1 Introduction

Organometallic chemistry deals with metal-carbon bonds and after the discovery of ferrocene, has become one of the most active areas of chemistry to be studied. Carbon can attach itself to metals in different ways of which the metal-carbon single (metal-alkyl), double (metal-carbene) and triple (metal-carbyne) bonds are examples. In addition, metals can coordinate to unsaturated carbon-carbon or carbon-heteroatom bonds in a "side-on" fashion, to give π-complexes.

1. π-complexes

1.1. Complexes with sandwich structures

The only true sandwich compounds with parallel rings are those of the types $(\eta^n\text{-}C_nH_n)_2M$ and $(\eta^n\text{-}C_nH_n)_2M^+$ (n represents the number of carbon atoms bonded to the metal). A large number of these complexes are known and ferrocene is the classical example.

(a)   (b)

Figure 1.1   Sandwich structures of (a) arene and (b) heteroarene complexes

1.2. Complexes with tilted sandwich structures

Three types of tilted sandwich compounds exist and they have one, two or three additional ligands. Titancene dichloride $[Ti(\eta^5-C_5H_5)_2Cl_2]$ is an example of a bent or open shell sandwich compound with two terminal ligands.

(a)   (b)   (c)

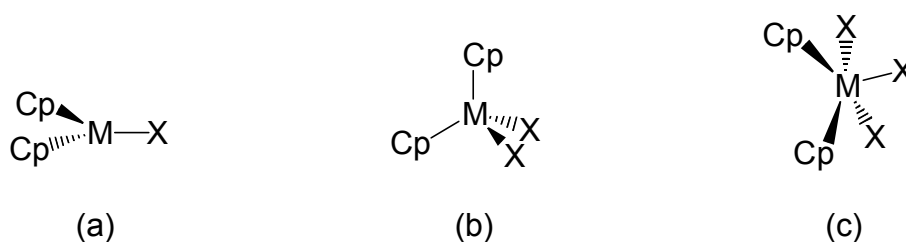**Figure 1.2**   Bent sandwich complexes with (a) one (b) two and (c) three additional
                              ligands

1.3. Complexes with half-sandwich structures

In π-arene complexes some of these structures exhibit a "piano stool" structure with the arene ring posing as the "seat" and the ligands as the "legs" of the stool. Also known are structures in the "milk stool" shape such as $[Ni(\eta^5-C_5H_5)NO]$. Although plenty of different structural examples exist, for this study the focus will be on the "piano stool" type. Complexes in discussion are of the type that contains arene or heteroarene moities and only one arene ring is π-bonded to a transition metal. The remaining coordination sites on the metal are occupied by ligands, e.g. Cl, CN, CO etc.
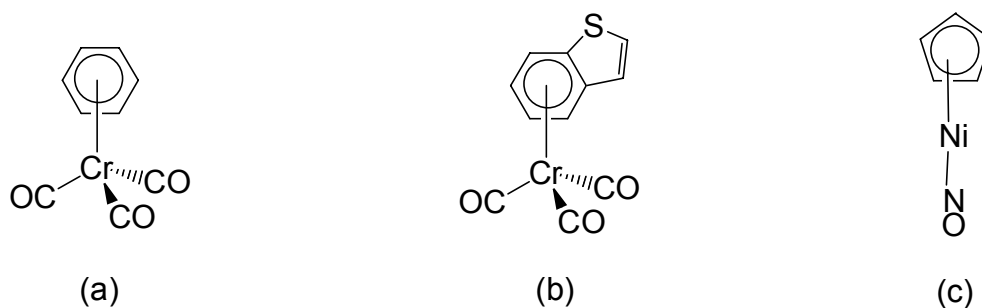

(a)   (b)   (c)

Figure 1.3   Examples of half-sandwich complexes: (a) arene and (b) heteroarene
                              complexes in the "piano stool" and (c) an arene complex in the
                              "milk stool" conformations

2. Carbene complexes

The term "carbene" refers to a divalent carbon species, that is, one in which a carbon atom forms two 2-electron bonds to adjacent atoms. The two remaining carbon electrons are then localized on the carbon atom, thus giving a sextet valence-electron configuration. This pair of carbon electrons may give rise to either a singlet or triplet spin ground state.[1] Complexes containing metal-carbon double bonds are generally referred to as metal-carbene complexes.

Even though carbenes are highly reactive species, some are stable and can be isolated.[2,3] Fischer and Maasböl were the first to synthesize and characterize a stable transition metal carbene complex[4] followed by the first nucleophilic carbene complexes that were prepared by Schrock in an effort to prepare a homoleptic tantalum(V) alkyl.[5] Thus, carbene complexes of two different types can be distinguished and they are named after their discoverers, i.e. Schrock and Fischer.

2.1. Fischer carbene complexes

In 1973 E.O. Fischer was awarded the Nobel Prize in Chemistry, not for discovering the first Fischer carbene complexes, but for solving the structure of ferrocene and other metallocenes.
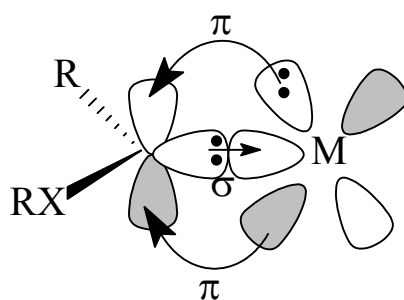

Figure 1.4   Important metal-orbital interactions in an electrophilic (Fischer) carbene
            complex (XR = heteroatom substituent)

Fischer carbene complexes have an electrophillic metal-coordinated sp^2-carbon atom and it can be considered as a neutral 2-electron ligand (L-type) derived from a singlet carbene

carbon atom. These complexes are generally afforded by the reaction of metal carbonyls of transition metals in low oxidation states like ruthenium, rhenium, iron, manganese, molybdenum, chromium and tungsten with an organolithium reagent (Figure 1.5).
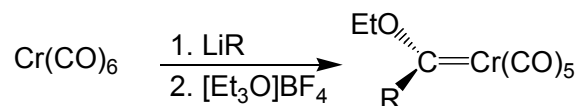
$$Cr(CO)_6 \quad \xrightarrow[\text{2. } [Et_3O]BF_4]{\text{1. } LiR} \quad \overset{EtO}{\underset{R}{\diagup}}C{=}Cr(CO)_5$$

Figure 1.5   Synthesis of a Fischer carbene complex

2.1.1   Application of Fischer carbene complexes

Note also, that due to the strong electron-withdrawing pentacarbonyl metal fragment, that decreases the metal to carbene carbon π-backbonding, it is clear that the carbene carbon possesses a positive charge. Fischer carbene complexes can undergo reactions at several sites, outlined in Figure 1.6. Much of the reactivity of Fischer carbene complexes is directly analogous to the reactivity of carboxylic acid derivatives. Both have electrophilic carbon centers with leaving groups.
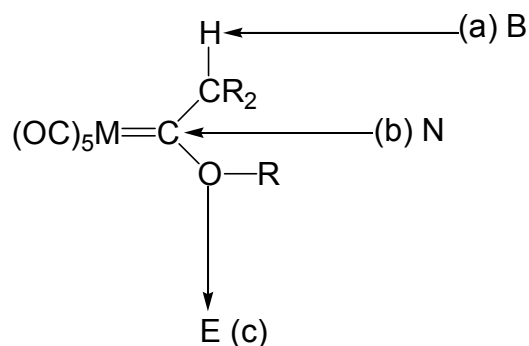
$$
\begin{array}{c}
H \longleftarrow \text{(a) B} \\
| \\
CR_2 \\
(OC)_5M{=}C \longleftarrow \text{(b) N} \\
| \\
O{-}R \\
\downarrow \\
E \text{ (c)}
\end{array}
$$

Figure 1.6   Reactivity of Fischer carbene complexes with bases (B), nucleophiles (N) and electrophiles (E)

Fischer carbene complexes with alkyl substituents can be deprotonated by bases (B) due to the acidity of the α-CH groups, to form metal carbene anions (route a), while nucleophilic (N) attack occurs at the elctrophilic carbene carbon atom (route b) e.g. aminolysis. Electrophiles (E), for instance Lewis acids, can coordinate to the alkoxy substituent (route c), leading to the formation of metal-coordinated carbyne complexes after C-O bond breakage. In the past few years interest in Fischer carbene complexes with respect to their

ability to act as templates for the synthesis of organic compounds has grown immensely. Several review articles and books have addressed this topic.[6-11]

Fischer carbene ligands exhibit a wide range of reactivity and can be readily modified. Some of the more common reaction pathways serve as examples.

The heteroatom of a Fischer carbene complex can often be exhanged by simple nucleophilic displacement (see Figure 1.6 route b); this is referred to as heteroatom substitution.[12]
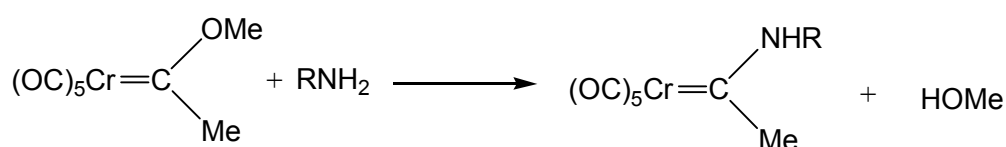

Figure 1.7   Heteroatom substitution[12]

The Dötz Reaction is another example. A carbene ligand containing a α-olefinic unit, an alkyne and carbon monoxide are converted into a benzannulated product.
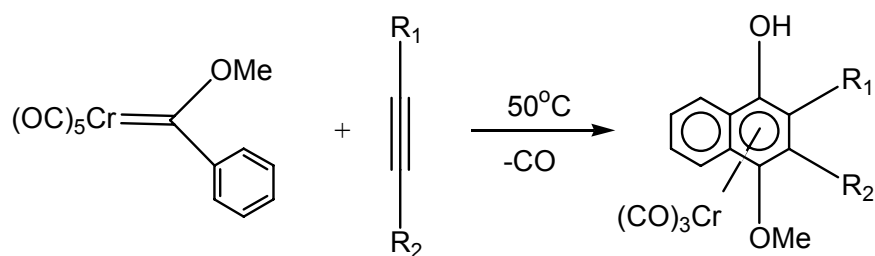

Figure 1.8   The Dötz reaction affording substituted naphthols

Dötz-type chemistry is well developed and has been used to prepare Vitamin E as well as some antibiotics. Fischer carbene complexes undergo many other kinds of annulation reactions where the Diels-Alder reaction is just another example.

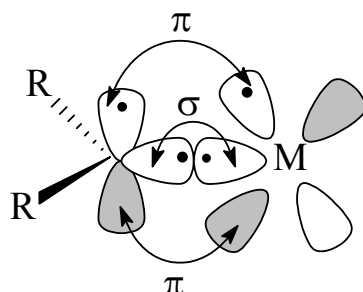## 2.2. Schrock carbene complexes

Figure 1.9   Important metal-orbital interactions in a nucleophilic (Schrock) carbene complex (R = alkyl substituents)

These complexes are afforded by using early transition metals in high oxidation states with strong donor and weak π-acceptor ligands.
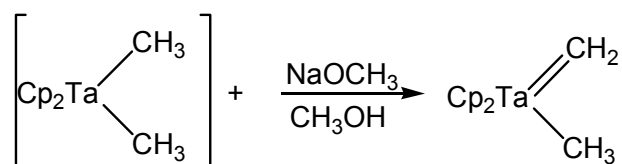

Figure 1.10   Example of a Schrock carbene complex

Schrock carbene complexes act as nucleophiles due to the partial negative charge that resides on the carbene carbon atom (Figure 1.10), as a result of polarization of shared electrons between an electropositive metal and a more electronegative carbene carbon atom. The carbene ligand is formally considered as a X_2-type ligand derived from a triplet carbene carbon atom, resulting in electron sharing in a metal-carbon σ- and π-bond.

2.2.1   Application of Schrock carbene complexes

Due to the nucleophilic character of Schrock carbene complexes, many reactions can take place for example by adding Lewis acid adducts (Figure 1.11) or addition to carbonyls, reactions similar to Figure 1.12 can be accomplished.
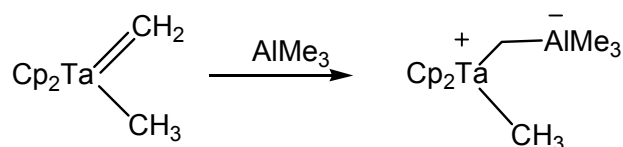
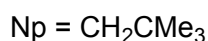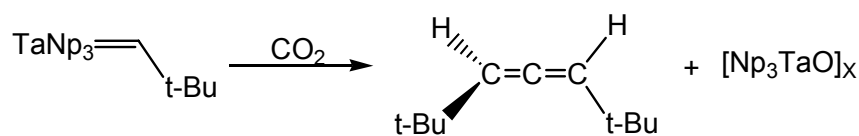**Figure 1.11**   Addition of a Schrock carbene complex to a Lewis acid

$Np = CH_2CMe_3$

Figure 1.12   Addition of a Schrock carbene complex to carbon dioxide

Schrock working at Du Pont in early 1970's, tried to synthesize $[Ta(CH_2CMe_3)_5]$, which was expected to be a stable compound because of the absence of β-hydrogen atoms. Instead he isolated the first stable metal-alkylidene complex, $[Ta(CH_2CMe_3)_3(=CHCMe_3)]$, which has the formal oxidation state of V.[13] The advantage of Scrock's carbene catalysts, of which the most efficient were reported in 1990,[14-16] is that they are extremely active and are especially known for their role in metathesis reactions.
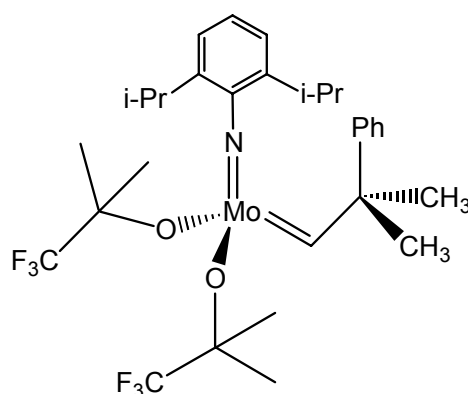
Figure 1.13   Commercially available Schrock carbene catalyst[14-16]

Schrock has invented a variety of catalysts, but the most important of these are arylimido complexes (imido ligands, also referred to as imides or nitrenes) of molybdenum with the general formula $(Ar'N)(RO)_2Mo=CHR'$ where Ar' is typically 2,6-diisopropylphenyl, R' can be virtually anything and R is neopentyl (Np) or neophyl (CH_2CMe_2Ph). These catalysts are exceedingly active, metathesizing over 1000 equivalents of cis-2-pentene for

one equivalent catalyst. Another advantage of these catalysts is that their reactivity can be tuned.

The Tebbe reagent $[Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_3]$ is particularly useful for the conversion of esters to vinyl ethers. It will olefinate carbonyls without enolizing α-stereocenters.[17] In the presence of a strong base such as pyridine, the reagent is functionally equivalent to $Cp_2Ti=CH_2$.
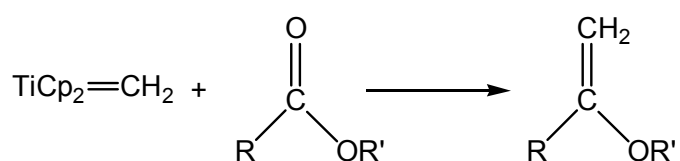

Figure 1.14   The conversion of an ester to vinyl ether, with the use of the Tebbe reagent

Another example where Schrock-type carbene complexes are used is in olefin matathesis. Olefin matathesis was first used in petroleum reformation for the synthesis of higher olefins in the Shell higher olefin process (SHOP). A metathesis reaction is a chain reaction involving a metal-carbene intermediate. The carbene ligand reacts with a coordinated olefin to a metallacyclobutane intermediate. This simple reaction type has enormous application in industry.
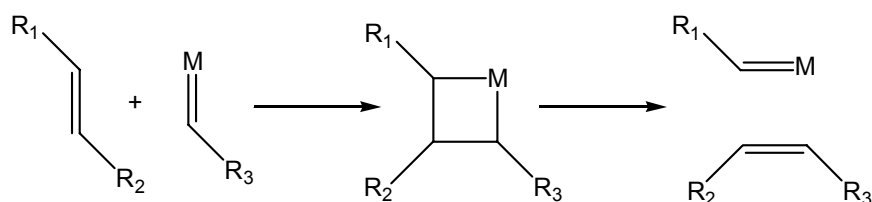
Figure 1.15   An example of a metathesis reaction

Three researchers in carbene chemistry shared this year's (2005) Nobel Prize in Chemistry; they are Y. Chauvin, R.H. Grubbs and R.R. Schrock. The Royal Swedish Academy of Sciences citation runs "for development of the metathesis method in organic synthesis".

Ring Opening Metathesis Polymerization (ROMP) is just another example of numerous metathesis reactions and is a subset of polymerization. The end of a growing chain acts as a reactive center that can react with additional monomers to propagate the chain to form a polymer. In ring-opening polymerization, the monomer is a cyclic compound which

causes the chain to propagate through cationic or anionic propagation. Examples of polymers produced by this method are Nylon 6 and polyethylene oxide. The catalysts used for ROMP are the same catalysts used for olefin metathesis.

The Grubbs[18] and Schrock[19] catalysts offer synthetic chemists novel opportunities, due to their tolerance of a large variety of functional groups, combined with their efficiency, and, for Grubbs' catalysts, their ease of handling in air. These catalysts have widespread use in organic chemistry.[20]

Clearly metal carbene complexes are of utmost importance in organic synthesis, by acting as templates and catalysts.[21]

3. Dimetallic Fischer carbene complexes

A lot of interest has developed in compounds containing two or more metals, due to the belief that these compounds could cooperate in catalytic transformations more effectively, because of their ability to promote new processes unknown for one metal acting on its own.[22-25] Principally, three possibilities exist in adding new metal centered fragments (represented by M') to Fischer carbene connecting atoms (Scheme 1.1).
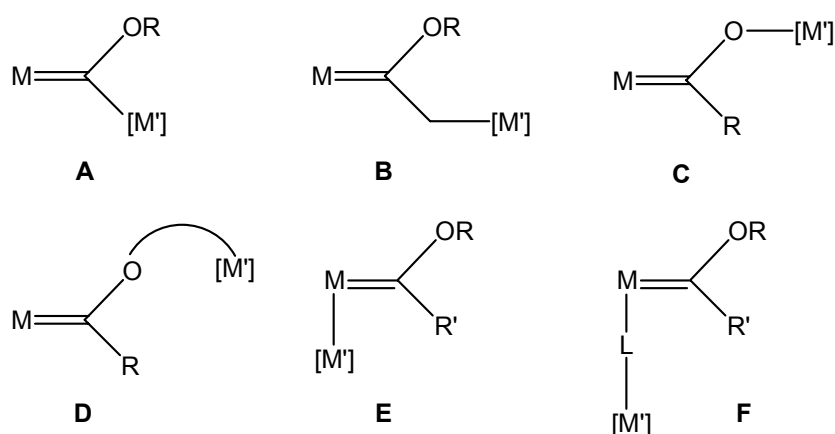
Scheme 1.1   Dimetallic Fischer carbene complexes

The first possibility is on the carbene carbon, either directly joined (**A**) or through a carbon chain or bridging unit (**B**). The second is through the heteroatom connected to the carbene carbon (**C**, directly and **D**, *via* a carbon or connecting chain). Thirdly, directly to the metal

center, by a metal-metal bond (**E**) or by a bidentate ligand joining both metal centers (**F**). For compounds analogous to **A** and **B**, the standard synthetic procedures are based on that developed for the preparation of mononuclear carbene complexes; it will follow one of the following methods:

(I)   From metal complexes that do not contain a preformed carbene ligand.

(II)   A mononuclear metal carbene complex containing a carbanion generated α to the carbene carbon, can be alkylated or acylated.

(III)   The additional metal center can be attached on the double or triple bond of metal carbene complexes that have unsaturated substituents.

(IV)   A metal nucleophile can be added to a carbyne complex.

(V)   Allenyl complexes can be used as precursors.

For compounds analogous to **C** and **D**, the classical Fisher route to carbene complexes is applicable, but alkylation involves a metal. Another possibility exists, and that is by starting with (η^4-diene)metallocenes and metal carbonyls, several dimetallic metaloxy-carbene complexes were afforded.[26-29] As for compounds analogous to that of **E**, the first synthesised carbene of this type was by King in 1963[30] (Figure 1.16). These reactions were carried out by reacting sodium pentacarbonyl manganate(-I) and either 1,3-dibromopropane or 4-butyryl chloride.

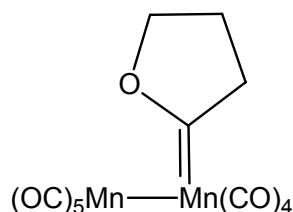**Figure 1.16**   King's dimetallic carbene complex[31]

 Fischer reported that the reaction of [$Mn_2(CO)_{10}$] with RLi (R = Me, Ph) followed by treatment with [R_3O]BF_4 yielded the first homodimetallic carbene complex that was characterized.[32,33]

$$Mn_2(CO)_{10} \xrightarrow{\text{RLi}} [Mn_2(CO)_9\{C(OLi)\}R] \xrightarrow[\text{H}_2\text{O}]{[Me_3O]BF_4}$$
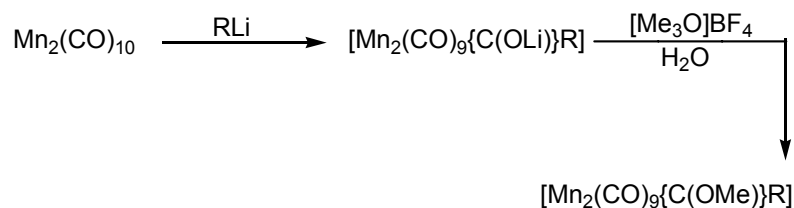
$$[Mn_2(CO)_9\{C(OMe)\}R]$$

Figure 1.17   Synthesis of one of the first homodimetallic carbene complexes

Complexes of the type **F**, can be generated by attaching metal fragments *via* bidentate ligands.

4. Aim of this study

The synthesis and characterization of Fischer carbene complexes with transition metal containing substituents have not yet been investigated systematically. In this study, the role of independent metal containing substituents in stabilizing the carbene carbon atom was addressed. Substituents were selected if they contained a conjugated π-system, creating a pathway for charge to be transferred from the metal to the carbene carbon atom. A second important factor that could affect the formation and/or stability of the trimetallic carbene complex was the steric bulk of the substituents. These metal-containing substituents may be too bulky and the carbene carbon atom too crowded for stability. Steric complications can be expected when the metal fragments are directly bonded to the carbene carbon (Schrock-type carbene complexes) or slightly less so when attached to a carboxy-carbene (Fischer-type carbene complexes). However, even for Fischer carbene complexes, we were concerned that the non-oxygen substituent may again, because of its bulkiness, cause too much steric hindrance for the trimetallic carbene complex to be stable enough to isolate. It was decided to create some space at the non-oxygen substituent by introducing a heteroaromatic ring that is π-bonded to a $Cr(CO)_3$ fragment. For this study carbene complexes of chromium and tungsten with carbonyl ligands as ancillary ligands were chosen, being representative of classes of carbene complexes of high stability.[7] As alkoxy substituent titanocene chloride was chosen for two reasons. The procedure for the synthesis of titanoxycarbene complexes in bimetallic complexes has been described in literature and the titanium(IV) centre has a high affinity for oxygen atoms.[34] As a third metal-containing fragment benzothiophene π-coordinated to chromium tricarbonyl was chosen for reasons of creating space at the carbene carbon atom as the $Cr(CO)_3$ fragment is

π-bonded to the benzene ring which is furthest from the point of attachment.[35]   To systematically study the electronic and steric effects of the different metal-containing substituents they were introduced in a stepwise manner.

$[M'], [M''] =$ metal fragments

○ = heteroarene
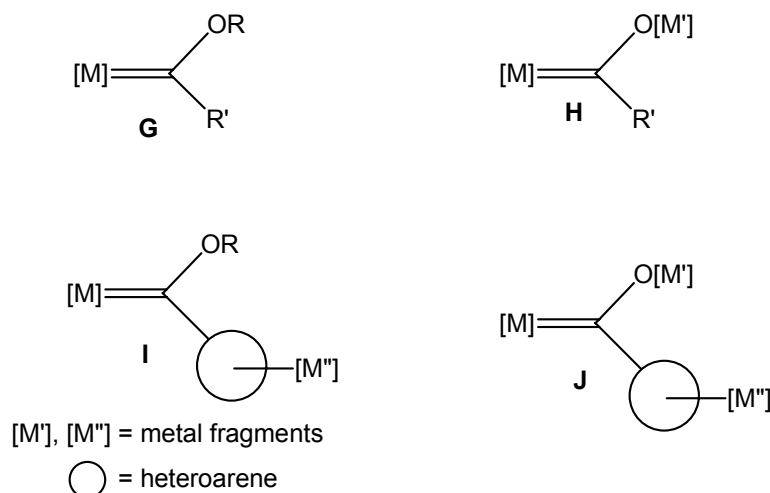
Scheme 1.2   Synthesized metal carbene complexes

The chapters in this thesis were organized in such a way that it deals with each metal substituent as an independent role player in the overall carbene complex.

In Chapter 1 a short overview is given of metal carbene and π-arene complexes. Emphasis is placed on the electronic properties of carbene complexes and their reaction profile.

Chapter 2 was dedicated to the synthesis and the molecular structures of the "reference carbene complexes". They contain either components of the metal substituents or will act as reference substituents to unravel the role of the metal-containing substituent. These are shown as carbene complexes of the type **G** (Scheme 1.2). Two different metal hexacarbonyls were used as precursors, lithiated benzo[*b*]thiophene as reactant and alkylation was done by $[Et_3O]BF_4$.

In Chapter 3 "alkylation" was performed with titanocene dichloride while benzo[*b*]thienyl remained the third substituent. These complexes are represented by **H** and the objective was to study the role of the titanocene fragment in the carbene complexes. Comparisons were made with respect to the ethoxycarbene complexes in Chapter 2.

In Chapter 4 the focus was on modifying the benzo[b]thienyl group to a π-benzo[b]thienyl complex and using this as carbene substituent. Complexes represented by **I** were synthesized to study the role of the π-benzo[b]thienyl-chromium-tricarbonyl substituent. Comparisons were made with respect to the benzo[b]thienyl complexes in Chapter 2. In Chapter 5 the anticipated three-metal-fragment carbene complexes, as represented by **J**, were the focus point of the investigations.

The study also included a large number of crystal structures and detailed NMR and infrared studies to explore the electronic and steric properties of the carbene substituents in the solid state as well as in solution.

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