Chapter 8. Reductive Elimination

- 1. Overview
- 2. Reductive elimination to form C-H bonds
- 3. Reductive elimination to form X-H bonds
- 4. Reductive elimination to form C-C bonds
- 5. Reductive elimination to form C-X bonds
- 6. Summary

1. Overview

Reductive Elimination = the reverse of Oxidative Addition

$$L_{n}M \stackrel{A}{\downarrow} B \longrightarrow L_{n}M + A-B$$

$$A \stackrel{B}{\downarrow} L_{n}M - ML_{n} \longrightarrow L_{n}M - ML_{n} + A-B$$

$$2 A - ML_{n} \longrightarrow L_{n}M - ML_{n} + A-A$$

Formation of products are <u>depends on the thermodynamics</u> of <u>oxidative addition and reductive elimination</u>.

Factors which affect the rates of reductive elimination

2. Reductive elimination to form C-H bond

- R.E.s to form C-H bonds occur via or without preceeding ligand dissociation.

- First products are σ-complexes. After that alkane dissociates or is displaced by incoming ligands.

$$L_{n}M \stackrel{R}{\longleftarrow} L_{n}M - L' + R - H$$

$$Complex \longrightarrow L_{n}M + R - H$$

Examples of R.E.s without ligand dissociation

$$(PPh_{3})_{2}Pt \xrightarrow{Me} \frac{-25 \text{ °C}}{Ph - me} \xrightarrow{Ph} Me - H + (PPh_{3})_{2}Pt(PhC \equiv CPh)$$

$$(PMe_{3})_{4}Ru \xrightarrow{CH_{2}Ph} \frac{g_{5} \text{ °C}}{H} + CH_{2}Ph + Me_{3}P \xrightarrow{Ru} CH_{2} CH_{2} CH_{2} CH_{3} CH_{3}P$$

$$(8.12)$$

$$Cp^{*} \xrightarrow{Me_{3}P} Cp^{*} Cp^{*} Cp^{*} Cp^{*} Cp^{*} Cp^{*} Cp^{*} Ch_{3}P$$

$$Me_{3}P \xrightarrow{Ir} Ph + Me_{3}P \xrightarrow{Ir} Ph$$

$$(8.13)$$

Examples of R.E.s via ligand dissociation

$$\begin{array}{c} H-carb\\ H(carb)Ir(PPh_3)_2(CO)CI \xrightarrow{PPh_3} H(carb)Ir(PPh_3)(CO)CI \xrightarrow{PPh_3} Ir(PPh_3)_2(CO)CI \xrightarrow{PPh_3} Ir(PPh_3)_2(CO)CI & (8.14)\\ (carb = 7-Ph-1, 7-C_2B_{10}H_{10}) & (8.15)\\ L = PMe_3 & L_2CIRh & H & L_2CIRh & H & R + RhL_3CI & (8.15)\\ L = PMe_3 & L_2CIRh & H & R + RhL_3CI & (8.16)\\ L = PMe_3 & CP_2Zr & L & H & R & (8.17)\\ L = PMe_3 & CP_2Zr & L & H & R & (8.17)\\ L = PMe_3 & CP_2Zr & L & H & R & (8.17)\\ L = PMePh_2 & R & R & RhL_3CI & R & R & RhL_3CI & R & RhL_3CI & RhL_3CI$$

 * Intermediate σ -comlex is suggested by the H/D scrambling through alkane complexes.

- Effects of ancillary ligands

Complexes with more e⁻-donating phosphines undergo R.E. more slowly than those with less e⁻-donating phosphines.

Table 8.1. The effect of ancillary ligand electronic effects on the rate of reductive elimination of benzene from $Cp^*Ah(PR_3)(Ph)(H)$.

Entry	PR ₃	Cone angle (deg)	T (°C)	k (s-1)	ΔG [‡] (kcal/mol)
1	PMe,	118	23	3.35(17) × 10 ⁻⁷	26.1
2	PMe Ph	122	23	1.08(5) × 10 ⁻⁶	25.4
3	PMe Bu	139	24.5	6.6 × 10⁻⁵	24.5
4	PMePh ₂	136	24.5	1.11(6) × 10 ⁻⁵	24.2

The rate constant for R.E. increase with increasing cone angle of the phosphine ligand.

Table 8.2. The effect of ancillary ligand steric properties on the rate of reductive elimination of benzene from Cp*Rh(PR₃)(Ph)(H).

Entry	PR_3	Cone angle (deg)	T (°C)	k (s-1)	ΔG [‡] (kcal/mol)
1	PMe,	118	23	3.4(2) × 10 ⁻⁷	26.1
2	P(n-Bu) _a	132	24.5	2.4(1) × 10 ⁻⁶	25.1
3	PMe,But	139	24.5	6.6 × 10 ⁻⁵	24.5

3. Reductive elimination to form X-H bond

- R.E.s to form X-H bonds occur upon addition of a dative ligand in most cases.

$$\begin{array}{c} \text{Cp*} \\ \text{Ph}_3\text{P}^{\text{Vir}} \text{OEt} \\ \text{H} \end{array} \xrightarrow{\hspace{1cm}} \begin{array}{c} \text{Cp*lr}(\text{PPh}_3)_2 \ + \ \text{H-OEt} \\ \text{Ph}_3\text{P} \end{array} \xrightarrow{\hspace{1cm}} \begin{array}{c} \text{Via} \\ \text{Ph}_3\text{P} \end{array} \xrightarrow{\hspace{1cm}} \begin{array}{c} \text{N}^3\text{-Cp*} \\ \text{Ph}_3\text{P} \end{array}$$

4. Reductive elimination to form C-C bond

- Few examples because of a high-energy transition state for the C-C bond forming R.E.s.
- Occur by concerted mechanisms (= cis coordination is necessary)
- Most common from complexes of group 10 metals (Ni^{II}, Pd^{II}, Pd^{IV}, Pt^{IV})
- Effects of parcitipating groups

the reaction rate:

aryl, vinyl groups (sp^2 -hybridized carbon) > alkyl carbon (sp^3 -hybridized carbon)

This trend is due to a difference in transition state energy, because ...

- 1. The two-dementionality of aryl & vinyl groups reduces steric hinderance.
- 2. An sp^2 -hybridized orbital is less directional than sp^3 .
- 3. Coordination of the product to the metal lower the barrier for R.E..

But this is not the case for PtIV complexes...

containing e⁻ rich reacting group > containing e⁻ poor reacting group

This trend is due to a more stable ground state when e⁻-withdrawing groups are present. And also accelated by the pairing of e⁻-rich and e⁻-poor groups bound to the metal

$$Ph_{2}$$

$$Ph_{2}$$

$$Ph_{2}$$

$$Ph_{2}$$

$$Ph_{2}$$

$$Relative rates:$$

$$X = p \cdot CN > p \cdot CF_{3} > p \cdot H > p \cdot Me > p \cdot OMe$$

$$Y = H > Ph > C(O)R > CF_{3} > CN$$

$$R^{1}$$

$$Ph_{2}$$

$$Ph_{2}$$

$$Ph_{3}$$

$$R^{2} + L_{n}PI(0) \qquad (8.39)$$

$$R^{1} = OMe, R^{2} = CF_{3} > R^{1} = R^{2} = OMe > R^{1} = R^{2} = CF_{3}$$

- Effects of bite angle

the reaction rate:

larger bite angle > smaller bite angle

$$\begin{array}{c} Ph_2 \\ P \\ Ph_2 \\ Ph_2$$

5. Reductive elimination to form C-X bond

- R.E.s to form C-X bonds occur by several mechanisms.

The difference of reaction mechanisms sometimes cause opposite trends for R.E.s. example:

- From aryl and alkylplatinum(IV) complexes

$$\begin{array}{c|c} Et_3P & Pt \\ Et_3P & Ph \\ \hline \\ C_6D_6 & (PEt_3)_2Pt(Ph)_2I(MeOH)]I^{\oplus} \\ \hline \end{array} \qquad \begin{array}{c|c} (PEt_3)_2Pt(Ph)_2I(MeOH)]I^{\oplus} \\ \hline \\ (PEt_3)_2Pt(Ph)II \\ \hline \end{array} \qquad (8.56)$$

$$X = I_1$$
 OAc, or OAr $P = 1, 2$ -bis(diphenylphosphine)ethane or 1, 2-bis(diphenylphosphine) benzene

$$CI \xrightarrow{Pt} CI \xrightarrow{CI \xrightarrow{CI^{\oplus} \text{(catalytic)}}} HO \xrightarrow{OH} + CI \xrightarrow{OH} + [PICI_4]^{2^{\oplus}}$$

$$(8.58)$$

- From arylpalladium(II) complexes

Ph₂
P A
RSBu^t
Ph₂
Rates:
$$R = Me < R < R < R$$
(8.62)

$$Ph_{3}P - Pd - PPh_{3}$$

$$Ph_{3}P - Pd - PPh_{3}$$

$$ArN(p-tol)_{2} + Pd(PPh_{3})_{n}$$
(8.63)

OMe
$$\frac{\Delta}{Fc(Bu^{t})_{2}P} \longrightarrow O \longrightarrow OMe + Pd(PFcBu^{t}_{2})_{2}$$

$$Fc(Bu^{t})_{2}P \longrightarrow O \longrightarrow OMe + Pd(PFcBu^{t}_{2})_{2}$$

$$Excess \qquad (Bu^{t})_{3}P \longrightarrow OMe + Pd(PBu^{t}_{3})_{2}$$

$$Fc = ferrocenyl$$

$$OMe$$

$$OMe$$

$$OMe$$

$$Fc(Bu^{t})_{2}P \longrightarrow OMe + Pd(PBu^{t}_{3})_{2}$$

$$OMe$$

$$OMe$$

$$OMe$$

$$Bu_{3}^{\prime}P-Pd-N \xrightarrow{CF_{3}} \underbrace{\frac{PBu_{3}^{\prime}}{25 \, {}^{\circ}C}}_{CF_{3}} \text{MeO} \xrightarrow{N}_{Ar}^{Ar}$$

$$(8.65)$$

(The analogous complex ligated by two \mbox{PPh}_3 ligands does not react at this temperature.)

- From acyl complexes

- From nickel(II) complexes to amines or ethers

$$(bpy)Ni \longrightarrow \begin{pmatrix} I(AcCp)_2Fe]^9 \\ 85\% \\ O_2 \\ 86\% \\ I_2 \\ \hline 77\% \end{pmatrix} \longrightarrow N-Tol$$

$$(bpy)Ni(COD) + \bigvee_{D} \bigvee_{R} \bigvee_{D} \bigvee_{D} \bigvee_{R} \bigvee_{D} \bigvee_{R} \bigvee_{D} \bigvee_{R} \bigvee_{D} \bigvee_{R} \bigvee_{D} \bigvee_{R} \bigvee_{R} \bigvee_{D} \bigvee_{R} \bigvee_{R} \bigvee_{D} \bigvee_{R} \bigvee$$

6. Summary

- The mechanisms of R.E. include the same pathways as for oxidative addition. (although in the reverse direction)
- Favorable from electron-poor, sterically hindered, odd coordination number-containing complexes.
- R.E.s to form C-H and H-H bonds are fast, while R.E.s to form C-C and C-X bonds are slow.
- Mainly studied about Rh, Ir, Ni, Pt, Pd.

