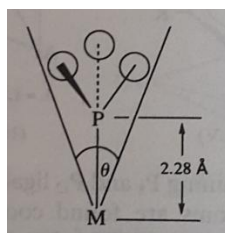


Phosphines as ligand

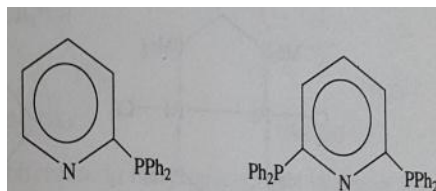
One of the most important classes of ligands in transition metal chemistry are the PR_3 , R_2Ar , PRAr_2 and PAr_3 molecules. Closely related are the P(OR)_3 and P(OAr)_3 molecules as well as mixed haloalkyl and haloaryl ligands. Analogous compounds are formed by As, Sb and to a small extent Bi. The donor ability decreases $\text{P} > \text{As} > \text{Sb} > \text{Bi}$, other things being equal.

The steric demand of a monophosphine ligand is difficult to define precisely, especially for those with more than one kind of group attached to P atom. A rough but useful estimate of the solid angle subtended at the metal atom to which the ligand is bound is the so called *cone angle*, θ , defined as follows.

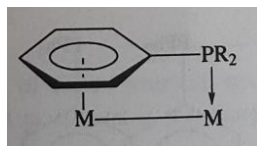


Monophosphines

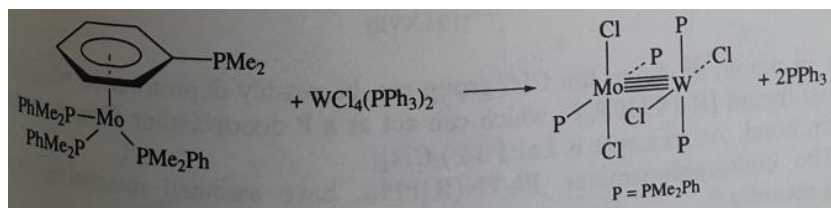
40 to 50 monophosphines are commercially available but two most common are triphenyl phosphines and trimethyl phosphines. Monophosphines can be combined with other ligands to afford many interesting following polydentate ligands.



Arylphosphines may also be bonded to metal atoms as substituted η^6 - arenes. The dangling PR_2 may then act as a donor to another metal atom, thus bridging across M-M bonded units.

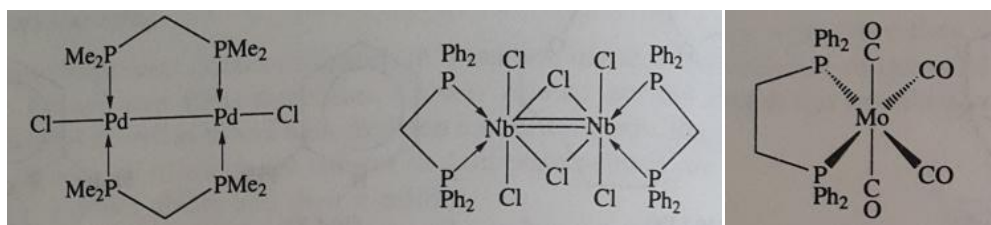


An interesting application of this is a reaction that may proceed through such intermediate to afford a synthesis for a Mo-W compound.

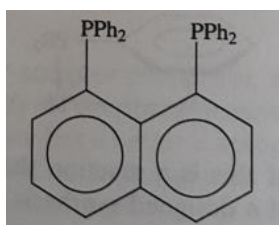


Diphosphines

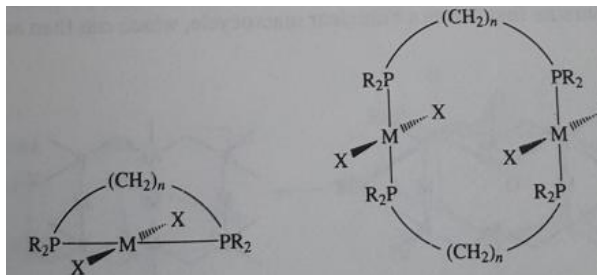
These ligands, of which the most widely used are $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ [bis(dimethyl phosphinoethane)(dmpe)], $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ [bis(diphenyl phosphinoethane)(dppe)], $\text{Me}_2\text{PCH}_2\text{PMe}_2$ [bis(dimethyl phosphinomethane)(dmpm)] and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ [bis(diphenyl phosphinomethane)(dppm)], can form either chelated or bridged complexes.



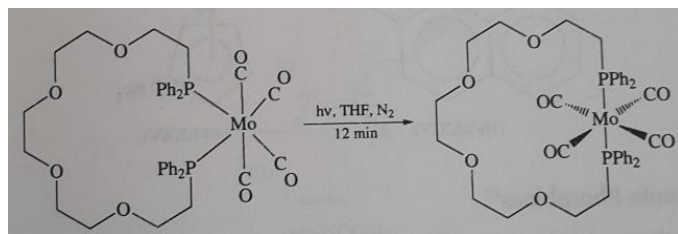
On the other hand, ligands can be designed to do only one thing. For example, following ligand is capable of chelation only.



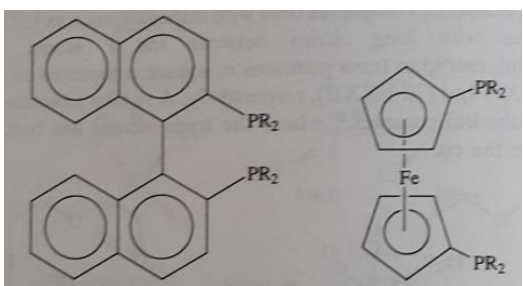
Diphosphines with long chains between the P atoms, for example, $\text{Bu}^t_2\text{P}(\text{CH}_2)_{5-8}\text{P}^t\text{Bu}_2$, can span trans positions in square planar complexes or give large ring systems.



A similar situation has also been found in an octahedral complex, where the trans isomer has been shown to be more stable than the cis.

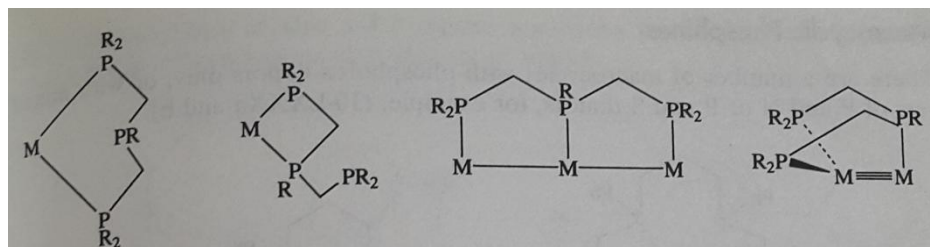


The reasons for the stabilities of these unusual systems are complexes. Other important biphosphines are the asymmetric binaphthyls and others as well as 1,1'-diphosferrocenes that can act as either chelating or bridging ligands.

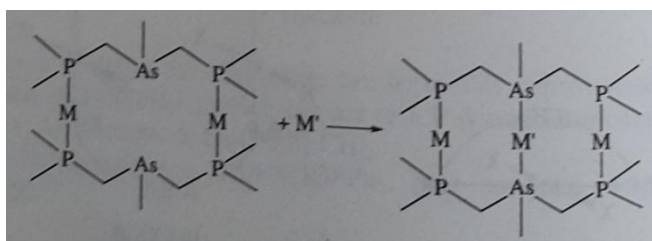


Polydentate Phosphines

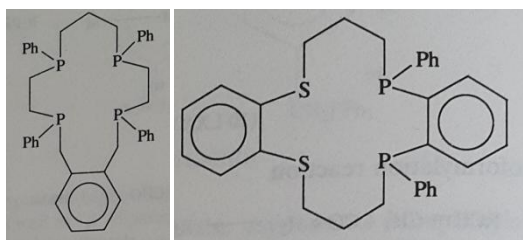
The important of these are the tripods, such as $\text{HC}(\text{CH}_2\text{PR}_2)_3$, as well as ligands such as $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$ or $\text{P}(\text{CH}_2\text{CH}_2\text{PMe}_2)_3$, which are potentially tetradentate. Linear tridentate phosphines can behave in a number of ways as shown below.



Also, there is the situation where a diphosphinoarsine first forms a binuclear macrocycle, which can then add another metal atom.



There are a number of macrocyclic ligands having phosphorus as donor as well as mixed set of P and N or P and S donors.



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