# The TM-L bond

Group number		4	5	6	7	8	9	10	11
1st row	3d	Ti	V	Cr	Mn	Fe	Со	Ni	Cu
2 <sup>nd</sup> row	4d	Zr	Nb	Мо	Тс	Ru	Rh	Pd	Ag
3 <sup>rd</sup> row	5d	Hf	Та	W	Re	Os	lr	Pt	Au
Oxid. state	0	4	5	6	7	8	9	10	
	Ι	3	4	5	6	7	8	9	10
	II	2	3	4	5	6	7	8	9
	III	1	2	3	4	5	6	7	8
	IV	0	1	2	3	4	5	6	7

The assumption that the TM valence electrons (outer electrons) are all d electrons is a good approximation.

≻ d<sup>n</sup>

#### Formal Oxidation State:

Charge left on the metal atoms after all ligands have been removed in their normal closedshell configuration (with their electron pairs)

#### d<sup>n</sup> Configuration:

Difference between the d configuration of the metal at zero oxidation state and the formal oxidation state of the complex

#### Coordination Number (CN):

The number of ligands directly bonded to the metal atom.

#### Coordinative Unsaturation:

Empty coordination sites where another ligand can be accommodated. Important for catalysis !

<u>Total Electron Count:</u> d electrons from the metal + electrons from the ligands

## M-L Bond: Hapticity and Electron Count





# Common Ligands in Transition-Metal Complexes

Ligand	Charge	Metal-Ligand	Involved electrons
Alkyl, Hal, OR, H	-1	M—Alk M—Hal	2
Fischer carbene	0	M=CR <sub>2</sub>	2
NO <sup>+</sup> (linear)	+1	⊕ M=N=O	2
PR <sub>3</sub> , NR <sub>3</sub> , ROR, CO, RCN, C=C, RCOR	0	M—PR <sub>3</sub> M—	2
Imido (bent) oxo	-2	M=N R M=O	4
Schrock carbene	-2	M=CR <sub>2</sub>	4
η <sup>3</sup> -allyl	-1	M 	4

# Common Ligands and their Electron Contribution

Ligand	Charge	Metal-Ligand	Involved electrons
diene	0	M	4
alkylidyne (carbyne)	-3	M≡C—R	6
imido (linear)	-4	M <b>⊟</b> N−R	6
η <sup>5</sup> -cyclopentadienyl	-1	M	6
arene	0	M	6
η <sup>8</sup> -cyclooctatetraenyl	0	M	8

#### The Special Case of Nitrosyl Ligand

In recognition of the covalent nature of the M–N–O interaction and the difficulty, not to say unreasonableness, of assigning formal oxidation states to the metal and the NO in nitrosyl complexes, Enemark and Feltham proposed a formalism which treated the metal nitrosyl as a single entity.<sup>12</sup> This was represented as  $\{M(NO)_x\}^n$ , in which *n* is the total number of electrons associated with the metal d and  $\pi^*$  (NO) orbitals. The number of d electrons is determined by the formal oxidation state of the metal atom, *assuming no charge on the NO group*. Some examples of this notation are given below:

[Mn(CN)5(NO)] <sup>3-</sup>	Mn <sup>II</sup>	$d^5$	$1 \pi^{\bullet} \text{NO e}^-$	{Mn(NO)} <sup>6</sup>
[Fe(NO)(oep)]	$Fe^{II}$	$d^6$	$1 \pi^{\bullet} \text{NO e}^-$	${Fe(NO)}^7$
$[Fe(NO)_2(SR)_2]^-$	$Fe^{I}$	$d^7$	$2 \times 1 \pi^{\bullet} \text{NO e}^{-}$	${Fe(NO)_2}^9$
[Co(NO)(NH <sub>3</sub> ) <sub>5</sub> ] <sup>2+</sup>	$Co^{II}$	$d^7$	$1 \pi^{\bullet} \text{NO e}^-$	$(Co(NO))^{8}$

Notwithstanding this pragmatic scheme, it is still necessary to reflect on the charge distribution between metal and NO, particularly with respect to the electronic and magnetic behavior of complexes, and one can still usefully apportion charges as, for example,  $\{M^{z-1}-(NO^+)\}$ ,  $\{M^z-(NO^{\bullet})\}$ , or  $\{M^{n+1}-(NO^-)\}$ , as is described later. In this regard, the position of the NO stretching frequency and, occasionally, <sup>14/15</sup>N NMR chemical shifts, can be informative.

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Mc Cleverty, J. A. Chem. Rev. 2004, 104, 403.
Enemark, J. H.; Feltham, R. D. Coord. Chem. Rev. 1974, 13, 339.
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Two theories are usually employed to explain such a bonding:

- a) The crystal field theory (later evolved into the Ligand Field Theory)
- b) The Molecular Orbital Theory

Pure crystal field theory assumes that the ligands are point charges and their interactions with the metal are merely electrostatic (ionic). On the other hand, the MO theory describes the TM-L bond as generated from the superposition between molecular orbitals of the ligand and atomic orbitals of the metal.

The 5 d orbitals in an isolated gaseous metal are degenerate. If we place a spherically symmetric field of negative charges around the metal, these orbitals remain degenerate, but all of them are raised in energy, as a result of the repulsion between the surrounding negative charges and the electrons on the d orbitals.



If now, rather than a spherical field, we consider an octahedral geometry (*CN* =6), and we assume that the Cartesian axes correspond to the bond directions, the 5 d orbitals will interact with six point charges located on the +x, -x, +y, -y, +z and -z axes. Due to the different directions of the d orbital lobes, the two  $e_g$  orbitals directed toward the axes ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) are more destabilized than the other three  $t_{2g}$  orbitals with lobes pointing in-between the main axes ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ).



The octahedral geometry corresponds to the *Oh* point group. Referring to the character table for the *Oh* point group reveals that the  $d_{x^2-y^2}$ ,  $d_{z^2}$  orbitals belong to the  $e_g$  irreducible representation and  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$  belong to the  $t_{2g}$  irreducible representation.

## **The Spectrochemical Series**

In a spherical field, the five d-orbitals are degenerate. However, as the ligands approach to the metal, the degeneration is lost and the extent of the effect mainly depends on the nature of the ligands. For an octahedral complex, the energy gap between the  $t_{2g}$  and the  $e_g$  levels, which are frontier orbitals, may fall in the visible, near ultraviolet or infrared regions of the electromagnetic spectrum. As a consequence, the electronic spectrum of a complex allows to determine the extent of the energy gap  $\Delta o$ . An empirical evaluation has been made which is known as the spectrochemical series.

This splitting is almost independent of the nature or the oxidation state of the metal. <u>The</u> <u>spectrochemical series is not consistent with the crystal field model alone</u>, which is based on purely electrostatic repulsions. Indeed, as we will see later,  $\pi$  interactions cannot be neglected. Scrock, R. R.; Osborn, J. A.; *J. Am. Chem. Soc.* **1976**, *98*, 2134, 2143, 4450



#### **The Spectrochemical Series**



The tetrahedral symmetry (CN = 4) can be obtained placing the point charges in four appropriate corners of a cube. In this case <u>the xy, yz, xz orbitals are destabilized as they</u> point towards the point charges, whereas the  $x^2-y^2$  and  $z^2$  are stabilized.

![](_page_11_Figure_2.jpeg)

The tetrahedral geometry corresponds to the *Td* point group.

Since only one half of the cube corners are involved, the point charges will produce a field one half as strong as the real cubic field. It should also be noted that the crystal field splitting in a tetrahedral symmetry is intrinsically smaller than in the octahedral symmetry as only four (instead of six) ligands interact with the metal ion. Approximately,:  $\Delta t = 4/9 \Delta o$ . This favors high spin configurations for the tetrahedral geometry.

The square planar geometry (CN = 4) can be obtained from the octahadral one by formally removing two apical point charges, for example along the z axis. This results in a maximal destabilization of the  $d_{x^2-y^2}$ , which points toward the charges. On the other hand, the  $d_{z^2}$  orbital is no more destabilized and mixes with s orbital. Furthermore, if the ligands are  $\pi$ -donors, donation into the empty pz orbital confers a double bond character to the fours ligands.

![](_page_12_Figure_2.jpeg)

In the MO approach, the molecular wavefunctions are a combination of the atomic orbitals, wherein the latter can physically overlap with each other. In particular, the orbitals of the ligands overlap with those of the metal to generate the coordination bonds.

Since the MOs are irreducible representations of the molecule's pointgroup, only certain atomic orbitals can interact together to form MOs with given bonding (or antibonding) character. The extent of the interaction between the atomic orbitals depends on the physical overlap as well as on their relative energies. The smaller is the energy difference, the greater is the interaction.

Since only the orbitals belonging to a given symmetry are allowed interact each other, it is important to classify all of them according to the irreducible representations of the pointgroup involved. This task requires a basic knowledge of the Group Theory (a mathematical tool) and is conveniently performed by the proper usage of table of the characters.

Jean Yves, *Les Orbitales Moléculaires dans les Complexes,* Les Éditions de l'École Polytechnique, Palaiseau, 2003 Gelessus, A.; Thiel W. Weber, W. *J. Chem. Educ.* **1995**, **72**, 505

In a generic TM-L bond an electron pair of the ligand is shared with the transition metal, which in turn can share its electron density with the ligand.

Each complex has a *geometry*, which, depending on the symmetry elements repeating atoms or group of atoms, corresponds to a given symmetry pointgroup. Each pointgroup has specific irreducible representations which are conveniently listed in the *character table*. By using this table, it is relatively easy to identify the set of the atomic metal orbitals which interact with symmetry combinations of the ligands. This qualitative approach greatly simplifies the chemical interpretation of the numerical results derived from MO calculations (semiempirical, ab-initio, DFT, etc.). Importantly, each MO must have the same feature of the corresponding irreducible

representation. Namely, it must behave symmetrically (or antisymmetrically) with respect to the application of the various symmetry elements of the pointgroup.

The MOs are distinguished according to their bonding/antibonding character relative to metal-ligand or intra-ligand interactions, as well as for their lone pair character, localized at the ligands or at the metal (non-bonding metal orbitals).

The usefulness of the MO classification by symmetry is such that even molecules with low or no symmetry can be conveniently analyzed in terms of an higher ideal symmetry in order to derive useful ideas about the chemical bonding. For instance, the properties of many pseudo-octahedral complexes can be rationalized with reference to the ideal *Oh* symmetry. According to the Group Theory nomenclature, the MOs may be: non-degenerate, doubly degenerate or triply degenerate. The respective symbols of the most common ones are:

"a", or "b": singly degenerate orbitals (*i.e.* symmetric or antisymmetric with respect to a rotation axis)

- "e": doubly degenerate orbitals
- "t": triply degenerate orbitals

The following specifications may also be encountered::

1 or 2: symmetric or antisimmetric with respect to a symmetry plane g: or u: (gerade or ungerade), *i.e.* symmetric or antisymmetric with respect to the center of inversion.

Let's now consider an <u>octahedral complex (CN = 6)</u> with all the M-L bonds aligned with the Cartesian axes. The metal has nine atomic orbitals: five (n-1)d, one ns, three np. The orbitals d<sub>z</sub><sup>2</sup>, d<sub>x</sub><sup>2</sup>.<sub>y</sub><sup>2</sup> (e<sub>g</sub> symmetry) p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub> (t<sub>1u</sub> symmetry) and s (a<sub>1g</sub>) symmetry have their lobes aligned with the direction of the main axes along which the metal-ligand bonds are formed. Thus, the above mentioned metal orbitals can overlap with the combination of the ligand lone pairs having the same symmetries. As a consequence, six  $\sigma$ -bonds are formed, belonging to the e<sub>g</sub>, t<sub>1u</sub>, and a<sub>1g</sub> symmetries. The remaining d<sub>xy</sub>, d<sub>xz</sub>, and d<sub>yz</sub> orbitals (t<sub>2g</sub> symmetry) have their lobes directed between the quadrants. They can be considered as metal non-bonding and, in the presence of suitable ligands, are available for  $\pi$ -bonding.

![](_page_16_Figure_2.jpeg)

Jean Yves, *Les Orbitales Moléculaires dans les Complexes*, Les Éditions de l'École Polytechnique, Palaiseau, 2003 Gelessus, A.; Thiel W. Weber, W. *J. Chem. Educ.* **1995**, **72**, 505

# The Octahedral Geometry: Point Group Oh

![](_page_17_Figure_1.jpeg)

The ligand field theory is a combination of molecular orbital concepts and crystal field arguments. Let us take again an octahedral complex. According to the crystal field theory, the purely electrostatic interactions between the metal and the incoming ligands bring about raising of the  $e_g$  and lowering of the  $t_{2g}$  levels, thereby generating the  $\Delta o$ .

![](_page_18_Figure_2.jpeg)

Jorgensen, C. K. Modern Aspects of Ligand Field Theory, Elsevier, New York, 1971

#### The Ligand Field Theory

Such a model, although well rationalizes the splitting of the five d orbitals according to the different geometries of the complex, is not realistic, as it overemphasizes the ionic contribution to the M-L interaction. This is the reason why the experimentally observed spectrochemical series is not consistent with such a theory. For example, the crystal field model cannot explain why carbon monoxide is associated to very strong field.

Molecular orbital theory tells us that if the ligand posses a p orbital or a  $\pi$ -bonding component orthogonal to the M-L axis,  $\pi$ -interaction between the t<sub>2g</sub> levels of the metal and those of the ligand may occur, thereby modifying the resulting energy gap.

More precisely, if the  $t_{2g}$  levels are empty and the ligand levels are occupied, transfer of electron density from the ligand to the metal will occur ( $\pi$ -bonding). Conversely, if the  $t_{2g}$  levels are filled and those of ligand are empty, a net transfer of electron density from the metal to the ligand will occur ( $\pi$ -back-bonding). These considerations rationalize the spectrochemical series. Indeed, the "strange" strong field ligands (CO, py, 2,2'-bipyridine, CN<sup>-</sup>, all have empty  $\pi$ -orbitals !

# The $\sigma$ -Bonding

Let us stick to a generic octahedral complex  $ML_6$ . The linear combination between the six valence atomic orbitals of the metal and an appropriate set of six molecular orbitals of the ligands accounts for the s part of the M-L<sub>6</sub> interaction.

![](_page_20_Figure_2.jpeg)

# The $\sigma$ -Bonding

![](_page_21_Figure_1.jpeg)

As a result, the following qualitative MO diagram of energetic levels is obtained.

Note that the  $t_{2g}$  set of orbitals  $(d_{xy}, d_{xz}, and d_{yz} does not interact with the ligands ($ *non bonding*). Indeed, with this octahedral geometry, there are no orbitals on the ligands that can overlap with them.

 $a_{1g}$ ,  $e_g$ ,  $t_{1u}$  sets of orbitals *in the complex* are closer in energy to the orbitals of the ligands. This means that electrons populating these orbitals will have essentially ligand character. The  $e_g$ \* set, on the other hand, will have essentially metal character, whereas the  $t_{2g}$  set will show totally metal character.

The higher the energy gap  $\Delta o$  between  $t_{2g}$  and  $e_g^*$ , the more stable the complex will be.

Thus, in the case  $\pi$ -acceptor ligands, a linear combination between the  $t_{2g}$  orbitals and an appropriate set of  $\pi$  orbitals of the ligands will assure extra stabilization of the complex.

![](_page_22_Figure_2.jpeg)

![](_page_22_Figure_3.jpeg)

 $t_{2q}$  become bonding  $\rightarrow$  low oxidation states are favored.

#### $\pi$ -Donors versus $\pi$ -Acceptors

 $\pi$ -acceptor ligand  $t_{2g}$  $e_q$  $e_g$  $e_g$  $t_{2g}$  $\Delta_0$  $\Delta_0$  $\Delta_0$  $\Delta_0$  $t_{2g}$  $t_{2g}$ 2a Μ M-L L ( $\pi$ -acceptor) M-L Μ

 $\pi$ -donor ligand

 $t_{2g}$  are lowered by  $\pi$ -back-donation.  $\Delta \tilde{o}$  increases  $\rightarrow$  high field.  $t_{2q}$  become bonding  $\rightarrow$  low oxidation states are favored.

- $t_{2g}$  are raised by  $\pi$ -donation.
- $\Delta \tilde{o}$  decreases  $\rightarrow$  weak field.
- $t_{2g}$  become anti-bonding and to stay empty high oxidation states are favored

 $e_g$ 

 $t_{2q}$ 

 $t_{2q}$ 

L ( $\pi$ -donor)

### Consequences of the $\pi$ -Back-bonding

Molecular orbital diagram of a class III octahedral complex, *i.e.* Cr(CO)<sub>6</sub>

![](_page_24_Figure_2.jpeg)

 $t_{2g}$  becomes bonding due to interactions with  $\pi$  orbitals of the ligands.  $e_g^*$  becomes more antibonding.

## $\sigma\text{-Donation}$ and $\pi\text{-Back-Donation}$

M-CO

#### **M-Alkene**

![](_page_25_Figure_3.jpeg)

![](_page_25_Figure_4.jpeg)

Dewar, Chatt, Duncanson, 1953

## $\sigma$ Donation, $\pi\text{-}\textsc{Donation},$ and $\pi\text{-}\textsc{Back-Donation}$

![](_page_26_Figure_1.jpeg)

![](_page_26_Figure_2.jpeg)

double  $\pi$ -donation

M—Hal:

M-NEC-R

filled  $\pi$ 

filled  $\pi$ 

filled n

![](_page_26_Figure_3.jpeg)

Pd(0) and Pd(II) are both capable of interacting with unsaturated systems such as alkenes or alkynes via  $\pi$ -bonding. The two types of complexes are however different in nature. **Pd(0)** is highly electron-rich and back-donates to the ligand (Pd  $\rightarrow$  L), whereas **Pd(II)** is *electrophilic*, and its main interaction is represented by  $\sigma$ -donation from the organic system to an empty orbital of palladium. A comparison of the orbital interactions between the alkene and the frontier orbitals of  $L_2Pd(0)$  and  $L_3Pd(II)$  fragments accounts for the different ability of the metal d orbitals to back-donate into the olefin  $\pi^*$  level [1] As the CACAO drawing shows (see next figure),<sup>[ii]</sup> the  $\pi$  fragment molecular orbital in L<sub>2</sub>Pd(0) is a hybrid formed by the d<sub>xv</sub> and  $p_v$  atomic orbitals, whereas the corresponding in L<sub>3</sub>Pd(II) is a pure d<sub>xv</sub> orbital one. Since the interaction between orbitals is governed by their relative energies and overlap, it is apparent that the Pd(0) fragment is able to produce a much better back-donation than the Pd(II) moiety.

[i] The FMOs (fragment molecular orbitals) of the principal transition metal fragments have been catalogued and those of the indicated fragments can be thought of as the hybrids which form upon removal of one ligand from planar L3M or L4M complexes, respectively. Albright. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*, **1985**, John Wiley, New York.

[ii] Mealli, C.; Proserpio, D. M. J. Chem. Ed., **1990**, 67, 399.

#### Alkene-Pd(0) versus Alkene-Pd(II) Complexes

![](_page_28_Figure_1.jpeg)

Courtesy from Mealli, C Poli, G. Giambastiani, G. Heumann, A. *Tetrahedron*, **2000**, *56*, 5959-5989

#### **Consequences of Metal-Back-Bonding**

![](_page_29_Figure_1.jpeg)

Strong back-bonding implies charge transfer from the metal to the ligand, *i.e.* change in the formal oxidation state (oxidative addition)

![](_page_29_Figure_3.jpeg)

#### Character table for point group Td

T <sub>d</sub>	Е	8C <sub>3</sub>	3C <sub>2</sub>	6S <sub>4</sub>	$6\sigma_d$	linear functions,	quadratic functions
A <sub>1</sub>	+1	+1	+1	+1	+1	-	x <sup>2</sup> +y <sup>2</sup> +z <sup>2</sup>
$A_2$	+1	+1	+1	-1	-1	-	-
Е	+2	-1	+2	0	0	-	(2z <sup>2</sup> -x <sup>2</sup> -y <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> )
T <sub>1</sub>	+3	0	-1	+1	-1	$(R_x, R_y, R_z)$	-
$T_2$	+3	0	-1	-1	+1	(x, y, z)	(xy, xz, yz)

D <sub>4h</sub>	Е	2C <sub>4</sub> (z)	<i>C</i> <sub>2</sub>	2C' <sub>2</sub>	2C"2	i	2S <sub>4</sub>	$\sigma_{h}$	2s <sub>v</sub>	2s <sub>d</sub>	linear functions	quadratic functions
A <sub>1g</sub>	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x <sup>2</sup> +y <sup>2</sup> , z <sup>2</sup>
$A_{2g}$	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R <sub>z</sub>	-
$B_{1g}$	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x <sup>2</sup> -y <sup>2</sup>
$B_{2g}$	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	ху
$E_{g}$	+2	0	-2	0	0	+2	0	-2	0	0	$(R_x, R_y)$	(xz, yz)
A <sub>1u</sub>	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-
$A_{2u}$	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-
B <sub>1u</sub>	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-
$B_{2u}$	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-
$E_{u}$	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-

#### Character table for point group $D_{4h}$

## Electronic Structure vs Geometry

![](_page_32_Figure_1.jpeg)

pz

 $p_x, p_y$ 

 $A_{2u}$ 

 $\mathsf{E}_{\mathsf{u}}$ 

#### Valence Electron Count in Transition Metal Complexes

TM complexes can be conveniently divided into 3 classes, according their different valence electron (VE) count. This is in turn directly related to the magnitude of  $\Delta$ .

**3d** TM having **low field ligands** show small  $\Delta$  values and belong to **Class I**. <u>t<sub>2g</sub> are non</u> bonding and may be occupied; <u>e\*<sub>g</sub> are weakly antibonding and may also be occupied</u>. Hexacoordination is attained regardless of the total VE count. As a result, VE of 12-21 are possible.

![](_page_33_Figure_3.jpeg)

Mitchell, P. R.; Parish, R. V.; J. Chem. Ed., 1969, 46, 811 Pilar, F. L.; J. Chem. Ed., 1978, 55, 2

**Class II** is made by **4d** and **5d** TM having **medium or strong field ligands** or by 3d TM with highly strong field ligands.  $t_{2q}$  are non bonding and may be occupied, whereas  $e_{q}^{*}$  are strongly antibonding and thus empty. Possible VE are  $\leq$  18.

![](_page_34_Figure_2.jpeg)

Mitchell, P. R.; Parish, R. V.; J. Chem. Ed., 1969, 46, 811 Pilar, F. L.; J. Chem. Ed., 1978, 55, 2

**Class III** is made by TM having **very strong field ligands**. In these complexes, which have high  $\Delta$  values,  $\underline{t_{2g}}$  is bonding (via back-bonding) and occupied by 6e<sup>-</sup>, whereas  $\underline{e^*_g}$  is strongly antibonding, and thus empty. As a result, a total VE count of 18 is observed. This event is known as the <u>**18 electrons rule**</u> (Sidgwick, 1927). Organometallic compounds, which normally feature high  $\Delta$  values, belong to this class.

![](_page_35_Figure_2.jpeg)

Mitchell, P. R.; Parish, R. V.; J. Chem. Ed., 1969, 46, 811 Pilar, F. L.; J. Chem. Ed., 1978, 55, 2

The geometry of TM complexes cannot be always deduced by the number of ligands coordinated to the metal, as is the case for main group element by the valence shell electron-pair repulsion theory (VSEPR, Gillespie-Nyholm theory).

For 18 VE complexes, for example, geometries predictable by the VSEPR theory are observed:

 $CN = 4, d^{10}, (18 \text{ VE}) : Ni(CO)4 : tetragonal$  $CN = 5, d^8, (18 \text{ VE}) : [Ni(CN)_5]^3 : square pyramid$  $CN = 5, d^8, (18 \text{ VE}) : Fe(CO)_5 : trigonal bipyramid$ 

![](_page_36_Picture_4.jpeg)

For species with less than 18 VE and with non zero oxidation state, VSEPR theory is not applicable. To qualitatively predict the geometry, imagine to start from the corresponding 18 VE complex and successively remove the dummy ligands together with their electron pairs.

CN = 4,  $d_{,}^{8}(16 \text{ VE})$ :  $[Ni(CN)_{4}]^{2}$ , square planar CN = 3,  $d^{8}$ , (14 VE):  $[(Ph_{3}P)_{3}Rh]^{+}$ , T structure

![](_page_36_Figure_7.jpeg)

Mingos D.M.P. J. Organomet. Chem., 2004, 689, 4420-4436.

## Some Examples

![](_page_37_Figure_1.jpeg)

 $ML_4$  d<sup>10</sup> complexes are coordinatively saturated (18e<sup>-</sup>) and adopt a tetrahedral geometry. On the other hand, d<sup>8</sup> complexes prefer an  $ML_4$  16e<sup>-</sup> square planar disposition rather then a 18e<sup>-</sup>  $ML_5$  configuration. This apparent violation of the 18 electrons rule is due to the fact that the non-bonding orbital p<sub>z</sub> is too high in energy to be filled. The coordination of a phosphine to a transition metal, as that of CO, depends on two components. P atom plays the role of donor via its lone pair ( $\sigma$ -donation). On the other hand, the metal, via its filled d orbitals can donate back electron density to into the  $\sigma^*$  P orbitals ( $\pi$ -back-donation). Back-bonding is not possible with N, and O donors.

![](_page_38_Figure_2.jpeg)

# $\sigma\text{-Donicity}$ of the Phosphorous Lone Pair

In a ligand, the higher the energy associated with the lone pair, the better the  $\sigma$ -donation. Conversely, the lower the energy of the  $\sigma^*$  orbitals involved in the  $\pi$ -back-donation, the better the  $\pi$ -back-donation. The lowest energy gap between the interacting electrons determines the dominant contribution. This explains why PF<sub>3</sub> is a weak  $\sigma$ -donor (low  $\sigma$ ) and a very good  $\pi$ -acceptor (low  $\sigma^*$ ).

From the experimental viewpoint, the acidity of the protonated phosphonium ion, or better, the value of the *oxidative potential*  $E^{\circ}$  of a phosphine { $R_3P \rightarrow R_3P^+ + e^-$ } can give (a thermodynamic) information of the  $\sigma$ -donicity of the phosphine lone pair.

![](_page_39_Figure_3.jpeg)

In a phosphine, the value of the  ${}^{31}P{}^{77}Se$  coupling constant of the corresponding phosphine-selenide R<sub>3</sub>P=Se is a function of the  $\sigma$ -donor ability of the parent phosphine R<sub>3</sub>P. Thus, an increase of this coupling constant indicates an increase in the s-character of the P lone pair (i.e. a diminished  $\sigma$ -donicity)

Allen, D.W.; Taylor, B.F. J. Chem. Soc. Dalton Trans. 1982, 51

<u>Do not forget</u>: amines are more basic (*i.e.*  $pk_a + HNEt_3$  in  $H_2O$  is 10.8 (9.0 in DMSO)) than phosphines. On the other hand, phosphines are more nucleophilic than amines, since they have higher HOMOs. Also, remember that basicity is a thermodynamic parameter, whereas nucleophilicity is a kinetic parameter.

The  $\pi$ -back-donation toward a coordinated phosphine can be measured by its *electronic affinity* value :

 $R_3P + e^- \rightarrow [R_3P]^-$ . Phosphines can be excellent  $\pi$ -acceptors.

![](_page_41_Figure_3.jpeg)

The  $\pi$ -acidity scale goes in the opposite direction with respect to the  $\sigma$ -donicity scale. Electron withdrawing substituents in phosphines decrease  $\sigma$ -donation and increase  $\pi$ -back-donation.

This is a strong  $\pi$ -acceptor: Mathey, F. *Chem. Rev.* **1988**, *88*, 429

Strohmeier, W.; Muller, F. J. Chem. Ber. 1967, 100, 2812-2821

## Steric Requirements: Tolman's Cone Angle $\theta$

Phosphines are pyramidal and their inversion barrier is ~140 kJmol<sup>-1</sup> (compare with amines: ~40 kJmol<sup>-1</sup>). This means that, in contrast with amines, phosphines that are stereogenic at phosphorous are <u>configurationally stable</u> at rt. Not unexpectedly, the longer the P-M separation, the weaker the coordination. Such a distance is not only a function of the electronic nature of the phosphine, but also of its steric requirements. As a consequence, a classification of the phosphines according to their intrinsic steric requirements is desirable. To this purpose, Tolman (1972) devised the cone angle, a measure which is a function of the extent of pyramidalization at the P atom as well as of the steric hindrance of the three substituents. To obtain Tolman's cone angle of a phosphine, a metal is arbitrarily placed along the lone pair direction at 2.28Å distance from P atom (average Ni-P distance). Then, by placing the origin at M, the tangents to the three substituents allow defining the cone angle  $\theta$ . If the phosphine is substituted with different R groups, an average value of  $\theta$  will be obtained.

The Tolman's cone angle is defined as the apex angle of a cylindrical cone, centered 2.28Å from the center of the P atom, which touches the outermost atoms of the model.

![](_page_42_Figure_3.jpeg)

Tolman, C.A. Chem. Rev. 1977, 313

## **Cone Angles of Selected Ligands**

![](_page_43_Figure_1.jpeg)

Note that phosphites have smaller cone angles than their corresponding phosphines. This is because oxygen atom acts as a spacer.

## Bidentate Ligands: the Bite Angle and the Flexibility Range

A correlation between the P-M-P bite angle in diphosphine complexes and selectivity has been observed in various catalytic reactions.

The P-M-P angle found in transition metal complexes of bidentate phosphines depends on the ligand's <u>natural bite angle</u> as well as on the requirement imposed by the metal center. The former factor is determined by the ligand backbone and the other ligands present, and is mainly steric, whereas the geometry preferred by the metal is dictated by electronic factors.

Calculation of ligand bite angles can be obtained either via a) molecular modeling or b) by measuring P....P distances from crystal structures. Since bite angles are a function of M-P bond length, meaningful comparisons between different ligands can be obtained using an arbitrarily chosen normalized M-P bond length. To this purpose, a Rh-P bond length of 2.1315Å has been chosen.

![](_page_44_Figure_4.jpeg)

Analysis of the complexes via molecular mechanics allows also to define a <u>flexibility range</u>, *i.e.* the accessible range of bite angles found within  $\leq$  12.5 kJ/mol excess strain energy from the calculated natural bite angle.

Casey, C.P.; Whiteker, G. T. *Isr. J. Chem., 1990,* **30**, 299 Kamer, P. C. J.; Van Leewen, P. W. N. M.; Reek, J. N. K. *Acc. Chem. Res.* **2001**, *34*, 895

## Bidentate Ligands: the Bite Angle and the Flexibility Range

F	Ph <sub>2</sub> P PPh <sub>2</sub>	OOO PPh <sub>2</sub> PPh <sub>2</sub>	PPh <sub>2</sub> PPh <sub>2</sub>	PPh <sub>2</sub>
Pito opglo	DPPE	DIOP	XANTPHOS	NORPHOS
(calcd. MM)	84.4°	102°	111.7°	123°
Flexibility range	70-95°	90 - 120°	97-135°	110-145°

![](_page_45_Figure_2.jpeg)

# Some Achiral P Ligands

![](_page_46_Figure_1.jpeg)

#### bidentate phosphines

![](_page_46_Figure_3.jpeg)

#### tetradentate phosphine

![](_page_46_Picture_5.jpeg)

## Some Chiral Phosphines and Analogues

![](_page_47_Figure_1.jpeg)

#### bidentate P ligands

![](_page_47_Figure_3.jpeg)

## Carbon monoxide

![](_page_48_Figure_1.jpeg)

![](_page_48_Figure_2.jpeg)

# CO Vibration as Internal Probe of Phosphine Donation

	v <sub>co</sub> (cm <sup>-</sup>	1)
Ni(CO) <sub>3</sub> PBu <sup>t</sup> <sub>3</sub>	2056.1	t
Ni(CO) <sub>4</sub>	2060	Increasing $\pi$ -back-
Ni(CO) <sub>3</sub> PMe <sub>3</sub>	2064.1	donation from the
Ni(CO) <sub>3</sub> PPh <sub>3</sub>	2068.9	metal to CO due to
Ni(CO) <sub>3</sub> P(OMe) <sub>3</sub>	2079.5	increasing σ-donation
Ni(CO) <sub>3</sub> P(OPh) <sub>3</sub>	2085.0	trom the phosphine to
Ni(CO) <sub>3</sub> PF <sub>3</sub>	2110.8	
СО	2143	
H₃B←CO	2164 (no	$\pi$ -back-donation to CO)

In a transition metal complex, such as Ni(CO)<sub>3</sub>PR<sub>3</sub>, the CO stretching frequency can be used as an indicator of the electron density at the metal. Indeed, the lower is the value of the CO stretching frequency, the greater is the back-bonding from the metal to the CO ligand, the higher is the electron density at the metal because it is enriched by the donor capability of the phosphine. In other words, the best phosphine donors allow maximal back-bonding from metal to CO. Each substituent R on the phosphine contributes to the frequency shift by a given increment  $\chi$ , from 0.0 cm<sup>-1</sup> for R = Bu<sup>t</sup> to 19.6 cm<sup>-1</sup> for R = CF<sub>3</sub>. The shifts are approximately additive :

 $v = 2056.1 + \Sigma \chi_i$ 

Carbenes are neutral species in which the carbenic carbon is divalent. Usually carbenes of the type  $CR_2$  are stable as triplets, due to the very close energy of the carbon s hybrid and the  $p\pi$  orbital for which there are two electrons available.

![](_page_50_Figure_2.jpeg)

Substituents that can donate electron pairs may stabilize the singlet state by delocalizing the pair into an empty p-orbital. If the energy of the singlet state is sufficiently reduced it will actually become the ground state. No viable strategies exist for triplet stabilization.

## **Fischer-type Carbene Ligands**

#### **Fischer-type carbenes**

The Fischer carbenes, discovered in 1964, [Fischer, E. O.; Maasbol, A. *Angew. Chem. Int.* **1964**, *3*, 580] are carbenes complexed to a transition metal. They are characterized by having a **metal in a low oxidation state**,  $\pi$ -accepting **auxiliary ligands**, and a **heteroatom** (O, N, or S) **on the carbene carbon**, which partially saturates the empty carbon  $p_{\pi}$  orbital. The lone pair of electrons in the trigonal carbon may be donated to a metal to form a sigma bond, and the empty  $p_z$  orbital accepts  $\pi$  electron density from the metal. In these carbenes the **HOMO is centered on the metal**, whereas the **LUMO (d** $\pi$ -**p** $\pi$  **antibonding) is more centered on the carbenic carbon atom**. The back-donation is limited. Hence, the **carbenic carbon has a residual electrophilic character**.

![](_page_51_Figure_3.jpeg)

 $\sigma$ -donor/ $\pi$ -acceptor neutral carbene ligand. Formally in singlet state.

#### NHC carbenes (Arduengo, 1991)

A carbene with two neighboring N atoms features strong electron donation from the lone pairs on the nitrogen atoms into the carbenic  $p_{\pi}$ .orbitals. This push-pull (-I, +M) effect of the nitrogen atoms results in a significant energy gap (up to 2 eV) between the  $\sigma$  hybrid and the carbon  $p_{\pi}$  orbital that favors the singlet state.

So, the NHC's are a particular type of Fischer-type carbenes and can behave as ligands for transition metals. The amount of  $\pi$ -backbonding is insignificant as the carbon  $p_{\pi}$  orbital already receives sufficient electron density from the adjacent N atoms.

![](_page_52_Figure_4.jpeg)

 $\sigma$ -donor neutral NHC carbene ligand in singlet state

J. Am. Chem. Soc. 1991, 113, 361-363

#### A Stable Crystalline Carbene

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![](_page_53_Figure_5.jpeg)

We report the synthesis, structure, and characterization of the first crystalline carbene. Carbene 1, 1,3-di-1-adamantylimidazol-2-ylidene, forms colorless crystals with sufficient kinetic and thermodynamic stability to be easily isolated and characterized. The deprotonation of 1,3-di-1-adamantylimidazolium chloride (2) in THF at room temperature with catalytic dimsyl anion ( $^{-}CH_2S(O)CH_3$ ) in the presence of 1 equiv of sodium hydride produces carbene 1 (eq 1). This deprotonation can also be accomplished with potassium *tert*-butoxide in THF to give a 96% yield of 1.

# Schrock-type Carbene Ligands

#### Schrock-type carbenes

In 1974 Schrock discovered [Schrock, R. R. J. Am. Chem. Soc. **1974**, *96*, 6796] a class of nucleophilic carbenes. These complexes are composed of **early transition metals** in **high oxidation states**, **non**- $\pi$ -accepting auxiliary ligands, and **no**  $\pi$ -donating substituents on the carbenic carbon. In principle, the isolated carbene unit is expected to show a triplet state with two unpaired electrons in the  $\sigma$  and  $p_{\pi}$  orbitals. However, these carbenes are formally considered as dianionic 4-electron donors ligands.

The d orbitals of the early transition metal lie at high energies. As a consequence, the HOMO of the complex is centered on the carbenic carbon, and the LUMO is centered on the metal. Hence, the carbene carbon has a nucleophilic character.

![](_page_54_Figure_4.jpeg)

![](_page_54_Figure_5.jpeg)

![](_page_54_Figure_6.jpeg)

 $\sigma$ -donor/ $\pi$ -donor dianionic carbene ligand

## Fischer- and Schrock-type Carbene Ligands

#### $M(d\pi)$ - $C(p\pi)$ interactions

![](_page_55_Figure_2.jpeg)

## Some Examples

#### **Fischer carbenes**

![](_page_56_Figure_2.jpeg)

#### Schrock carbenes

![](_page_56_Figure_4.jpeg)

#### NHC carbenes

![](_page_56_Figure_6.jpeg)

# Typical Usage and/or Reactivity of TM Carbenes

Fischer carbenes:

![](_page_57_Figure_2.jpeg)

#### Schrock carbenes

![](_page_57_Figure_4.jpeg)

#### NHC carbenes

spectator ligands for organometallic catalytic processes

![](_page_57_Figure_7.jpeg)

IR measurement of carbonyl absorption frequencies of NHC carbonyl metal and their phosphine analogues showed significantly increased donor capacity of NHC relative to phosphines, even to trialkylphosphines Due to their  $\sigma$ -donor ability and their strong M-C bond, NHC have been applied as spectator ligands in various catalytic transformations in place of phosphines

# Some Commercially Available NHC Catalysts

These commercially available stable NHC-based complexes are excellent catalysts for crosscoupling reactions (Negishi, Suzuki-Miyaura, Buchwald–Hartwig, Mizoroki-Heck, Kumada). As an exercise find metal oxidation state and electron configuration for the three complexes

![](_page_58_Figure_2.jpeg)

## The Ru Carbenes for Ru-Catalyzed Metathesis

![](_page_59_Figure_1.jpeg)