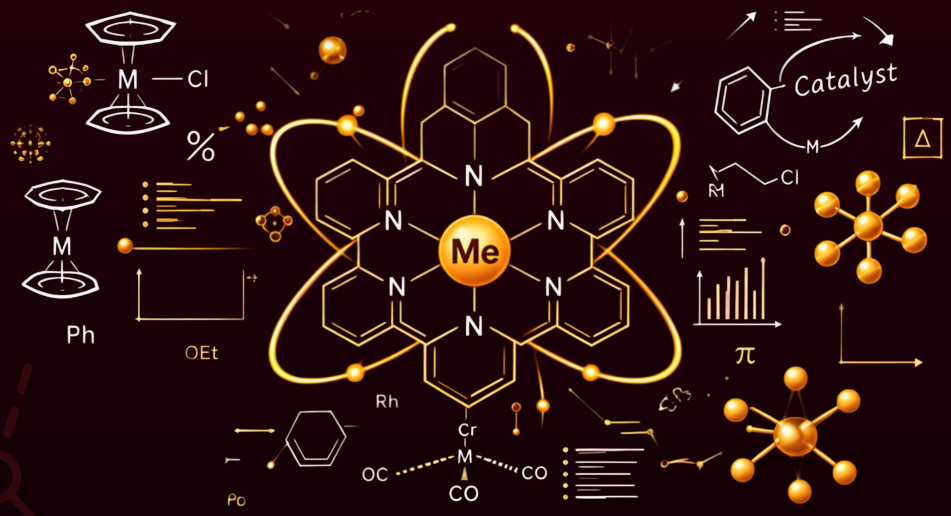
Organometallic Chemistry

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CHEMISTRY SPARK PUBLICATION

ORGANOMETALLIC

CHEMISTRY

MADE EASY

Concepts · Short Tricks · Mind Maps · PYQs

CSIR-NET | GATE | IIT-JAM

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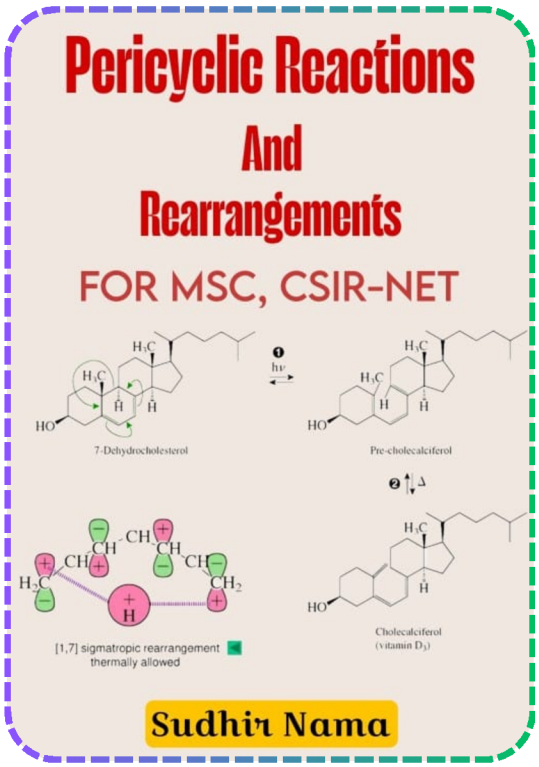
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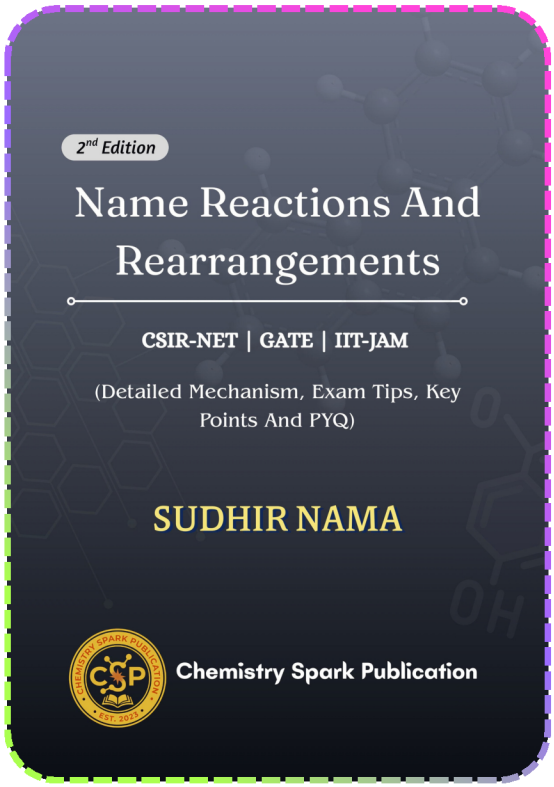
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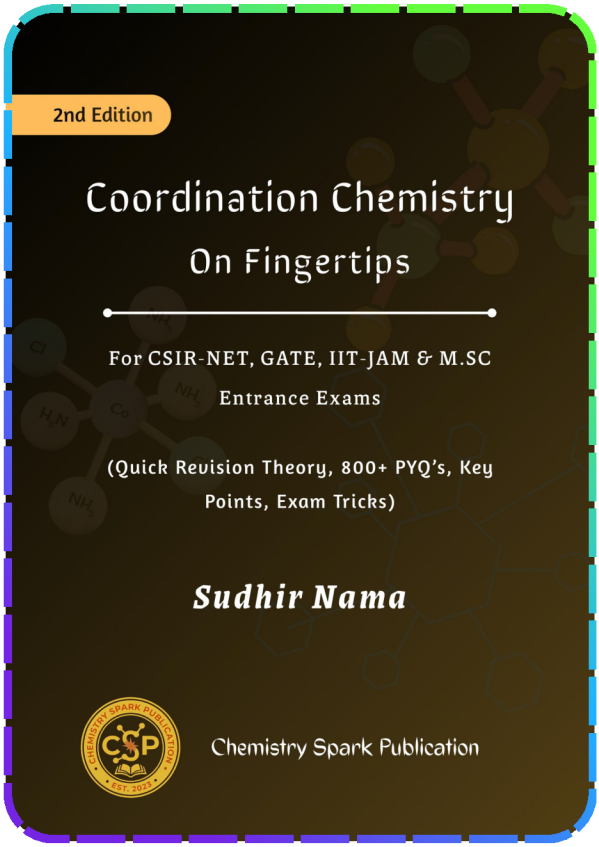
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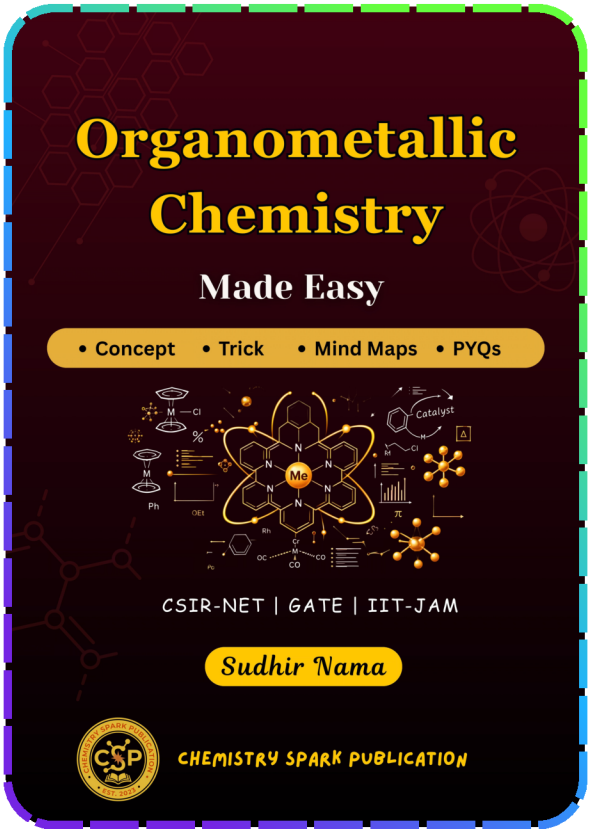
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Contents

I · FOUNDATIONS 1

1. Introduction, History and Nomenclature 2
2. The 18-Electron Rule and Electron Counting 12
3. A Field Guide to Organometallic Ligands 24

II · THE METAL CARBONYL STORY 36

4. Bonding in Metal Carbonyls 37
5. Preparation, Properties and Reactions of Metal Carbonyls 47

III · STRUCTURE, DYNAMICS AND REACTIVITY 55

6. Ferrocene and the Sandwich Family 56
7. Fluxionality and Spectroscopic Characterisation 74
8. Elementary Reactions of Organometallic Complexes 79

IV · CATALYSIS 99

9. Homogeneous Catalysis 100

V · ADVANCED TOPICS 150

10. Stability of Organometallic Compounds 151
11. Metal Clusters, Wade's Rules and Metal–Metal Bonds 156
12. The Isolobal Analogy 189

VI · RAPID REVISION AND PRACTICE 197

13. Rapid Revision Kit: Flashcards and Summary Tables 198
14. Topic-Wise Special Question Set 2 212
15. Previous Year Questions: CSIR-NET, GATE And IIT-JAM 219

PART

I

Foundations

Chapter 1 — Introduction, History and Nomenclature

Chapter 2 — The 18-Electron Rule and Electron Counting

Chapter 3 — A Field Guide to Organometallic Ligands

CHAPTER 1

Introduction, History and Nomenclature

What are Organometallic Compounds?

Organometallic compounds are substances that contain at least one bond between a metal (M) and a carbon atom (C) of an organic group.

The metal can be a transition metal, a main-group element, a lanthanide or an actinide.

The M–C bond can be ionic, covalent, or have π-character (e.g., η^5-Cp, η^6-arene).

A Short History of the Field (and the Nobel Prizes Behind It)

Organometallic chemistry never set out to be glamorous. It began by accident, grew through puzzling compounds whose structures nobody could explain, and matured into one of the most decorated areas of the subject. A quick walk through the timeline tells you where each idea actually came from, and examiners love testing these milestones.

Year	Landmark	Why it matters
1760	Louis Cadet prepares foul-smelling organoarsenic compounds (cacodyl) from cobalt arsenide minerals	The first organometallic substances made — unknowingly
1827	William Zeise isolates Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]\cdot H_2O$	The first π-complex: an alkene bound through its C=C bond
1849–1852	Edward Frankland prepares dialkylzinc and alkylmercury halides; coins the word "organometallic"	Frankland is regarded as the father of organometallic chemistry
1853	Löwig and Schweizer prepare $(C_2H_5)_4Pb$, $(C_2H_5)_3Sb$ and $(C_2H_5)_3Bi$	Main-group organometallics begin to appear
1863	Friedel and Crafts prepare organochlorosilanes	The roots of silicone chemistry
1868	Schützenberger isolates $[PtCl_2(CO)_2]$	The first metal carbonyl complex
1890	Ludwig Mond makes $Ni(CO)_4$	The first binary carbonyl — and the Mond nickel-purification process
1898–99	Philippe Barbier tries Mg/alkyl-halide chemistry on a ketone (published 1899, Compt. Rend. 128, 110); his student Grignard perfects it	The stepping stone to RMgX
1900	Victor Grignard develops RMgX reagents	The workhorse of organic synthesis for a century
1909	Pope prepares the tetramer $[(CH_3)_3PtI]_4$	The first σ-bonded organotransition-metal compound

Year	Landmark	Why it matters
1951	Kealy and Pauson (and, independently, Miller, Tebboth and Tremaine — published 1952) discover ferrocene	The sandwich structure, proposed by Wilkinson and Fischer in 1952, opened modern organometallic chemistry
1964	E. O. Fischer makes the first carbene complex, $(CO)_5W{=}C(OMe)Ph$	The first M=C double bond
1973	First carbyne complex, $(CO)_4BrCr{\equiv}CPh$	The first M≡C triple bond
1984	Kubas characterises the first dihydrogen complex	A coordinated H–H bond — the σ-complex era begins

CSIR-NET POINTER

Nobel prizes you should be able to name: Grignard and Sabatier (1912, Grignard reagents and catalytic hydrogenation); Ziegler and Natta (1963, polymerisation catalysts); E. O. Fischer and G. Wilkinson (1973, sandwich compounds); Lipscomb (1976, boranes); Brown and Wittig (1979, organoboron and phosphorus chemistry); Knowles, Noyori and Sharpless (2001, asymmetric hydrogenation/oxidation); Chauvin, Grubbs and Schrock (2005, alkene metathesis); Heck, Negishi and Suzuki (2010, Pd-catalysed C–C coupling).

NOTE

Organometallics in everyday life: MMT (methylcyclopentadienyl manganese tricarbonyl) replaced tetraethyllead as the anti-knock additive in petrol; tributyltin oxide (TBTO) is painted onto ship hulls as an anti-foulant that stops barnacles and algae; and vitamin B_{12} keeps organometallic chemistry running inside your own cells.

The definition is worth quoting word for word: an organometallic compound contains at least one direct metal–carbon bond. Ligands such as CO, NO, N_2, PR_3 and H_2 can coexist inside such complexes, but none of them on its own makes a compound organometallic — and C-bound cyanides, which do contain a direct M–C bond, are nevertheless conventionally studied as coordination compounds. Binary metal carbonyls, by long convention, are embraced by the subject, M–C bond present in every one, so the Mond process counts as organometallic history. Vitamin B_{12} in its coenzyme form (adenosylcobalamin) carries a natural Co–C σ bond, hence its reputation as nature's oldest organometallic compound; in cyanocobalamin a CN^- ligand occupies the upper axial site that carries the Co–C bond in the coenzymes.

Types of Ligands in Organometallic Chemistry

Ligand Type	Examples	Nature of Bonding
Alkyl	$-CH_3$, $-C_2H_5$	σ-donor
Alkenyl/Alkynyl	$-CH{=}CH_2$, $-C{\equiv}CH$	σ-donor (X-type); alkynyl can additionally π-donate

Ligand Type	Examples	Nature of Bonding
Aryl	–Ph, $–C_6H_4Me$ (tolyl)	σ-donor (X-type; η^6-arenes are the π ligands)
Carbonyl (CO)	$Fe(CO)_5$, $Ni(CO)_4$	σ-donor + π-acceptor
Cyclopentadienyl (Cp)	$(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$	π-donor (multi-hapto, η^5)
Arene	$(\eta^6–C_6H_6)Cr(CO)_3$	π-donor
Carbenes	Fischer/Schrock type	σ + π-donor or π-acceptor

Classification of Organometallic Compounds

Three ways to classify an organometallic compound	
By nature of the M–C bond	σ-bonded — R–M, e.g. $CH_3–Li$ π-bonded — alkenes, alkynes, arenes Bridging ligands — μ-CO, μ-CH_3
By metal type	Main group — $Al(CH_3)_3$, $ZnEt_2$ Transition metals — $Fe(CO)_5$, $Ni(CO)_4$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$
By ligand hapticity (η)	η^1 — coordination through a single atom ($CH_3–M$) η^2 — coordination through a C=C bond ($C_2H_4–M$) η^5 — cyclopentadienyl ring η^6 — arene ring

Organometallics by Composition: Simple and Mixed Types

A very practical way of sorting organometallic compounds looks at how many kinds of groups are attached to the metal:

- Homoleptic (symmetrical): the metal carries identical organic groups at every position — e.g., diethylmercury, $(C_2H_5)_2Hg$, or dimethylzinc, $(CH_3)_2Zn$.
- Heteroleptic (unsymmetrical): two different organic groups are bound to the same metal — e.g., ethylmethylmercury, $CH_3–Hg–C_2H_5$.
- Mixed: one organic and one inorganic group on the metal — the Grignard reagents, e.g., C_2H_5MgBr, are the classic examples.

Type	Metal environment	Example
Homoleptic (symmetrical)	Two identical organic groups	$(C_2H_5)_2Hg$

Type	Metal environment	Example
Heteroleptic (unsymmetrical)	Two different organic groups	$CH_3–Hg–C_2H_5$
Mixed	One organic + one inorganic group	C_2H_5MgBr (Grignard reagent)

Classification by the Nature of the Metal–Carbon Bond

The nature of the M–C bond gives the most exam-relevant classification:

- Ionic organometallics come mainly from the most electropositive metals, the alkali, alkaline-earth, lanthanide and actinide elements. They are best written as salts, with Na^+Cp^-, $Cs^+CH_3^-$ and $Ph_3C^-Na^+$ as typical examples. Expect colourless, non-volatile crystalline solids that are violently reactive towards air and moisture, and that usually dissolve only in polar or coordination solvents rather than hydrocarbons.
- Covalent σ-bonded (2-centre 2-electron) organometallics are built on a normal 2c–2e bond, the carbon of the organic group sharing an electron pair with the metal. Metals of intermediate electronegativity dominate this territory, $(CH_3)_2Zn$, $(C_2H_5)_2Hg$ and $Pb(CH_3)_4$ among them. The M–C σ bond is present in every metal carbonyl as well — donated by the carbon lone pair, with π back-donation layered on top — so it is not an alkyl-type σ bond.
- π-bonded organometallics work differently. Unsaturated organic fragments such as alkenes, alkynes, aromatic rings and Cp^- bind through their delocalised π systems, so the metal ends up attached to several carbon atoms at once; ferrocene, dibenzenechromium and Zeise's salt all belong to this family.
- Finally, the multicentre (electron-deficient) cases. Alkyls of Li, Be, B and Al simply do not carry enough electrons for classical 2c–2e bonds, so they aggregate instead, with alkyl groups bridging between metals. Tetrameric $(CH_3Li)_4$ and dimeric $Al_2(CH_3)_6$, with its 3c–2e bonds, are the textbook examples.

Classification by the Position of the Metal in the Periodic Table

The third standard basis of classification asks not what is attached, but which metal is doing the attaching — and the answer predicts the bonding style before you draw a single structure.

- For the s-block metals Li, Na and K the M–C bond is strongly ionic (M^+C^-), the more covalent Be and Mg cases aside. These compounds are violently air- and moisture-sensitive, they cluster into aggregates in the solid state (MeLi is a tetramer with multicentre bonds), and their everyday job in synthesis is carbanion transfer.

- p-Block organometallics (B, Al, Sn, Pb…) are electron-precise, with predominantly covalent σ M–C bonds that ordinary two-centre valence structures describe perfectly well. Organoaluminiums are bridge-dimeric, as in the Me_3Al dimer; organoleads gave the world the historic anti-knock additive tetraethyllead; and organoboranes power hydroboration.
- d-Block organometallics: the heart of the subject. Low oxidation states, π-acceptor ligands, the 18-electron rule, and most of homogeneous catalysis — carbonyls, metallocenes, alkylidenes and alkylidynes all live here.
- f-Block organometallics (lanthanides, actinides): the M–C bonds are largely ionic, coordination numbers run high, and there is no 18-electron rule to lean on — though the actinides can show genuine 5f/6d covalency. The stars here are the Cp_3Ln species and uranocene, $(\eta^8\text{-}C_8H_8)_2U$.

The Whole Classification at a Glance

Basis of classification	Categories	One-line reminder
Hapticity (how many ligand atoms bind)	η^1 through η^8	"How many carbons are fastened to the metal?"
Composition (what is bound)	symmetrical R_nM; unsymmetrical $R_nR'_xM$; mixed R_nMX_x	"What is the ligand set around the metal?"
Position of the metal	s-block ionic; p-block σ-covalent; d-block π-complex; f-block ionic, no 18e rule	"Which metal family — and therefore which bonding style?"
Nature of the M–C bond (bonus basis)	ionic; 2c–2e σ; π (σ-donor/π-acceptor); multicentre electron-deficient	"What kind of bond holds it together?"

CSIR-NET POINTER

Read the question stem carefully for the classification basis: "on the basis of hapticity" points at one ligand's binding mode; "on the basis of composition" at the ligand set; "on the basis of position of the metal" at the periodic-table block. The same compound can appear in all three lists with different labels — e.g., ferrocene is mixed-composition-free symmetrical $(Cp)_2Fe$, an η^5 π-complex, and a d-block organometallic all at once.

Structures of Two Landmark Organometallics (Frequently Asked)

Structure of Methyl Lithium, $(CH_3Li)_4$

In hydrocarbon and diethyl ether solutions, methyllithium is found mainly as a tetramer. The four Li atoms occupy the corners of a tetrahedron and each triangular face is capped by one methyl group, so every CH_3 group ends up bridging three lithium atoms; strongly donating solvents and chelating additives can break the aggregate down.

How is that held together? By a set of localised molecular orbitals: the symmetric combination of the three Li 2s orbitals of one face overlaps with an sp^3 hybrid orbital of the methyl carbon, producing a single orbital that holds one electron pair. That is a four-centre two-electron (4c–2e) bond.

Because the carbon-based orbital lies lower in energy than the Li orbitals, the bonding pair is concentrated on the CH_3 group. The fragment is therefore strongly carbanionic, and some analyses put the Li–CH_3 interaction at roughly 90% ionic character.

Exam takeaway: electron-deficient main-group organometallics (Li, Be, Al) reach stability through multicentre bonding — the same theme that appears in diborane and in $Al_2(CH_3)_6$.

Structure of Zeise's Salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$

Zeise's salt, potassium trichloro(η^2-ethene)platinate(II), was first isolated in pure form by William Zeise in 1827 — commonly cited as the first organometallic compound to be obtained pure.

The Pt(II) centre is d^8, square planar and 16-electron (counting the η^2-ethene as a 2-electron donor).

The bonding is synergic, just as it is in metal carbonyls. The filled π orbital of ethene donates into an empty metal dσ orbital, while the filled metal dπ orbitals back-donate into the alkene's empty π* orbital.

You can see the consequences in the structure. The C–C bond lengthens from 133.7 pm in free ethene to ≈ 137.5 pm when coordinated, and the two carbons bend back, rehybridising towards sp^3, so the hydrogens tilt away from the metal. In the IR, ν(C=C) drops from ~1623 cm^{-1} in the free alkene to ~1516 cm^{-1} once it is coordinated.

The Pt–Cl bond trans to the ethene is significantly longer than the two cis Pt–Cl bonds — a structural signature of the strong trans influence of a π-acceptor ligand.

Conceptual Trick: Hapticity vs Denticity

Denticity = number of donor atoms coordinated to the metal

Hapticity (η) = number of contiguous atoms of one ligand directly bonded to the metal — conventionally applied to π-bonded ligands (η^1-alkyl, -carbene and -carbyne are the σ-bonded edge cases)

One η^2 entry students forget is the side-on σ-complex: an intact H_2 bound through its σ bond (η^2-H_2, Kubas 1984) and the agostic C–H that leans in toward a hungry metal both count as η^2. CSIR-NET has asked the hapticity of the H_2 ligand directly — the answer is η^2.

KEY NOTE

Example: In $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$

Cp ligand is η^5, CO is monodentate, CH_3 is σ-donor

The Hapticity Catalogue: η^1 to η^8

Every organic ligand slots into one of eight hapticity families, and the catalogue below runs through all eight. Once the families are familiar, the hapticity of a ligand in an unfamiliar formula can simply be read off.

Hapticity	Typical ligands	Flagship examples
η^1 (monohapto)	alkyl R, acyl C(O)R, CO, CS, carbene $=CR_2$, carbyne $\equiv CR$	any σ-alkyl; M–CO complexes
η^2 (dihapto)	alkenes; alkynes (through one π system)	Zeise's salt $K[PtCl_3(\eta^2\text{-}C_2H_4)]$
η^3 (trihapto)	allyl C_3H_5 (π-allyl mode)	$(\eta^3\text{-}C_3H_5)Pd$ complexes in Tsuji–Trost chemistry
η^4 (tetrahapto)	butadiene, cyclobutadiene, COD, norbornadiene, cycloheptatriene as diene	$Ni(\eta^4\text{-}COD)_2$; $(\eta^4\text{-}C_4H_4)Fe(CO)_3$
η^5 (pentahapto)	cyclopentadienyl (the default Cp), cyclohexadienyl	ferrocene $(\eta^5\text{-}Cp)_2Fe$
η^6 (hexahapto)	benzene and arenes; cycloheptatriene	$(\eta^6\text{-}C_6H_6)_2Cr$; $(\eta^6\text{-}C_7H_8)Cr(CO)_3$
η^7 (heptahapto)	cycloheptatrienyl / tropylium-type ring	$[(\eta^7\text{-}C_7H_7)Mo(CO)_3]^+$
η^8 (octahapto)	cyclooctatetraene (COT)	uranocene $(\eta^8\text{-}COT)_2U$

- Do not confuse η with κ. Hapticity (η) counts contiguous atoms of one ligand engaging the metal through a π system; κ marks the individual donor atoms of a polydentate ligand — κ^2-N,N′-ethane-1,2-diamine grips through two nitrogens, whereas $\eta^2\text{-}C_2H_4$ engages two carbons of the same C=C bond. A ligand can be both: allyl is η^3 through the π system or κ^1 through one carbon.
- A ligand that changes its hapticity on demand is called a fluxional ligand: Cp slipping $\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$, the allyl flexing $\eta^3 \rightarrow \eta^1$. Either way, the rearrangement opens a coordination site without losing the ligand.

CSIR-NET POINTER

If a formula omits the hapticity (plain "Cp", plain "allyl"), assume the highest: Cp means η^5, allyl means η^3. Examiners build MCQ traps on exactly this default.

Important Examples

Compound	Structure Type	Notes
$Ni(CO)_4$	18 e^-, tetrahedral	Very toxic, volatile
$Fe(CO)_5$	18 e^-, trigonal bipyramidal	Photosensitive — photolysis releases CO (a route to $Fe(CO)_4$ fragments)
$(C_5H_5)_2Fe$ (Ferrocene)	Sandwich compound	Aromatic, stable
$(\eta^6\text{–}C_6H_6)Cr(CO)_3$	Arene complex	18 e^-, piano-stool geometry

Mind Map

```
Organometallic Compounds
├── Based on M–C Bond
│   ├── σ-Bonded: R–M
│   ├── π-Bonded: Alkenes, Arenes
│   └── Bridged: μ–CO, μ–CH₃
│
├── Ligand Types
│   ├── σ-donor: CH₃⁻, C₂H₅⁻
│   ├── π-acceptor: CO, CN⁻
│   └── π-donor: Cp, arene
└── Hapticity (η)
    ├── η¹: R–M
    ├── η²: C₂H₄–M
    ├── η⁵: Cp–M
    └── η⁶: C₆H₆–M
```

Shortcuts and Memory Aids

KEY NOTE

18-electron rule (valence-shell stability rule):

Total valence electrons (metal + ligands) = 18 → Stable complex

KEY NOTE

Cp ligand contributes 6 electrons

$(\eta^5\text{-}C_5H_5)^-$ is a 6 π-electron aromatic anion — ionic method: 6 e^- directly; covalent method: 5 e^- from the Cp• radical plus 1 e^- for the negative charge

KEY NOTE

CO contributes 2 electrons

(σ-donation + π-backbonding)

KEY NOTE

Quick Estimation Trick:

For transition-metal carbonyls — Group number of metal + (2 × number of CO ligands) = 18.

If satisfied, the complex is likely stable.

CSIR-NET Style Practice Questions

Q1. Which of the following complexes obey the 18-electron rule?

Options:

A. $Fe(CO)_5$

B. $Ni(CO)_4$

C. $Cr(CO)_6$

D. $Mn(CO)_5$

Answer: (A), (B) and (C)

Q2. What is the hapticity of the cyclopentadienyl ligand in ferrocene?

Options:

A. η^1

B. η^2

C. η^5

D. η^6

Answer: C (η^5)

Q3. Which of the following ligands is both σ-donor and π-acceptor?

Options:

A. CH_3^-

B. NH_3

C. CO

D. H_2O

Answer: C (CO)

Nomenclature of Organometallic Compounds

Naming follows the grammar of coordination nomenclature with two extra conventions: hapticity (η) for the number of contiguous ligand atoms bound to the metal, and μ for ligands that bridge two or more metals.

- Ligands are listed alphabetically, then the metal with its oxidation state in Roman numerals: $(\eta^5\text{-}C_5H_5)_2Fe$ is bis(η^5-cyclopentadienyl)iron(II).
- Formulas follow the usual convention: metal first, then the ligands in alphabetical order by symbol — the reverse of the naming order, where the ligands precede the metal. An older convention puts anionic ligands first in the formula, and both orderings appear in the literature and in exam options. Round brackets enclose polyatomic or organic ligand formulas, (CO), (C_5H_5) and (PPh_3) for instance, while simple ligands such as Cl^- or NH_3 are written bare.
- Hapticity is written η^n before the ligand name (η^2-ethene, η^5-cyclopentadienyl); bridging uses μ_n (μ-CO, μ_3-H).
- Anionic ligands keep their usual names (chloro, methyl, hydrido); neutral ones keep theirs (carbonyl, triphenylphosphane).

Worked examples

Formula	Systematic name	Counting note
$(\eta^5\text{-}C_5H_5)_2Fe$	bis(η^5-cyclopentadienyl)iron(II) — "ferrocene"	Fe(II) d^6 + 12 e^- (two Cp^-) = 18 e^-
$[Rh(CH_3)(PMe_3)_4]$	methyltetrakis(trimethylphosphine)rhodium(I)	Rh(I) d^8 + CH_3^- + 4 PMe_3 = 18 e^-
$[IrBr_2(CH_3)(CO)(PPh_3)_2]$	dibromocarbonylmethylbis(triphenylphosphine)iridium(III)	Ir(III) d^6; ligands supply 12 e^- = 18 e^-
$K[PtCl_3(\eta^2\text{-}C_2H_4)]$	potassium trichloro(η^2-ethene)platinate(II) — Zeise's salt	Pt(II) d^8 square planar, 16 e^-
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	tetracarbonylbis(η^5-cyclopentadienyl)diiron(I) — the all-terminal Fp dimer	each Fe: 18 e^- with an Fe–Fe bond

The bridged form of $Co_2(CO)_8$ shows the μ convention at work: di-μ-carbonyl-bis(tricarbonylcobalt(0))(Co–Co) — μ ligands are cited first, then the rest alphabetically, and the M–M bond is named in brackets at the end.

CSIR-NET POINTER
The marks for "write the IUPAC name" sit in three places: the η^n prefix, the alphabetical ligand order and the metal oxidation state. For a formula from the name, watch μ and η first.

CHAPTER 2

The 18-Electron Rule and Electron Counting

The 18-Electron Rule in Depth

Start from the octet rule you already know. In main-group $PbEt_4$, lead uses its four valence electrons for four σ bonds and attains an 8-electron closed shell. A hypothetical $PbEt_6$ would pile ten electrons around lead (4 from Pb + 6 from the ethyl groups), exceeding the octet — and lead, unlike a transition metal, has no low-lying valence orbitals to house the extra electrons. $PbEt_4$ is exactly octet-complete, which is why it, and never $PbEt_6$, served as the petrol anti-knock additive. The 18-electron rule is the same argument scaled up for transition metals: one s + three p + five d orbitals make nine valence orbitals, and 2 × 9 = 18 electrons close the shell, $(n-1)d^{10}ns^2np^6$.

> KEY NOTE
> Why 18 Electrons?

Eighteen is simply a full house — the transition metal's answer to the noble-gas shell.

Electron Count Method (2 Approaches)

Neutral Atom Method (Most CSIR-Friendly)

Count the valence electrons of the neutral metal atom.

Add electrons donated by each ligand.

Adjust for the overall charge: add one electron per unit of negative charge, subtract one per unit of positive charge.

Oxidation State Method (Less Used Here)

Calculate oxidation state first.

Use metal^{n+} electrons = Group number – oxidation state.

Add the ligand electrons (2 e^- per X- or L-type donor, 6 e^- per Cp^-, etc.).

> KEY NOTE
> Electron Contribution by Common Ligands

Ligand	e^- Donated	Notes
CO	2	σ-donor + π-acceptor
NO^+	2	Treated like CO
PR_3 (Phosphines)	2	Similar to CO
Cl^-, Br^-, I^-	2	σ-donors
Cp^- (η^5-$C_5H_5^-$)	6	5 π e^- + 1 σ e^-
C_2H_4 (η^2-alkene)	2	π-donor
CH_3^-, R^- (alkyls)	2	σ-donor (as R^-)
H^-	2	Like halides
NH_3, H_2O	2	Neutral σ-donors
Note	NO^+ counted here by the ionic method (2 e^-); the neutral count used elsewhere in this book is 3 e^-	

KEY NOTE
Examples: Electron Count

$Fe(CO)_5$

Fe = Group 8 → 8 e^-

5 CO = 5 × 2 = 10 e^-

Total = 18 e^- ✓

$Ni(CO)_4$

Ni = Group 10 → 10 e^-

4 CO = 4 × 2 = 8 e^-

Total = 18 e^- ✓

$(C_5H_5)_2Fe$ (Ferrocene)

Fe^{2+} (ionic method) = 8 − 2 = 6 e^-

2 Cp^- = 2 × 6 = 12 e^-

Total = 6 + 12 = 18 e^- ✓

→ The neutral method gives the same answer: Fe 8 e^- + 2 Cp• (5 e^- each) = 18 e^-

KEY NOTE
Exceptions to the 18-Electron Rule

Compound	Reason for Exception
$RhCl(PPh_3)_3$ (Wilkinson's catalyst)	16 e^- — late-metal square-planar d^8 complexes are commonly stable at 16 e^-
$V(CO)_6$ (17 e^-)	Electron-deficient
$TiCl_4$ (8 e^-; a coordination compound, shown for comparison)	Incomplete d-shell
$[V(CO)_6]^-$	18 e^- — one-electron reduction of 17 e^- $V(CO)_6$ closes the shell

KEY NOTE
Rule of thumb: the electron count helps predict stability, but it is not absolute — some stable species violate it, and some 17/16-electron species are perfectly isolable reactive intermediates.

The EAN Rule (Effective Atomic Number)

The EAN rule is Sidgwick's effective atomic number rule — exams phrase it exactly that way: reach a noble-gas configuration (36 for krypton, 54 for xenon) and the complex counts as satisfied.

The EAN rule is the older statement of the idea behind the 18-electron rule. Add the electrons remaining on the metal to the electrons donated by the ligands, and the sum should equal the atomic number of the next noble gas. That total is the effective atomic number of the metal.

EAN = (atomic number of the metal − its oxidation state) + electrons donated by the ligands

In modern language, a complex is electronically saturated when the metal's valence shell is filled to $(n-1)d^{10}$ ns^2 np^6. That means eighteen electrons spread over nine valence orbitals, one s plus three p plus five d, which is exactly the 18-electron rule.

Counting conventions for metal carbonyls:

- count the metal's valence electrons, then add one electron per unit of negative charge on the complex (or subtract one per positive charge);

- every terminal CO contributes 2 e^-;
- each bridging CO (μ-CO) contributes 1 e^- to each metal it joins;
- each M–M bond contributes 1 e^- to each metal.

Carbonyl	Counting (per metal)	EAN	Valence e^-	Remark
$Ti(CO)_6$	Ti(0): 4 + 12	34	16	not stable as a neutral species
$V(CO)_6$	V(0): 5 + 12	35	17	stable but paramagnetic (exception)
$[V(CO)_6]^-$	5 + 1 (charge) + 12	36	18	one-electron reduction closes the shell
$Cr(CO)_6$	6 + 12	36	18	stable, octahedral
$[Mn(CO)_5]^-$	7 + 1 + 10	36	18	stable anion
$Mn_2(CO)_{10}$	7 + 10 + 1 (Mn–Mn)	36	18	all CO terminal
$[Fe(CO)_4]^{2-}$	8 + 2 + 8	36	18	Collman's reagent
$Fe(CO)_5$	8 + 10	36	18	stable, trigonal bipyramidal
$Fe_2(CO)_9$	8 + 6 + 3 (μ-CO) + 1 (Fe–Fe)	36	18	three bridging CO (the Fe–Fe bond assumed here is debated; see the cluster chapter)
$[Co(CO)_4]^-$	9 + 1 + 8	36	18	nucleophilic anion
$Co_2(CO)_8$	9 + 6 + 2 (μ-CO) + 1 (Co–Co)	36	18	bridged form (solid state)
$Ni(CO)_4$	10 + 8	36	18	stable, tetrahedral

Neutral metals reaching EAN 36 (krypton) in this table belong to Groups 6–10 — the anionic $[V(CO)_6]^-$ is the Group 5 exception below. $Ti(CO)_6$ and $V(CO)_6$ fall short. $V(CO)_6$ is the famous 17-electron exception, and a one-electron reduction to $[V(CO)_6]^-$ restores the 18-electron count.

Limitations of the EAN / 18-Electron Rule

- Square-planar d^8 complexes of the late transition metals (Rh(I), Ir(I), Pd(II), Pt(II), Au(III)) are perfectly stable at 16 e^-.
- Many early transition-metal organometallics are stable with far fewer than 18 e^- — high-valent d^0 species such as Cp_2TiCl_2 are the standard example (its dialkyl Cp_2TiMe_2 likewise).
- Very bulky ligands can make an 18-electron count sterically impossible.
- Medium and large clusters are handled better by Wade-type skeletal-electron counting than by a per-metal EAN.

- The rule does not apply to organometallics of the main-group metals, lanthanides or actinides.
- Electron counting never tells you whether a CO is terminal or bridging — that needs structural or spectroscopic evidence.
- Counting is a stability guideline, not a law: 17- and 16-electron species are often exactly the reactive intermediates that make catalysis work.

Metal Carbonyl Complexes

A metal carbonyl is a complex in which CO binds a transition metal in a low oxidation state, usually zero. The standard examples sit just below, and the bonding that explains their behaviour follows in the next section.

Examples

Benchmark mononuclear carbonyls	
1	**$Fe(CO)_5$ —** trigonal bipyramidal (D_3h)
2	**$Ni(CO)_4$ —** tetrahedral (Td)
3	**$Cr(CO)_6$ —** octahedral (O_h)

Features

- Low oxidation state metals — most often zero
- Colourless, volatile and toxic
- Usually obey the 18-electron rule
- Show π-backbonding into the CO ligand

Mononuclear and Polynuclear Carbonyls

By nuclearity (the number of metal atoms per molecule) the carbonyls split into two families:

- Mononuclear: one metal atom per molecule — $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $V(CO)_6$, $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$.
- Polynuclear: two or more metal atoms per molecule — $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_6(CO)_{16}$.

Notice the pattern here, because it repeats across the whole table. Metals with an even atomic number, Cr, Fe and Ni, form mononuclear 18-electron carbonyls. Metals with an odd atomic number, Mn and Co, cannot reach 18 e^- with terminal COs alone, so they pair their

odd electrons into M–M bonds instead, which is how $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ come about — vanadium being the standing counter-example, $V(CO)_6$ tolerating 17 e^- as a stable monomer.

Physical Properties of Metal Carbonyls (Exam Favourites)

- Most mononuclear carbonyls are volatile liquids ($Ni(CO)_4$ boils at just 43 °C, $Fe(CO)_5$ at 103 °C) or sublimable solids like $Cr(CO)_6$, and they run colourless to pale yellow; as nuclearity climbs the colour deepens, from golden $Fe_2(CO)_9$ and orange $Co_2(CO)_8$ all the way to black $Rh_6(CO)_{16}$. Essentially insoluble in water, they nonetheless dissolve readily in benzene, ether, acetone and CCl_4. Nearly all are diamagnetic, the lone exception being $V(CO)_6$, the blue-black 17 e^- monomer; volatile as they are, they sublime under vacuum before they decompose.
- Thermal behaviour: carbonyls melt or decompose at low temperature and sublime under vacuum; $Ni(CO)_4$ decomposes on heating to 180–200 °C, which is the basis of the Mond process for refining nickel.
- Air sensitivity: $Co_2(CO)_8$ and $Fe_2(CO)_9$ are oxidised by air even at room temperature, whereas $Cr(CO)_6$ and $Mo(CO)_6$ have to be heated before they are attacked.
- Toxicity: $Ni(CO)_4$ is dangerously toxic even at trace levels — a standard laboratory-safety point.

Why Exactly 18? The Molecular-Orbital Justification

The 18-electron rule is not numerology — it follows from the number of bonding molecular orbitals a complex can build.

- In an octahedral complex, the six σ-donor interactions generate six σ-bonding MOs. Bring in π-acceptor ligands such as CO and the metal t_2g set becomes bonding too, through M→L π-backdonation, so three more join the tally. Nine bonding MOs in all, with room for 9 × 2 = 18 electrons.
- A square-planar complex builds four bonding and four non-bonding d-based MOs, so a 16-electron configuration is the natural closed shell there — and the d^8 metals of Groups 9–11, Rh(I), Ir(I), Pd(II), Pt(II) and Au(III), accordingly thrive at 16 e^-.
- Push the count beyond 18 and the extra electrons have nowhere to go but antibonding orbitals, so such complexes tend to lose an electron and behave as reducing agents. Fall short of 18 and bonding MOs are left unfilled, so those species grab electrons and act as oxidising agents.

Periodic position	Typical electron count	Examples
Early transition metals (Groups 3–5)	Usually fewer than 18 e^-	Sc, Ti, V; Y, Zr, Nb; La, Hf, Ta
Middle metals (Groups 6–8)	Usually 18 e^-	Cr, Mn, Fe; Mo, Tc, Ru; W, Re, Os
Late metals (Groups 9–10)	16 or 18 e^-	Co, Ni; Rh, Pd; Ir, Pt

TRICK

17-electron complexes are one electron short and tend to behave as oxidising agents; 19-electron complexes carry one electron too many and tend to act as reducing agents. Both are paramagnetic. This single line answers a recurring CSIR-NET multiple-choice pattern: "Which of the following is a strong reducing/oxidising agent?"

Donor-Pair vs Neutral-Atom Counting: A Side-by-Side Comparison

Feature	Donor-pair (ionic) method	Neutral-atom (covalent) method
Ligand picture	Ligands donate in pairs and may be charged (CO neutral 2 e^-; Cl^-, H^-, CH_3^- are 2 e^- donors)	Every ligand is treated as a neutral radical: Cl, H, CH_3 donate 1 e^-; CO and PR_3 donate 2 e^-
Metal contribution	Group number − oxidation state	All valence electrons of the neutral metal atom
Charge handling	Built into the oxidation-state assignment	Add/subtract electrons for the overall charge at the end
Advantage	Gives both the electron count and the oxidation state	The electron count is immediate — no formal charges needed
Disadvantage	Overestimates the charge separation on the metal	Overestimates the covalence; hides the oxidation state
Special cases	Cp^- = 6 e^- donor	η^5-Cp• = 5 e^-; delocalised fragments give 1 e^- per haptic carbon

NOTE

Both methods must give the same final electron count — always. If they disagree, you have mixed conventions somewhere (the classic ferrocene trap: Fe(0) + 2 × Cp^- "20 e^-" mixes the two models and is wrong).

NOTE

Electron counting is bookkeeping, not a bonding analysis. It predicts which totals recur and which structures are likely, but it cannot prove that a particular drawn bond exists — bridging ligands, delocalisation and multicentre bonding all sit outside the simple Lewis picture, and $Fe_2(CO)_9$ in Chapter 11 is the standing reminder. Use the count to anticipate; use the structural evidence to decide.

- So which method, when? The neutral (covalent) method suits low-valent complexes with unsaturated π-ligands, and it spares you the oxidation-state gymnastics. The oxidation-state method suits high-valent complexes with N-, O- and halide donors, and it is the method of choice whenever the metal's oxidation state changes across a reaction step, which is exactly what happens in catalytic cycles.

The Master Ligand Table — Electron Donation in Both Counting Methods

Ligand	Neutral/covalent count	Ionic count
CO (carbonyl), CS, PR_3, NR_3, isocyanide CNR	2	2
η^2-alkene, η^2-alkyne	2	2
Carbene, $=CR_2$	2	2
Carbyne, ≡CR	3	2 (as CR^+)
NO, linear	3	2 (as NO^+)
NO, bent	1	2 (as NO^-)
H, halide X, alkyl R, aryl, acyl C(O)R	1	2 (as anion)
Amide NR_2, alkoxide OR, thiolate SR, phosphide PR_2	1	2 (as anion)
η^1-allyl, η^1-Cp	1	2 (as anion)
η^3-allyl	3	4
η^3-Cp	3	4
η^5-Cp	5	6 (as Cp^-)
η^4-diene (butadiene, COD, norbornadiene)	4	4
η^4-cyclobutadiene	4	6 (as $C_4H_4^{2-}$)
η^6-arene (benzene)	6	6
η^6-cycloheptatriene	6	6
η^8-COT (cyclooctatetraene)	8	10 (as $C_8H_8^{2-}$)
η^7-cycloheptatrienyl (tropylium-type)	7	6 (as $C_7H_7^+$ tropylium)
μ-CO, μ-H, μ-alkyl (3c–2e bridges)	1 per metal	1 per metal
μ-X, μ-OR, μ-NR_2, μ-PR_2 (lone-pair bridges)	3 total (1 to one metal, 2 to the other)	2 per metal (4 total)
Bridging μ-alkyne	2 per metal	2 per metal
M–M bond	1 to each metal	1 to each metal

Isocyanides, RNC, bind through carbon just like CO and are made from alkyl halides with AgCN. They are stronger σ-donors but weaker π-acceptors than CO, so their ν(CN) sits 100–150 cm^{-1} above the ν(CO) of the corresponding carbonyl, and they stabilise higher oxidation states. Like CO they count as 2 e^- L-type ligands in both counting methods.

CSIR-NET POINTER
Two uses of this table: (1) count any complex in either method in seconds; (2) for charged complexes, finish the neutral count first and then subtract the positive charge / add the negative charge to the total — never adjust inside the ligand entries.

Worked Electron Counts: Both Methods, Side by Side

Electron counting is the most useful habit this subject teaches. A quick count tells you whether a complex is likely to be stable, whether a metal–metal bond must exist, and whether a ligand sits terminal or bridging. The two counting methods each have their partisans, and they always give the same final count; what you must never do is mix them inside a single calculation. The classic worked examples below are solved both ways, so cover a column and test yourself.

Complex	Ionic (oxidation-state) method	Neutral (covalent) method	Count
$HMn(CO)_5$	Mn(I) d^6: 6 + H^- (2) + 5 CO (10) = 18	Mn: 7 + H (1) + 5 CO (10) = 18	18 e^-
$(\eta^5\text{-}C_5H_5)_2Fe$ (ferrocene)	Fe(II) d^6: 6 + 2 Cp^- (12) = 18	Fe: 8 + 2 η^5-Cp (10) = 18	18 e^-
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$	Fe(II) d^6: 6 + Cp^- (6) + 2 CO (4) + Cl^- (2) = 18	Fe: 8 + η^5-Cp (5) + 2 CO (4) + Cl (1) = 18	18 e^-
$CH_3Mn(CO)_5$	Mn(I) d^6: 6 + CH_3^- (2) + 5 CO (10) = 18	Mn: 7 + CH_3 (1) + 5 CO (10) = 18	18 e^-
$(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)Mo(CO)_2$	Mo(II) d^4: 4 + η^3-allyl (4) + Cp^- (6) + 2 CO (4) = 18	Mo: 6 + η^3-allyl (3) + η^5-Cp (5) + 2 CO (4) = 18	18 e^-
$(\eta^3\text{-}C_3H_5)Co(CO)_3$	Co(I) d^8: 8 + η^3-allyl (4) + 3 CO (6) = 18	Co: 9 + η^3-allyl (3) + 3 CO (6) = 18	18 e^-
$(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2Ti$	Ti(IV) d^0: 0 + 2 η^5-Cp^- (12) + 2 η^1-Cp^- (4) = 16	Ti: 4 + 2 η^5-Cp (10) + 2 η^1-Cp (2) = 16	16 e^-
$V(CO)_6$	V(0) d^5: 5 + 6 CO (12) = 17	V: 5 + 6 CO (12) = 17	17 e^- — the famous exception

- Why do odd-electron fragments dimerise? Think back to the methyl radical. Two 7-electron CH_3• radicals pair their odd electrons into the C–C bond of ethane, and each

carbon completes its octet. Two 17-electron $Mn(CO)_5$ fragments do exactly the same, pairing their odd electrons into an Mn–Mn bond until each manganese reaches 18. Even-electron metals have no such problem: they simply bind the appropriate number of CO ligands, six for Cr, five for Fe, four for Ni.

- Count predicts shape. Once the electron count is settled, the coordination number fixes the geometry: 6 gives octahedral, 5 gives trigonal-bipyramidal or square-pyramidal, and 4 gives tetrahedral or square planar. Sketch these shapes instantly when a count demands them.

> **NOTE**
> Notice the Ti example: when one counting route feels awkward (η^1-Cp at 2 electrons ionic, 1 electron neutral), the other route often reads more naturally — the two methods are interchangeable sanity checks for each other.

More Famous Exceptions (Sterics at Work)

- $Pt(PCy_3)_2$ — 14 electrons, linear two-coordinate Pt(0): the crowding of two tricyclohexylphosphines is so severe that only two ligands fit; a textbook steric exception.
- $(\eta^5\text{-Cp})_2(\eta^1\text{-Cp})_2Ti$ — tetrakis(cyclopentadienyl)titanium: two rings bind η^5, but the remaining two are forced into η^1 slippage, leaving Ti a 16-electron centre. The molecule shows hapticity slippage being used as a way out of an electron-count corner.
- Take $(\eta^5\text{-Cp})Cr(CO)_2(PPh_3)$. It is a 17-electron monomer that resists dimerisation because the bulky phosphine blocks the Cr–Cr approach; replace PPh_3 by compact CO and the 18-electron dimer $[CpCr(CO)_3]_2$ forms readily. Steric bulk can lock an electron-count violation in place.
- Counting odd-electron metals, once more. $V(CO)_6$ (17 e^-) is reduced by sodium to $Na[V(CO)_6]$ (18 e^-). $CoCp_2$ (19 e^-) is oxidised to the 18 e^- cobaltocenium cation, and $NiCp_2$ (20 e^-) follows the same drift towards 18. Odd-electron species are electron-transfer reagents in disguise.

Practice Set: Solve for the Unknown

Use the 18-electron rule to find the missing number (answers follow).

- (a) $TcBr(CO)_n$ — find n. (b) $Na_2[Fe(CO)_n]$ — find n. (c) $[Mn(CO)_n]^-$ — find n.
- (d) $[Co(CO)_3]^z$ — find the charge z. (e) $[Ni(CO)_3(NO)]^z$ — find z (count linear NO as a 3 e^- neutral donor). (f) $[IrCl_2(CS)_2(PPh_3)_2H]^z$ — find z.
- (g) Identify the 3d metal M in the Fischer carbene $(CO)_5M{=}C(OMe)Ph$.

CSIR-NET POINTER — ANSWERS

- (a) n = 5 (Tc: 7 + 1 + 2n = 18).
- (b) n = 4 (Fe(−II): 8 + 2 + 2n = 18; the dianion $[Fe(CO)_4]^{2-}$ is Collman's reagent).
- (c) n = 5 (7 + 1 + 2n = 18).
- (d) z = −3 (neutral count 9 + 6 = 15, three electrons short, so a 3− charge supplies them).
- (e) z = +1 (10 + 6 + 3 − 1 = 18).
- (f) z = +2 (neutral count 9 + 2 + 4 + 4 + 1 = 20, so remove 2).
- (g) M = Cr, the Group 6 metal: 6 + 10 + 2 = 18 — the parent of all Fischer carbenes.

Problem Bank: Electron-Counting Classics (with Answers)

- P1. Verify that Cr in $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ obeys the 18-electron rule, but that V in $V(CO)_6$ does not.
- P2. Show that both $H_2Fe(CO)_4$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ contain 18-electron metal centres.
- P3. Show that $Fe(CO)_4(\eta^2\text{-}C_2H_4)$ and $HMn(CO)_4(PPh_3)$ are 18-electron species.
- P4. Show that $[Rh(PMe_3)_4]^+$ is a 16-electron centre, and comment on whether this "violation" is expected.
- P5. Using only the 18-electron rule, predict an M–M single bond in $M_2(CO)_{10}$ (M = Mn, Tc, Re).
- P6. For $[(\eta^5\text{-Cp})(CO)Fe(\mu\text{-}CO)]_2$, show that an Fe–Fe bond is expected — and state what assumption your count depends on.
- P7. Find the electron count and oxidation state of Pt in the anion of Zeise's salt, $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$.
- P8. Show that both $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ (cycloheptatriene) and $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]^+$ (tropylium) are 18-electron species.
- P9. Is $[Mo(CO)_7]$ likely to be stable?
- P10. Which of $Fe(CO)_5$, $[V(CO)_6]^{2-}$, $[Co(CO)_4]^-$, $[Mn(CO)_6]^+$ is the strongest reducing agent?

CSIR-NET POINTER — ANSWERS

- P1: Cr: 6 + 6 (η^6-arene) + 6 (3 CO) = 18 ✓. V: 6 + 12 = 17 — a genuinely 17-electron monomer, which is why $V(CO)_6$ compensates with fast associative substitution rather than a metal–metal bond.
- P2: $H_2Fe(CO)_4$: Fe(II) d^6 + 2×2 + 8 = 18. $[CpFe(CO)_2]^-$: Fe(0) d^8 + 6 + 4 = 18.
- P3: $Fe(CO)_4(C_2H_4)$: 8 + 8 + 2 = 18. $HMn(CO)_4(PPh_3)$: 7 + 1 + 8 + 2 = 18.
- P4: Rh(I) d^8: 8 + 8 = 16 — expected, square-planar d^8 complexes of Group 9 thrive at 16 e^-.
- P5: each M: 17 e^- → one M–M bond completes 18.
- P6: each Fe (covalent): 8 + 5 (Cp) + 2 (CO) + 2 (two μ-CO at 1 e^- each) = 17 → Fe–Fe bond expected; the count hinges on treating each bridging CO as a 1 e^- donor to each metal.
- P7: Pt(II) d^8 + 6 (3 Cl^-) + 2 (η^2-alkene) = 16 e^-.
- P8: η^6-C_7H_8: 6 + 6 + 6 = 18; η^7-$C_7H_7^+$: 6 + 6 + 6 = 18 (the tropylium cation is a 6 π-e aromatic donor).
- P9: No — 6 + 14 = 20 e^-, and seven-coordinate Mo(0) carbonyls are not realised.
- P10: $[V(CO)_6]^{2-}$ — it counts 5 + 12 + 2 = 19 e^-, and 19-electron species are strong reducing agents.

CHAPTER 3

A Field Guide to Organometallic Ligands

3.1 The Carbonyl Family and its Heavier Cousins

Carbon monoxide is the reference ligand of organometallic chemistry: a weak base, yet a superb ligand for low-oxidation-state metals because of its π-acceptor ability. Six variations on CO chemistry are regularly examined:

- A semibridging CO leans towards two metals without being symmetrically shared between them: it accepts backdonation mainly from one metal and donates to the other. Its ν(CO) falls between the terminal and the symmetrically bridging regions, which is how you spot one in an IR spectrum.
- The σ/π-bridging (asymmetric) carbonyl takes bridging to an extreme, donating its σ lone pair to one metal and its π density to a second. Overall it acts as a four-electron donor across the two metals.
- The oxygen end can also bind. In O-bonded (isocarbonyl) mode, CO attaches to a second metal or to a Lewis acid such as $AlCl_3$, giving a bent M–C–O–M′ link. Attaching the Lewis acid weakens and lengthens C–O and drops ν(CO) by roughly 100–200 cm^{-1}.
- The heavier analogues CS, CSe and CTe behave as σ-donors and π-acceptors much as CO does. Their π* orbitals sit lower in energy, so π-acceptor strength grows down the series CO < CS < CSe < CTe, and isostructural Ru complexes show progressively shorter Ru–C bonds for the same reason.
- Cyanide, CN^-, is isoelectronic with CO and a centuries-old ligand (Prussian blue). It is a stronger σ-donor and a much weaker π-acceptor than CO, but sits close to CO in the spectrochemical series.
- Isocyanides (RNC), isoelectronic with CO and N_2, are stronger σ-donors and weaker π-acceptors than CO, so ν(CN) actually rises on coordination — the classic MCQ inversion of the CO trend.

CSIR-NET POINTER
Order of π-acceptor strength among CO-like ligands: CTe > CSe > CS > CO > CN^- (the isoelectronic set); among the phosphines, PF_3 is the closest mimic of CO.

3.2 Phosphines: The Tunable Ligand

Phosphines, PR_3, contain no M–C bond, yet you cannot prise them apart from organometallic chemistry: nearly every classic catalyst, Wilkinson's, Vaska's, Grubbs's, is built on them. Like CO they are 2-electron σ-donors with π-acceptor character, except that the acceptor orbitals are the P–R σ* combinations.

- Substituent control: electron-donating R groups (alkyl) make the phosphine a strong σ-donor; electron-withdrawing groups make it a better π-acceptor. The resulting π-acceptor order is $PF_3 > P(OR)_3 > PPh_3 > PMe_3 > P(t\text{-}Bu)_3$.
- Steric control is measured by the Tolman cone angle, the angle of the cone swept by the substituents around the metal. Three benchmarks are worth memorising: $PCl_3 \approx 124°$, $PPh_3 \approx 145°$, $P(t\text{-}Bu)_3 \approx 182°$. With bulky phosphines, ligand dissociation and reductive elimination speed up, whereas small phosphines allow tight binding and high coordination numbers.

How wide a monodentate phosphine spreads is measured by the cone angle; the P–M–P corner a chelating diphosphine forces on the metal is the bite angle (dppe ≈ 85°, dppf ≈ 99°, wide-bite Xantphos ≈ 111°). That angle then steers square-planar versus trigonal-bipyramidal geometry and, with it, linear versus branched selectivity in hydroformylation. "Cone angle or bite angle — which ligand property?" is a standard one-mark pair.

- Electronic tuning — the Tolman electronic parameter (TEP): measured through the ν(CO) of $Ni(CO)_3L$; a more basic phosphine pushes electron density onto the metal, raises backdonation and lowers ν(CO).

> **TRICK**
> Remember the pairing: bulky ligands favour dissociation, reductive elimination and open sites (catalysis); small, strongly donating ligands favour oxidative addition and tight binding. Exam questions on "which ligand speeds up which step" are answered by this one line.

3.3 Hydride and Dihydrogen Complexes

A hydride ligand, H^-, bonds through the hydrogen 1s orbital, so the M–H interaction is necessarily a σ interaction. In electron counting, hydride is a 2 e^- donor by the ionic method and a 1 e^- neutral donor by the covalent method.

- Preparation: oxidative addition of H_2 to a low-valent complex; protonation of an anion at the metal; reduction with $NaBH_4$ or $LiAlH_4$.
- Homoleptic hydrides exist: $[ReH_9]^{2-}$ is the textbook nine-coordinate example — a tricapped trigonal prism.

- The breakthrough came in 1984, when Kubas characterised $W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)$ (with Mo analogues), the first complexes carrying an intact, side-on H_2 ligand. The σ(H–H) orbital donates into an empty metal orbital while the metal back-donates into the H_2 σ* orbital, a genuine three-centre two-electron interaction and exactly the Dewar–Chatt picture transplanted from alkenes.
- Coordinated H_2 shows H–H distances of 82–90 pm, stretched from 74.14 pm in free H_2. If the metal is too electron-rich, backdonation into σ* ruptures the bond and a dihydride forms instead.

> **CSIR-NET POINTER**
> Classic viva/MCQ: $Mo(CO)_3(P^iPr_3)_2$ keeps H_2 intact because CO ligands drain electron density from the metal; in a phosphine-rich complex such as $MoH_2(CO)(Et_2PC_2H_4PEt_2)_2$ the electron-rich metal back-donates so strongly into σ*(H–H) that the bond breaks — two separate hydrides result. Stabilising a dihydrogen complex therefore calls for electron-poor metal centres and strong π-acceptor co-ligands (CO, NO).

Proving that the H_2 stayed intact comes down to two numbers. The $^1H–^2D$ coupling of an intact $\eta^2\text{-}H_2$ ligand is tiny ($J \approx 1–2$ Hz), because the two hydrogens never exchange sites; a classical dihydride, with H and D in separate positions, shows $J(H–D) \geq 30$ Hz. The $\eta^2\text{-}H_2$ protons also sit far upfield ($\delta \approx -5$ to -25), extreme even by hydride standards. Both facts are recurring NET/GATE questions.

3.4 Dinitrogen Complexes

N_2 is isoelectronic with CO, and for decades chemists hunted a "dinitrogen carbonyl analogue". The breakthrough came unexpectedly in 1965, when Allen and Senoff isolated $[Ru(NH_3)_5(N_2)]^{2+}$ from the reaction of ruthenium salts with hydrazine. Then in 1967 $[CoH(N_2)(PPh_3)_3]$ became the first complex made directly from N_2 gas.

- N_2 is a weaker σ-donor and a weaker π-acceptor than CO — $M–N_2$ bonds are correspondingly weak and ν(N–N) (≈ 1900–2150 cm^{-1} in complexes) shifts only modestly from free N_2 (2331 cm^{-1}).
- Binding is almost always terminal and end-on ($\eta^1\text{-}N_2$), through one nitrogen atom, exactly analogous to terminal CO.

Binding is almost always terminal and end-on, but know the alternatives for completeness: side-on $\eta^2\text{-}N_2$ (electron-rich, early metals) and bridging $\mu\text{-}\eta^1\text{:}\eta^1$ between two metals — the mode that comes closest to activating N_2 for cleavage.

- How are they made? Mostly by displacing H_2 from polyhydrides under N_2 pressure, $[MH_n(PR_3)_n] + N_2 \rightarrow [MH_{n-2}(N_2)(PR_3)_n] + H_2$, a reaction that models the first step of

nitrogenase action (the enzymatic reaction is competitively inhibited by H_2, consistent with this equilibrium). Hydrazine routes also work, as does conversion of coordinated NO into N_2, as in $[Fe(CN)_5NO]^{2-} + N_2H_4 \rightarrow [Fe(CN)_5(N_2)]^{2-}$ (hydrazine oxidation by-products omitted).

CSIR-NET POINTER
Why does N_2 bind so much more weakly than CO? Its HOMO is lower in energy (poorer donor) and its π^* is higher (poorer acceptor). This one comparison — donor/acceptor ability of N_2 vs CO — is a recurring CSIR-NET conceptual question.

3.5 Nitrosyl (NO) Complexes

NO is the other great π-acceptor. Unlike CO, it binds in two geometries that differ by two electrons of bookkeeping.

Mode	Electron counting (ionic)	Electron counting (covalent)	Geometry at N	IR ν(N–O)
Linear M–N–O	NO^+, a 2 e^- donor	3 e^- donor	sp, linear	1600–1900 cm^{-1}
Bent M–N–O	NO^-, a 2 e^- donor	1 e^- donor	sp^2, bent (~120°)	1525–1690 cm^{-1}

- NO^+ is isoelectronic with CO, so linear NO is its close cousin; $Cr(NO)_4$, tetrahedral and isoelectronic with $Ni(CO)_4$, is the classic example of a homoleptic nitrosyl.
- Bent NO is formally NO^- with the lone pair on nitrogen sp^2-hybridised; both modes can even coexist in one complex. Bridging NO is counted as a 3 e^- neutral donor.
- Sodium nitroprusside, $[Fe(CN)_5(NO)]^{2-}$, releases NO in vivo and is used as a vasodilator — the therapeutic effect comes from the ligand itself.
- The heavier analogue NS (thionitrosyl) also binds in linear, bent and bridging modes. Because more negative charge concentrates on N in NS, it is a stronger σ-donor and a weaker π-acceptor than NO. Selenonitrosyl (NSe) complexes remain extremely rare.

WATCH OUT
Do not assign linear/bent NO from IR alone — the two ranges overlap and crystal packing can bend an essentially linear M–N–O. Structural (X-ray) data decide. For counting questions, remember: linear = NO^+ (2 e^- ionic) and bent = NO^- (2 e^- ionic); by the covalent model, 3 e^- and 1 e^- respectively.

Structural and Spectroscopic Fingerprints of Nitrosyls

When IR cannot settle linear versus bent, structural data can: the M–N bond of a bent nitrosyl is longer than that of a linear one, since the bent form manages only σ bonding while the linear form does σ + π. $[ClRu(PPh_3)_2(lin\text{-}NO)(bent\text{-}NO)]^+$ carries both modes on one metal, and its M–N distances are 173.8 pm (linear) and 185.9 pm (bent) while the N–O lengths are nearly identical, 116.2 and 117.0 pm. For reference, N–O distances in free NO^+, NO and NO^- are 106, 115 and 120 pm, so a coordinated nitrosyl always sits between bond orders 2 and 3. Complexes carrying both modes at once are known, e.g. $Cl(PPh_3)_2Ir(lin\text{-}NO)(bent\text{-}NO)$.

A few IR numbers earn their keep in the exam hall: free NO ≈ 1876 cm^{-1}, free NO^+ ≈ 2377 cm^{-1}, and terminal M–NO spread over 1900–1500 cm^{-1}. Bridging NO exists too, exactly like bridging CO. $NaBH_4$ reduction of $CpCr(NO)_2Cl$ gives $[CpCr(\mu\text{-}NO)(NO)]_2$, with terminal ν(NO) ≈ 1672 cm^{-1} and bridging ν(NO) ≈ 1505 cm^{-1}.

- Some complexes interconvert the two forms in solution, where L is a neutral 2 e^- donor, the diphosphine or diarsine of such complexes. The equilibrium $CoL_2Cl_2(lin\text{-}NO) \rightleftharpoons CoL_2Cl_2(bent\text{-}NO)$ swaps an 18-electron Co(I) species for a 16-electron Co(III) one, with ν(NO) ≈ 1750 cm^{-1} (linear) and 1650 cm^{-1} (bent). Because those values sit close enough to overlap, ν(NO) alone is not a foolproof diagnostic.

The 3CO = 2NO Substitution Rule

In electron-counting terms two linear NO ligands (3 e^- each, covalent model) exactly replace three CO ligands (2 e^- each). Nitrosyls therefore substitute carbonyls in fixed ratios:

$$\mathbf{Co_2(CO)_8 + 2\ NO \rightarrow 2\ Co(CO)_3(NO) + 2\ CO}$$

$$\mathbf{Fe_2(CO)_9 + 4\ NO \rightarrow 2\ Fe(CO)_2(NO)_2 + 5\ CO}$$

$$\mathbf{Mn_2(CO)_{10} + 2\ NO \rightarrow 2\ Mn(CO)_4(NO) + 2\ CO}$$

- Under forcing photolysis, every CO can be replaced: $Cr(CO)_6$ + 4 NO → $Cr(NO)_4$ (all four NO linear) + 6 CO — the tetrahedral nitrosyl isoelectronic with $Ni(CO)_4$.
- The very first bent nitrosyl to be structurally characterised came from Vaska's complex: $Ir(PPh_3)_2(CO)Cl + NO^+BF_4^- \rightarrow [Ir(PPh_3)_2(CO)(bent\text{-}NO)Cl]^+$ — a square-pyramidal cation with a bent Ir–N–O link.

CSIR-NET POINTER

The neatest demonstration of NO's electronic flexibility: $[Co(diars)_2(lin\text{-}NO)]^{2+} + SCN^- \rightarrow [Co(diars)_2(NCS)(bent\text{-}NO)]^+$. Adding a 2 e^- ligand to an 18 e^- complex would give a forbidden 20-electron species — so instead the linear (3 e^-) NO folds to bent (1 e^-), releasing exactly two electrons of capacity, the metal formally climbs from Co(I) to Co(III), and BOTH complexes count 18 electrons throughout. That is the whole trick of nitrosyl "non-innocence" in one equation.

- Because NO is non-innocent, the oxidation state and d^n count of a nitrosyl are ambiguous. The Enemark–Feltham number $\{MNO\}^n$ — metal d electrons plus the π* electrons of NO — sidesteps the problem: $[Fe(CN)_5(NO)]^{2-}$ is $\{FeNO\}^6$ and linear. The EF number comes out the same whichever way you write the NO. That is the whole point of the notation. Adding electrons to the MNO unit raises n; nitrosyls with $n \leq 6$ are usually linear, $n = 7$ intermediate, $n \geq 8$ bent. Modern papers classify nitrosyls this way.

3.6 Dioxygen Complexes

Oxygen is both a ligand and a reagent in transition-metal chemistry; respiration, corrosion and every aerobic oxidation run through metal–dioxygen intermediates. MO theory explains why free O_2 is a paramagnetic triplet: its two highest-energy electrons occupy separate π* orbitals. Light can promote it to the reactive singlet state, and on a metal its reduction level depends on how many electrons the metal pushes in.

Species	Bond order	O–O distance	Magnetic behaviour
O_2 (dioxygen, neutral)	2	121 pm	Paramagnetic (triplet)
O_2^- (superoxide, 1 e^- added)	1.5	~133 pm	Paramagnetic
O_2^{2-} (peroxide, 2 e^- added)	1	~149 pm	Diamagnetic

- Binding modes: end-on η^1 (superoxo), side-on η^2 (peroxo), and the bridging modes $\mu\text{-}\eta^1{:}\eta^1$ (end-on across two metals) and $\mu\text{-}\eta^2{:}\eta^2$ (side-on peroxo bridging both metals of a dinuclear centre).
- Vaska's complex binds O_2 reversibly as a side-on peroxo Ir(III) adduct and releases it again on heating. Formally an oxidative addition, though an unusual one because O_2 has no σ bond to break, it was the first example of reversible O_2 binding at a transition-metal complex, an in-vitro oxygen carrier. In haemoglobin and myoglobin, O_2 binds end-on to the heme Fe(II). Haemocyanin does it differently: the O_2 bridges the two copper centres as a $\mu\text{-}\eta^2{:}\eta^2$ peroxo, oxidising them from Cu(I) to Cu(II), and that peroxo-to-Cu(II) charge transfer is what turns the colourless deoxy form blue.

CSIR-NET POINTER
Superoxide vs peroxo in one line each: superxo — longer O–O, paramagnetic, one electron transferred; peroxo — longer still, diamagnetic, two electrons transferred. ν(O–O) falls and O–O length rises in the order $O_2 > O_2^- > O_2^{2-}$.

NOTE
The full bioinorganic story of O_2 transport (Bohr effect, cytochromes, Fe–S proteins) belongs to bioinorganic chemistry, outside this book's organometallic scope — but the binding modes above are regularly examined in inorganic papers.

3.7 Alkyl, Alkenyl, Alkynyl and Aryl Ligands (X-type σ-Ligands)

These are the classical organometallic fragments: a carbon atom bonded to the metal by a normal 2c–2e σ bond. In electron counting they are X-type, 2 e^- donors as R^- (ionic) and 1 e^- donors as R• (covalent).

- M–C bonds are polarised M(δ+)–C(δ−): the more electropositive the metal, the more carbanionic (and reactive) the alkyl. sp- and sp^2-hybridised carbons (alkynyl, aryl) are the least nucleophilic.
- Transition-metal alkyls decompose mainly by β-hydride elimination and reductive elimination (both are covered in Chapter 8) — so stable alkyls either lack β-hydrogens (methyl, neopentyl, benzyl, CH_2SiMe_3) or are kinetically shielded by bulky ligands.
- Homoleptic alkyls are rare: $Ti(CH_3)_4$ decomposes near −40 °C, whereas 6-coordinate $W(CH_3)_6$, protected by strong W–C bonds (it adopts a distorted trigonal prism rather than the expected octahedron), melts at ~30 °C and survives briefly at room temperature, and $Cr[CH_2Si(CH_3)_3]_4$ is a stable four-coordinate example — kinetic and steric protection, not the 18-electron rule, is what separates the survivors.

3.8 Alkene Complexes: the Dewar–Chatt–Duncanson Model

An alkene binds a metal through two synergic donations. Its filled π orbital gives electron density to an empty metal dσ orbital, and a filled metal dπ orbital back-donates into the alkene π* orbital. A d^0 metal has no d electrons to back-donate, and simple alkene complexes of d^0 metals are therefore not observed.

- The stronger the backdonation, the longer the C=C becomes and the more the two carbons rehybridise towards sp^3, bending the substituents away from the metal (Zeise's salt: ≈ 137.5 pm vs 133.7 pm free).
- Strained alkenes (cyclopropene, norbornene) bind unusually tightly — coordination releases some of their strain energy.
- Umpolung, the reversal of reactivity, matters here. Free alkenes are electron-rich and attacked by electrophiles; once coordinated to a metal, especially an electron-poor one,

they turn electron-poor instead and are attacked by nucleophiles. The Wacker process and many C–C coupling reactions depend on exactly this inversion.

3.9 Alkyne Complexes

- An alkyne has two mutually perpendicular π systems, so it can act either as a 2 e^- donor, one π bond used, like an alkene, or as a 4 e^- donor with both π systems donating. The second, side-on donation is weaker, and it gives the complex a "metallacyclopropene" character in which the alkyne is formally a dianion.
- Consequences: coordinated C≡C distances stretch from about 120 pm (free) to 124–135 pm, and the R–C–C–R unit bends away from linearity — the stronger the donation, the more the coordinated alkyne behaves like an alkene (its C≡C bond order drops towards two).
- Alkynes also bridge two metals as 2 e^- donors to each, an arrangement describable as a 1,2-dimetallatetrahedrane. Terminal alkynes rearrange on some metals to vinylidene (=C=CHR) complexes. And alkyne cyclotrimerisation on CpCo-type fragments remains a classic route to substituted benzenes.

3.10 Allyl Complexes

- The allyl ligand, $C_3H_5^-$, switches between η^1 and η^3 modes: η^1-allyl is an X-type ligand that behaves exactly like an alkyl; η^3-allyl is an LX-type 4 e^- donor (ionic; 3 e^- covalent).
- The three allyl π-MOs map neatly onto metal orbitals. ψ_1 (bonding, filled) donates σ-fashion into dz^2, ψ_2 (nonbonding, filled) donates π-fashion into dxz, and ψ_3 (empty, antibonding) accepts backdonation from dyz. Both terminal carbons interact identically, so the η^3 geometry comes out symmetrical.
- $\eta^3 \rightleftharpoons \eta^1$ slippage is the ligand's way of "parking" one double bond to free a coordination site, and it is the signature step of allyl chemistry in catalysis (e.g., Tsuji–Trost allylic substitution).

3.11 Diene and Polyene Ligands

- Chelating dienes bind two C=C bonds at once and gain the extra stability of the chelate effect. bis(η^4-cycloocta-1,5-diene)nickel(0), $Ni(cod)_2$, is far more stable than tris(ethene)nickel(0), $Ni(C_2H_4)_3$ — little wonder, then, that cod and nbd (norbornadiene) serve as the standard "placeholder" ligands in synthesis.

- η^4-butadiene: both filled MOs donate (one σ-like, one π-like) and the π* accepts backdonation; the free diene's s-cis conformation is locked on the metal.
- Cyclobutadiene, antiaromatic and unisolable when free, becomes a stable η^4 ligand — coordination gives the ring its 6π aromatic electron count. This "aromaticity by coordination" is a favourite exam concept.
- Cyclooctatetraene (COT) usually binds η^4 (like a diene) but can be persuaded into full η^8 binding with f-block and early metals.

η^8-COT's flagship is uranocene, $U(\eta^8\text{-}C_8H_8)_2$, the f-block sandwich — the answer examiners expect when η^8 appears.

- The MO view of η^4-butadiene runs on three channels: ψ_1 (fully bonding) donates σ-fashion to the metal, ψ_2 (one node) donates π-fashion, and the empty ψ_3 accepts backdonation, a Dewar–Chatt-like interaction with one extra channel. A further δ-type interaction between a metal d orbital and ψ_4 has been proposed on symmetry grounds, but it has no experimental support. A symmetry-allowed interaction, though, is not necessarily a significant one.

3.12 Cyclopentadienyl and the Metallocenes

- Cp^-, $C_5H_5^-$, is the second most important ligand in organometallic chemistry after CO. It is an aromatic 6 π-electron anion, a 6 e^- donor in the ionic model (5 e^- covalent), and it prefers η^5 binding though it can slip to η^1 and η^3 when the metal needs it to.
- Metallocenes $(\eta^5\text{-}C_5H_5)_2M$ are prepared from metal salts plus NaC_5H_5 (or Cp derivatives). Ferrocene (Fe, 18 e^-) is the stable archetype. Cobaltocene (19 e^-) and nickelocene (20 e^-) push their extra electrons into weakly antibonding orbitals, so their M–C distances grow and their M–Cp bond enthalpies drop; their chemistry is accordingly dominated by reactions that restore 18 electrons. Cobaltocene, itself a standard one-electron reducing agent, oxidises readily to the cobaltocenium cation, while nickelocene accepts ligands after ring slippage.
- Substituted Cp ligands pull their weight too. Cp* ($C_5Me_5^-$) is more electron-rich, more donating and bulkier than Cp, the standard tool for stabilising reactive fragments. Bent metallocenes (Cp_2MX_n, e.g., Cp_2TiCl_2) hold their two rings tilted, and they are the 16 e^- engines of Ziegler–Natta-type polymerisation.

CSIR-NET POINTER

Exotic sandwich facts worth one mark each: decamethyldizincocene, $(\eta^5\text{-}C_5Me_5)_2Zn_2$, is the first stable molecule with a Zn–Zn bond and zinc(I); and "inverse sandwich" complexes exist with a π-ligand in the middle and metals outside.

3.13 Arene Complexes

- Benzene is a neutral L_3-type 6 e^- donor in its common η^6 mode, with $(\eta^6\text{-}C_6H_6)_2Cr$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ as the classic examples. Arenes donate more strongly than CO, in fact: a single arene out-donates three COs, and the IR proves it, with ν(CO) running lower in arene carbonyls than in the homoleptic carbonyls.
- Ring slippage: $\eta^6 \rightarrow \eta^4 \rightarrow \eta^2$ "slipping" generates an open site on the metal without full dissociation — a key trick in arene-complex catalysis (and a parallel to $\eta^3 \rightleftharpoons \eta^1$ allyl slippage).
- η^4-arenes come out bent and non-aromatic. η^2-arene binding dearomatises just one double bond, so η^2-benzene behaves like a simple alkene (and η^2-furan like a vinyl ether); η^4-binding turns the arene into a diene donor. With polycyclic aromatics, binding settles wherever the free portion of the ligand keeps the maximum remaining aromaticity.
- Coordination also makes arenes better electrophiles, because an electron-poor metal enables nucleophilic aromatic substitution that the free arene would never undergo. One caveat, though: aromatic heterocycles such as pyridine usually bind through the N lone pair rather than the π system.

3.14 Carbene Complexes: Fischer vs Schrock

A carbene complex contains an M=C double bond. Free $:CH_2$ has only six electrons on carbon, and it can exist as a singlet (lone pair plus empty p orbital) or a triplet (two unpaired electrons). The two families of carbene complexes descend from these two states: Fischer carbenes from the singlet, Schrock carbenes from the triplet.

Property	Fischer carbene	Schrock carbene (alkylidene)
First made	1964, E. O. Fischer — $(CO)_5W{=}C(OMe)Ph$	several years later, R. R. Schrock
Metal and ligands	low oxidation state, late metal, π-acceptor co-ligands (CO)	high oxidation state, early metal (Ti, Ta, Mo, W), σ-donor co-ligands
Substituents on carbene C	a heteroatom (OMe, NR_2, SR) or aryl	only C and H substituents
Carbene carbon	electrophilic	nucleophilic
Bonding picture	σ-donation from a singlet carbene + M→C π-backdonation	covalent sharing from a triplet-like fragment
Typical chemistry	attacked by nucleophiles at Cα; substitutions at the heteroatom	alkene metathesis (Schrock and Grubbs catalysts), olefination

- The classic Fischer-carbene synthesis goes in two steps. PhLi attacks a CO of $Cr(CO)_6$ to give the acylmetallate $[PhC(O)Cr(CO)_5]^-$, and methylation with MeI or $Me_3O^+BF_4^-$ then gives $(CO)_5Cr{=}C(OMe)Ph$. X-ray diffraction settles the structure: the Cr=C distance of 204 pm sits well below a normal Cr–C single bond at ~220 pm, which is the double-bond evidence.
- The heteroatom stabilises the carbene by delocalising the π pair over M=C–O — a three-atom π system. That delocalisation is what makes $Cr(CO)_5[C(OCH_3)C_6H_5]$ far more stable than the heteroatom-free analogue.
- N-heterocyclic carbenes (NHCs) are the modern third family: strong σ-donors with negligible π-acceptance, they push phosphines out of many catalysts (the "second-generation" Grubbs catalyst).
- A note on oxidation states, because this trips people up. Count the M=C carbon as a neutral 2-electron donor, Fischer style, and you get one answer; count it as a dianionic alkylidene, Schrock style, and the oxidation state comes out two higher. Both conventions appear in the literature, so always check which one a question is using.

CSIR-NET POINTER
The question usually reads: "Which of the following is TRUE for a Fischer carbene?" Expect — low oxidation state metal, heteroatom substituent, electrophilic carbene carbon, π-acceptor co-ligands. Every one of those four flags the Fischer camp; invert them all for Schrock.

3.15 Carbyne, Carbide and Carbon-Chain Complexes

- Carbyne (alkylidyne) complexes carry an M≡C triple bond, formally analogous to alkynes. The first one, $(CO)_4ClCr{\equiv}CPh$, arose by treating the Fischer methoxycarbene with Lewis acids BX_3: the acid attacks the methoxy oxygen, CO departs, and the halide lands trans to the carbyne. The Cr≡C distance of 168 pm is dramatically shorter than the 204 pm of the parent carbene, and the M–C–R angle is essentially 180°.
- The bonding is straightforward: an sp lone pair on the carbyne carbon donates σ-fashion, and two carbon p orbitals accept two π donations. Hence the alkylidyne ligand counts as a 3 e^- donor in the covalent (neutral, CR•) model and a 6 e^- donor as CR^{3-} in the ionic model. (A Fischer-style convention also appears in the older literature, one that treats the ligand as cationic $:CR^+$, a 2 e^- donor putting the metal one oxidation state below the neutral $:CR_2$ model and four below the CR^{3-} ionic model; always check which one a question is using.)

- Carbynes catalyse alkyne metathesis through metallacyclobutadiene intermediates — the triple-bond analogue of the metathesis you met for alkenes.
- Carbide complexes hide a bare carbon atom at the metal — formally C^{4-} in the ionic picture, a neutral four-electron donor in cluster counting. Cumulene and polyyne bridges, C_n chains strung between two metals, are studied as molecular wires, since the HOMO–LUMO gap shrinks as the carbon chain lengthens.
- Carbon chains can act as ligands in their own right. Cumulenylidene complexes (M=C=C=···C:) carry cumulated double bonds, while polyynediyl (alternating C–C≡C–C) and polyenediyl bridges string two metals together through a conjugated carbon wire. Among the longest cumulenylidenes reported are the heptahexaenylidenes. As the chain lengthens the HOMO–LUMO gap narrows, just as it does in polyenes, and that narrowing is what makes these complexes candidates for one-dimensional molecular wires and nanoscale optical devices.
- Short 2- and 3-carbon chains have recently found roles as ligand backbones in catalysts: the same chain chemistry, put to practical use.

3.16 Agostic Interactions and σ-Complexes

- Sometimes a C–H bond of an already-attached ligand simply leans in and donates its σ electrons to the metal. Brookhart and Green coined the word in 1983, from the Greek agōstos, “to hold close to oneself”. It is a genuine three-centre two-electron M–H–C bond, and it donates 2 e^- to the metal count.
- Agostic bonds stabilise coordinatively unsaturated (14–16 e^-) species, and β-agostic arrangements are the waypoints of β-hydride elimination. Their tell-tale NMR signature is a strongly upfield-shifted ^{1}H resonance together with reduced ^1J(C–H) coupling.
- The same logic with an intact molecule instead of a tethered C–H gives σ-complexes: coordinated dihydrogen (Section 3.3) and even coordinated alkanes are σ-complexes — C–H σ donation in, σ* acceptance out.

NOTE
One idea ties this chapter together: every ligand family is a variation on two moves — donate a filled orbital to the metal, and accept backdonation into an empty one. CO, N_2, NO^+, PF_3, H_2, C–H and C=C all play the same duet with different partners.

PART

II

The Metal Carbonyl Story

Chapter 4 — Bonding in Metal Carbonyls

Chapter 5 — Preparation, Properties and Reactions of Metal Carbonyls

CHAPTER 4

Bonding in Metal Carbonyls

1. Nature of the M–CO Bond

No family in organometallic chemistry has been studied as thoroughly as the metal carbonyls. The M–CO bond is unlike anything in classical coordination chemistry, ν(CO) makes their IR spectra immediately diagnostic, and most of organometallic synthesis is built on them.

Dual Bonding Mode (Synergic Bonding)

CO binds transition metals through two mutually reinforcing interactions:

The two components of the synergic M–CO bond	
σ-Donation (C: → M)	the lone pair on the carbon of CO donates into an empty metal orbital
π-Backbonding (M → CO π*)	a filled metal dπ orbital donates back into the empty π* orbital of CO

These interactions are synergic: backbonding strengthens the M–CO bond but weakens the C≡O bond.

2. Molecular Orbital Description

The CO ligand's π* orbitals accept electron density from the metal:

- More electron-rich metals → greater backbonding → stronger M–CO bond
- This weakens the C≡O bond → lower ν(CO) in the IR spectrum

The CO Ligand through its Molecular Orbitals

CO is the archetypal σ-donor and π-acceptor, and its frontier orbitals explain why it binds through carbon and why the M–CO bond is so strong:

- The HOMO of CO (5σ) is concentrated on the carbon end and is weakly antibonding — σ donation through carbon is therefore highly effective.
- The LUMO of CO (2π*) lies unusually low in energy for so stable a molecule, so metal dπ → π* backdonation is strong.

Take the resonance view. The M–CO bond is a blend of M←C≡O, pure σ donation with C–O close to a triple bond, and M=C=O, carbene-like with strong π backdonation and C–O double-bond character. Greater backdonation shifts the balance towards M=C=O, so the M–C bond shortens and strengthens, the C–O bond lengthens and weakens, and ν(CO) falls.