Pi Ligands

Pi ligands are a class of organometallic ligand with extended π systems that include linear molecules including ethylene, and allyl, and cyclic molecules such as cyclopentadienyl. As a dative L-type ligand, these molecules have a direct affect on the reactivity of the organometallic complex.

Linear Pi Systems

Properties

Figure \(\PageIndex{1}\): Bonding and back bonding between ethylene and a metal ion.

Linear π systems include alkenes, alkynes, and other unsaturated compounds containing π bonds. The ligand donates electron density from its π bonding orbitals to the d-σ orbitals on the metal center in a σ fashion; therefore the ligands HOMO is interacting with the metals LUMO. There is also back donation from the metal centers d orbital to the ligands π* orbitals in a π fashion, and in this case the metals HOMO is interacting with the ligands LUMO. With these types of interactions the ligand is a σ donor and π acceptor. In this type of bonding, the C-C bond strength within the ligand is weakened and the bond is lengthened in comparison to its free form. This can be attributed to the donation of electron density removing π-bonding electron density within the ligand, and the donation of electrons to the π* orbitals in the ligand. [1][2]

Synthesis

These types of complexes are typically synthesized through ligand substitution in which an existing ligand is replaced by the π ligand. Ligand substitution can be either associative or dissociative depending on which ligand moves first. In the associative mechanism, the new ligand binds to the metal, followed by the departure of another. In the dissociative mechanism, a ligand is a removed before the incoming ligand can bind to the metal center. [3]
Reactivity

- **Nucleophilic addition**: Addition of a nucleophile in the trans position with respect to the metal that is also bound to the π ligand.
- **Migratory insertion**: A nucleophile that is already bound to the metal ion and the π ligand combine to form one ligand. In this case the nucleophile and the metal are cis across the π system.

Cyclic Pi systems

Properties

Cyclic or arene π systems are either actor or spectator ligands that typically bind to metals through more than 2 atoms. The bonding is similar to that of the linear π systems, consisting of a more typical bond formed by the donation of electron density from the π orbitals of the ligand to the dσ of the metal, and back donation from the dπ of the metal to the π* of the ligand. However, donation from the ligand to the metal is much more common since arenes are highly conjugates making them stronger electron donors. De-aromatization occurs in some cases in order to form a more stable structure. This is called ring-slippage or the removal of one π bond from the system, which leaves the atoms bond to the metal coplanar and the remaining atoms are out of plane. In some cases this forms a stable structure, while in others is used as a means to open a coordination site for further reactivity. Typically these ligands are hydrocarbons, and rarely are heterocycles which contain a lone pair of electrons that can react on their own. [1]

Synthesis

One way in which cyclic π ligand-metal complexes are formed is through salt metathesis. This is a type of double replacement reaction where a ligand attached to the metal is exchanged for the π ligand, resulting in the desired organometallic complex and a salt. For example the generic reaction, \( \text{MCl}_2 + 2\text{NaCp} \rightarrow \text{MCp}_2 + 2\text{NaCl} \), where the chloride ligands are replaced with the more favorable cyclopentadienyl ligand. Another method is applying heat to trigger a retro-Diels-Alder reaction in order to form an ionic form of the ligand that can more easily bond with a metal. Aromatic ligands are chelating ligands, therefore they can easily replace other ligands in a metal complex that are weaker electro donors such as CO. This method of synthesis is entropically favorable, and therefore just requires the application of heat to move forward. [1]

Reactivity

- Coordinating to a metal increases the ligands electrophilicity, therefore increasing its ability to under go nucleophillic addition.
- Electrophilic aromatic addition is also possible as the metal can stabilize both cation and anions.
- Steric hindrance is increased in this type of complex, allowing for a greater selectivity in reactions.
- Bonding to the metal decreases the electron density of the ligand, leaving it vulnerable to nucleophillic aromatic substitution. The new ligand must be as good or better at coordinating the metal and an oxidant can be utilized to release the aromatic ligand. Oxidants decrease the complexes ability to back bond, making the arene less enthalpically favorable.
Sandwich Complexes

Sandwich complexes are organometallic complexes where the metal is bound to two cyclic π systems forming a "sandwich". Typically these complexes follow the 18 electron rule, except for 1st row transition metals that can have electron counts from 15-20 electrons, and lanthanides and actinides that do not follow the rule.

Metallocenes

Metallocenes are a subgroup of sandwich complexes that consist of a metal bonded to two cyclopentadienyl (Cp) ligands. Common configurations include η¹-, η³- and η⁵- bonding modes. If the electron count is higher than 18 electrons there is occupation in antibonding orbitals, increasing the distance between the ligand and the metal and thus decreasing the amount of energy needed to dissociate. The Cp ligands can be eclipsed or staggered as shown in the Figure. Paramagnetic metallocenes can form ions, allowing the complex to form ionic bonds, replace the Cp ligand, or to add to the complex. [2]
Ferrocene is the most widely studied metallocene with in the field of organometallics. Looking to the molecular orbital diagram, orbitals that are occupied by electrons are stabilized by the interactions with iron, and are typically that of s and p type orbitals. The orbitals of the most interest are that of the HOMO ($d_{z^2}$) and the LUMO ($d_{xz}$, $d_{yz}$). In the case of the HOMO the orbital has mostly metal characteristics as it is cone-shaped and has very little overlap with the orbitals of the ligand, making it almost non-bonding. The LUMO however has a large overlap of the d orbital on the metal and p orbitals of the carbons on the Cp ligands, allowing for π bonding. [2]

Following the 18 electron rule also makes for a more stable compound than that of other metallocenes or sandwich compounds. Comparing to sandwich structures containing benzene in the place of Cp, ferrocene performs electrophillic aromatic substitution at a much faster rate. Benzene being much more reactive than Cp also makes it more vulnerable to elimination. Metallocenes that have electron counts greater than 18 are also more vulnerable to elimination in order to achieve the desired electron count.

References