of number of metal atoms.

Bond type	$\nu(CO)/cm^{-1}$
M—CO	2150-1900
$M_2(\mu_2\text{-}CO)$	1900-1750
$M_3(\mu_3\text{-}CO)$	1750-1600

μ_2-CO ligand donates **one electron** to each of the two metal centres. μ_3-CO ligand donates 2/3 of electron to each of the three metal centres.