

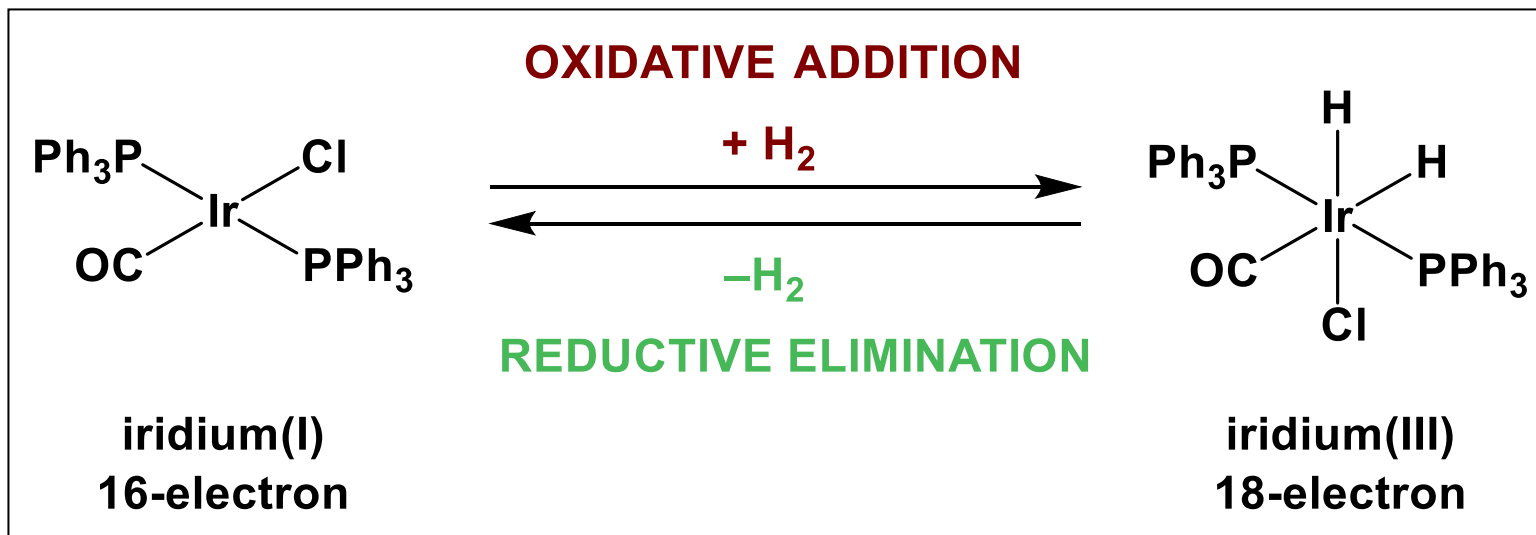
Oxidative Addition/Reductive Elimination

OXIDATIVE ADDITION

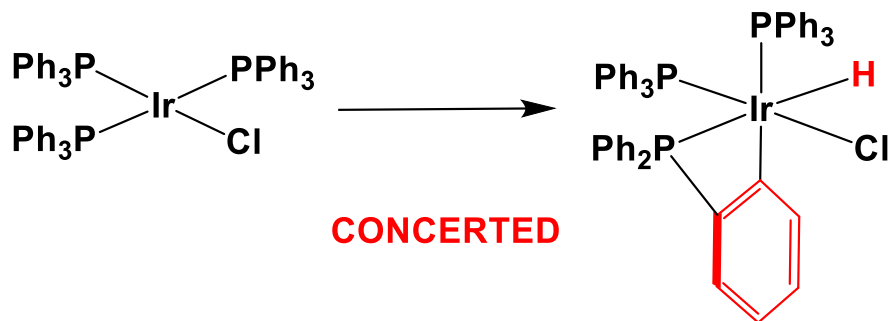
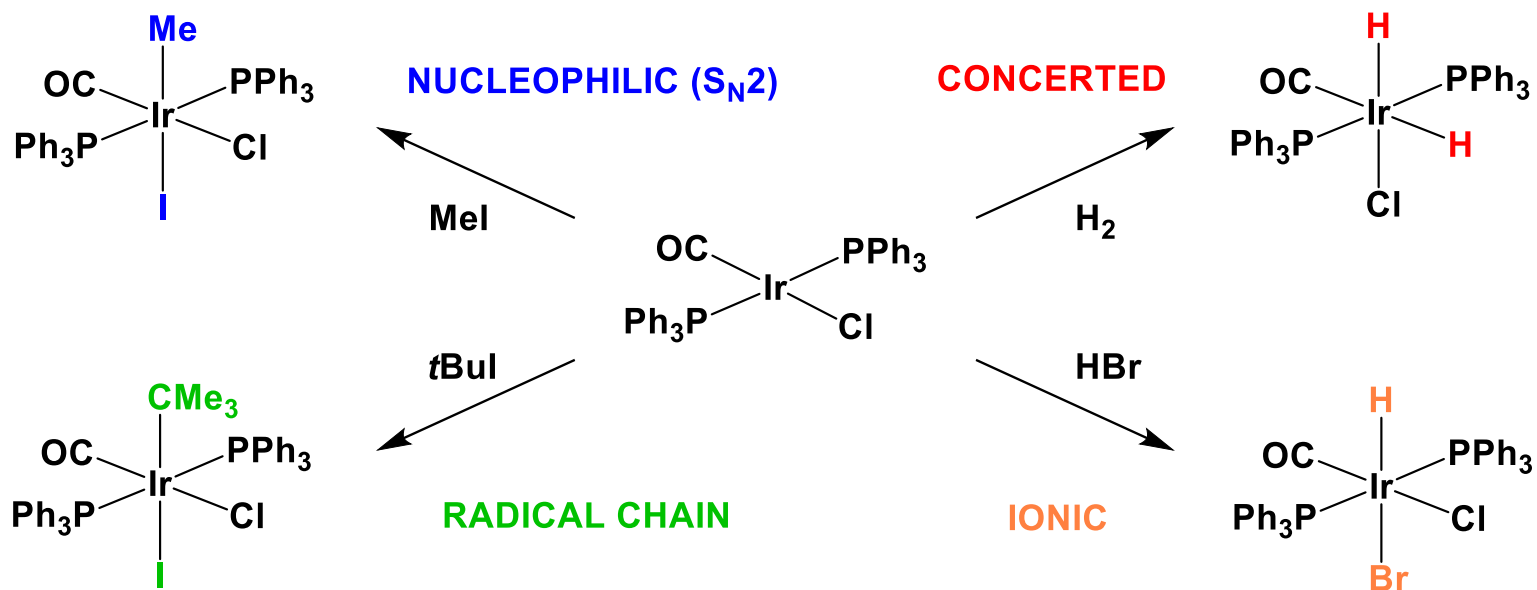
- Addition of R-X (e.g. H₂, HSiR₃, HBR₂, ArI, HCl) to the metal.
- Metal oxidation state increases by 2 units (e.g. Ir^I → Ir^{III}).
- Various mechanisms possible (concerted, S_N2, Radical x 2, Ionic – see later).
- Familiar main group example = Mg + ArBr → ArMgBr Grignard.

REDUCTIVE ELIMINATION

- Opposite of Oxidative Addition



Oxidative Addition Mechanisms



Intramolecular OA = Cyclometallation
(or just metallation)

Oxidative Addition Mechanisms - Overview

OA Mechanism	Type of L_xM	Type of X-Y	Features
Concerted (3-centre addition)	(1) coord. Unsat., (2) sterically uncongested, (3) $3^{rd} > 2^{nd} \gg 1^{st}$ row TM, (4) filled orbital capable of interacting with the s^* orbital of incoming X-Y → Often d^8 complexes [e.g. $IrCl(CO)(PR_3)_2$].	Fairly non-polar substrates: $H-H$, R_3C-H , R_3Si-H strained R_3C-CR_3 , $Ar-X$ not very common	(1) <i>cis</i> -addition (2) retention of config. at $RR'R''C-Y$ (3) 2^{nd} order, $\Delta S^\ddagger \sim -30$ e.u., rate <i>not</i> greatly affected by solvent polarity.
Nucleophilic (S_N2)	Nucleophilic metals e.g. $IrCl(CO)(PR_3)_2$, $Ni(PR_3)_4$, $Pd(PR_3)_n$	Polarized substrates: R_3C-X ($1^\circ > 2^\circ > 3^\circ$) ($MeI > EtI > iPrI$), Also Cl_2 , Br_2 , I_2	(1) <i>cis</i> - or <i>trans</i> -addition (2) inversion of config. at $RR'R''C-Y$ (3) 2^{nd} order, $\Delta S^\ddagger \sim -40$ to -50 e.u., rate accelerated in polar solvents.
Radical (chain or non-chain mechanisms)	Non-chain = $Ni(PPh_3)_3$, $Pt(PPh_3)_3$ Chain = $IrCl(CO)(PMe_3)_2$ Binuclear = $Mn_2(CO)_5$, $Co(CN)_5^{3-}$	R_3C-X , R_3Sn-X ($3^\circ > 2^\circ > 1^\circ$)	(1) <i>cis</i> - or <i>trans</i> -addition (2) racemization of $RR'R''C-Y$ (3) <i>only the radical chain mechanism is accelerated by radical initiators and retarded by radical inhibitors</i>
Ionic (H^+ or X^- attacks first)	(a) $18 e^- Pt(PPh_3)_4 + H^+Cl^-$ (H^+ attacks first) (a) $16 e^- Ir(COD)(PR_3)_2^+ + H^+Cl^-$ (Cl^- attacks first)	$H-X$ (largely dissociated in solution)	

Oxidative Addition Mechanisms - Overview

- **In general :** Non polar substrates (*e.g.* H–H, C–H, Si–H) → Concerted
Halogens (Cl₂, Br₂, I₂) → Nucleophilic
Alkyl halides → Nucleophilic (S_N2) or Radical
Acids (HCl, HBr, HI) → Ionic
- For Alkyl Halides, distinguish a S_N2 or radical mechanism by determining whether 3°, 2° or 1° R–X react faster, whether the reaction leads to racemization or inversion at RR'R''C–X, and whether the reaction is accelerated by radical initiators and retarded by radical inhibitors.
- For a radical mechanism, distinguish between a chain or non-chain process by whether the reaction is affected by radical initiators or inhibitors.
- If it is necessary to distinguish between a concerted or S_N2 mechanism, determine whether X and Y are *cis*- or *trans*-disposed in the product, whether the reaction leads to retention or inversion of stereochemistry in RR'R''C–X, and whether the reaction is accelerated in polar solvents.