Lecture 7. Polymer compound V elements and VI, VII, VIII of the periodic system.

Compounds with metal-carbon bonds

The variety of hydrocarbon ligands found in d-block organometallic chemistry range from simple σ-bonded alkyl ligands, double-bonded carbenes, and triply bonded carbynes to a host of polyene ligands, some of which are described in the remainder of this section.

SIMPLE ALKYL LIGANDS

A simple alkyl ligand forms an M−C single bond, and in doing so the alkyl group acts as a one-electron monohapto ligand. Many such compounds are known, but they are less common in the d block than in the s and p blocks. This may in part be a result of the modest M−C bond strengths. Another reason for the limited stability of alkyl ligands in many d-block complexes is a set of reactions that can be quite rapid, such as β-hydrogen elimination, CO insertion, and reductive elimination. As described below, these reactions transform simple hydrocarbon ligands into other groups.

The β-hydrogen elimination reaction is an important feature of the hydrocarbon chemistry of both d- and p-block organometallics. The reaction consists of the abstraction of a hydrogen atom from the organic ligand with the formation of two products, one of which contains a metal-hydrogen bond and the other of which is an alkene. $L_nM-CH_2CH_3 \rightarrow L_nM-H + H_2C=CH_2$ (L_n represents the n ligands not involved in the hydrogen elimination.) The reverse of this reaction, alkene insertion into the M−H bond, is illustrated by the hydroboration and hydrosilation reactions discussed above. Both the β-hydrogen elimination and addition of M−H across a C=C double bond are thought to proceed through a cyclic intermediate involving a three-centre, two-electron bond where a hydrogen atom bridges between the carbon and the metal atoms.

Since a compound with no hydrogen atoms on the β-carbon atom cannot undergo β-hydrogen elimination, benzyl, $CH_2(C_6H_5)$, and methyltrimethylsilyl, $CH_2Si(CH_3)_3$ (shown below) ligands are generally more robust than ethyl ligands when attached to d-block metal atoms. Similarly, the lack of β-hydrogen atoms on the methyl group accounts for the greater stability of complexes containing the methyl ligand rather than the ethyl ligand.
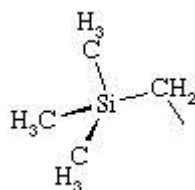
A reaction frequently referred to as CO insertion leads to carbon-carbon bond formation between the carbon atom of a carbonyl ligand and the carbon atom of an alkyl ligand, which is the methyl group in the following example.
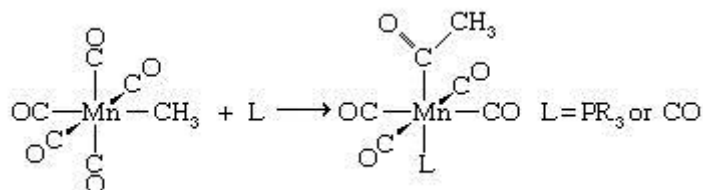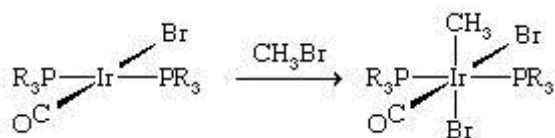

The CO insertion reaction is involved in all the transformations of $[Fe(CO)_4R]^-$ into organic molecules.

Another type of reaction that can transform an attached organic ligand (as well as other groups) is reductive elimination.
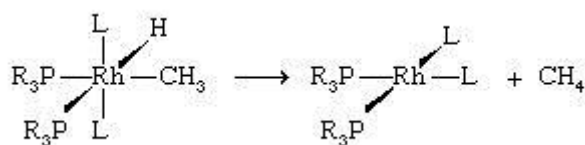

The converse of reductive elimination is oxidative addition.

The reactions discussed above, insertion of C=C into an M−H bond, β-hydrogen elimination, and CO insertion, are often employed for the synthesis of organic molecules in the laboratory and in industry. They also account for some of the individual steps in some important catalytic cycles (*see below* Organometallic compounds in catalysis).

ALKYLIDENE LIGANDS

Alkylidene ligands, such as CH_2, CHR, or CR_2, form the M=C *d-p* double bonds (i.e., bonds between the *d* orbitals of the metal and the *p* orbitals of the carbon), and their metal compounds are often called carbenes. The first stable metal carbene complex was discovered in the laboratory of the German chemist Ernst O. Fischer in Munich by the reaction of a metal carbonyl with an alkyllithium compound. In this reaction, the alkyl group is transferred (as an R⁻ group) to the carbon atom of the coordinated carbonyl, and subsequent addition of carbocation reagent results in attachment of an R⁺ group to theoxygen.
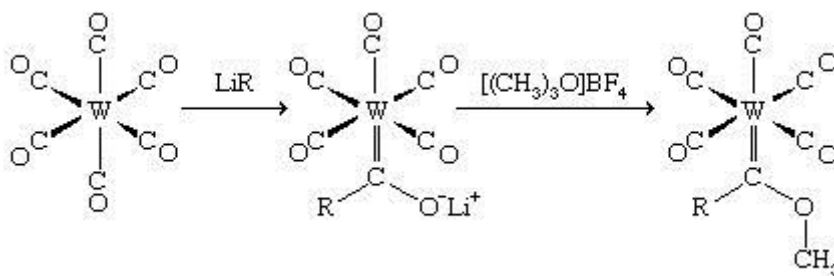
This type of carbene complex is common for the atoms of metals in groups 6–8, and they are called Fischer carbenes. The Fischer carbenes can be modified by electron-rich groups. For example, the attack of an amine on the electron-poor carbon atom of a Fischer carbene results in the displacement of the OR group to yield a new carbene (Me represents the methyl group, $-CH_3$).
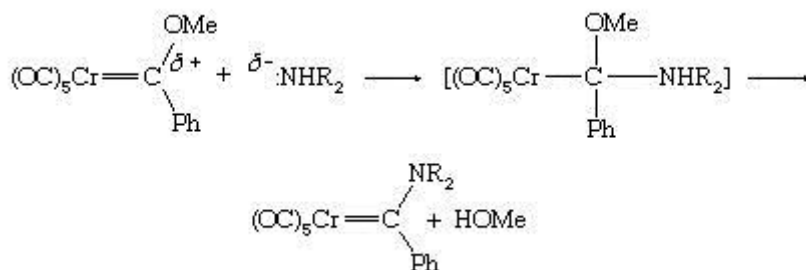

The attack of an electron-rich amine (indicated by δ- in the above equation) on the carbon atom in the Fischer carbene is attributed to the significant electronegativity of the middle to late *d*-block metals, which makes the carbon atom of the carbene electron-poor (indicated by δ+ in the above equation).

The reactions of Fischer carbene complexes with alkynes has considerable utility in organic synthesis. For example, naphthyl compounds (i.e., those derived from the fused ring system $C_{10}H_8$) can be synthesized by the reaction of methoxy phenyl Fischer carbenes with analkyne.
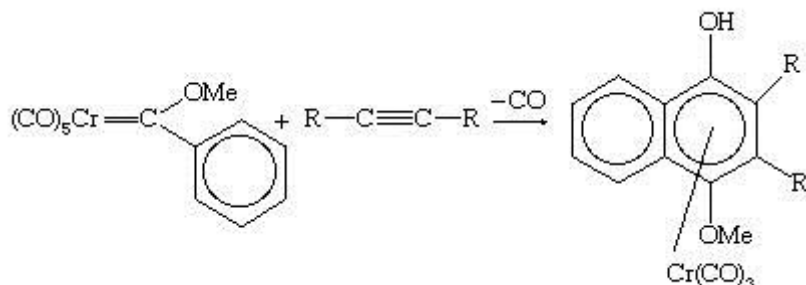

The chromium can be removed from the organic product by mild oxidation. Another route to a carbene is the deprotonation of an alkyl ligand, producing a carbene that contains onlyhydrocarbon ligands.
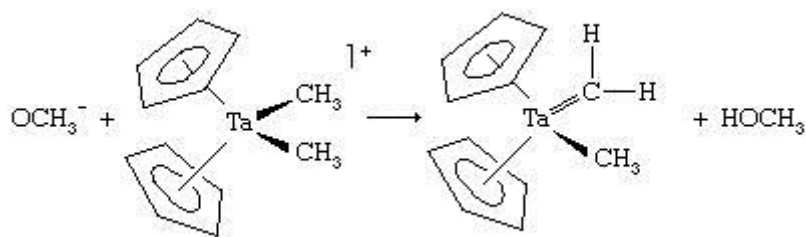
These ligands that contain only carbon and hydrogen are commonly attached to metal atoms from the early part of the d block such as titanium (Ti) and tantalum (Ta). The complexes are known as Schrock carbenes for their discoverer, American chemist Richard Schrock. The chemistry and spectroscopy of the Schrock carbenes indicate that these compounds have the opposite polarity of the Fischer carbenes. The carbon behaves as if it were electron-rich, because the $M^{\delta+}=C^{\delta-}$ bond is polarized so as to put negative charge on the metal-bound carbon, for the early d-block metals readily give up electrons. As a result, the carbon attached to the metal atom in a Schrock carbene reacts with electron-seeking reagents, such as $Me_3Si^{\delta+}Br^{\delta+}$, at the carbene carbon (Cp is a common abbreviation for the cyclopentadienyl ligand, $-C_5H_5$).

$$Cp_2Ta(CH_2)(CH_3) + Me_3SiBr \longrightarrow [Cp_2Ta(CH_2SiMe_3)(CH_3)]^+ + Br^-$$
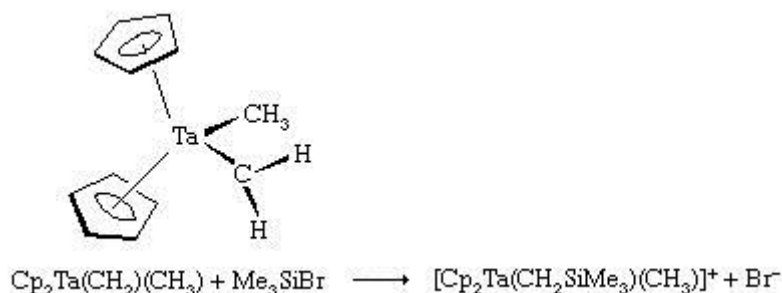
An interesting reaction of the Schrock carbenes is the alkene metathesis reaction:

$$CpCl_2Ta=C(H)CMe_3 + H_2C=CH_2 \longrightarrow$$
$$CpCl_2Ta=CH_2 + H_2C=C(H)(CMe_3)$$
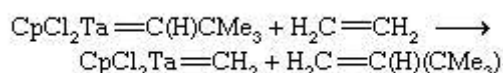
This reaction appears to proceed through a four-membered ring intermediate containing carbon atoms and the metal atom.
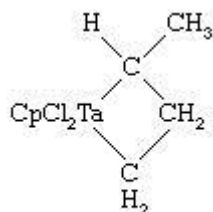

ALKYLIDYNE LIGANDS

Alkylidyne ligands have the general formula CH or CR. They are bound to the metal by an M≡C triple bond involving one σ bond and two d-p π bonds. The simplest member of this series is methylidyne, CH, and the next simplest, CCH$_3$, is ethylidyne. One route to methylidynes, discovered in Fischer's laboratory, involves the abstraction of an alkoxide group (OR) from a Fischer carbene by BBr$_3$.
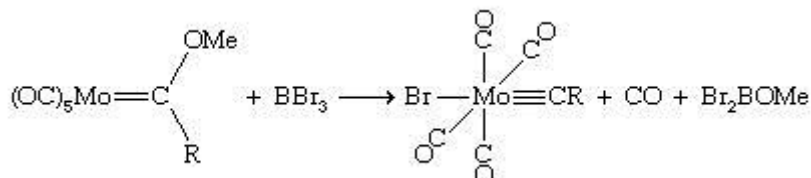

ALKENE AND ALKYNE LIGANDS

An alkene ligand contains a π bond between carbon atoms, C=C, which can serve as an electron pair donor in a metal complex, as in the case of Zeise's salt (*see above* Historical developments). This complex may be prepared by bubbling ethylene, C$_2$H$_4$, through an aqueous solution of $[PtCl_4]^{2-}$ in the presence of divalent tin, Sn(II), which aids in the removal of the chloride ion (Cl$^-$) from the coordination sphere of the divalent platinum, Pt(II).

$$K_2[PtCl_4] + H_2C{=}CH_2 \xrightarrow{\text{SnCl}_2} K[PtCl_3(\eta^2\text{-}C_2H_4)] + KCl$$
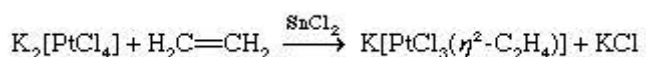
The alkene ligand bonds to the metal centre by both electron donation and acceptance, similar to the situation with carbon monoxide. Electron donor-and-acceptor character between the metal and the alkene ligand appear to be fairly evenly balanced in most ethylene complexes of the d metals.

The allyl ligand, $-CH_2-CH{=}CH_2$, can bind to a metal atom in either of two configurations: as an η^1-ligand or an η^3-ligand. Because of this versatility in bonding, η^3-allyl complexes are often highly reactive. Examples of η^1- and η^3-allyl complexes are, respectively, shown here.

Fe(η^1-C$_3$H$_3$)(CO)$_2$(η^5-Cp)   Co(η^3-C$_3$H$_5$)(CO)$_3$
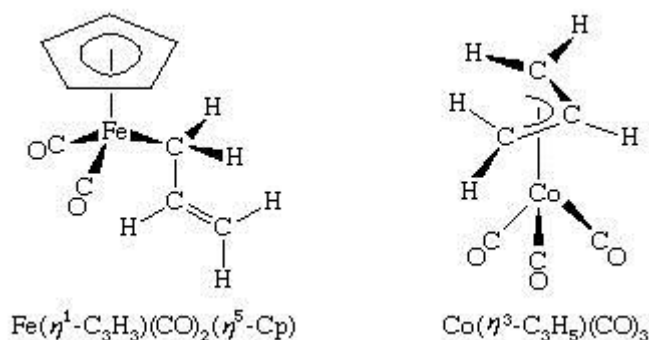
Acetylene, H−C≡C−H, has two π bonds and hence is a potential four-electron donor. Substituted acetylenes form very stable polymetallic complexes in which the acetylene can be regarded as a

four-electron donor. An example is η^2-diphenylethynehexacarbonyldicobalt, in which four of the six electrons in the triple bond of the ethyene ligand, R−C≡C−R, are shared with the two cobalt atoms (Ph represents the phenyl ligand, −C$_6$H$_5$). As in this example, the alkyl or aryl groups (R) on the acetylene impart stability to the metal complex—in contrast to simple acetylene (HC≡CH) complexes, where the hydrogen atoms are reactive.


$Co_2(PhC_2Ph)(CO)_6$
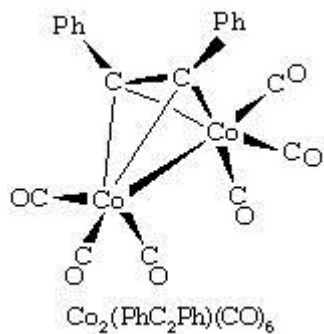
POLYENE LIGANDS

Diene (−C=C−C=C−) and larger polyene ligands present the possibility of several points of attachment to a metal atom. The resulting polyene complexes are usually more stable than the equivalent monohapto complex with individual ligands. For example, bis(η^4-cycloocta-1,5-diene)nickel is more stable than the corresponding complex containing four ethylene ligands.
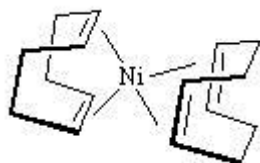

Cycloocta-1,5-diene (cod), a fairly common ligand in organometallic chemistry, is introduced into the metal coordination sphere by ligand displacement reactions; for example, PdCl$_2$(NCPh)$_2$ + cod → codPdCl$_2$ + 2NCPh. Metal complexes of cod are often used as starting materials because the cod ligand can bind in various ways to the metal and the complexes are intermediate in stability. Many of them are sufficiently stable to be isolated and handled, but cod and similar ligands can be displaced by stronger ligands. For example, Ni(cod)$_2$ reacts with CO to form Ni(CO)$_4$ and the free cod molecule. This reaction is a convenient source of the extremely toxic Ni(CO)$_4$, for it can be generated directly in a flask where it is then available to undergo a subsequent reaction.

$\mathrm{Cr}(\eta^6\text{-}C_6H_6)_2$
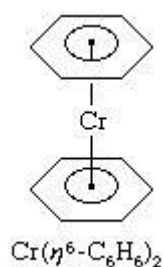
CYCLIC POLYENE LIGANDS

These rings, which have alternating double and single bonds, are among the most important ligands in organometallic chemistry; the most common members of this group range from cyclobutadiene (C_4H_4) to cyclooctatetraene (C_8H_8). Their organometallic compounds include the metallocenes ferrocene and bisbenzenechromium and bis(cyclooctatrienyl)uranium (commonly called uranocene), shown here.

$\mathrm{U}(\eta^8\text{-}C_8H_8)_2$
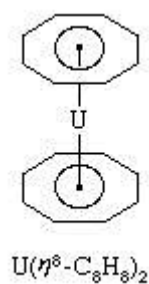
A metallocene consists of a metal atom between two planar polyhapto rings (as in ferrocene), and because of this structure they are informally called sandwich compounds. Cyclic polyenes are also known to form complexes in which they bind to a metal atom through some but not all of their carbon atoms.

The cyclobutadiene ligand is a four-electron donor. It is unstable as the free (i.e., uncombined) hydrocarbon, but it is known to exist in stable complexes, including $Ru(C_4H_4)(CO)_3$.


$\mathrm{Ru}(C_4H_4)(CO)_3$
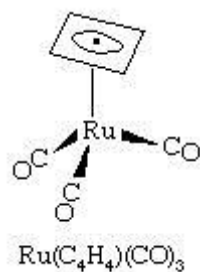
This is one of many cases in which coordination to a metal atom stabilizes an otherwise unstable molecule. Because of its instability, cyclobutadiene must be generated in the presence of the metal to which it is to be coordinated. This can be accomplished in several ways, one of which is

the dimerization of a substituted acetylene. Interestingly, the C_4R_4 is bound to the cobalt in preference to the trimerization product, C_6R_6.
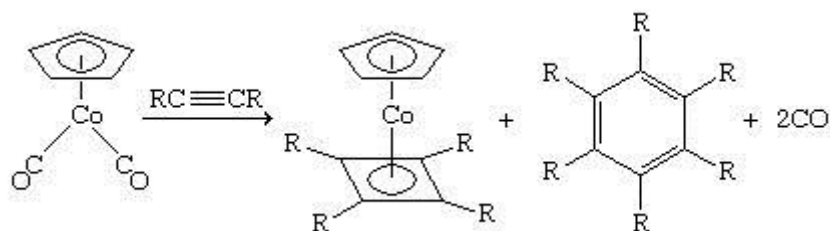
The cyclopentadienyl ligand (C_5H_5, abbreviated Cp) has played a major role in the development of organometallic chemistry. In some metal cyclopentadienyl compounds, the metal is bonded to only one of the five carbon atoms, and in these complexes the Cp is designated as a monohapto, η^1-, ligand, which contributes one electron to form a σ bond with the metal, as in
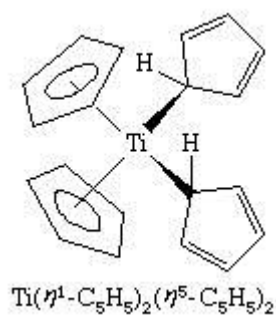
Others contain a trihapto (η^3-) cyclopentadienyl ligand, which donates three electrons. The most common case, however, is when Cp is a pentahapto ligand contributing five electrons. Two of the bonding modes for Cp are illustrated in the following structure, which contains both η^3- and η^5-C_5H_5 ligands.
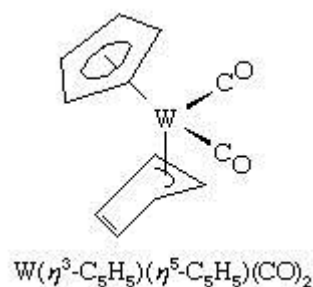
The bis(η^5-cyclopentadienyl)-sandwich complexes of iron, cobalt, and nickel are readily prepared by the reaction of sodium cyclopentadienide with the corresponding d-metal halide.

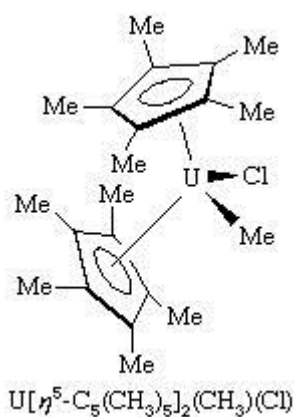$$2Na[C_5H_5] + MnCl_2 \xrightarrow{\text{THF}} Mn(C_5H_5)_2 + 2NaCl$$
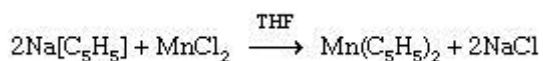
Because of their great stabilities, the 18-electron group-8 compounds ferrocene, ruthenocene, and osmocene maintain their ligand-metal bonds under rather harsh conditions, and it is possible to carry out a variety of reactions on the cyclopentadienyl ligands while they are attached to the central metal. In some cases, they undergo reactions similar to those of simple aromatic hydrocarbons, such as Friedel-Crafts substitution, which is a characteristic reaction of benzene, C_6H_6.
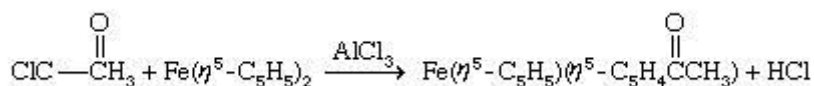
It is also possible to replace the hydrogen atom on a C_5H_5 ring with a lithium atom using the highly reactive reagent butyllithium.$LiC_4H_9 + Fe(\eta^5\text{-}C_5H_5)_2 \rightarrow Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4Li) + C_4H_{10}$This lithiated product is an excellent starting material for the synthesis of other ring-substituted products.

A closely related set of so-called bent sandwich compounds, in which the Cp rings are not parallel, are important in the organometallic chemistry of the early and middle d-block elements and the f-block elements (lanthanoids and actinoids). The Schrock carbene $Ta(\eta^5\text{-}C_5H_5)_2(CH_3)(CH_2)$, shown above, is one such example. Bent sandwich compounds are important in the organometallic chemistry of the f-block elements, but to achieve stability the pentamethylcyclopentadienyl ligand, $C_5(CH_3)_5$, is generally employed with these elements, as, for example, in the following uranium compound.

$U[\eta^5\text{-}C_5(CH_3)_5]_2(CH_3)(Cl)$

Reference:

http://www.britannica.com/science/organometallic-compound#toc277970