Unit 17 · Organometallic Compounds

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Organic Chemistry (Units 8–17 together): 33 of 75 marks; 2 MCQs, 3 short and 2 long questions
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: Zeise's salt: a π-bonded complex of **ethene**, the first organometallic compound made (of a transition metal)
- **MCQ (1 mark)**
  - ethane from a Grignard reagent (C_2H_5MgX + water); CH_3MgBr + propanone → 2-methylpropan-2-ol
  - Zeise's salt: formula, name; CH_3MgBr + HCN → ethanal; R–X + Mg → RMgX; alkyl cyanide → ketone
  - $CH_3Cl + 2Li \rightarrow CH_3Li + LiCl$; $CH_3COCl + CH_3MgBr$; which ester gives a 2° alcohol (a methanoate)
- **Short (5 marks, in parts)**
  - what a Grignard reagent is; with methanal and CO_2; 1°, 2°, 3° alcohols from RMgX + the right carbonyl
  - organometallic compounds: Li, Cd, Cu examples; the M–C bond; Zeise's salt's formula, name, use, likeness to RMgX
- **Long (8 marks)**: Grignard's preparation, why dry ether, from an aryl halide; what happens with water, an ester, an acid chloride; from CH_3MgBr: methane, ethanol, acetic acid, isopropyl alcohol, propanol; the alcohols C_3H_8O

Key terms

Organometallic compound: at least one **direct metal–carbon bond** (CH_3CH_2MgBr yes; CH_3COONa, CH_3CH_2OMgBr no).

Transmetallation: an organic group moves from one metal to another (RLi + CuI; RMgX + $CdCl_2$).

Gilman reagent: lithium dialkylcuprate, R_2CuLi.

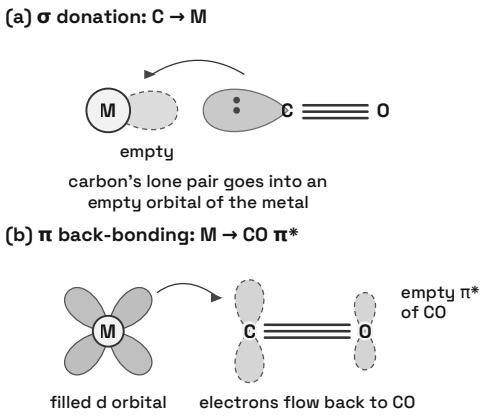
Grignard reagent: alkylmagnesium halide, RMgX, in dry ether.

π **back-bonding**: a filled metal d orbital gives electrons into an empty π^* of CO or an alkene.

η^2: ligand bonded through two carbons together (ethene in Zeise's salt).

The metal–carbon bond

- metal less electronegative than C (2.55): **polar covalent**, Mδ+–Cδ–; carbon δ–: acts as a **carbanion**: base and nucleophile (reverse of Cδ+–Xδ– in a haloalkane)
- Li 0.98 (difference 1.57) > Mg 1.31 (1.24) > Cd 1.69 (0.86) > Cu 1.90 (0.65): **R–Li most reactive**, R_2Cd and R_2CuLi gentle (stop at one step)
- Na, K: nearly ionic, R^-M^+
- metal alkyls: σ **bond** only (C gives a pair to an empty metal orbital)
- metal carbonyls $Ni(CO)_4$, $Fe(CO)_5$ and alkene complexes: σ **donation** + π **back-bonding**, each strengthens the other



σ donation and π back-bonding between a metal and CO.

Uses: Ziegler–Natta ($TiCl_4 + Al(C_2H_5)_3$) → polythene, polypropylene; Mond process ($Ni(CO)_4$ at 50 °C, decomposed at 230 °C, 99.99% Ni); Grignard, RLi, cuprates in synthesis; organomercury, organotin seed dressings (now banned: Iraq 1971–72); vitamin B_{12} (Co–C), technetium-99m sestamibi; ferrocene in glucose strips; $Ga(CH_3)_3$ for LEDs

Lithium, copper, cadmium

- **R–Li**: $CH_3CH_2Cl + 2\,Li \xrightarrow{\text{dry ether}} CH_3CH_2Li + LiCl$: strongest base and nucleophile; n-BuLi starts synthetic rubber
- **R_2CuLi**: $2\,CH_3Li + CuI \xrightarrow{\text{dry ether}} (CH_3)_2CuLi + LiI$: **Corey–House**, joins two different groups
- **R_2Cd**: $2\,CH_3MgBr + CdCl_2 \longrightarrow (CH_3)_2Cd + 2\,MgBrCl$: acid chloride → **ketone**, stops there
- $CH_3Cl + 2\,Li \longrightarrow CH_3Li + LiCl$ (two Li); RLi burn in air, react violently with water

- Corey–House: $(CH_3)_2CuLi + CH_3CH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_3 + CH_3Cu + LiBr$ (Wurtz gives three alkanes from two different RX)
- cuprates: RCu, R_2CuLi, mixed R_1R_2CuLi, cyanocuprates $RCu(CN)Li$, $R_2Cu(CN)Li_2$
- $(CH_3)_2Cd + 2\,CH_3COCl \longrightarrow 2\,CH_3COCH_3 + CdCl_2$; cadmium poisonous (itai-itai)

Grignard reagent

Preparation: $CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$; $C_6H_5Br + Mg \xrightarrow{\text{dry ether or THF}} C_6H_5MgBr$

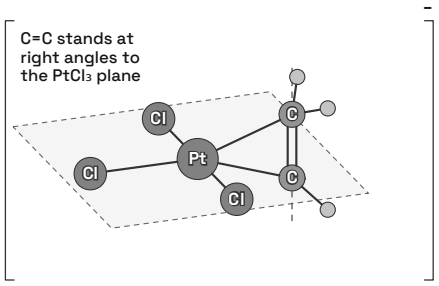
- Mg gives **one electron** to C–X: R· + ·MgX, which combine (fish-hook arrows); rate RI > RBr > RCl
- **dry ether**: water (any O–H, N–H) destroys it; ether O lone pairs bond to Mg, $RMgX(OEt_2)_2$, and hold it in solution
- not from ethane: no halogen; first $C_2H_6 + Cl_2 \xrightarrow{\text{light}} C_2H_5Cl + HCl$, then Mg
- reacts as $\mathbf{R^-}$: takes H^+ (→ alkane) or adds to the $\delta+$ C of C=O, C≡N (new C–C)

Reagent	After H_2O/H^+	Example (from CH_3MgBr)
H_2O, ROH, NH_3	alkane	CH_4
HCHO	**1**° alcohol	ethanol
RCHO	**2**° alcohol	CH_3CHO → propan-2-ol
R_2CO	**3**° alcohol	propanone → 2-methylpropan-2-ol
CO_2	acid (one C more)	ethanoic acid
HCN	aldehyde	ethanal
R′CN	ketone	CH_3CN → propanone
ester (2 RMgX)	3° alcohol (methanoate: 2°)	$HCOOC_2H_5$ → propan-2-ol
acid chloride	ketone, then 3° alcohol	CH_3COCl → propanone → $(CH_3)_3COH$
oxirane	1° alcohol (two C more)	propan-1-ol

- $CH_3MgBr + H_2O \longrightarrow CH_4 + Mg(OH)Br$; $C_2H_5MgBr + C_2H_5OH \longrightarrow C_2H_6 + Mg(OC_2H_5)Br$
- $HCHO + RMgX \longrightarrow RCH_2OMgX$; $RCH_2OMgX + H_2O \longrightarrow RCH_2OH + Mg(OH)X$
- $CH_3MgBr + CO_2 \longrightarrow CH_3COOMgBr$; $CH_3COOMgBr + H_2O \longrightarrow CH_3COOH + Mg(OH)Br$
- $CH_3CN + CH_3MgCl \longrightarrow (CH_3)_2C{=}NMgCl$ (imine salt; stops: N^- takes no second R); hydrolysis → $CH_3COCH_3 + NH_3$
- HCN: its acidic H (pKa 9.2) reacts first in a real flask; exam answer the aldehyde
- $C_6H_5COOCH_3 + 2\,C_2H_5MgBr + 2\,H_2O \longrightarrow C_6H_5C(OH)(C_2H_5)_2 + CH_3OH + 2\,Mg(OH)Br$ (3-phenylpentan-3-ol); ketone reacts faster than ester: can't stop
- acid chloride faster than ester (Cl makes C more $\delta+$); stop at the ketone with R_2Cd or R_2CuLi
- add in **dry ether**, water and acid only **afterwards**
- butan-2-ol: $CH_3CH_2MgBr + CH_3CHO$, or $CH_3MgBr + CH_3CH_2CHO$

Zeise's salt

- **$K[PtCl_3(C_2H_4)]\cdot H_2O$**, potassium trichlorido(η^2-ethene)platinate(II) monohydrate; Zeise, Copenhagen, **1830** ($PtCl_4$ in ethanol, then KCl); lemon-yellow
- **first organometallic compound of a transition metal**, first metal–alkene complex
- anion $[PtCl_3(C_2H_4)]^-$: Pt(II) d^8, **square planar**; ethene on the fourth corner, its **C=C perpendicular** to the $PtCl_3$ plane, both C equally bonded (π-bonded)
- bonding (Dewar–Chatt–Duncanson): ethene's π → empty Pt orbital (σ), Pt d → ethene π^* (back-bonding): C=C a little longer
- family: Wacker process (ethene → ethanal, Pd), Ziegler–Natta
- like RMgX: a metal bonded straight to carbon



The anion of Zeise's salt.

Ferrocene $Fe(C_5H_5)_2$: Fe between two parallel rings (sandwich); orange, stable in air; Wilkinson and Fischer, Nobel 1973

COMMON MISTAKES

✗ R–X + Li → R–Li + LiX
✓ + **2**Li.

✗ CH_3CH_2Br is methyl bromide
✓ **bromoethane** (ethyl bromide).

✗ ketone + RMgX in presence of water
✓ in **dry ether**; water and acid afterwards.

✗ Zeise's salt without its charge, ethene in the $PtCl_3$ plane
✓ $[PtCl_3(C_2H_4)]^-$, C=C **at right angles** to the plane.

✗ Ziese, Zieglar, palatinate
✓ **Zeise**, **Ziegler**, **platinate**.

✗ methoxy benzoate
✓ **methyl** benzoate.