

13.1: Metal-Carbenes

Learning Objectives

In this lecture you will learn the following

- The metal–ligand multiple bonding and their relevance in.
- The Fischer type carbene complexes.
- The Schrock type carbene complexes.

The organometallic compounds containing metal–ligand multiple bonds of the types, $M=X$ and $M\equiv X$ ($X = C, N, O$) are of current interest as they are valuable intermediates in many important catalytic cycles. In this regard, considerable attention has been paid towards developing an understanding of the metal–ligand multiply bonded systems like that of the metal carbene $L_nM=CR_2$ type complexes and of the metal carbyne $L_nM\equiv CR$ type complexes. A detailed account of the metal–carbene complexes is presented in this chapter.

Metal carbene complexes

Carbenes are highly reactive hexavalent species that exist in two spin states, *i.e.* (i) in a singlet form ($=$), in which two electrons are paired up and (ii) in a triplet form (\equiv), in which the two electrons remain unpaired. Of the two, the singlet form is the more reactive one. The instability of carbene accounts for its unique reactivity like that of the [insertion reaction](#), which has aroused significant interest in recent years. The singlet carbene and the triplet carbene bind differently to metals, with the singlet one yielding Fischer type carbene complexes while the triplet one yielding Schrock type carbene complexes (Figure 13.1.1).

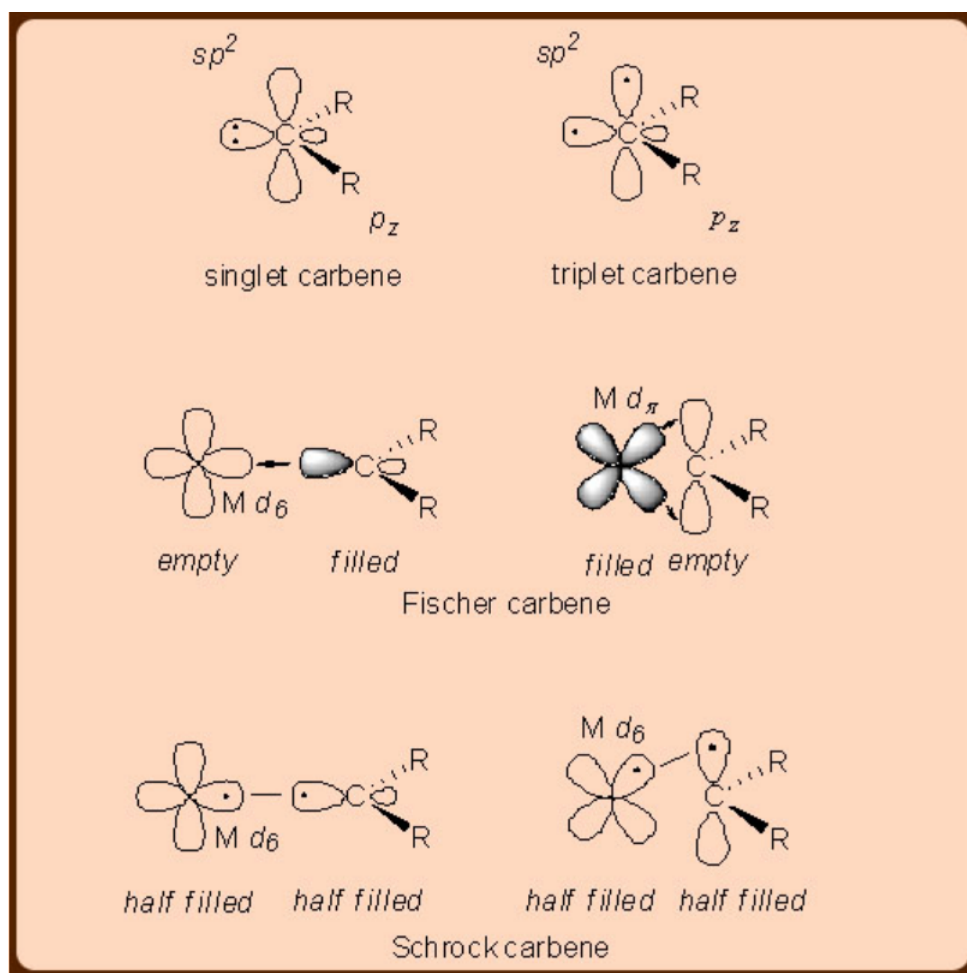


Figure 13.1.1: Metal–ligand multiple bonding in the Fischer and Schrock carbene system.

The $L_nM=CR_2$ type Fischer carbene complexes comprise of two dative covalent interactions that include (i) a $L_nM \leftarrow CR_2$ type ligand to metal σ -donation and (ii) a $L_nM \rightarrow CR_2$ type metal to ligand π -back donation. The Fischer type carbene complexes are usually formed with metal centers at a low oxidation state. These are also commonly observed for the more electron rich late-transition metals that participate in the $L_nM \rightarrow CR_2$ type metal to ligand π -back donation. Another characteristic of the Fischer type carbene complex is the presence of the heteroatom substituents like $R = OMe$ or NMe_2 on the carbene CR_2 moiety which makes the carbene carbon significantly cationic (δ^+) to facilitate the $L_nM \rightarrow CR_2$ type metal to ligand π -back donation.

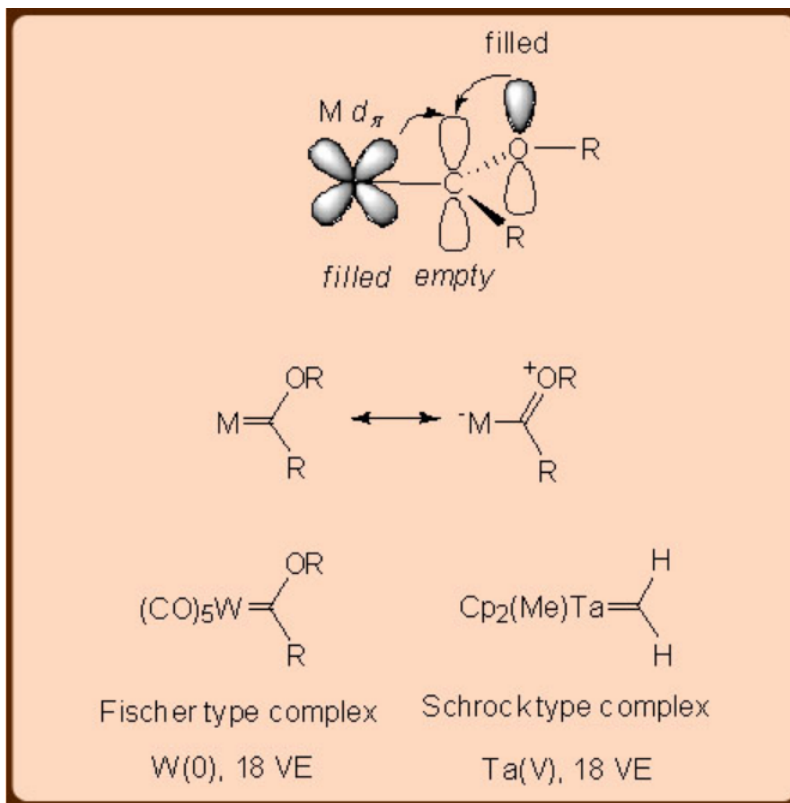
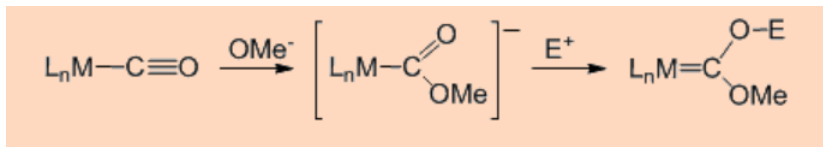


Figure 13.1.2: Fischer and Schrock type complexes.

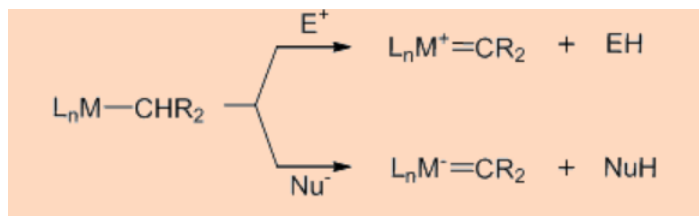
Similarly, the $L_nM=CR_2$ type Schrock carbene complexes comprise of two covalent interactions that involve one electron donation towards the σ -bond from each of the metal L_nM and the carbene CR_2 fragments. Schrock carbene complexes are thus formed with the metal centers having high oxidation state and are usually observed for electron deficient early-transition metals (Figure 13.1.2).

Carbene complexes can be prepared by the following methods.

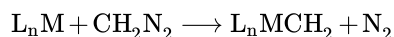
i. by the reaction with electrophiles



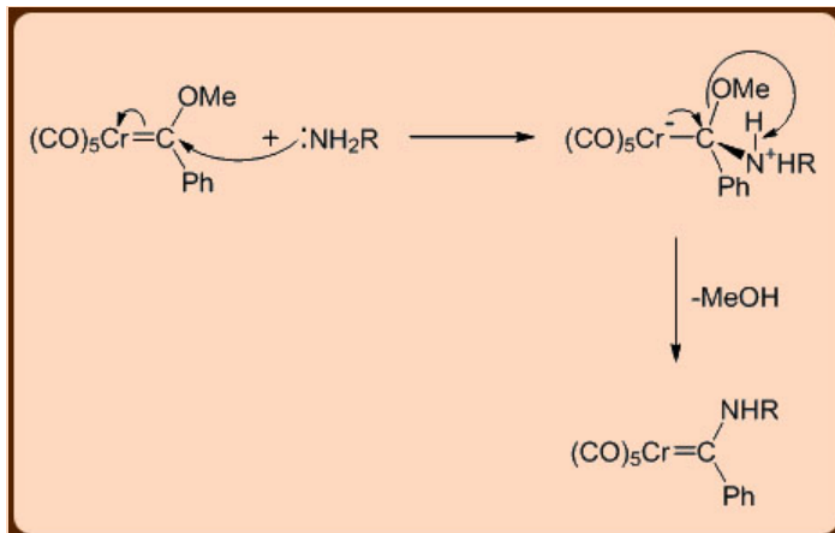
ii. by H^-/H^+ abstraction reactions as shown below



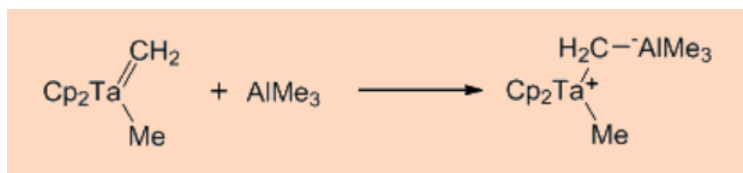
iii. from low-valent metal complexes



Because of the electronically different metal–ligand interaction that exist between the L_nM and the carbene CR_2 moiety, the reactivity of Fischer and Schrock carbene complexes are completely different. For example, the Fischer type carbene complexes undergo attack by nucleophiles at its carbene–C center.



The Schrock type carbene complexes on the other hand undergo attack by electrophiles at its carbene–C center.



Summary

The metal–ligand multiple bonding is of significant interest as many of the compounds containing such bonds are important intermediates in various catalytic cycles. The metal–ligand doubly bonded carbene systems can exist in two varieties like the Fischer type and the Schrock type carbene complexes. Due to their different electronic structures, the reactivities of these Fischer type and the Schrock type carbene complexes differ significantly, with the former undergoing nucleophilic attack while the later undergo electrophilic attack at their respective carbene–C centers.

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