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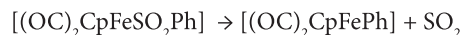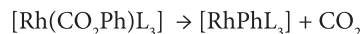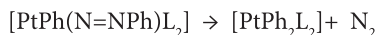
Deinsertion

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.
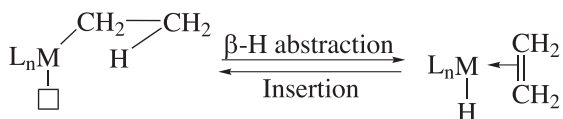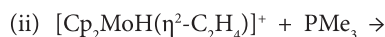

Some examples for deinsertion of N_2, CO_2 or SO_2 are given below. These reactions take place by the action of heat or light. (L = PPh_3)
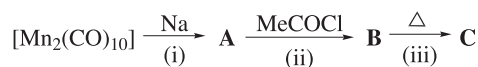
$$[PtPh(N=NPh)L_2] \rightarrow [PtPh_2L_2] + N_2$$

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

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

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.

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

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

# 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 $L_n(X)(Y)M^{(n+2)+}$.

$$L_nM^{(n+2)+} \underset{\text{O.A.}}{\overset{\text{R.E.}}{\rightleftharpoons}} L_nM^{n+} + X{-}Y$$
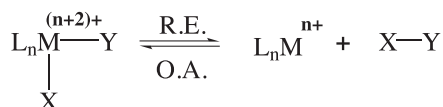
X and Y groups are combined to form X—Y, just before they are eliminated from the metal. Some reactions are reversible, e.g., addition and elimination of H_2 and O_2. R.E. is the last step in catalytic cycles.

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   VEC = 16e
C.N. = 6   C.N. = 4
O.N. = +4   O.N. = +2
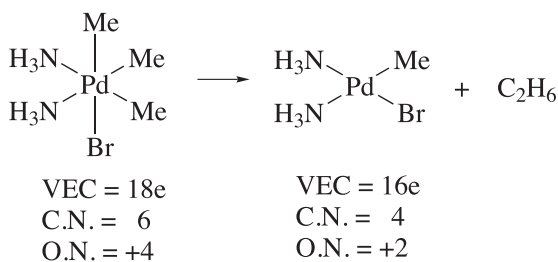
During this process, Pd(IV) is reduced to Pd(II), octahedral → square-planar, and $d^6 \rightarrow d^8$. Some of the common conversions are given below: e.g.,

Rh(III) → Rh(I), Ir(III) → Ir(I),

Co(III) → Co(I), Pt(IV) → Pt(II),

Pd(II) → Pd(0), Ni(II) → Ni(0).
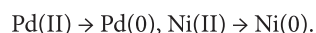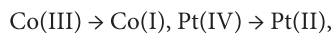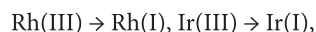
The groups that are easily combined (and then eliminated) include R—H, R—R' to give **alkanes**; H—C(=O)R to give **aldehydes**; R'—C(=O)R to give

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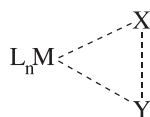
Creation of this **transition state** is crucial: as reductive elimination occurs *via* a **concerted** process, hence, all bond breaking and bond-forming occur simultaneously in a single step.

In square-planar complexes, **trans groups** must rearrange to cis positions before the elimination step to take place; e.g., *trans*-[PtH(CH$_2$CN)(PPh$_3$)$_2$] reductive eliminates MeCN, after **isomerising** it into the *cis*-isomer, *cis*-[PtH(CH$_2$CN)(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$_3$, [(η^5-C$_5$Me$_5$)ZrMe$_2$] eliminates an ethane molecule.

Problems

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

   (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$)

   (i)   [(η^5-C$_5$Me$_5$)ZrMe$_2$] + 2 PPh$_3$ →

   (ii) [(η^5-C$_5$Me$_5$)Zr(H)Me] + dppe →

   (iii) *fac*-[PdIMe$_3$(dppe)] → (heat)

   (iv) *fac*-[RhI$_3$(COMe)(CO)$_2$]$^-$ → (heat)

   (v)   *trans*-[PtI$_2$(Ph)$_2$(PEt$_3$)$_2$] → (heat)

2. [TiMe$_4$] decomposes above −50 °C, but [TiMe$_4$(Me$_2$PCH$_2$CH$_2$PMe$_2$)] is stable at room temperature. Explain.
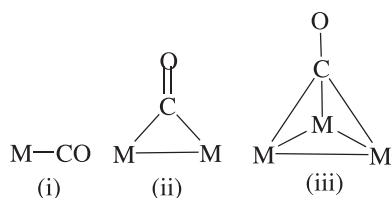
Metal Carbonyls

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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$_2$(μ$_2$-CO), and (iii) **triply** or face **bridging** M$_3$(μ$_3$-CO).

The **carbonyl stretching frequency** ν(CO) decrease in the following order, M—CO >M$_2$(μ$_2$-CO) >M$_3$(μ$_3$-CO): as back donation increases with the increase of number of metal atoms.

Bond type	ν(CO)/cm^{-1}
M—CO	2150-1900
M$_2$(μ$_2$-CO)	1900-1750
M$_3$(μ$_3$-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.