

1 Introduction

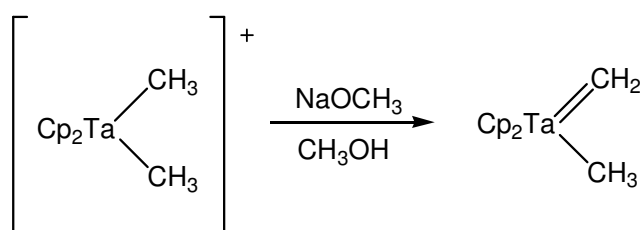
1.1 Overview of carbene complexes

Since the inception of organometallic carbene complexes in the early 1960's, the metal-to-carbon double bond has been extensively studied and numerous examples with different metals and substitution patterns are known. The transition metal carbene complexes are not only chemically versatile^[1;2], but also possess unique physical properties. This is illustrated by the growing search for new materials in nonlinear optics, which stimulated expansive studies of organometallic materials incorporating metal-to-carbon double bonds^[3].

Organometallic carbene complexes as described by Fischer in his Nobel Prize lecture^[4] are highly reactive derivatives of divalent carbon and as such are widely used as organic synthons^[5]. Transition metals stabilize carbenes by coordination yielding two types of complexes with contrasting reactivities, named after their discoverers: the 'Fischer-type' carbenes^[6] where the carbene carbon is electrophilic and the 'Schrock-type' carbene complexes^[7] where the polarity is reversed.

1.2 Schrock carbene complexes

The first nucleophilic carbene complex was prepared by Schrock in an effort to prepare a homoleptic tantalum(V) alkyl^[7]. Schrock carbene complexes are usually characterized by an early transition metal in high oxidation state, with strong donor and weak π -acceptor ligands.



Scheme 1.1 Synthesis of a typical Schrock carbene complex

1.2.1 Theoretical bonding model

The progress in quantum chemical methods for the calculation of electronic structure and theoretical studies gave insight into the nature of the chemical bond in transition metal carbene complexes. Frenking and Frölich^[8] have recently reviewed the state-of-the-art methods of computational chemistry applied to the bonding in transition metal compounds.

Bonding in Schrock complexes are described as a "covalent bond" between a 3B_1 triplet carbene and a triplet metal fragment^[9], implying that the electronic ground state of a carbene ligand can be used to predict binding interactions with a transition metal. Carbene ligands such as methylene and dialkylcarbenes that have a triplet ground state will preferentially form covalent bonds with triplet metal fragments.

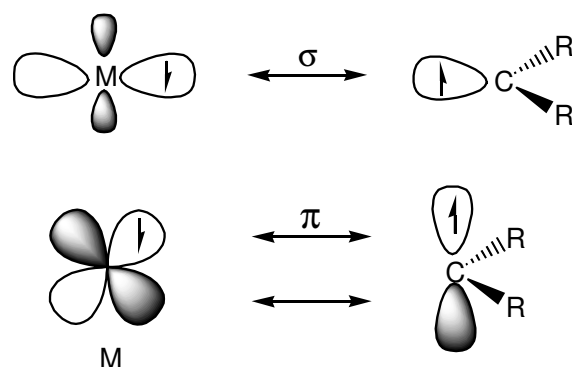
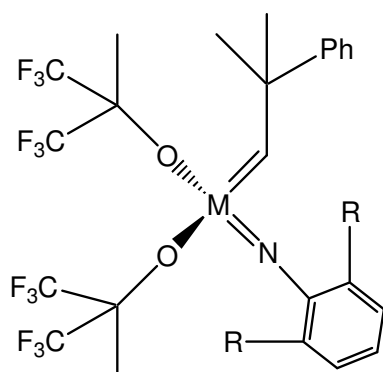


Figure 1.1 Orbital interactions of a Schrock carbene ligand

Besides the neutral resonance form (Figure 1.1) a nucleophilic resonance form $L_nM^+-CR_2^-$ can explain the experimental observations that these compounds react mostly as nucleophiles. A partial negative charge resides on the carbene carbon atom as a result of polarization of shared electrons between an electropositive metal and a more electronegative carbene carbon atom. The carbene ligand is therefore formally considered as an X_2 -type ligand, resulting in electron sharing in a metal-carbon σ - and π -bond.

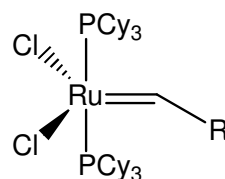
1.2.2 Applications

Perhaps the most well-known uses of Schrock carbene complexes are their activity in olefin metathesis^[10-12] and their ability to act as substitutes for phosphorous ylides in the Wittig reaction^[13]. Schrock and co-workers developed the popular catalyst, the tungsten and molybdenum alkylidene complexes^[14] while the ruthenium carbene complexes were introduced by Grubbs and co-workers^[15] (Figure 1.2). As a result, Grubbs, Schrock and Chauvin shared the 2005 Nobel Prize in Chemistry, for the "development of the metathesis method in organic synthesis", the citation given by the Royal Swedish Academy of Sciences.



M = Mo, W

Schrock catalyst



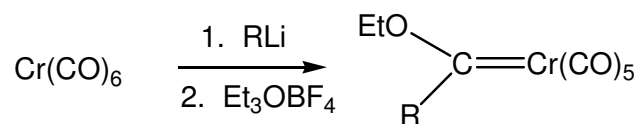
R = Ph, CH=CPh₂, etc.

Grubbs catalyst

Figure 1.2 Commercially available metathesis catalysts

1.3 Fischer carbene complexes

The first stable transition metal carbene complex was synthesized by Fischer^[6]. Typical Fischer-type carbene complexes contain a low valent Group VI to VIII transition metal stabilized by π -acceptors, and are characterized by an electrophilic carbene carbon atom, the metal-coordinated sp^2 -carbon atom.



Scheme 1.2 Synthesis of a typical Fischer carbene complex

According to Fischer^[16] carbene complexes can be prepared from non-carbene complex precursors and by modification of pre-existing carbene complexes. Carbene complexes that can be obtained from non-carbene (carbonyl, allyl, etc.) complex precursors, can be synthesized from two

different methods: (i) transformation of a non-carbene ligand and (ii) addition of a carbene ligand precursor to a metal complex from pre-existing carbene complexes, of which five reactions are possible. They are (i) the transfer of a carbene ligand from one metal to another, (ii) modification of the carbene ligand, (iii) insertion of an unsaturated organic molecule into the metal carbene bond, (iv) change of the oxidation state of the central metal and (v) modification of the metal-ligand framework.

Due to the ability of Fischer carbene complexes to act as reagents for the synthesis of organic compounds, much interest has been shown in the activity of these carbene complexes. Several review articles and books have addressed this topic^[16-22] which has been explored extensively and applied in various organic syntheses.

1.3.1 Theoretical bonding model

The generally accepted bonding model employs the singlet and triplet states of the fragments CR_2 and L_nM as building blocks for the carbene complexes. For Fischer carbene complexes, the model describes the metal-to-carbon bond in terms of "donor-acceptor interactions" between a (1A_1) singlet carbene and a singlet metal fragment. Carbene ligands with π -donor groups and a singlet ground state will preferentially engage in donor-acceptor interactions with singlet metal fragments^[23]. In particular, dihalocarbenes, which have singlet ground states and large singlet to triplet excitation energies, are considered to be donor-accepting bonding and thus "Fischer type". The resulting electrophilic carbene carbon can be considered as a neutral 2-electron ligand (L-type).

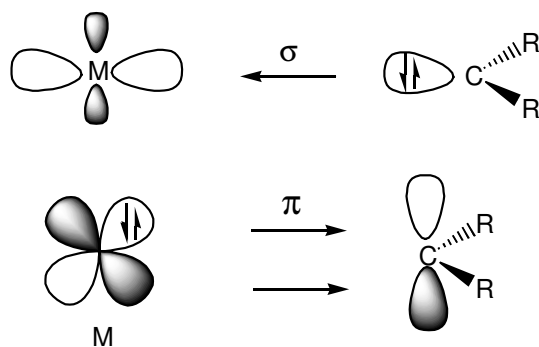


Figure 1.3 Orbital interactions of Fischer type carbene complex ligand

1.3.2 Applications

Many important reactions of Fischer carbene complexes have been recorded, of which nucleophilic attack on the carbene carbon, carbyne synthesis and modification of carbene substituents are but a few. The Fischer-type carbene complexes are characterized by an electrophilic carbene carbon atom, the metal-coordinated sp^2 -carbon atom. These carbene complexes can undergo reactions at several sites on the carbene ligand, as outlined in Figure 1.4

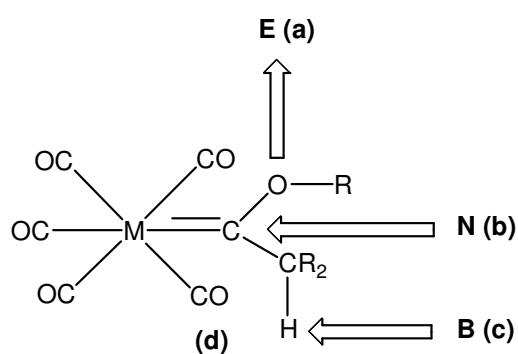


Figure 1.4 Modifications of Fischer carbene complexes

Electrophiles (E), for instance Lewis acids, are coordinated to the alkoxy substituent (route a), leading to the formation of metal-coordinated carbyne complexes. Nucleophilic attack (N) occurs at the electrophilic carbene carbon

atom (route b), e.g. aminolysis. Alkylcarbene complexes are deprotonated by bases (B) to form metal carbene anions (route c), owing to the acidity of the α -CH groups, while carbonyl substitution by other ligands, e.g. phosphine ligands^[24;25], can occur via route d.

Fischer carbene ligands exhibit a wide manifold of reactivity and can be readily modified. A widely applied reaction is the so-called Dötz reaction^[22]. The benzannulation ([3+2+1] carbonylative cycloaddition with alkynes) of alkoxy-carbene complexes with unsaturated substituents (vinyl or aryl) to give cyclohexadienes or phenols, is one of the most unique type of carbene reactions. Chromium complexes are the metal templates of choice, as they allow excellent chemo- and regioselectivity under mild conditions. Benzannulation is an attractive methodology for the synthesis of natural products with hydroquinoid, quinoid or fused phenolic structures.

Other reactions of importance for organic synthesis are [2+2], [3+2] and [4+2] cycloadditions, sigmatropic rearrangements, coupling of anions of the carbene ligand with C-X σ -bonds, coupling of anions of the carbene ligand with C-X π -bonds, Michael additions to α,β -unsaturated carbene complexes and nucleophilic substitutions at and cleavage of the carbene ligand^[26].

The reactions of Fischer carbene complexes are multifaceted and consequently a wide range of products is accessible. One feature often utilised in synthetic strategy is the fact that in these reactions either the metal-carbon bond is retained in the product whilst a ligand is modified or the bond undergoes reaction. Thus, in order to mediate an otherwise difficult transformation, the organic framework is attached to the metal through a carbene carbon, this moiety is modified and then cleaved from the metal to yield the desired product.

1.4 Aim

Carbene chemistry of transition metals such as chromium and tungsten is well developed and can easily be controlled and manipulated^[27], but for transition metals such as manganese and cobalt, discoveries made are still often serendipitous.

The general aim of this project is to investigate aspects of the synthesis, characterization and structural features of Group VII transition metal carbene complexes, specifically manganese, and to a lesser extent, its comparison with the rhenium analogues. The Fischer method will be used to synthesize binuclear ethoxycarbene complexes with a range of heteroaromatic substituents. The structure and properties of such new complexes will address a number of very important aspects in manganese carbene chemistry that will be investigated:

- i) positioning of the carbene ligand with respect to the metal-metal bond,
- ii) the role of the heteroarene ring in stabilizing the carbene ligand of the complex,
- iii) the stability of the metal-metal bond under reaction conditions employing organolithium reagents,
- iv) possible route to the synthesis of mononuclear carbene complexes containing halogen ligands.

The assembly of complexes containing both a carbene and a halide ligand could potentially be used as precursor for carbon-carbon coupling catalysts or templates in organic syntheses, after modification of the carbene ligand. A metal-metal cleaving reaction is to be investigated, where it is planned to use halogens to oxidatively cleave the Mn-Mn bond to yield mononuclear carbene complexes containing a halide ligand.

1.5 References

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