4.2: Main group elements of 2nd and 3rd periods and their compounds

(a) Boron

Refined elemental boron is a black solid with a metallic luster. The unit cell of crystalline boron contains 12, 50, or 105 boron atoms, and the B_{12} icosahedral structural units join together by 2 center 2 electron (2c-2e) bonds and 3 center 2 electron (3c-2e) bonds (electron deficient bonds) between boron atoms (Figure 4.2.1). Boron is very hard and shows semiconductivity.
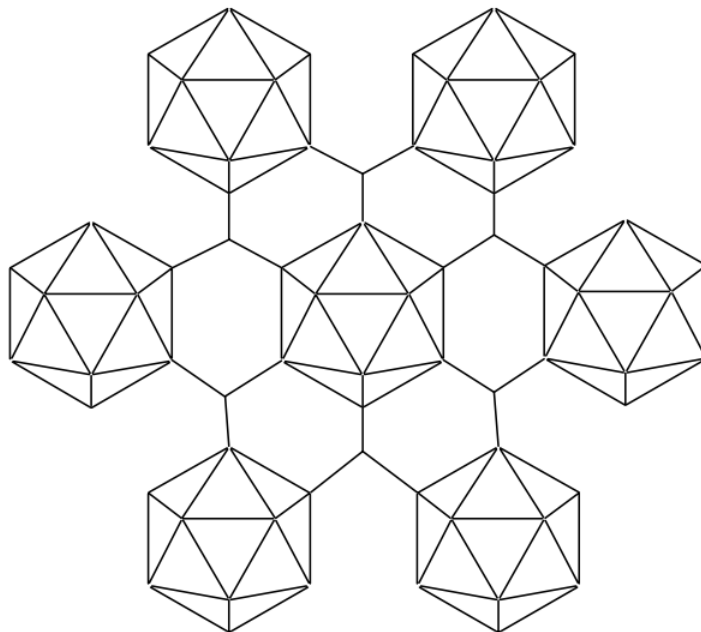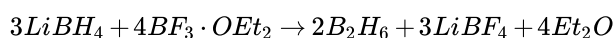

Figure 4.2.1: - The structure of the elemental boron with B_{12} icosahedra.

The chemistry of **boranes** (boron hydrides) started from the research of A. Stock reported during the period 1912-1936. Although boron is adjacent to carbon in the periodic table, its hydrides have completely different properties from those of hydrocarbons. The structures of boron hydrides in particular were unexpected and could be explained only by a new concept in chemical bonding. For his contribution to the very extensive new inorganic chemistry of boron hydrides, W. N. Lipscomb won the Nobel prize in 1976. Another Nobel prize (1979) was awarded to H. C. Brown for the discovery and development of a very useful reaction in organic synthesis called hydroboration.

Because of the many difficulties associated with the low boiling points of boranes, as well as their activity, toxicity, and air-sensitivity, Stock had to develop new experimental methods for handling the compounds *in vacuo*. Using these techniques, he prepared six boranes B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, and $B_{10}H_{14}$ by the reactions of magnesium boride, MgB_2, with inorganic acids, and determined their compositions. However, additional research was necessary to determine their structures. At present, the original synthetic method of Stock using MgB_2 as a starting compound is used only for the preparation of B_6H_{10}. Since reagents such as lithium tetrahydroborate, $LiBH_4$, and sodium tetrahydroborate, $NaBH_4$, are now readily available, and **diborane**, B_2H_6, is prepared according to the following equation, higher boranes are synthesized by the pyrolysis of diborane.

$$3LiBH_4 + 4BF_3 \cdot OEt_2 \rightarrow 2B_2H_6 + 3LiBF_4 + 4Et_2O$$

A new theory of chemical bonding was introduced to account for the bonding structure of diborane, B_2H_6. Although an almost correct hydrogen-bridged structure for diborane was proposed in 1912, many chemists preferred an ethane-like structure, $H_3B\text{-}BH_3$, by analogy with hydrocarbons. However, H. C. Longuet-Higgins proposed the concept of the electron-deficient **3-center 2-electron bond** (3c-2e bond) and it was proven by electron diffraction in 1951 that the structure was correct (Figure 4.2.2).
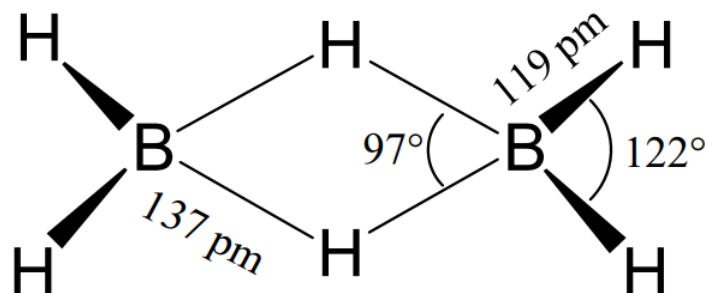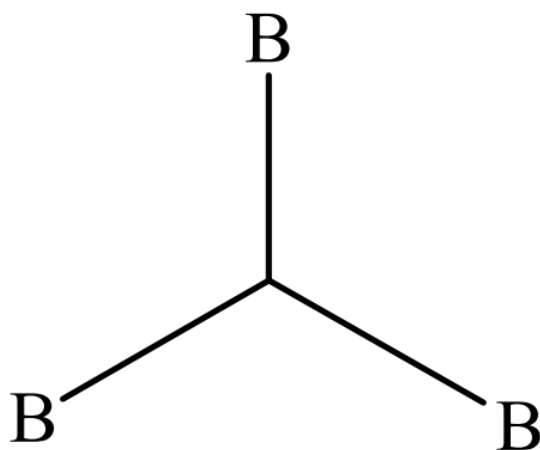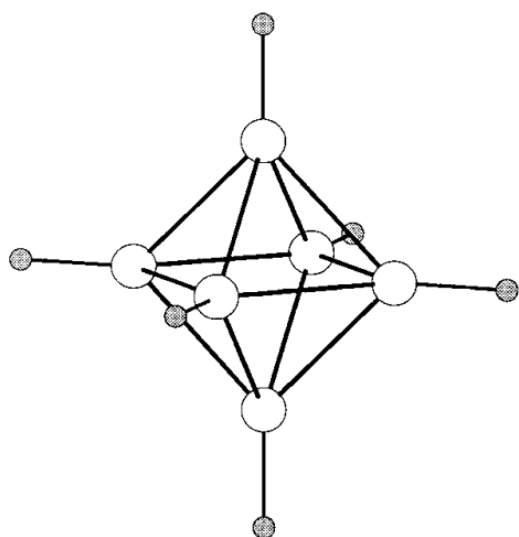
Figure 4.2.2: - Structure of diborane.

It has been elucidated by electron diffraction, single crystal X-ray structure analysis, infrared spectroscopy, etc. that boranes contain 3-center 2-electron bonds (3c-2e bond) B-H-B and
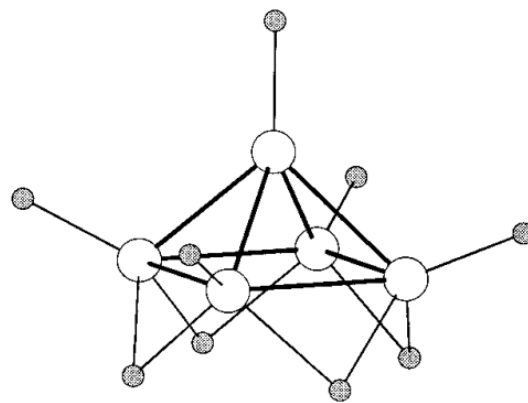

besides the usual 2 center 2 electron covalent bonds (2c-2e bond) B-H and B-B. Such structures can be treated satisfactorily by molecular orbital theory. Boranes are classified into *closo, nido, arachno*, etc. according to the skeletal structures of boron atoms.

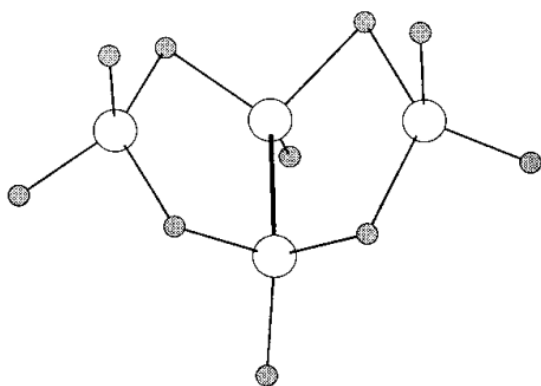***Closo*-borane** $[B_nH_n]^{2-}$ has the structure of a closed polyhedron of n boron atoms bonded to n hydrogen atoms, as seen in the examples of a regular octahedron $[B_6H_6]^{2-}$ and an icosahedron $[B_{12}H_{12}]^{2-}$. The boranes of this series do not contain B-H-B bonds. Boranes B_nH_{n+4}, such as B_5H_9, form structures with B-B, B-B-B, and B-H-B bonds and lack the apex of the polyhedron of *closo* boranes, and are referred to as **nido** type boranes. Borane B_nH_{n+6}, such as B_4H_{10}, have a structures that lacks two apexes from the *closo* type and are more open. Skeletons are also built by B-B, B-B-B, and B-H-B bonds, and these are called **arachno** type boranes. The structures of typical boranes are shown in Figure 4.2.3.
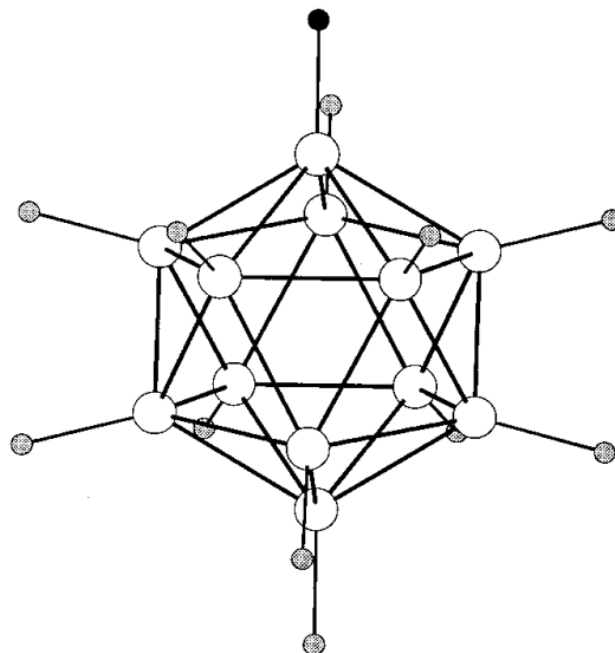
(a) *closo*-$[B_6H_6]^{2-}$

(b) *nido*-$[B_5H_9]$

(c) *arachino*-$[B_4H_{10}]$

(d) *closo*-$[B_{12}H_{12}]^{2-}$

Figure 4.2.3: - Structures of boranes.

Not only diborane but also higher boranes are **electron-deficient compounds** that are difficult to explain using Lewis' electronic structure based on simple 2-center 2-electron covalent bonds.

> **?** **Exercise 4.2.2**
>
> Why is diborane called an electron deficient compound?
>
> **Answer**
>
> It is because there are only 12 valence electrons of boron and hydrogen atoms, although 16 electrons are necessary to assign two electrons each to eight B-H bonds.

K. Wade summarized the relation of the number of valence electrons used for skeletal bonds and the structures of boranes and proposed an empirical rule called the **Wade rule**. According to this rule, when the number of boron atoms is n, the skeletal valence electrons are 2(n+1) for a *closo* type, 2(n+2) for a *nido* type, and 2(n+3) for an *arachno* type borane. The relationship between the skeletal structure of a cluster compound and the number of valence electrons is also an important problem in the cluster compounds of transition metals, and the Wade rule has played a significant role in furthering our understanding of the structures of these compounds.

(b) Carbon

Graphite, diamond, fullerene, and amorphous carbon are carbon allotropes. Usually a carbon atom forms four bonds using four valence electrons.

Graphite

Graphite is structured as layers of honeycomb-shaped 6 membered rings of carbon atoms that look like condensed benzene rings without any hydrogen atoms (Figure 4.2.4). The carbon-carbon distance between in-layer carbon atoms is 142 pm and the bonds have double bond character analogous to aromatic compounds. Since the distance between layers is 335 pm and the layers are held together by comparatively weak van der Waals forces, they slide when subjected to an applied force. This is the origin of the lubricating properties of graphite. Various molecules, such as alkali metals, halogens, metal halides, and organic compounds intercalate between the layers and form intercalation compounds. Graphite has semi-metallic electrical conductivity (about 10^{-3} Ωcm parallel to layers and about 100 times more resistant in the perpendicular direction).
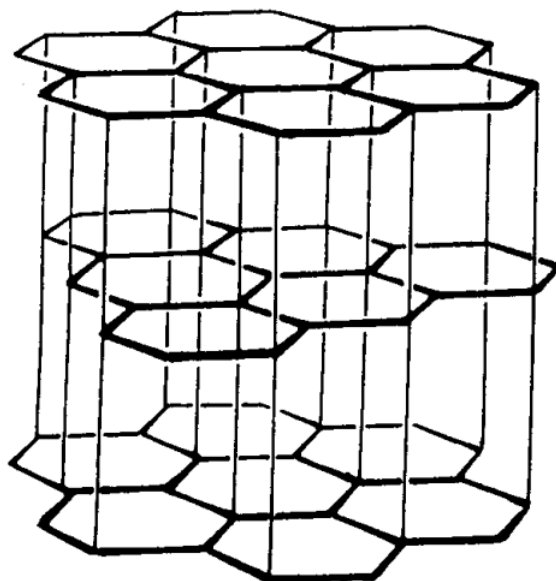

Figure 4.2.4: - Structure of graphite.

Diamond

Its structure is called the diamond-type structure (Figure 4.2.5). A unit cell of diamond contains eight carbon atoms and each carbon atom is 4-coordinate in a regular tetrahedron. Diamond is the hardest substance known, with a Mohs hardness 10. Diamond has very high heat conductivity although it is an electrical insulator. Although previously a precious mineral only formed naturally, industrial diamonds are now commercially prepared in large quantities at high temperatures (1200 °C or higher) and under high

pressures (5 GPa or more) from graphite using metal catalysts. In recent years, diamond thin films have been made at low temperatures (about 900 °C) and under low pressures (about 102 Pa) by the pyrolysis of hydrocarbons, and are used for coating purposes, etc.
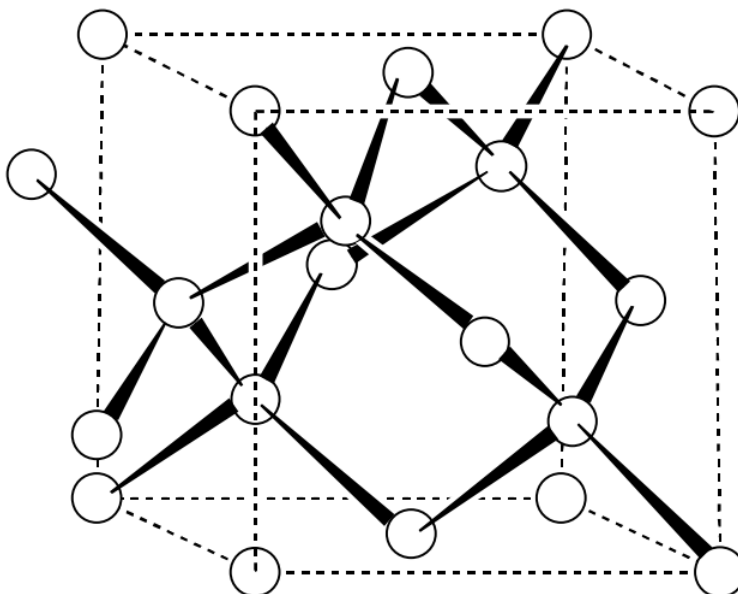

Figure 4.2.5: - Structure of diamond.

Fullerene

Fullerene is the general name of the 3rd carbon allotrope, of which the soccer ball-shaped molecule C_{60} is a typical example (Figure4.6). R. E. Smalley, H. W. Kroto and others detected C_{60} in the mass spectra of the laser heating product of graphite in 1985, and fullerene's isolation from this so-called "soot" was reported in 1991. It has the structure of a truncated (corner-cut)-icosahedron and there is double bond character between carbon atoms. It is soluble in organic solvents, with benzene solutions being purple. Usually, it is isolated and purified by chromatography of fullerene mixtures. Wide-ranging research on chemical reactivities and physical properties such as superconductivity, is progressing rapidly. Besides C_{60}, C_{70} and carbon nanotubes are attracting interest.
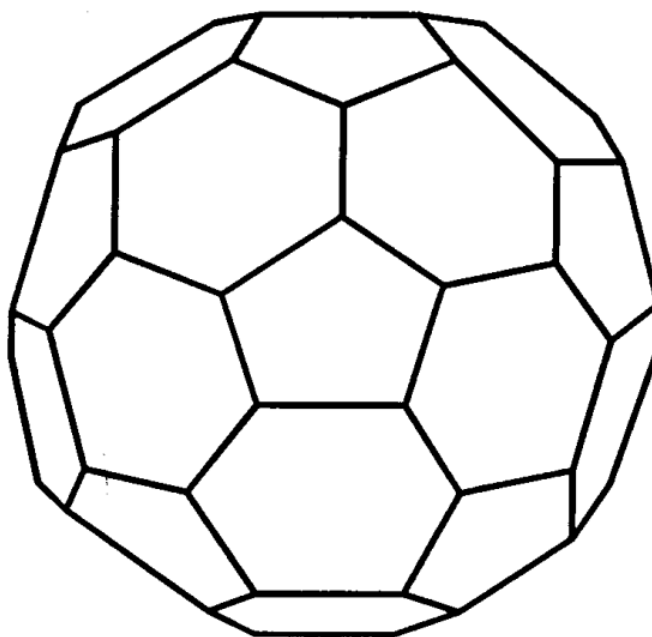

Figure 4.2.6: - Structure of C_{60}.

(c) Silicon

Silicon is the most abundant element in the earth's crust after oxygen. Most of this silicon exists as a component of silicate rocks and the element is not found as a simple substance. Therefore, silicon is produced by the reduction of quartz and sand with high-grade carbon using electric arc furnaces. Higher-grade silicon is obtained by hydrogen reduction of SiHCl3, which is produced by the hydrochlorination of low purity silicon followed by rectification. The silicon used for semiconductor devices is further refined by the crystal Czochralski or zone melting methods. The crystal (mp 1410 o C) has a metallic luster and the diamond type structure.

There are three isotopes of silicon, ^{28}Si (92.23%), ^{29}Si (4.67%), and ^{30}Si (3.10%). Because of its nuclear spin of I = 1/2, ^{29}Si is used for NMR studies of organic silicon compounds or silicates (solid-state NMR).

Silicates and organosilicon compounds show a wide range of structures in silicon chemistry. Section 4.3 (c) describes the properties of silicates. Organosilicon chemistry is the most active research area in the inorganic chemistry of main group elements other than carbon. Silicon chemistry has progressed remarkably since the development of an industrial process to produce organosilicon compounds by the direct reaction of silicon with methyl chloride CH_3Cl in the presence of a copper catalyst. This historical process was discovered by E. G. Rochow in 1945. Silicone resin, silicone rubber, and silicone oil find wide application. In recent years, silicon compounds have also been widely used in selective organic syntheses.

Although silicon is a congener of carbon, their chemical properties differ considerably. A well-known example is the contrast of silicon dioxide SiO_2 with its 3-dimensional structure, and gaseous carbon dioxide, CO_2. The first compound $(Mes)_2Si=Si(Mes)_2$ (Mes is mesityl $C_6H_2(CH_3)_3$) with a silicon-silicon double bond was reported in 1981, in contrast with the ubiquitous carbon-carbon multiple bonds. Such compounds are used to stabilize unstable bonds with bulky substituents (kinetic stabilization).

> **? Exercise 4.2.3**
>
> Why are the properties of CO_2 and SiO_2 different?
>
> **Answer**
>
> Their properties are very different because CO_2 is a chain-like three-atom molecule and SiO_2 is a solid compound with the three dimensional bridges between silicon and oxygen atoms.

(d) Nitrogen

Nitrogen is a colorless and odorless gas that occupies 78.1% of the atmosphere (volume ratio). It is produced in large quantities together with oxygen (bp -183.0 °C) by liquefying air (bp -194.1 °C) and fractionating nitrogen (bp -195.8 °C). Nitrogen is an inert gas at room temperatures but converted into nitrogen compounds by biological nitrogen fixation and industrial ammonia synthesis. The cause of its inertness is the large bond energy of the N≡N triple bond.

The two isotopes of nitrogen are ^{14}N (99.634%) and ^{15}N (0.366%). Both isotopes are NMR-active nuclides.

(e) Phosphorus

Simple phosphorus is manufactured by the reduction of calcium phosphate, $Ca_3(PO_4)_2$, with quartz rock and coke. Allotropes include white phosphorus, red phosphorus, and black phosphorus.

White phosphorus is a molecule of composition of P_4 (Figure 4.2.7). It has a low melting-point (mp 44.1 °C) and is soluble in benzene or carbon disulfide. Because it is pyrophoric and deadly poisonous, it must be handling carefully.
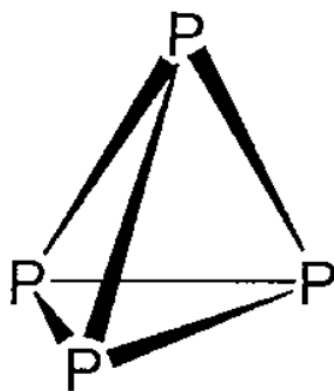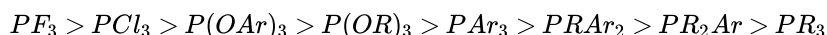
Figure 4.2.7: - Structure of white phosphorus.

Red phosphorus is amorphous, and its structure is unclear. The principal component is assumed to be a chain formed by the polymerization of P_4 molecules as the result of the opening of one of the P-P bonds. It is neither pyrophoric nor poisonous, and used in large quantities for the manufacturing of matches, etc.

Black phosphorus is the most stable allotrope and is obtained from white phosphorus under high pressure (about 8 GPa). It is a solid with a metallic luster and a lamellar structure. Although it is a semiconductor under normal pressures, it shows metallic conductivity under high pressures (10 GPa).

Phosphorus compounds as ligands

Tertiary phosphines, PR_3, and phosphites, $P(OR)_3$, are very important ligands in transition metal complex chemistry. Especially triphenylphosphine, $P(C_6H_5)_3$, triethyl phosphine, $P(C_2H5)_3$, and their derivatives are useful ligands in many complexes, because it is possible to control precisely their electronic and steric properties by modifying substituents (refer to Section 6.3 (c)). Although they are basically sigma donors, they can exhibit some pi accepting character by changing the substituents into electron accepting Ph (phenyl), OR, Cl, F, etc. The order of the electron-accepting character estimated from the C-O stretching vibrations and ^{13}C NMR chemical shifts of the phosphine- or phosphite-substituted metal carbonyl compounds is as follows (Ar is an aryl and R is an alkyl).

$$PF_3 > PCl_3 > P(OAr)_3 > P(OR)_3 > PAr_3 > PRAr_2 > PR_2Ar > PR_3$$

On the other hand, C. A. Tolman has proposed that the angle at the vertex of a cone that surrounds the substituents of a phosphorus ligand at the van der Waals contact distance can be a useful parameter to assess the steric bulkiness of phosphines and phosphites. This parameter, called the **cone angle**, is widely used (Figure 4.2.8). When the cone angle is large, the coordination number decreases by steric hindrance, and the dissociation equilibrium constant and dissociation rate of a phosphorus ligand become large (Table 4.2.2). The numerical expression of the steric effect is very useful, and many studies have been conducted into this effect.
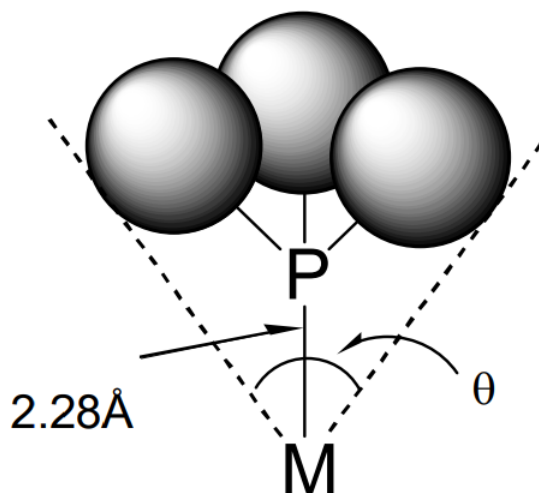

Figure 4.2.8: - Cone angle.

Table 4.2.2 Cone angles ($\theta°$) of tertiary phosphines and phosphites

Ligands	Cone angles
$P(OEt)_3$	109
PMe_3	118
$P(OPh)_3$	121
PEt_3	132
PMe_2Ph	136
PPh_3	145
P^iPr_3	160
P^tBu_3	182