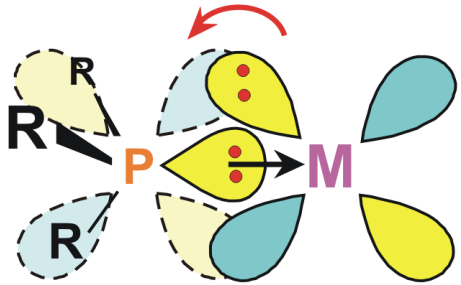
Phosphine Ligands – PR_3

empty d orbitals on phosphine can act as π-acceptor orbitals } not very important unless R-groups are electron-withdrawing



neutral $2e^-$ donor

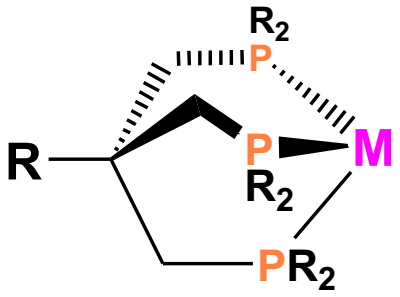
Phosphine ligands

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

R = carbon groups { phosphine (US) / phosphane (Germany/Europe)

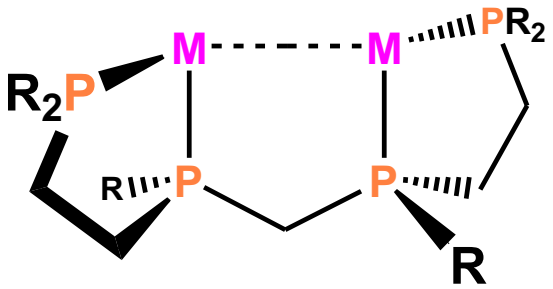
R = OR groups → phosphite

- large changes in the donor/acceptor properties of the phosphine (from excellent donor/poor π-acceptor to poor donor/excellent π-acceptor)
- large changes in the steric profile of the phosphine (from fairly small to enormous)
- generation of a large number of polydentate polyphosphines (bis-, tris-, tetra-, penta-, and hexaphosphine ligands are all known) that can adopt specific coordination geometries (cis-enforcing, facial tridentate, bridging, bridging and chelating, etc.)



M(η^3-tripod)

facial coordinating



racemic-M_2(P4)

binucleating phosphine

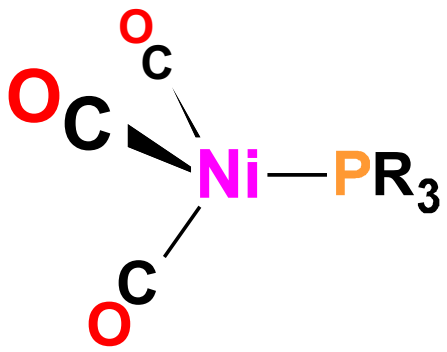
able to bridge and chelate 2 metals

Tolman's Cone Angle and Electronic Parameter

The **electron-donating ability** of a phosphine ligand was determined by measuring the ν_{CO} of a $Ni(CO)_3(PR_3)$ complex:

Lowest CO stretching frequency:

most donating phosphine

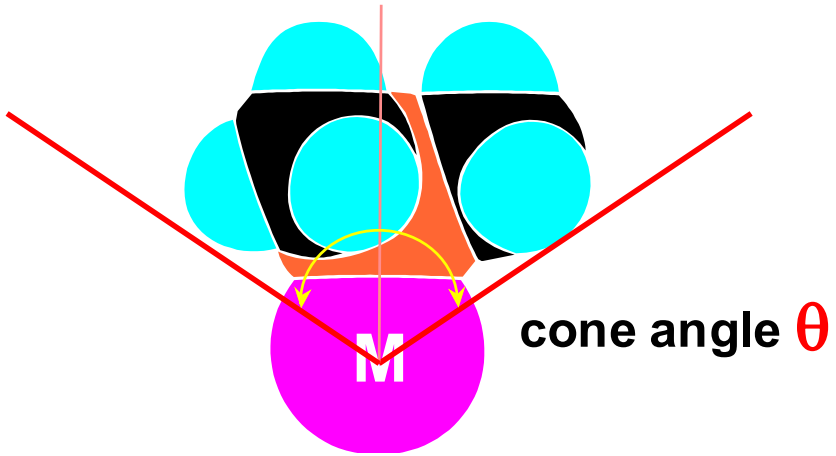


Highest CO stretching frequency:

least donating phosphine

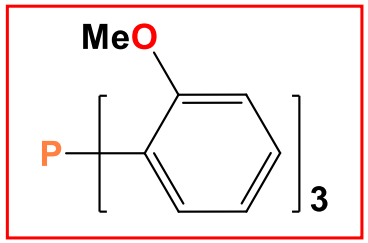
(best π-acceptor)

The **size** or **steric bulk** of a phosphine ligand was determined from simple 3-D space-filling models of the phosphine ligand coordinated to a Ni atom:

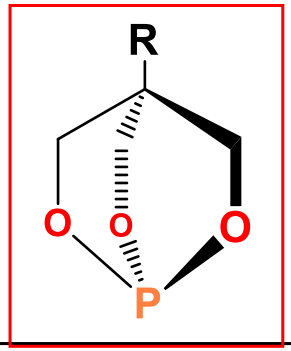


Tolman's Electronic Parameter ν (most donating to least)

PR_3	mixed	$P(OR)_3$	PX_3	ν, cm^{-1}
$P(t\text{-}Bu)_3$				2056.1
PCy_3				2056.4
$P(o\text{-}OMe\text{-}C_6H_4)_3$				2058.3
$P(i\text{-}Pr)_3$				2059.2
PBu_3				2060.3
PEt_3				2061.7
	PEt_2Ph			2063.7
PMe_3				2064.1
	PMe_2Ph			2065.3
$P(p\text{-}OMe\text{-}C_6H_4)_3$	$PPh_2(o\text{-}OMe\text{-}C_6H_4)$			2066.1
PBz_3				2066.4
$P(o\text{-}Tol)_3$				2066.6
$P(p\text{-}Tol)_3$	$PEtPh_2$			2066.7
	$PMePh_2$			2067.0
$P(m\text{-}Tol)_3$				2067.2
	$PPh_2(NMe_2)$			2067.3
	$PPh_2(2,4,6\text{-}Me\text{-}C_6H_2)$			2067.4
	$PPhBz_2$			2067.6
	$PPh_2(p\text{-}OMe\text{-}C_6H_4)$			2068.2
	PPh_2Bz			2068.4
PPh_3				**2068.9**



$P(CH=CH_2)_3$	$PPh_2(p\text{-}F\text{-}C_6H_4)$		2069.5
	$PPh(p\text{-}F\text{-}C_6H_4)_2$		2070.0
$P(p\text{-}F\text{-}C_6H_4)_3$			2071.3
	$PPh_2(OEt)$		2071.6
	$PPh(O\text{-}i\text{-}Pr)_2$		2072.2
$P(p\text{-}Cl\text{-}C_6H_4)_3$			2072.8
	PPh_2H		2073.3
	$PPh(OBu)_2$		2073.4
$P(m\text{-}F\text{-}C_6H_4)_3$			2074.1
	$PPh(OEt)_2$		2074.2
	$PPh_2(C_6F_5)$		2074.8
		$P(O\text{-}i\text{-}Pr)_3$	2075.9
		$P(OEt)_3$	2076.3
	$PPhH_2$		2077.0
		$P(OMe)_3$	2079.5
	$PPh(OPh)_2$		2079.8
		PPh_2Cl	2080.7
		PMe_2CF_3	2080.9
		$P(O\text{-}2,4\text{-}Me\text{-}C_6H_3)_3$	2083.2
		$P(OPh)_3$	2085.3
		$P(OCH_2)_3CR$	2086.8
	$P(C_6F_5)_3$		2090.9
		PCl_3	2097.0
		PF_3	2110.8



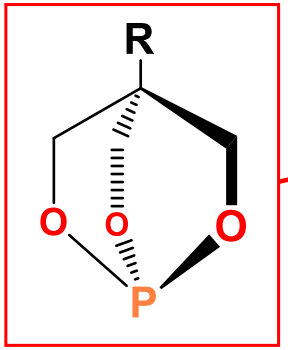
Problem: Order the following phosphines from strongest to weakest σ donor:

$P(OEt)_3$ PPh_3 PPr_3 PCl_3 $PPh(OMe)_2$

The strongest σ-donor has the most alkyl groups, which are considered to be donating to the phosphorus center (actually the least electron-withdrawing). The more electronegative (electron-withdrawing) groups attached to the P center, the more positive charge on the P center and the more contracted and lower the energy of the P lone pair. This makes it a poorer σ-donating group.

$PPr_3 > PPh_3 > PPh(OMe)_2 > P(OEt)_3 > PCl_3$

Tolman's Cone Angle θ (smallest to largest)



PR_3	mixed	$P(OR)_3$	PX_3	θ (°)
			PH_3	87
	$PPhH_2$	$P(OCH_2)_3CR$		101
			PF_3	104
	$Me_2PCH_2CH_2PMe_2$	$P(OMe)_3$		107
		$P(OEt)_3$		109
	$P(CH_2O)_3CR$			114
	$Et_2PCH_2CH_2PEt_2$			115
PMe_3				118
	$Ph_2PCH_2PPh_2$			121
		PMe_2CF_3	PCl_3	124
	$Ph_2PCH_2CH_2PPh_2$			125
	PPh_2H	$P(OPh)_3$		128
			PBr_3	131
PEt_3, PPr_3, PBu_3	$PPh_2(OMe)$			132
	PEt_2Ph, $PMePh_2$			136
	$Cy_2PCH_2CH_2PCy_2$			142
PPh_3				**145**

	$PPh_2(t\text{-Bu})$		157
	$PPh_2(C_6F_5)$		158
$P(i\text{-Pr})_3$			160
PBz_3			165
PCy_3	$PPh(t\text{-Bu})_2$		170
		$P(O\text{-}t\text{-Bu})_3$	175
$P(t\text{-Bu})_3$			182
	$P(C_6F_5)_3$		184
$P(o\text{-Tol})_3$			194
$P(\text{mesityl})_3$			212

Commonly Used Monodentate Phosphines

PPh_3 (145°, medium donor), triphenylphosphine, tpp "The KING"

- air-stable, white crystalline material, no odor to speak of

Increasing σ-Donor Ability:

$PMePh_2$ (136°), PMe_2Ph (122°), PMe_3 (118°), PEt_3 (132°)

$P(Cy)_3$ (170°) tricyclohexylphosphine, $P(t\text{-}Bu)_3$ (182°)

- the alkyl phosphines are strong σ-donors; low MW ones usually colorless liquids, somewhat to very air-sensitive, horrible smelling (unless very high MW and non-volatile)

Poor σ-Donors, Good π-Acceptors:

Phosphites: $P(OMe)_3$ (107°), $P(OEt)_3$ (110°), $P(OPh)_3$ (128°)

- phosphites are relatively poor σ-donors, but can be fairly good π-acceptor ligands (about half as good as CO); low MW ones are usually colorless liquids, higher MW compounds are white solids; usually air-stable but moisture sensitive; sometimes sweet smelling

PF_3 (104°) } v. poor donor; strong π-acceptor, almost as good as CO