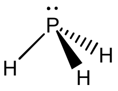
Phosphine Ligands

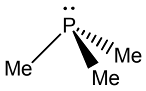
- Tertiary phosphines, PR_3, are an important class of ligands because their ***electronic and steric properties can be altered in a systematic and predictable way*** over a very wide range by varying the R group(s).

- Tertiary phosphines also ***stabilize an exceptionally wide variety of metal complexes*** of interest to the organometallic chemist as their phosphine complexes $(R_3P)_nM{-}L$.

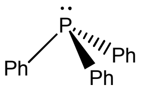
- Phosphines are more commonly ***spectator*** rather than actor ligands.



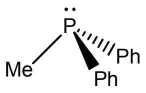
phosphine



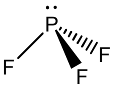
trimethylphosphine



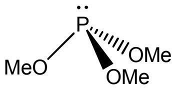
triphenylphosphine



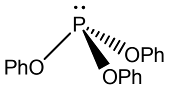
methyldiphenylphosphine



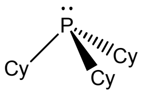
trifluorophosphine



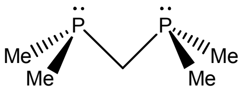
trimethylphosphite



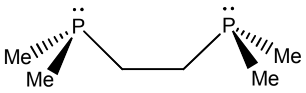
triphenylphosphite



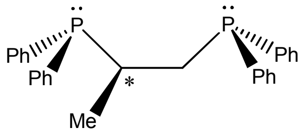
tricyclohexylphosphine



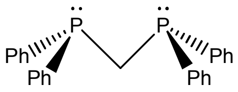
dimethylphosphinomethane
(dmpm)



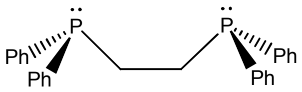
dimethylphosphinoethane
(dmpe)



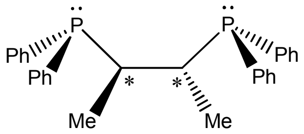
PROPHOS



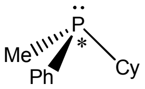
dimethylphosphinomethane
(dmpm)



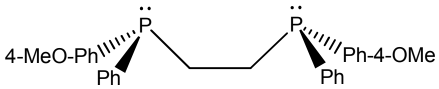
dimethylphosphinoethane
(dmpe)



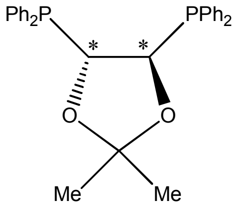
S,S-chiraphos



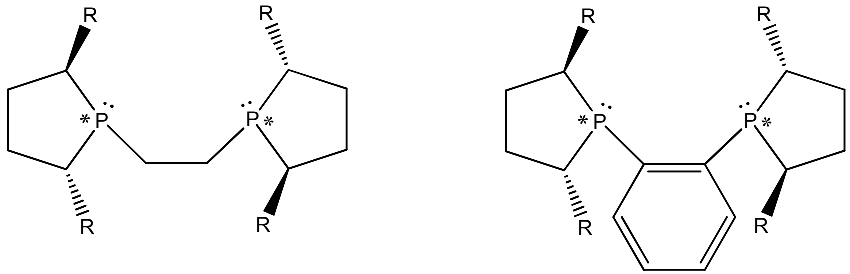
PAMP



DIPAMP

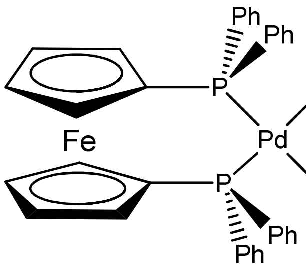


DIOP

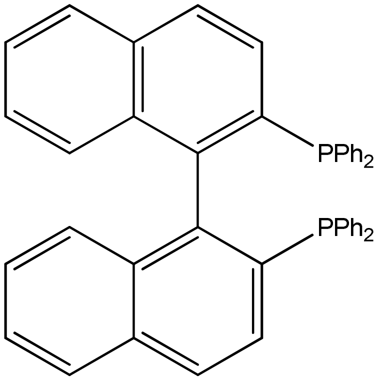


DuPHOS

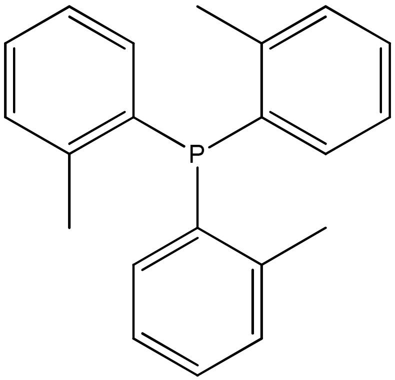
- The range and complexity of phosphine ligands has increased dramatically in recent years due to the development of C-X coupling reactions such as Buchwald-Hartwig reaction.



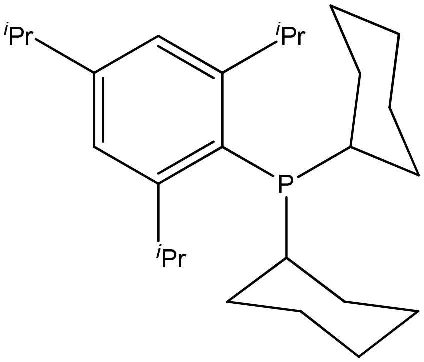
1,1'-diphenylphosphinoferrocene
(dppf)



2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
rac-BINAP



tri-ortho-tolylphosphine



(2,4,6-triisopropylphenyl)dicyclopentylphosphine

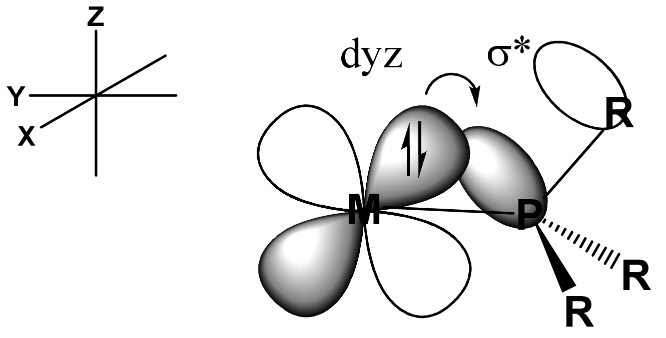
- Like NR_3, phosphines have a lone pair on the central atom that can be donated to a metal.
- Unlike NR_3, they are also ***π-acids***, to an extent that depends on the nature of the R groups present on the PR_3 ligand.
- For alkyl phosphines, the π acidity is weak; aryl, dialkylamino, and alkoxy groups are successively more effective in promoting π acidity.
- In the extreme case of PF_3, the π acidity becomes as great as that found for CO!

In the case of CO the π^* orbital accepts electrons from the metal.

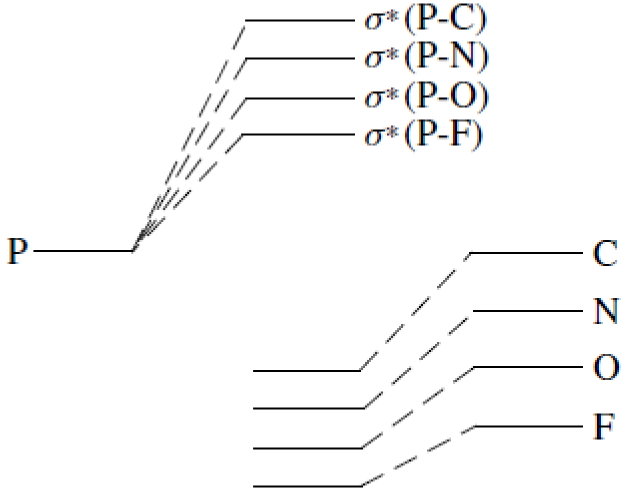
The σ^* orbitals of the P−R bonds play the role of acceptor in PR_3.

- Whenever the R group becomes more electronegative, the orbital that the R fragment uses to bond to phosphorus becomes more stable (lower in energy).
- This implies that the ***σ^* orbital of the P−R bond also becomes more stable***.
- At the same time, ***the phosphorus contribution to σ^* orbital increases***, and so the size of the σ^* lobe that points toward the metal increases
- Both of these factors make the empty σ^* more accessible for back donation.
- The final order of increasing π-acid character is

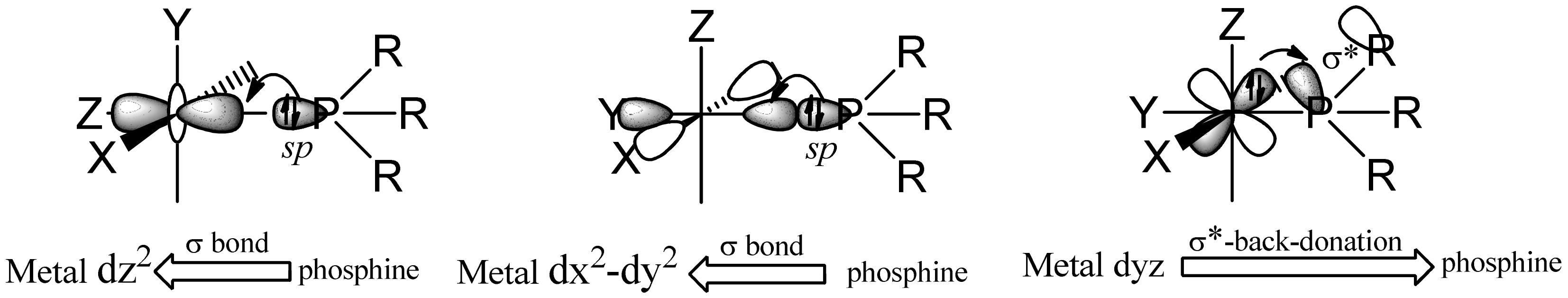
$$\mathbf{PMe_3 \approx P(NR_2)_3 < PAr_3 < P(OMe)_3 < P(OAr)_3 < PCl_3 < PF_3 \approx CO}$$



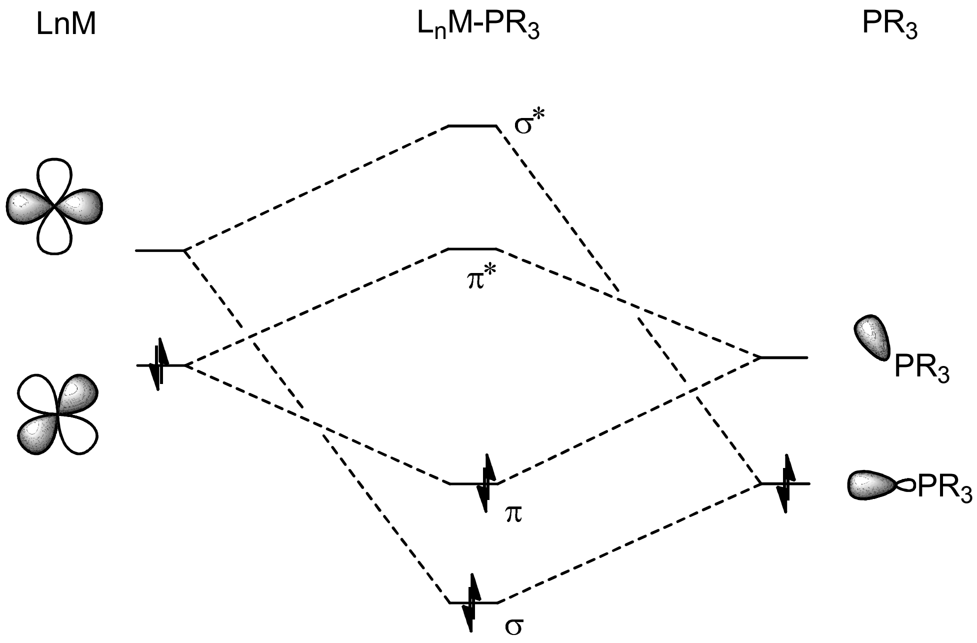
M(dyz) + P(σ*) = M-P π bond



- The empty P–R σ^* orbital plays the role of acceptor in metal complexes of PR_3.
- As the atom attached to the P atom becomes more electronegative, the empty P–X σ^* orbital becomes more stable (lower in energy) making it a better acceptor of electron density from the metal centre.



- Occupation of the P−R σ^* orbital by back donation from the metal also implies that ***the P−R bonds <u>should</u> lengthen slightly on binding***.
- In practice, this is ***masked by a simultaneous shortening of the P−R bond*** due to donation of the P lone pair to the metal, and the consequent decrease in P(lone pair)–R(bonding pair) repulsions.
- Once again, as in the case of CO, the M−L π bond is made at the expense of a bond in the ligand, but this time it is a σ, not a π, bond.

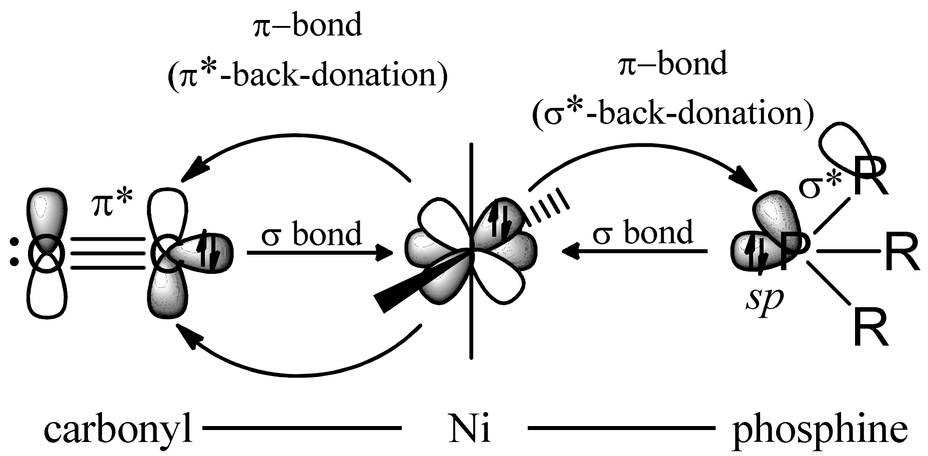


Tolman Electronic Parameter

Phosphorus Ligand (L)	CO ν, cm^{-1}
P(t-Bu)$_3$	2056
PCy$_3$	
P(i-Pr)$_3$	2059
P(NMe$_2$)$_3$	2062
PMe$_3$	2064
PPhMe$_2$	2065
PBz$_3$	2066
PPh$_2$Me	2067
PPh$_3$	2069
PPh$_2$(OEt)	2072
P(p-C$_6$H$_4$Cl)$_3$	2073
PPh(OEt)$_2$	2074
P(OEt)$_3$	2077
PH$_3$	2083
PCl$_3$	2097
PF$_3$	2111

CO stretching frequencies measured for Ni(CO)$_3$L where L are PR$_3$ ligands of different σ-donor abilities. [ν(CO) =2143 cm^{-1}]

The electronic effect of various PR$_3$ ligands can be adjusted by changing the R group as, quantified by Tolman, who compared the ν(CO) frequencies of a series of complexes of the type LNi(CO)3, containing different PR$_3$ ligands.



The increase in electron density at the nickel from PR$_3$ σ-donation is dispersed through the M-L π system *via π-backbonding. Much of the electron* density is passed onto the CO π* and is reflected in decreased *ν*(CO) stretching frequencies which corresponds to weaker CO bonds.

$$\nu = \frac{1}{2\pi c}\left[\frac{f}{(M_xM_y)/(M_x+M_y)}\right]^{1/2}$$

Tolman *Chem. Rev. 1977 (77) 313*

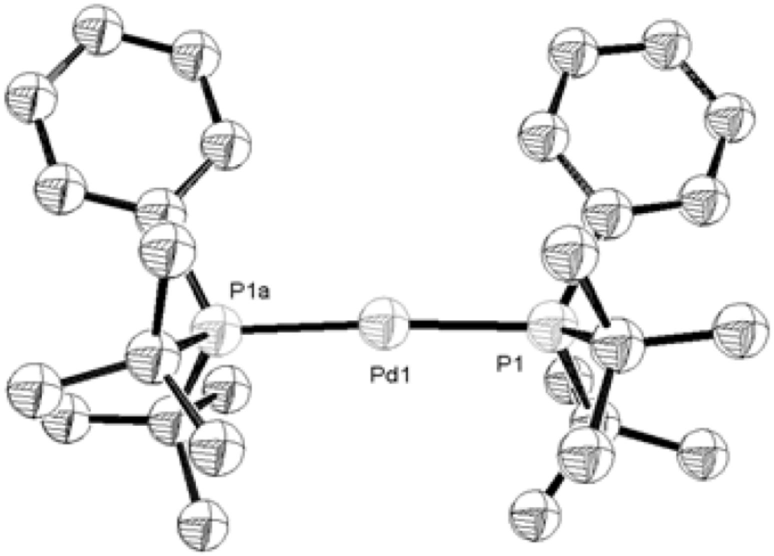
Tolman Cone Angle

- The second important feature of PR_3 as a ligand is the ***variable steric size***, which can be adjusted by changing R.
- CO is so small that as many can bind as are needed to achieve 18e. In contrast, the same is rarely true for phosphines, where ***only a certain number of phosphines can fit around the metal***.
- This can be a great advantage in that by using bulky PR_3 ligands, we can favor forming low-coordinate metals or we can leave room for small but weakly binding ligands,
- The usual maximum number of phosphines that can bind to a single metal is
  - two for PCy_3 or P*(i-Pr)*$_3$
  - *three or four for* PPh_3
  - *four for* PMe_2Ph
  - five or six for PMe_3

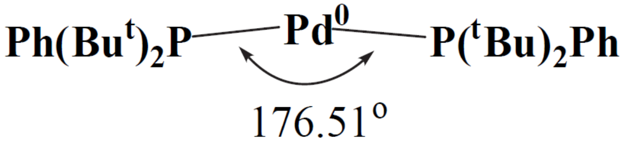
- ***Coordination Number*** **(CN) – the number of bonding groups at metal centre**
  - ***Low CN favored by:***

    1. Low oxidation state (e^- rich) metals.

    2. Large, bulky ligands.

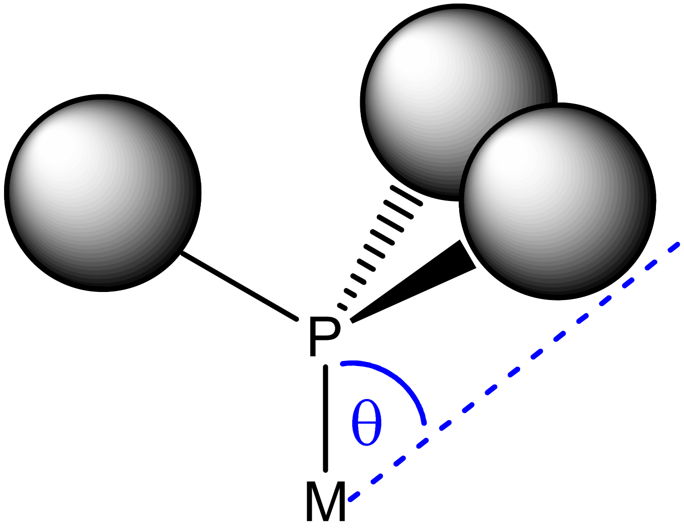


Although $Pd(P(^tBu)_2Ph)_2$ is *coordinatively unsaturated electronically*, the steric bulk of both $P(^tBu)_2Ph$ ligands prevents additional ligands from coordinating to the metal.



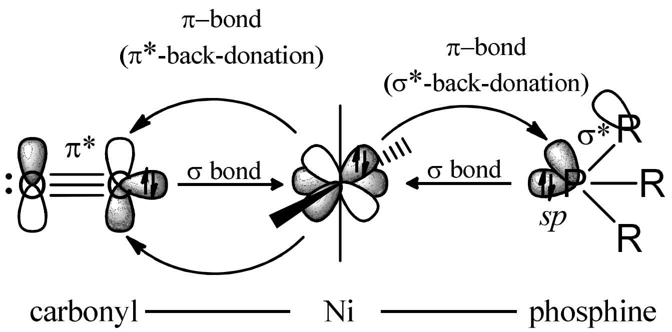
Otsuka *JACS*, 1976 (98)5850.

- The cone angle is obtained by taking a space-filling model of the $M(PR_3)$ group, folding back the R substituents as far as they will go, and measuring the angle of the cone that will just contain all of the ligand, when the apex of the cone is at the metal.
- Although the procedure may look rather approximate, the angles obtained have been very successful in rationalizing the behavior of a wide variety of complexes.



θ = Tolman's cone angle

Tolman Plot of Electronic Parameter and Cone Angle



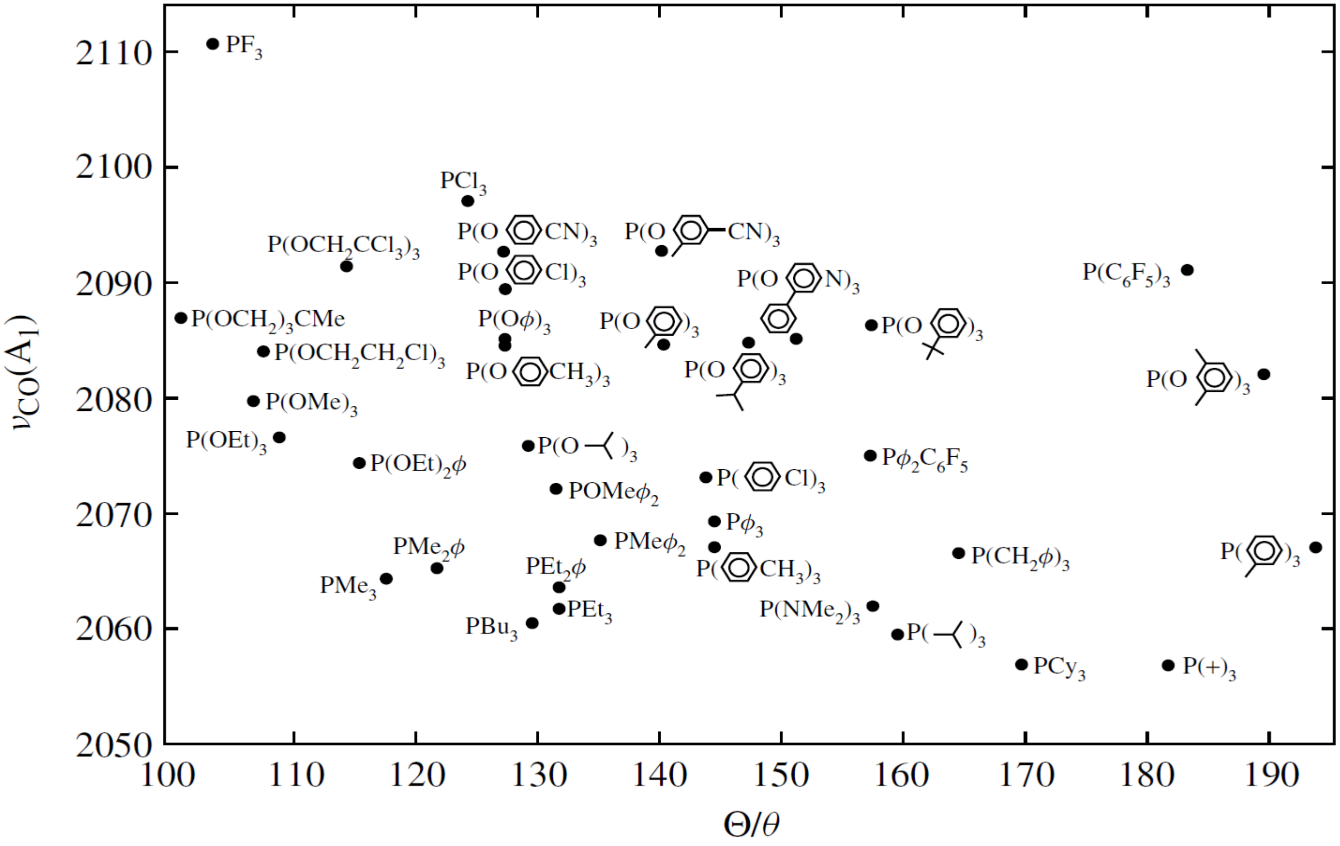


FIGURE 4.4 Electronic and steric effects of common P-donor ligands plotted on a map according to Tolman (ν in cm^{-1}, θ in degrees).

- An important part of organometallic chemistry consists in **varying the steric and electronic nature of the ligand environment of a complex** to promote whatever properties are desired: activity or selectivity in homogeneous catalysis, reversible binding of a ligand, facile decomposition, or high stability.

- Using the Tolman plot we can relatively easily change electronic effects without changing steric effects
  - ➢ e.g., by moving from PBu_3 to $P(OiPr)_3$

- Also, we can relatively easily change steric effects without changing electronic effects
  - ➢ e.g., by moving from PMe_3 to $P(o\text{-tolyl})_3$

Metal Carbenes

- The concept of a double bond between transition metals and carbon constitutes *one of the most important elements in the field of organometallic chemistry*
- The notion of a metal–carbon double bond was first brought forward by Fischer and Maasbol in 1964 with the synthesis of $(CO)_5W{=}C(Ph)(OMe)$
- Soon after the discovery of Fischer type complexes their chemistry was systematically explored and they have been since ***well established as valuable species in organic synthesis as well as in catalytic processes***
- Schrock later prepared a number of tantalum complexes including $(Np)_3Ta{=}CH(CMe_3)$ and $(\eta^5\text{-}Cp)_2MeTa{=}CH_2$

E.O. Fischer, A. Maasbol, *Angew. Chem.* **1964**, 76, 645.

K. H. Dotz, *Angew. Chem. Int. Ed. Engl.* **1984**, 23, 587.

W. D. Wulff, '*Metal-Carbene Cycloadditions*' in '*Comprehensive Organic Synthesis*', Wiley-Interscience:New York, **1988**.

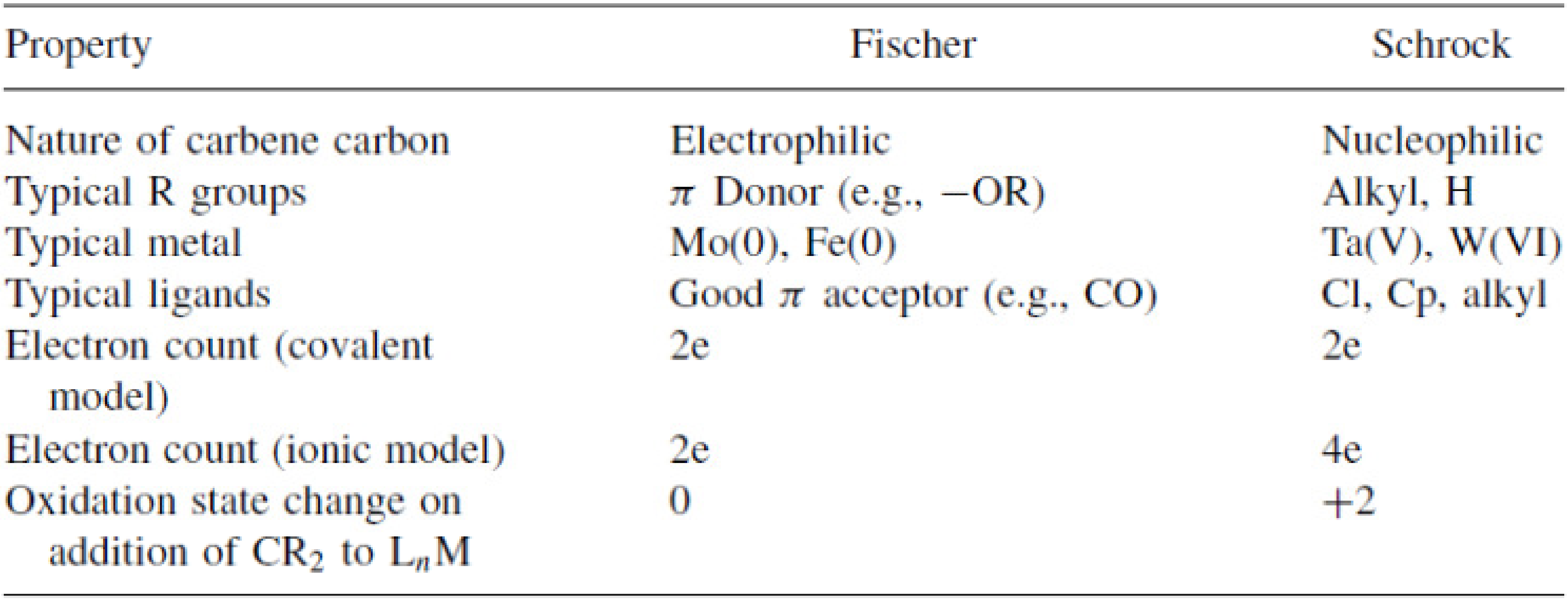
L. S. Hegedus, '*Transition Metals in the Synthesis of Complex Organic Molecules*', **1994**, University Science Books.

R. R. Schrock, *J. Amer. Chem. Soc.* **1975**, 97, 6578.

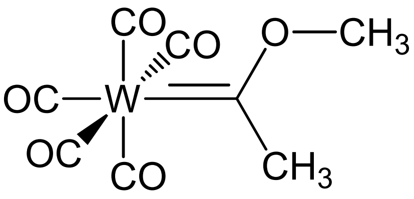
R. R. Schrock, *Acc. Chem. Res.* **1979**, 12, 98.

- Two different patterns of reactivity emerged during the development of these systems resulting in their classification as Fischer and Schrock type carbenes.
- Each represents a different formulation of the bonding of the CR_2 group to the metal and real cases fall somewhere between the two.

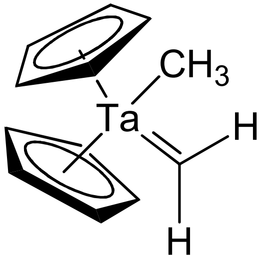
Fischer type vs. Schrock type carbene complexes



Property	Fischer	Schrock
Nature of carbene carbon	Electrophilic	Nucleophilic
Typical R groups	π Donor (e.g., –OR)	Alkyl, H
Typical metal	Mo(0), Fe(0)	Ta(V), W(VI)
Typical ligands	Good π acceptor (e.g., CO)	Cl, Cp, alkyl
Electron count (covalent model)	2e	2e
Electron count (ionic model)	2e	4e
Oxidation state change on addition of CR_2 to L_nM	0	+2



W(0) , 18 VE

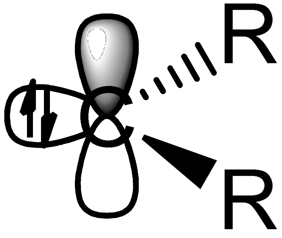


Ta(0) , 18 VE

If we consider the Schrock carbene as a Fischer carbene with strongly enhanced M→C p-back bonding, the 2 electrons originally in M(d_{π}) transfer to the C(p_z) orbital, oxidizing the metal by 2 units and giving a CR_2^{2-} ligand.

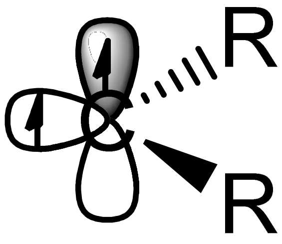
- The more electropositive early transition metal complexes have less stable M(d_{π}) orbitals, i.e. easier to oxidize. For example d^2 metals are especially strong *p*-donors.

- The system can thus be visualized as a metal stabilized carbanion acting as both a σ and π donor to the metal.



singlet carbene

sp^2



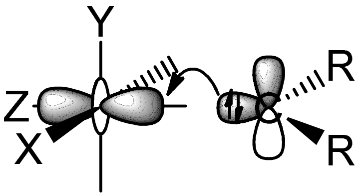
triplet carbene

sp^2

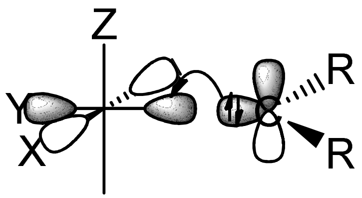
- Free carbene CH_2 has ***two distinct spin isomers:*** singlet and triplet

  – not resonance forms (sinlget ↔ triplet resonance forbidden)
- Singlet and triplet forms have different H-C-H angles
- In the singlet state $2e^-$ are paired up in the sp^2 orbital leaving the p_z orbital unoccupied
- In the triplet state both the sp^2 and *p* orbitals are singly occupied

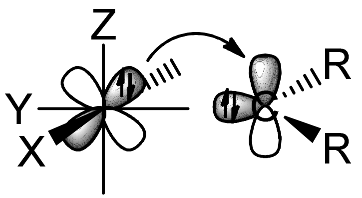
Fischer vs. Schrock



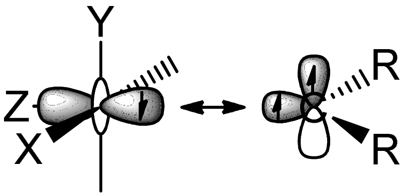
Metal $dz^2 \xLeftarrow{\sigma\text{ bond}}$ singlet carbene sp^2



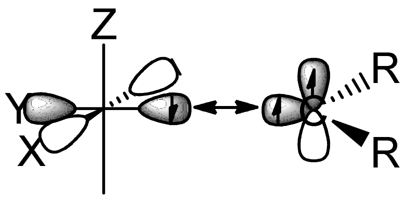
Metal $dx^2\text{-}dy^2 \xLeftarrow{\sigma\text{ bond}}$ singlet carbene sp^2



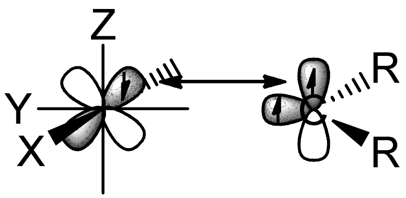
Metal dyz $\xRightarrow{\pi\text{-back-donation}}$ singlet carbene p_z



Metal $dz^2 \xLeftrightarrow{\sigma\text{ bond}}$ triplet carbene sp^2



Metal $dx^2\text{-}dy^2 \xLeftrightarrow{\sigma\text{ bond}}$ triplet carbene sp^2



Metal dyz $\xLeftrightarrow{\pi\text{-bond}}$ triplet carbene p_z

- In the Fischer (singlet) case, direct *C→M donation predominates* and the carbon tends to be positively charged.
- In the Schrock (triplet) case, *two covalent bonds are formed, each polarized toward the carbon* giving it a negative charge.

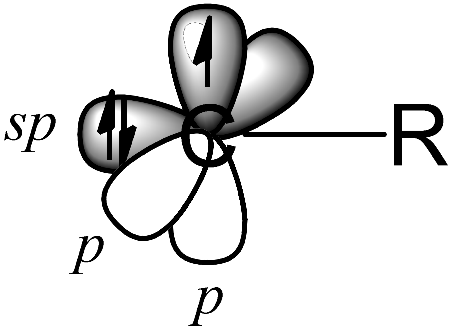
- Taylor and Hall used ab-initio calculations to differentiate between the electronic structures of Fischer and Schrock type carbene complexes.
- Calculations on a variety of free carbenes indicated that
  - **heteroatom and phenyl substituents preferentially stabilize a singlet ground state**.
  - **alkyl and hydride substituents stabilized a triplet ground state at the carbene carbon**.
- Carbenes are both thermodynamically and kinetically unstable therefore forming very strong metal-carbene bonds disfavoring dissociation

  e.g. just as paramagnetic triplet **:**CH_2 can dimerize to form diamagnetic $H_2C=CH_2$, it also binds to a triplet L_nM fragment to give a diamagnetic $L_nM=CH_2$ complex.

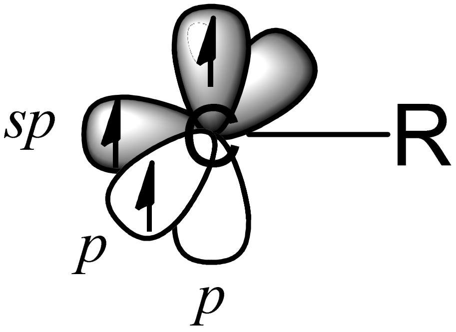
T. E. Taylor, M. B. Hall, *J. Amer. Chem. Soc.* **1984**, 106, 1576-1584.

Metal Carbynes

- Have similar bonding formulations as per Fischer and Schrock carbenes
- The free carbyne can be of doublet (Fischer) or quartet (Schrock) multiplicity



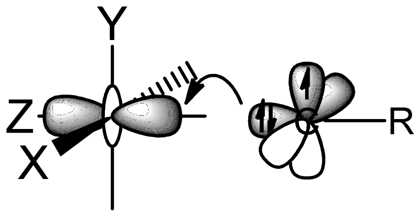
doublet carbyne (*sp*)



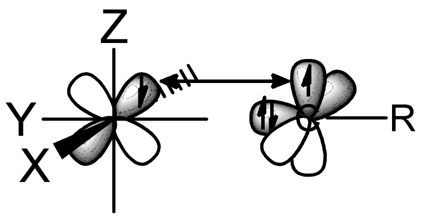
quartet carbyne (*sp*)

- The carbyne ligand is linear
- Carbyne carbon is *sp* hybridized
- The M≡C bond is very short (1.65 – 1.90 Å)
- Characteristic low-field ^{13}C NMR resonance in the range +250 to +400 ppm

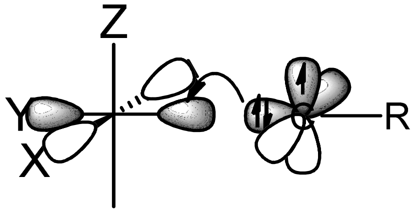
Fischer Carbynes



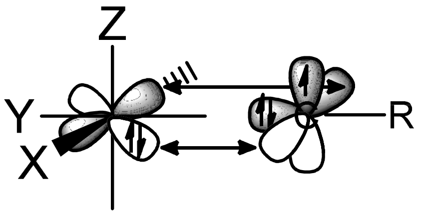
Metal dz^2 $\xLeftarrow{\sigma \text{ bond}}$ doublet carbyne *sp*



Metal dyz $\xLeftrightarrow{\pi\text{-bond}}$ doublet carbyne p_z



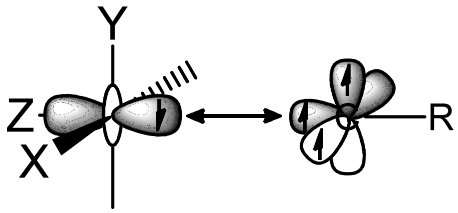
Metal dx^2-dy^2 $\xLeftarrow{\sigma \text{ bond}}$ doublet carbyne *sp*



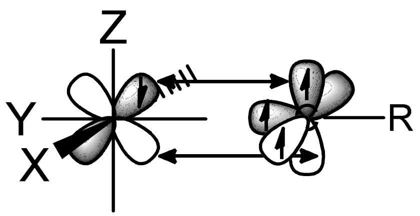
Metal dxy $\xRightarrow{\pi\text{-back-donation}}$ doublet carbyne p_x

- A doublet (Fischer) carbyne is *sp* hybridized
- Contains one filled *sp* orbital capable of donating 2e$^-$ to a metal centre
- Contains one singly occupied *p* orbital capable forming an additional π bond
- The remaining empty *p* orbital is capable of M→C π back donation
- 3e$^-$ donor covalent model (or 4e$^-$ donor ionic model)

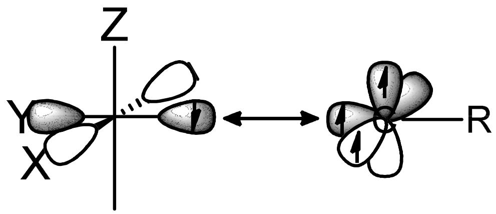
Schrock Carbynes



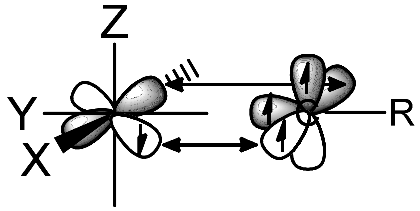
Metal $dz^2 \xLeftrightarrow{\sigma \text{ bond}}$ quartet carbyne *sp*



Metal dyz $\xLeftrightarrow{\pi\text{-bond}}$ quartet carbyne p_z



Metal $dx^2\text{-}dy^2 \xLeftrightarrow{\sigma \text{ bond}}$ quartet carbyne *sp*



Metal dxy $\xRightarrow{\pi\text{-back-donation}}$ quartet carbyne p_x

- A quartet (Schrock) carbyne is also *sp* hybridized
- Contains three singly occupied orbitals (one *sp* and two *p*) capable of forming three covalent M-C bonds (one s and two p bonds)
- $3e^-$ ligand in covalent model (*or* $6e^-$ ionic model)