





Fischer type carbene:

- middle to late transition metals
- low oxidation state
- π acceptor ligands at M (CO, NO)
- π donor substituents (OMe, NMe₂)





Structural features of Schrock type carbenes:

 $Cp_2Ta(=CH_2)(CH_3)$



The Ta= CH_2 bond is distinctly shorter than the Ta- CH_3 single bond!

Schrock type carbene:

- early transition metals
- high oxidation state
- ligands with strong σ , π donor capacity
- substituents with no π acceptor capacity (H, CR₃, SiR₃)





Let's compare carbenes of Fischer and Schrock type:



Fischer Carbenes	Schrock Alkylidenes
Nucleophillic attacks at carbon	Electrophillic attacks at carbon
atom of carbene (carbon is	atom of alkylidene (carbon is
electron deficient)	electron-rich)
Electrophillic attacks on metal center (metal is more electron-rich, often d ⁶ 18 e ⁻ system)	Nucleophillic attacks on metal center (metal is electron-deficient, usually d ² or d ⁰ 16 or 14 e ⁻ count)
Carbene is <u>stabilized</u> by	Alkylidene is <u>destabilized</u> by
heteroatom groups that can π -	heteroatom groups that can π -
bond to it. Likes NR ₂ , SR, OR, or	bond to it. Strongly prefers H or
Ph groups.	simple alkyl groups.
Later transition metals favored,	Early transition metals favored,
especially with d ⁶ counts (carbene	especially with d ⁰ centers
as neutral 2e ⁻ donor ligand)	(alkylidene as dianionic 4e ⁻ donor)

NMR data for carbenes:

¹³C resonance for carbenes occurs to low field: 200-350 ppm, ¹H resonance for M=CHR occurs at +10...+20 ppm

Compound	¹³ C, δ (nnm)	Class
Cp ₂ Ta(=CH ₂)(Me)	224	Schrock
(t-BuCH ₂) ₃ Ta(= <mark>C</mark> H(t-B	u) 250	Schrock
(OC) ₅ Cr(=CH(NMe ₂))	246	Fischer
(OC) ₅ Cr(=CPh(OMe))	351	Fischer
(OC) ₅ Cr(=CPh ₂)	399	Fischer

IR data: carbene complexes are characterized usually only through v_{CH} IR absorption ($v_{M=C}$ is seldom unambiguously identified)

Mo=CH₂ 3080 and 2945 cm⁻¹



Olefinic ligands

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First organometallic compound – Zeise salt, 1831



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K[PtCl_3(CH_2=CH_2)] H_2O
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Alkenes act as neutral 2e⁻ donors (per C=C double bond). Due to the presence of empty π^* antibonding orbitals, there is the possibility of some π -backbonding:

			$CH_2 = CH_2$	1.337
		Dewar-Chatt- Duncanson bonding	K[PtCl ₃ (CH ₂ =CH ₂)]	1.375
		model (1953)	Cp* ₂ Ti(CH ₂ =CH ₂)	1.438
σ -donation via the filled alkene π-system	π -back donation via the empty alkene π^* -system		CH ₃ —CH ₃	1.540

<u>IR-spectroscopy</u> in analysis of olefinic complexes

Electronic effects with alkenes can often be somewhat easily monitored using IRspectroscopy. The more π -backbonding, the *weaker* the C=C double bond and the *lower* the C=C stretching frequency in the IR-spectrum

The table shows a series of alkene compounds with differing amounts of σ -donation and π -backbonding

Ethylene Complex	ν _{c=c} (cm⁻¹)
Free Ethylene	1623
[Ag(H2C=CH2)2]+	1584
Fe(CO)4(H2C=CH2)	1551
[Re(CO)4(H2C=CH2)2]+	1539
[CpFe(CO)2(H2C=CH2)]+	1527
Pd2Cl4(H2C=CH2)2	1525
[PtCl3(H2C=CH2)]-	1516
CpMn(CO)2(H2C=CH2)	1508
Pt2Cl4(H2C=CH2)2	1506
CpRh(H2C=CH2)2	1493

<u>Factors</u> influence *thermodynamic stability* of olefinic complexes:

- 1) Electron-withdrawing groups on the alkene generally increase the strength of the metal-alkene bonding
- 2) In cases where *cis-trans* isomerism is possible, the more stable complex is almost always formed by the *cis*-alkene (steric factor)
- 3) Third-row metals form the strongest bonds and most stable complexes



Arene ligands



Arenes typically coordinate in an η^6 fashion and as such are **neutral 6 e- donors**, although they can adopt lower coordination modes (η^4 and η^2).



An interesting aspect of metal-arene complexes is that π -back donation plays a relatively important role in the bonding and chemistry.





Electron-withdrawing $Cr(CO)_3$ or $Mn(CO)_3$ fragments facilitate nucleophilic addition and substitution and other processes.

Sandwich bis-arene complexes





Bis-arene complexes are close to bis-cyclopentadiene complexes, but arene ligand is less tightly bonded to the metal center.



Cr-C₆H₆ bond energy is 40 kcal/mol

Fe-C₅H₅ bond energy is 52 kcal/mol

Ansa-metallocenes and metallocenophanes:

When two rings (Cp or arene) are bridged together we have new class of organometallic compounds – ansametallocenes. They have an application in the synthesis of stereoregular polymers, treating cancer and so on.



Carbonyl ligand

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Ludwig Mond, 1888

Examples of complexes: Fe(CO)₅, Ni(CO)₄, Co₂(CO)₈, Mn₂(CO)₁₀, Cr(CO)₆



powerful π -acceptor ligand!

excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

Standard Bonding Modes:



terminal mode 2e[−] neutral donor





 $\begin{array}{lll} \mu_2 - \textit{bridging mode} & \mu_3 - \textit{bridging mode} \\ 2e^- neutral donor & 3e^- r \end{array}$

μ₃− *bridging mode* 3e[−] neutral donor

Carbonyl IR Stretching Frequencies



The **position** of the carbonyl bands in the IR depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being π -backbonded to the CO.

The **number** (and intensity) of the carbonyl bands one observes depends on the number of CO ligands present and the symmetry of the metal complex.

Bonding Modes: As one goes from a terminal CO-bonding mode to μ_2 -bridging and finally μ_3 -bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.



The carbonyl region in the IR spectrum can be very distinctive and useful for help in assigning structures and for indicating the relative amount of electron density present on the metal:





Carbonyl NMR Shifts



Terminal carbonyl ligands generally gives rise to ¹³C NMR resonances in the region 160-230 ppm, the chemical shift (δ) being most significantly dependent on the metal center. In general, heavier metals cause shifts to the higher field. Bridging carbonyls typically resonate to lower field.

$$\begin{array}{c|c} & & & & 1^{3}C \text{ NMR shifts: } M = Fe & \delta = 211 \text{ ppm} \\ & & & M = Ru & \delta = 200 \text{ ppm} \\ & & & M = Os & \delta = 183 \text{ ppm} \end{array}$$

Bonding M-CO could be drawn as a set of resonance forms:

$$M^{-} \leftarrow C \equiv 0^{+} \leftrightarrow M \equiv C \equiv 0 \leftrightarrow {}^{+}M \equiv C = 0^{-}$$

X-Ray:

$$[Cllr(CO)_{5}]^{2+} \qquad d_{lr-C} = 2.02 \text{ Å} \qquad d_{lr-C} = 1.87 \text{ Å}$$
$$[(CO)_{2}lr(CS)(PPh_{3})_{2}]^{+} \qquad d_{C-S} = 1.51 \text{ Å}$$

II.b. Ligands with other atoms attached to metal (H, halogens, CO, phosphines)

Phosphorus(III) ligands

Examples:

Phosphines: PMe₃, PPh₃

 $H_2C - CH_2$ / $Ph_2P PPh_2$

M-P bond formation is close to M-(CO):







Phosphine ligands

excellent soft-donor ligands with a wide variety of easily adjusted steric and electronic factors

neutral 2e⁻ donor

But in compare with CO phosphines have more donor ability: $PMe_3 > PPh_3 > P(OMe)_3 > P(OPh)_3 > P(NR_2)_3 > CO \sim PF_3$



Tolman, 1977		cone angle θ
Phosphine/Phosphite	Cone angel	Ph ₃ P PPh ₃ Pd
PH ₃	87 ⁰	 PPh ₃
PF ₃	104 ⁰	Ph ₃ P PPh ₃ Pd
P(OMe) ₃	107 ⁰	Ph ₃ P PPh ₃
PMe ₃	118 ⁰	
PPh ₃	145 ⁰	P - Pd - P
P(mesytil) ₃	212 ⁰	

Structural features of phospine metal complexes

Some typical first row M-PR3 average bond distances:

Ti-P	2.6 Å
V-P	2.5 Å
Cr-P	2.4 Å
Ni-P	2.1 Å

NMR – ³¹P characteristics of phosphine complexes

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<sup>31</sup>P NMR shifts: + 245...-163 ppm
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0

 δ , ppm

-10

¹H-NMR scale:

+10

NMR – characterization of hydride complexes:

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Most hydride ligands show ¹H NMR signal in hydride region – from -3 to -25 ppm, although it could be find in a wider range – from +25 to -60 ppm. But it could not be a valid criteria of the "acidity" of metal-hydrogen bond

HCo(CO)₄ ¹H NMR
$$\delta = -10.7 \text{ ppm}$$

HCo(CO)₄ \leftrightarrow H⁺ + Co(CO)₄⁻
¹H-NMR scale:
+10 0 -10

Coupling constants – hydrides can couple with the atom, where this has $\frac{1}{2}$ spin:



with other hydride ligand (if they are not equivalent) ${}^{2}J_{HH}$ =1-10 Hz

with phosphorus atom (phosphines, phosphites) ²J_{HP}=15-30 Hz for *cis*-, 90-150 Hz for *trans*-orientation

with metal atom (Pt, Rh, W)

¹J_{PtH}=500-1500 Hz



Structural Features (X-ray, neutron diffraction)

Hydride is the smallest ligand and as a result, M-H distances are typically quite short: 1.8 to about 1.5 Å, depending on the metal.

Hydrides can be quite difficult to observe via X-ray diffraction (the most common technique used to determine structures) due to the very small number of electrons on the hydride vs. adjacent atoms, especially the metal. Since X-rays are scattered by electron density, not by atomic nuclei it is the M-H bonding electrons that are detected, so that X-ray methods systematically underestimate the true M-H internuclear distance by approximately 0.1 Å

Therefore, neutron diffraction studies are considered best for accurately locating and identifying hydrides on metal centers (proton itself scatters neutrons relatively efficiently), even so much larger crystals are usually needed for neutron work (1 mm³ vs. 0.01 m³)





Reactivity of hydride complexes



Halogen ligands (halide donors)



The halides are anionic donors that generally only donate 2e to a metal center. Due to their relatively high electronegativity they are not especially good σ -donor ligands. Although they can theoretically act as π -donor ligands, once again, the higher electronegativity limits them to simple 2e donor ligands.



Fluoride is generally NOT a good ligand except for very high oxidation state metal centers. It is too electronegative to donate much of its electron density.



When coordinating to a single metal center usually we regard halides as 2e donors. 4e can be more easily donated by I then by any other halide, even so exceptions are possible:



Coordinatively unsaturated metal halides often exist as insoluble polymers connected by bridging halides. $PdCl_2$ is a classic example. Ligands such as CH_3CN can displace the bridging halide to give the soluble square planar complex $(CH_3CN)_2PdCl_2$.







Alkoxides commonly act as bridging ligands for electropositive metals. To avoid formation of bridges, bulky alkoxides must be used. With high valent transition metals, π -donation becomes important.





Important information about bonding type gives M-O-C angle:



Usually in ethers (like Et2O) the C-O-C angle is about 110⁰

But in the metal-alkoxyde systems M-O-C angle is often approaching 120° or even 180°



An angle near 120 $^{\circ}$ suggests that the O is sp² hybridized and acting as a 4 electron donor.



An angle near 180 ° suggests that the O is sp hybridized and acting as a 6 electron donor. In this case the alkoxide can be considered to be isoelectronic with the Cp ligand.





For organic compounds: maximum 8 electrons on C:



For metal complexes: maximum 18 electrons on M:

S	d	p

Complexes with 18 e⁻ counts are referred to as <u>saturated</u>, because there are no empty low-lying orbitals to which another incoming ligand can coordinate. Complexes with less than 18e⁻ are called <u>unsaturated</u> and can electronically bind additional ligands NO⁺ (nitrosyl)



Neutral 2e- donors:PR3 (phosphines), CO (carbonyl), R2C=CR2 (alkenes),RC=CR (alkynes, can also donate 4 e), N=CR (nitriles)

Anionic 2e donors: CI (chloride), Br (bromide), I (iodide), CH3 (methyl), CR3 (alkyl), Ph (phenyl), H (hydride)

The following can also donate **4** e if needed, but initially count them as 2e donors (unless they are acting as bridging ligands):

OR (alkoxide), SR (thiolate), NR2 (amide), PR2 (phosphide)

Anionic 4e⁻donors: C3H5⁻ (allyl), O²⁻ (oxide), S2⁻ (sulfide), NR2⁻ (imide), CR2⁻ (alkylidene) and from the previous list: OR⁻ (alkoxide), SR⁻ (thiolate), NR2⁻ (amide), PR2⁻

Anionic 6e donors: Cp (cyclopentadienyl), O2 (oxide)



Electron Count Oxidation State Coordination Number

- Basic tools for understanding structure and reactivity.
- Doing them should be "automatic".
- Not always unambiguous ⇒ don't just follow the rules, understand them!



The basis of counting electrons

- Every element has a certain number of valence orbitals:
 - 1 (1s) for H
 - 4 (*n*s, $3 \times n$ p) for main group elements
 - 9 (*n*s, $3 \times n$ p, $5 \times (n-1)$ d) for transition metals





The basis of counting electrons

- Every orbital wants to be "used", i.e. contribute to binding an electron pair.
- Therefore, every element wants to be surrounded by 2/8/18 electrons.
- The strength of the preference for *electron-precise* structures depends on the position of the element in the periodic table.



The basis of counting electrons

- Too few electrons:
 - An empty orbital makes the compound very electrophilic,
 - i.e. susceptible to attack by nucleophiles.
- Too many electrons:
 - There are fewer covalent bonds than one would think (not enough orbitals available). An ionic model is required to explain part of the bonding. The "extra" bonds are relatively weak.
- Metal-centered (unshared) electron pairs: Metal orbitals are fairly high in energy. A metal atom with a lone pair is a strong σ-donor (nucleophile) and susceptible to electrophilic attack.



Use a localized (valence-bond) model to count electrons

H₂ H · · · H Every H has 2 e. OK

CH₄ H has 2 *e*, C 8. OK



C_2H_4

C has 8 e. OK

singlet CH₂

C has only 6 e, and an empty p_z orbital: extremely reactive ("singlet carbene"). Unstable. Sensitive to nucleophiles and electrophiles.

triplet CH₂

C has only 6 *e*, is a "biradical" and extremely reactive ("triplet carbene"), but not especially for nucleophiles or electrophiles.



:





CH_3^+

C has only 6 *e*, and an empty p_z orbital: extremely reactive. Unstable. Sensitive to h_{H}

 CH_3^-

C has 8 *e*, but a lone pair. Sensitive to electrophiles.



Cl-

CI has 8 *e*, 4 lone pairs. *OK* Somewhat sensitive to electrophiles.





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BH<sub>3</sub>
    B has only 6 e, not stable as monomer,
    forms B_2H_6:
B_2H_6
    B has 8 e, all H's 2 (including the bridging<sup>H</sup>
    H!). 2-electron-3-center bonds! OK
AICI<sub>3</sub>
    Al has only 6 e, not stable as monomer,
    forms Al<sub>2</sub>Cl<sub>6</sub>:
AI_2CI_6
    Al has 8 e, all Cl's too (including the
    bridging CI!). Regular
    2-electron-2-center bonds! OK
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$2 \text{ MeAICI}_2 \rightarrow \text{Me}_2\text{AI}_2\text{CI}_4$





PCI_5

P would have 10 *e*, but only has 4 valence orbitals, so it cannot form more than 4 "net" P-CI bonds. You can describe the bonding using ionic structures (hyperconjugation).

Easy dissociation in PCI_3 en CI_2 .



HF_2^- Write as FH·F⁻, mainly ion-dipole interaction.







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Exercises

Give electron count and oxidation state for the following compounds. Draw conclusions about their (in)stability.

Me ₂ Mg	$Pd(PMe_3)_4$	MeReO ₃
ZnCl ₄	$Pd(PMe_3)_3$	ZnMe ₄ ²⁻
Co(CO) ₄ -	Mn(CO) ₅ ⁻	Cr(CO) ₆
V(CO) ₆ -	V(CO) ₆	Zr(CO) ₆ ⁴⁺
PdCl(PMe ₃) ₃	RhCl ₂ (PMe ₃) ₂	OsO ₄ (pyridine)
Ni(PMe ₃)Cl ₄	Ni(PMe ₃)Cl ₃	$Ni(PMe_3)_2Cl_2$