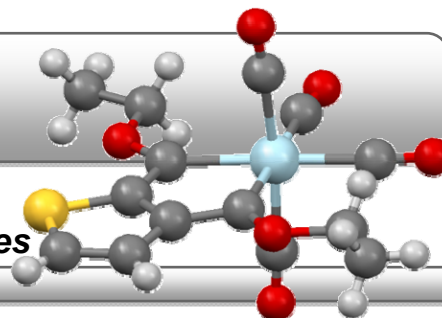


Chapter 1: Introduction and Theory

Organometallic chemistry of divalent carbon complexes



General Introduction

Organometallic compounds containing carbon metal double bonds have received wide spread interest from the time that the first metal carbene complex was fully characterized by Fischer and Maasböl in 1964¹ (Figure 1.1). Since the induction into the study of carbon metal double bonds, extensive applications in catalytic and template organic synthesis² have been found of which those of monocarbene complexes are the most widespread. The group VI carbene complexes and palladium catalysts³ often undergo formation of a biscarbene intermediate, which allows for the catalytic formation of an olefin. The stability of carbene complexes plays an obvious role in its applicability as a synthetic tool and is dependent on the metal and carbene substituents⁴.

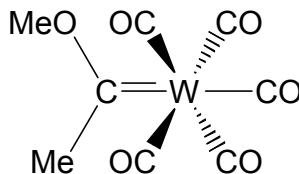


Figure 1.1: The first fully characterized metal carbene complex¹.

¹ E.O. Fischer, A. Maasböl, *Angew. Chem. Int. Ed. Engl.*, **1964**, 3, 580

² J. Barluenga, M.A. Fernández-Rodríguez, E. Aguilae, *J. Organomet. Chem.*, **2005**, 690, 539

³ I. Fernández, M.J. Mancheño, R. Vincente, L.A. López, M.A. Sierra, *Chem. Eur. J.*, **2008**, 14, 11222

⁴ Ch. Elschenbroich, A. Salzer, *Organometallics: a concise introduction 2nd edition*, **1992**, Verlagsgesellschaft, New York

From the time of Fischer the scope of metal carbene complexes has grown to such an extent that two individual classes of carbene complexes were distinguishable: Schrock carbene complexes (Figure 1.2) and Fischer carbene complexes⁵ (Figure 1.1). The differentiation between the respective types of carbene complexes was found to be by the nature of the carbon metal double bond itself. This differentiation was made by the characteristics of the substituents attached to the carbene carbon atom and the influence that the above mentioned imparts on the carbene ligand.

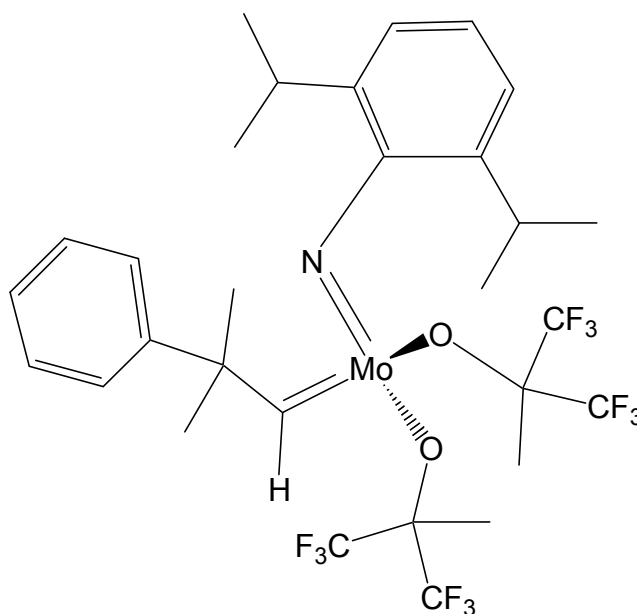


Figure 1.2: A typical Schrock carbene complex⁶.

Research on Fischer carbene complexes has focused on especially N-heterocyclic carbene complexes (NHC-complexes). These types of complexes have found application as auxiliary carbene ligands in 3rd generation Grubbs catalysts (Figure 1.3). NHC-complexes, a sub-class of Fischer carbene complexes, are now a predominant topic of research in metal carbene chemistry neglecting the synthesis of novel classic Fischer and Schrock type carbene

⁵ G. Frenking, M. Solà, S.F. Vybioshchikov, *J. Organomet. Chem.*, **2005**, 690, 6178

⁶ D.H. McConville, R.J. Wolf, R.R. Schrock, *J. Am. Chem. Soc.*, **1993**, 115, 4413

complexes⁷. While carbene complexes are finding application as active or auxiliary ligands in organic synthesis and catalysis, which are able to enforce stereoselective control, they have not yet entered the arena of material sciences. No carbene supramolecular compounds have been reported, such as assemblies of carbene units and only a few carbene complexes are known to be part of a metal organic framework⁸. In addition, no dendrimers with carbene functionalities were recognized and no carbene complexes showing liquid crystal type properties have been reported. There are no examples of carbene complexes with photochromic effects and in fact, very few studies on multimetal carbene complexes or cluster carbene complexes have been reported.

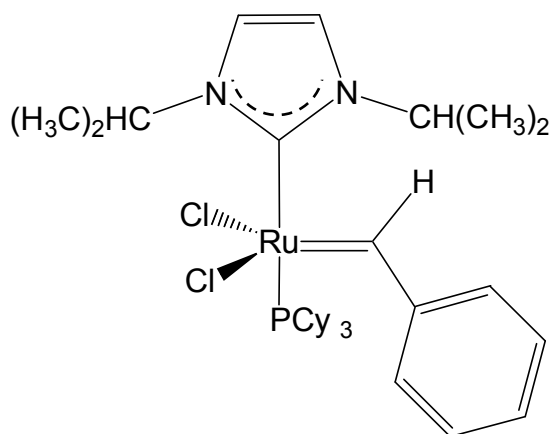


Figure 1.3: A third generation Grubbs catalyst⁹.

Some combinatorial chemistry includes attachment of a Fischer carbene complex to solid supports¹⁰. Additional exploration of these versatile complexes² as part of a supramolecular structure was essential. Creative new methods for synthesis and structural investigation of these types of compounds must be explored to produce multifunctional compounds with unique features and properties.

⁷ A.J. Arduengo III, *Acc. Chem. Res.*, **1999**, 32, 913

⁸ J.C. Garrison, R.S. Simons, C.A. Tessier, W.J. Youngs, *Organomet. Chem.*, **2003**, 673, 1

⁹ (a) P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 2039

(b) P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.*, **1996**, 118, 100

¹⁰ K.H. Dötz, J. Stendel, Jr., *Chem. Rev.*, **2009**, 109, 3227

History

More than 150 years ago Dumas reacted methanol with water-abstracting reagents in an attempt to synthesize methylene¹¹, a divalent carbon. In 1855, forty-five years before the first radical was characterized by Gomberg¹², Hermann¹³ suggested a divalent carbene carbon as the reaction intermediate in chloroform hydrolysis (Figure 1.4). At this time, the recognition of carbon as being tetravalent, was not yet established¹⁴.

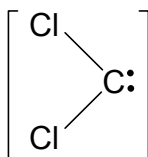


Figure 1.4: The first carbene carbon suggested by Hermann¹³.

Nef¹⁵ suggested the same reaction intermediate forty-two years later for the Reimer-Tienmann reaction, of the transformation of pyrrole to α -chloropyridine, in chloroform. In 1925 Chugaev¹⁶, reacted hydrazine with a cyanide complex to yield a bridged hydrazine metal complex, this was the first synthesis of a metal carbene complex, but Chugaev was unable to characterise the complex with the techniques available at that time and in 1972, Rouschias suggested the metal carbene complex alternative (Figure 1.5)¹⁷. In 1922, the Nobel laureate Staudinger¹⁸.

¹¹ P. De Frémont, N. Marion, S.P. Nolan, *Coord. Chem. Rev.*, **2009**, 253, 862, and references cited therein

¹² M. Gomberg, *J. Am. Chem. Soc.*, **1900**, 22, 757

¹³ M. Hermann, *Liebigs Ann. Chem.*, **1855**, 95, 211

¹⁴ H. Werner, *Landmarks in Organo-Transition metal chemistry*, **2009**, 64-65, 235

¹⁵ J.U. Nef, *Ann.*, **1887**, 298, 202

¹⁶ L. Chugaev, M. Skanavy-Grigorizeva, A. Posniak, *Z. Anorg. Allg. Chem.*, **1925**, 148, 37

¹⁷ G. Rouschias, B.L. Shaw, *J. Chem. Soc. D*, **1970**, 183

¹⁸ (a) H. Staudinger, O. Kupfer, *Ber.*, **1911**, 44, 2194,

(b) H. Staudinger, O. Kupfer, *Ber.*, **1912**, 45, 501

started investigating the synthesis of divalent carbon and the interest in free carbene chemistry started to intensify¹⁴.

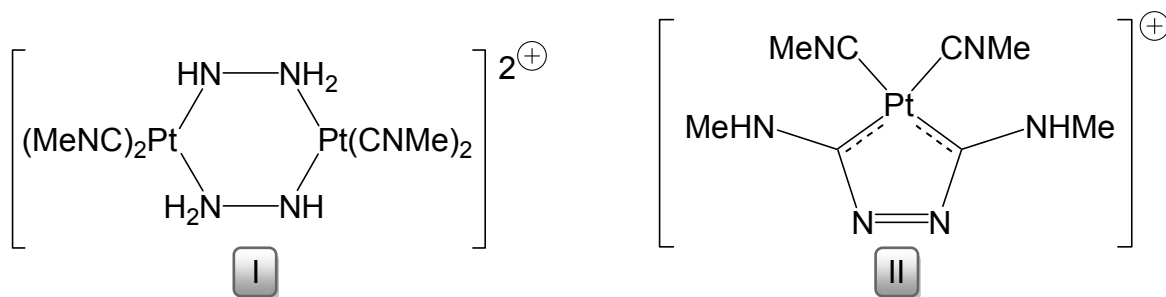


Figure 1.5: (I) was a structure proposed to be Chugaev's salt, (II) was the revised structure by Rouschias^{17, 19}.

Only about one hundred years after Hermann¹³, in 1953, did Knox and Doering²⁰ prove the existence of the dibromomethylene intermediate, which spurred a new interest in carbene chemistry (Figure 1.)¹¹. However, a stable carbene was not yet isolated.

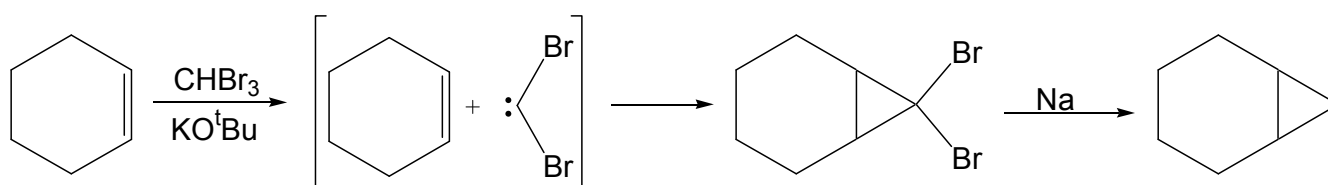


Figure 1.6: The dibromocarbene intermediate in the cyclopropanation of an alkene²⁰.

Not only was the divalent carbon of interest as a powerful organic synthon but it was also used as an organometallic reagent. Only ten years after the research of Knox and Doering²⁰, was King²¹ able to synthesize the first carbene complex in 1963 (Figure 1.7)²².

¹⁹ A. Burke, A.L. Balch, J.H. Enemark, *J. Am. Chem. Soc.*, **1970**, 92, 2555

²⁰ (a) W. von Doering, L.H. Knox, *J. Am. Chem. Soc.*, **1953**, 75, 297

(b) W. von Doering, L.H. Knox, *J. Am. Chem. Soc.*, **1954**, 76, 6162

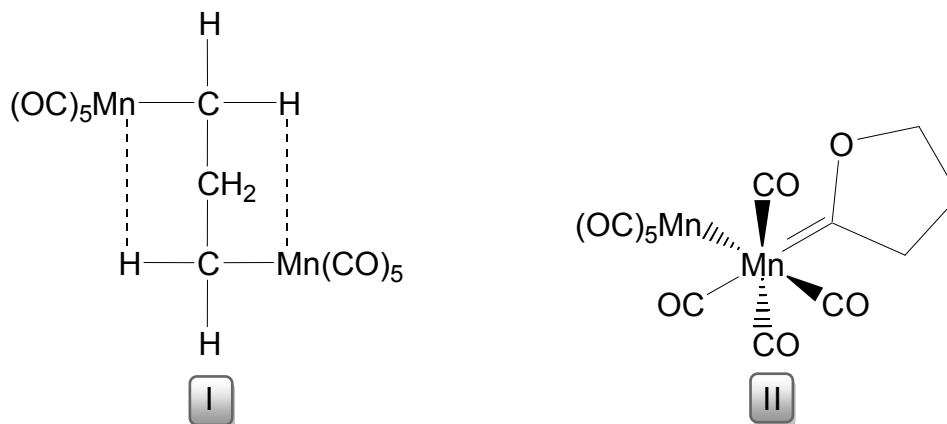


Figure 1.7: (I) Proposed structure by King²¹ and (II) corrected structure by Casey²³.

Only one year later, Fischer and Maasböl¹ fully characterized the first tungsten carbene complex (Figure 1.1) after which Casey²³ elucidated the manganese carbene synthesized by King²². The discovery by Fischer¹, renewed the interest into divalent carbon as part of a metal system, of organic and organometallic chemists alike and not long afterwards up to four NHC's were complexed to a single metal (Figure 1.8)²⁴.

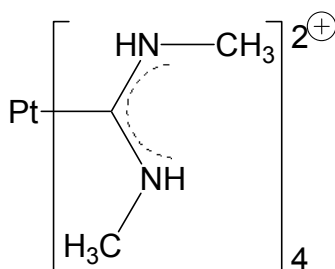


Figure 1.8: Platinum tetracarbene complex synthesized by Miller and co-workers²⁴.

²¹ R.B. King, *J. Am. Chem. Soc.*, **1963**, 85, 1922

²² M.A. Sierra, *Chem. Rev.*, **2000**, 100, 3591

²³ C.P. Casey, *J. Chem. Soc. Chem. Commun.*, **1970**, 1220

²⁴ J.S. Miller, A.L. Balch, *Inorg. Chem*, **1972**, 11, 2069

In 1968 Wanzlick²⁵ reported the synthesis of a diaminocarbene complex. In that same year, Öfele²⁶ also reported stable diaminocarbene complex (Figure 1.9). However, they did not isolate the free carbene molecule itself¹⁴.

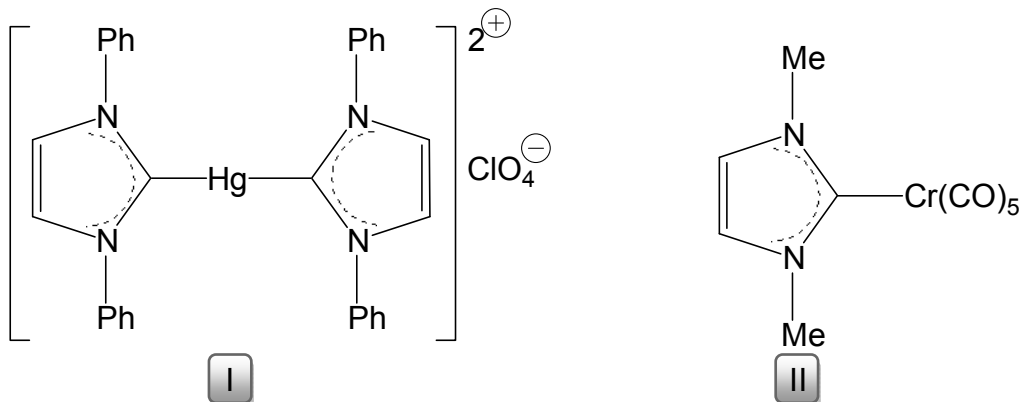


Figure 1.9: NHC-complex published by Wanzlick²⁵ (I) and by Öfele²⁶ (II).

In 1974, 6 years later, Schrock²⁷ reported a carbene complex without stabilisation at the α -position of the carbene carbon (Figure 1.10)²⁷. The high oxidation state metal-alkylidene complex had characteristics so unique that these types of carbene complexes were known as Schrock carbene complexes⁹.

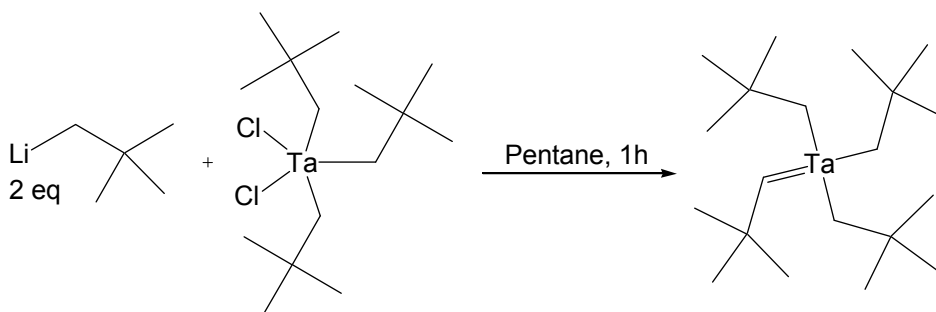


Figure 1.10: Synthesis of the first Schrock carbene complex²⁷.

²⁵ H.W. Wanzlick, H.J. Schoenherr, *Angew. Chem. Int. Ed. Engl.*, **1968**, 7, 141

²⁶ K. Öfele, *J. Organomet. Chem.*, **1968**, 12, P42

²⁷ R.R. Schrock, *J. Am. Chem. Soc.*, **1974**, 96, 6796

In this same year, Fischer²⁸ synthesized the first carbyne complex. In 1991, after many failed attempts, Arduengo^{29,30} isolated and crystallized the first stable carbene molecule¹⁴ and because of their exceptional electronic and steric properties branched the research of Fischer carbene complexes (Figure 1.11).

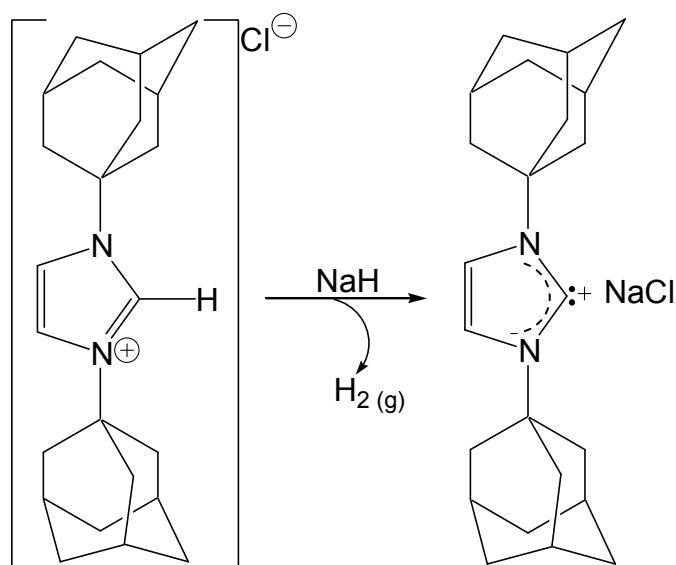


Figure 1.11: Synthesis of the first isolable free carbene molecule^{29,7}.

The investigation into NHC-complexes has grown exponentially since the initial isolation of a stable free carbene and the variety and diversity of stable carbenes were evident as well as metal carbene complexes. The influence of metal carbene chemistry on society was so comprehensive that both R.R. Shrock and E.O. Fischer received the Nobel Prize for chemistry in 2005 and 1973 respectively¹⁴.

²⁸ E.O. Fischer, F.J. Gammel, D. Neugebauer, *Chem. Ber.*, **1980**, 113, 1010

²⁹ (a) A.J. Arduengo III, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **1991**, 113, 361

(b) A.J. Arduengo III, R.L. Harlow, M. Kline, *J. Am. Chem. Soc.*, **1991**, 113, 280

³⁰ A.J. Arduengo III, F. Davidson, H.V.R. Dias, J.R. Goerlich, D. Khasnis, W.J. Marshall, T.K. Prakasha, *J. Am. Chem. Soc.*, **1997**, 119, 12742

Carbene carbons and carbene complexes

Since the conception and full characterization of divalent carbon, it has received much attention. The reason for this was the exceptional characteristics of the carbene carbon as well as its applicability as an organic synthon³¹. Carbene carbons are neutral divalent⁴ or dicoordinate carbons with six valence electrons^{13, 32}.

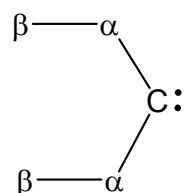


Figure 1.12: Free carbene characteristics are influenced by the α and β position substituents on the carbene carbon atom.

Free carbenes show different characteristics compared to metal bound carbene ligands. The philicity of a free carbene with heteroatoms on the α -position (singlet carbenes), results in a nucleophilic carbene carbon and the opposite is true for triplet carbenes, which contains no heteroatoms³³. An empirical philicity scale was used to characterise carbenes as electrophiles, nucleophiles or ambiphiles^{33,34} (amphiphiles³⁵). The success with this type of measurement was more prominent with singlet carbene complexes³³. There was difficulty in classifying certain types of carbene complexes such as di-halo carbene complexes, which may tend to be electrophilic or nucleophilic (Figure 1.13).

³¹ C. Crause, PhD Thesis, *Synthesis and application of carbene complexes with heteroaromatic substituents*, **2004**, University of Pretoria.

³² D. Bourissou, O. Geurret, F.P. Gabbaï, G. Bertrand, *Chem. Rev.*, **2000**, *100*, 39

³³ G. Bertrand, *Carbene Chemistry: From fleeting intermediates to powerful reagents*, **2002**, Marcel Dekker, Inc. New York

³⁴ R.A. Moss, *Acc. Chem. Res.*, **1980**, *13*, 58

³⁵ J.W. Herndon, *Coord. Chem. Rev.*, **2000**, *206-207*, 237

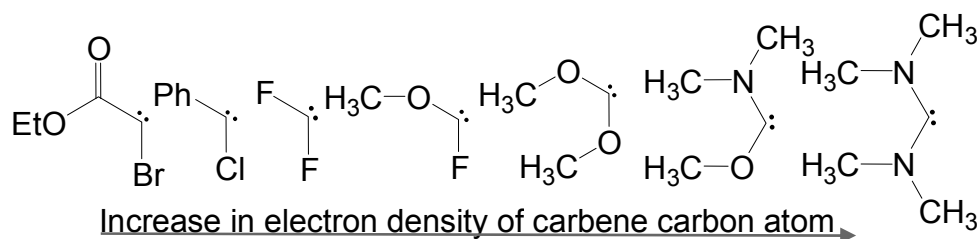


Figure 1.13: Philicity scale of a series of carbenes, from electrophiles to nucleophiles³⁴.

For a free carbene, there are two different electronic states (ground-state spin multiplicities)³², a singlet and triplet state⁹. A singlet carbene carbon has three orbitals triangular in geometry, two with paired electrons and the third has a lone pair of electrons. The fourth orbital, a p-orbital is perpendicular to the plane and empty. A triplet state has two orbitals with paired electrons and two orbitals with unpaired electrons and was considered a diradical³² (Figure 1.14). As was expected, the carbene carbon will readily want to complete its octet to reach a more stable state with the utilization of all the valence orbitals. Stability between the triplet and singlet state was also important. Stabilization of the singlet carbene carbon was achieved by addition of strong donating groups at the α position to the carbene carbon atom. The coordination of the free carbene to a transition metal also adds stability to the carbon atom⁴ and results in a neutral complex.

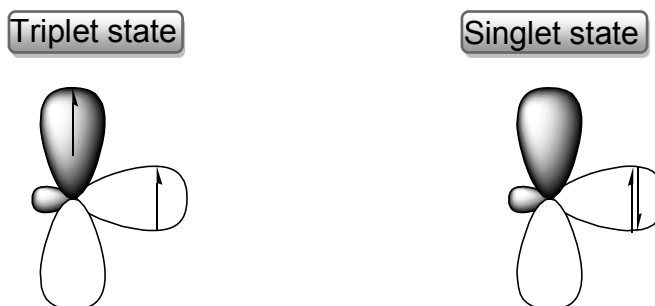


Figure 1.14: The electronic states of the two different types of free carbenes³⁶.

³⁶ (a) R. Hoffmann, *J. Am. Chem. Soc.*, **1968**, *90*, 1475

(b) R. Hoffmann, G.D. Zeiss, G.W. Van Dine, *J. Am. Chem. Soc.*, **1968**, *90*, 1485

General characteristics for a carbene carbon atom⁴:

- An approximate sp^2 hybridization of carbene carbon atom
- A trigonal planar geometry
- A shorter distance for the carbene carbon metal bond in a complex than a metal-carbon single bond, but longer than the σ donor/ π -acceptor bond displayed by a carbonyl ligand.
- When the α -position to the carbene carbon was a heteroatom (X), the C-X bond was shorter than that of a C-X single bond. Due to the resonance contribution, there was π -bonding from a lone pair on X to the empty carbene p-orbital.
- There were also different characteristic for specific types of transition metals complexed to the carbene carbon

The result was a relatively large difference in carbene character and orbital overlap allowing for specific differentiation between them. This demarcation leads to two different types of carbene complexes: the Fischer carbene complex, which has a carbene carbon in a singlet state, coordinated to low oxidation state metal and a heteroatom at the α -position to the carbene, which renders the carbene carbon electrophilic^{37,38} (Figure 1.15). The Schrock carbene complex contains a carbon in a triplet state, bound to a metal in a high oxidation state with no stabilization from the atoms on the α -position making the carbene carbon nucleophilic³⁹. When the use of coordination numbers or oxidation states fails to describe metal ligand bonding sufficiently, the covalent bond classification (CBC) was used, as described by Green⁴⁰.

(c) R. Hoffmann, R. Gleiter, *J. Am. Chem. Soc.*, **1968**, *90*, 5457

³⁷ (a) C.P. Casey, R.A. Boggs, R.L. Anderson, *J. Am. Chem. Soc.*, **1972**, *94*, 8947

(b) K. Weiss, E.O. Fischer, *Chem. Ber.*, **1973**, *106*, 1277

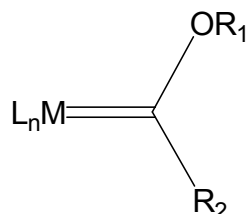
³⁸ S.F. Vyboishchikov, G. Frenking, *Chem. Eur. J.*, **1998**, *4*, 1428

³⁹ R.R. Schrock, *Acc. Chem. Res.*, **1979**, *12*, 98

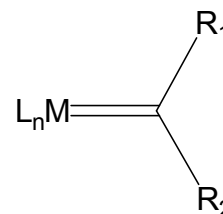
⁴⁰ M.H.L. Green, *J. Organomet. Chem.*, **1995**, *500*, 127

Line structure

Fischer carbene complex



Schrock carbene complex



Orbital representation

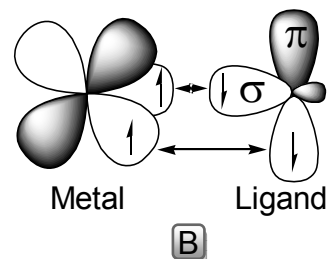
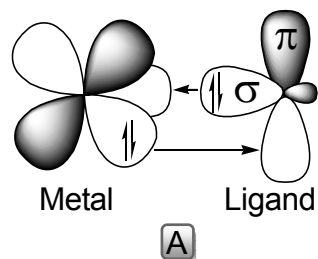


Figure 1.15: General bonding pattern found for (a) Fischer carbene complex and (b) Schrock carbene complex.

A Fischer carbene complex was described as a $\bar{L}\bar{Z}$ type ligand because the carbene carbon atom donates an electron pair datively to the metal and the metal in return, donates an electron pair to the carbene carbon atom \bar{Z} (Figure 1.15, A). Schrock carbene complexes were described as \bar{X}_2 type ligands because each bond was considered covalent and two electrons were shared from the same ligand (Figure 1.15, B).

Fischer carbene complexes

Synthesis

Treatment of a lithiated substrate with a metal carbonyl or isocyanide⁴¹ group followed by alkylation is one of the most frequent used methods to prepare a Fischer carbene complexes (Figure 1.16)³⁵.

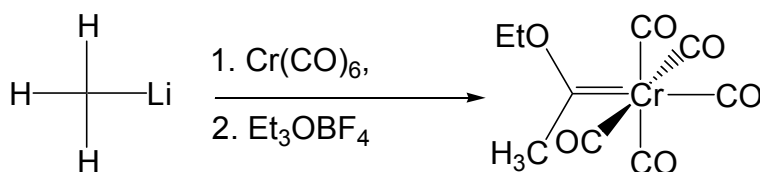


Figure 1.16: Synthesis of Fischer carbene complex with a lithium derivative as starting material¹.

An assortment of methods was applied to synthesize both Fischer and Schrock carbene complexes⁴. An alternative method of the alkylation of a neutral acyl complex requires an exceptionally strong alkylating agent such as magic methyl. Overall, there are three general methods for carbene synthesis:

- Transformation of a metal ligand (Figure 1.16) (Fischer¹)
- Combination of a coordinatively unsaturated metal with a carbene precursor (Semmelhack-Hegedus route¹⁰)
- Modification of an already present carbene complex⁴².

⁴¹ K. Öfele, M. Herberhold, *Angew. Chem. Int. Ed. Engl.*, **1970**, 9, 739

⁴² K.H. Dötz, *Angew. Chem. Int. Ed. Engl.*, **1984**, 23, 587

Various examples include:

- Reaction of carbonyl ligands with a lithiated substrate and consequent alkylation (Fischer¹)
- Addition of alcohol to an isocyanide complex (Chatt⁴³)
- Cleavage and insertion of a metal into an electron-rich olefin (Lappert⁴⁴)
- Addition of carbonyl metalates to geminal chlorides (Öfele⁴⁵)
- Interception of free carbenes by metals (Herrmann⁴⁶)
- Metal-alkyl deprotonation at the α -position (Schrock⁴⁷)
- Metal-alkyl hydride abstraction (Gladysz⁴⁸)
- Carbene transfer from one metal to another (Fischer⁴⁹)

The successes of these reactions were dependent on steric and electronic characteristics of starting materials used, but in general, high yields were obtained⁴². The scope of carbene complexes is not only limited to monocarbene complexes or a system with only one metal fragment, a range of combinations is possible (Figure 1.17 (a) and (f))¹⁰. The total of metal centres on a carbene fragment is limited (Figure 1.17, (b)), but more than one carbene has been placed on one metal centre, such as a mononuclear biscarbene complex (Figure 1.17, (c))⁵⁰. Introduction of a second metal moiety has been accomplished by addition to the carbene carbon substituent (Figure 1.17 (e)).

⁴³ J. Chatt, *J. Chem. Soc. Dalton, Trans.*, **1969**, 1322

⁴⁴ M.F. Lappert, *J. Chem. Soc. Dalton Trans.*, **1977**, 2172

⁴⁵ K. Öfele, *Angew. Chem. Int. Ed. Engl.*, **1968**, 7, 950

⁴⁶ W.A. Herrmann, B. Reiter, H. Biersack, *J. Organomet. Chem.*, **1975**, 97, 245

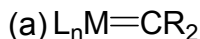
⁴⁷ R.R. Schrock, *J. Am. Chem. Soc.*, **1975**, 97, 6577

⁴⁸ J.A. Gladysz, W.A. Kriel, G. Yu Lin, G.S. Bodner, *J. Am. Chem. Soc.*, **1983**, 105, 4958

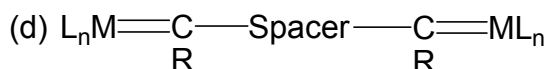
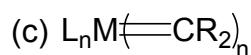
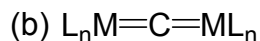
⁴⁹ E.O. Fischer, H.J. Beck, *Angew. Chem. Int. Ed. Engl.*, **1970**, 9, 72

⁵⁰ Y.M. Terblans, PhD Thesis, *Thiophene bimetallic carbene complexes*, **1996**, University of Pretoria

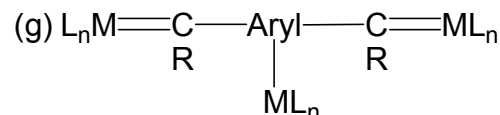
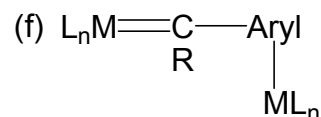
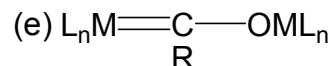
Monocarbene complexes



Biscarbene complexes



Multimetal systems

Figure 1.17: Possible combinations for synthesis of carbene containing complexes⁵⁰.

Dinuclear biscarbene complexes (Figure 1.17 (d) and (g)) with a molecular spacer was a popular choice and addition of other types of carbon metal bonds (metal coordination). In general, the synthetic procedure for the synthesis of biscarbene complexes was similar to that of the monocarbene complex. Various methods for synthesizing dinuclear biscarbene complexes include⁵¹:

- Reacting a dilithiated substrate with the appropriate transition metal containing carbonyl ligands⁵²
- Michael addition: lithiation of the α -carbon on a Group VI (Cr, W) alkoxy carbene complex followed by conjugate addition of α/β -unsaturated carbene complexes⁵³
- Reacting diiodoalkanes with a α -lithiated tungsten carbene complex⁵⁴
- Reacting tetrachlorocyclopropene with a α -lithiated chromium carbene complex⁵⁵

⁵¹ E. Keuster, L.S. Hegedus, *Organometallics*, **1999**, 18, 5318

⁵² H. Wang, W.D. Wulff, *J. Am. Chem. Soc.*, **1998**, 120, 10573

⁵³ (a) D.W. Macomber, M.H. Hung, A.G. Verma, *Organometallics*, **1988**, 7, 2072

(b) D.W. Macomber, M.H. Hung, P. Madhukar, M. Liang, *Organometallic*, **1991**, 10, 737

⁵⁴ D.W. Macomber, P. Madhukar, *J. Organomet. Chem.*, **1992**, 433, 279

- Aldol condensation between aromatic dialdehydes and chromium alkoxy carbene complexes⁵⁶
- Stille coupling⁵⁷
- photoinduced substitution or substitution by irradiation of metal carbonyl ligands (Figure 1.18)⁴¹
- Other methods include thermal reactions of tetraaminoalkanes with a metal hexacarbonyl⁵⁸

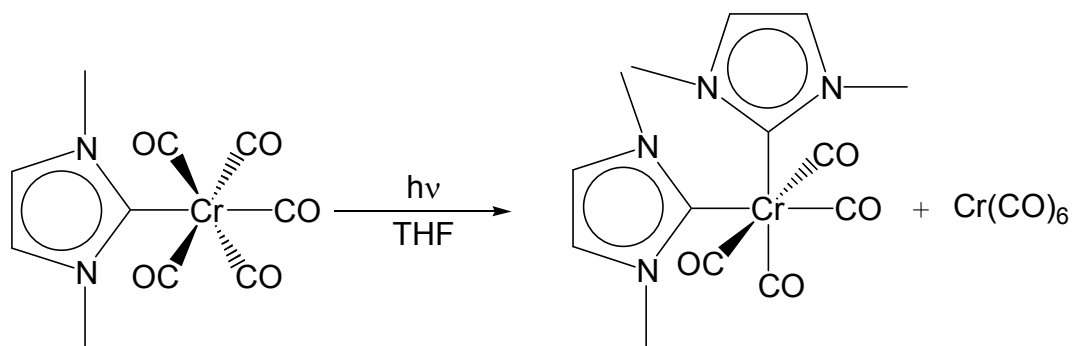


Figure 1.18: Synthesis of the first mononuclear biscarbene complexes on a group VI transition metal⁴¹.

Various types of biscarbene complexes have been synthesized using these methods including mononuclear biscarbene complexes. An alternative method for synthesizing a biscarbene complex is the modification of an existing method. These methods implemented large complexes with many possible areas of reactivity. Apart from modification reactions of monocarbene complexes the use of catalysts to facilitate carbon-carbon coupling reactions has assisted in preparing biscarbene complexes. This type of synthetic procedure is possible because the group 6 aminocarbene complexes are not as prone to transmetalation as the alkoxy carbene complex (Figure 1.19). Another method involves copper as a catalyst implementing Hay's⁵⁹ oxidative coupling to give an alkynylchromium biscarbene complex⁶⁰.

⁵⁵ R. Aumann, B. Jasper, R. Fröhlich, S. Kotila, *J. Organomet. Chem.*, **1995**, 502, 137

⁵⁶ R. Aumann, H. Heinen, *Chem. Ber.*, **1987**, 120, 537.

⁵⁷ C. Hartbaum, E. Mauz, G. Roth, K. Weissenbach, H. Fischer, *Organometallics*, **1999**, 18, 2619.

⁵⁸ J. Barluenga, A.A. Trabanco, I. Pérez-Sánchez, R. De la Campa, J. Flórez, S. García-Granda, Á. Aguirre, *Chem. Eur. J.*, **2008**, 14, 5401

⁵⁹ A.S. Hay, *J. Org. Chem.*, **1962**, 27, 3320.

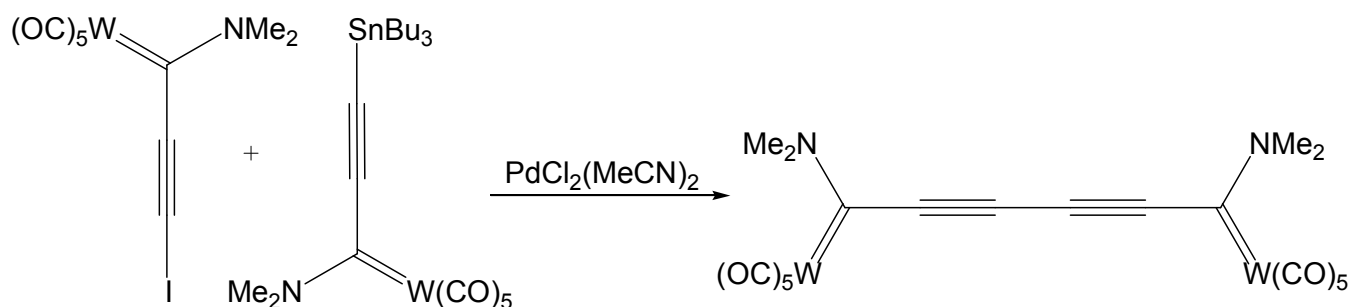


Figure 1.19: Stille methodology utilized in the synthesis of a bis-carbene complex⁵⁷.

Mononuclear bis-carbene complexes are not as common as dinuclear carbene complexes due to the lack of general synthetic procedures⁶⁰. Low yields are obtained by the reaction of metal hexacarbonyl with two equivalents of BuLi and then reacting with an electrophile⁵⁸. The most common examples of mononuclear bis-carbene complexes are NHC complexes. The general problem when trying to synthesize a mononuclear bis-carbene complex containing carbonyl ligands is the fact that the carbene carbon is the most reactive site in the molecule⁵⁸. A possible solution is in the deprotonation of an α -substituent on a carbene carbon atom, resulting in a decrease of the carbene electrophilicity and allowing for a nucleophilic attack on a carbonyl ligand⁶¹. For this, the nucleophile must be selected carefully. The use of BuLi, alkynyllithium, substituted alkyllithiums and phenyllithium give reactions with alternative products. Reacting 1,2-dilithiated precursors afforded 5-membered chelate rings with bis-carbene ligands (Figure 1.20)⁵⁸.

⁶⁰ B. Baeza, L. Casarrubios, P. Ramírez-López, M. Gómez-Gallego, M.A. Sierra, *Organometallics*, **2009**, *28*, 956

⁶¹ G.M. Wieber, L.S. Hegedus, C. Gale, *Organometallics*, **1995**, *14*, 3574

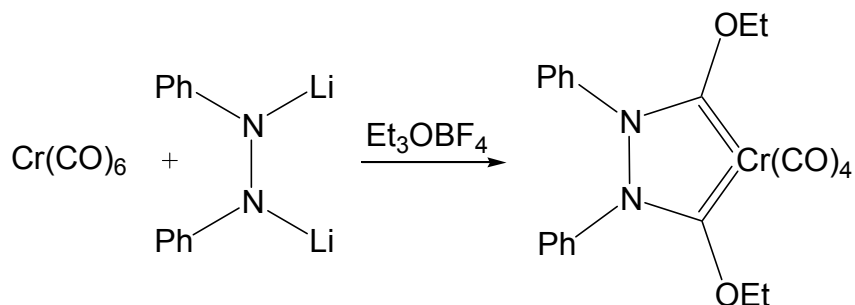


Figure 1.20: Synthesis of a stable isolable mononuclear biscarbene complex⁶².

This leaves an area of opportunity, in other words to create a synthetic procedure that is time and cost efficient. The use of dilithiated compounds to synthesize biscarbene complexes has been employed but no examples of sequential preparation of heterodimetallic biscarbene complexes utilizing this method have been reported⁶³. The method used to prepare dilithiated complex by Fischer^{63b, c} makes use of complex procedures.

Characteristics: Electronic structure

Electronic and steric effects control the ground-state spin multiplicity of the free carbene while inductive and mesomeric effects influence the electronic state. The latter show a more prominent control³². This is mainly due to the influence of the substituents on the carbene carbon atom and is of great interest because they control the reactivity of the carbene ligand. The electron placement of a singlet carbene has the empty π -orbital perpendicular to the

⁶² N.H.T. Huy, C. Pascard, E.T.H. Dau, K.H. Dötz, *Organometallics*, **1988**, 7, 590

⁶³ (a) E.O. Fischer, W. Röhl, N.H.T. Huy, K. Ackermann, *Chem. Ber.*, **1982**, 115, 2951.

(b) N.H.T. Huy, P. Lefloch, F. Robert, Y. Jeannin, *J. Organomet. Chem.*, **1987**, 327, 211.

(c) K. H. Dötz, P. Tomuschat, M. Nieger, *Chem. Ber.*, **1997**, 130, 1605.

(d) T. Albrecht, J. Sauer, H. Nöth, *Tetrahedron Lett.*, **1994**, 35, 561.

(e) R. Neidlein, S. Gürtler, C. Krieger, *Helv. Chim. Acta*, **1994**, 77, 2303.

(f) D.M. Anderson, G.S. Bristow, P.B. Hitchcock, H.A. Jasim, M.F. Lappert, B.W. Skelton, *J. Chem. Soc., Dalton Trans.*, **1987**, 2843.

substituents plane³³ and the substituents on the α and β position of the carbene carbon atom typically has at least one heteroatom which provide π -donor character⁶⁴.

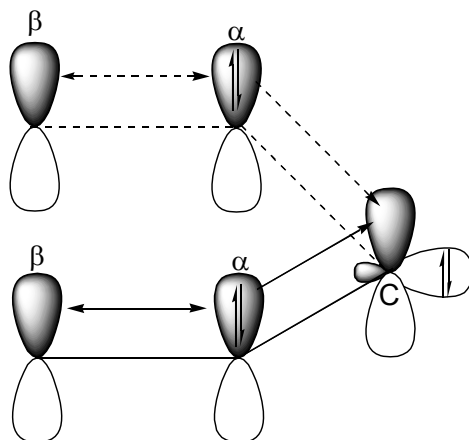


Figure 1.21: Stabilization of the carbene carbon atom by α and β substituents on the carbene carbon atom⁶⁴.

In the extreme case where both α -substituents are heteroatoms, the empty p-orbital of the carbene carbon atom is stabilized by lone pairs on either or both heteroatoms and is in turn stabilized by negative inductive effects from the atom in the β position^{65,33}. These contributions make the singlet carbene a neutral isolable complex with the ability to donate two electrons⁶⁶ (Figure 1.21). Substitution of the electron rich heteroatom with a lesser electron donating substituent resulted in a less stable complex. The Dewar-Chatt-Duncanson model was employed to describe the synergic interaction of a Fischer metal-carbene bond³⁷. Both the metal and the carbene carbon were in a singlet state to allow bonding⁶⁵. The primary interaction was the σ -donation from the carbene carbon atoms sp^2 orbital to the metal σ -hybrid orbital and π -back donation from the metal d-orbital to the empty p-orbital of the carbene

⁶⁴ (a) H.W. Wanzlick, H.J. Kleiner, *Angew. Chem.*, **1961**, 73, 493

(b) H.W. Wanzlick, E. Schikora, *Chem. Ber.*, **1961**, 94, 2389

(c) H.W. Wanzlick, *Angew. Chem.*, **1962**, 74, 129

(d) H.W. Wanzlick, F. Esser, H.J. Kleiner, *Chem. Ber.*, **1963**, 96, 1208

(e) H.W. Wanzlick, H.J. Kleiner, *Chem. Ber.*, **1963**, 96, 3024

⁶⁵ K.H. Dötz, *Metal carbenes in organic synthesis*, **2004**, Springer-Verlag, Germany

⁶⁶ J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, *Principles and applications of organotransition metal chemistry*, **1987**, University Science Books, USA.

carbon atom (Figure 1.22). The π -back donation from the metal in certain cases is comparatively small compared to the contribution of the substituents on the carbene carbon as in the case of NHC complexes⁵. The electronic state of the carbene carbon was also related to the relative energies of the σ and π orbitals³². A large energy separation between these orbitals favours a singlet carbene³². Attachment of a functional group to the carbene carbon such as a metal serves to stabilize and activate the carbene moiety for further reactions¹⁰.

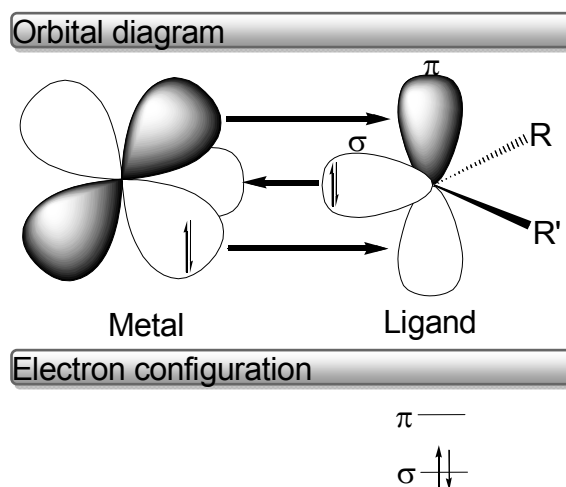


Figure 1.22: Interaction of the hybridized sp^2 orbital and π orbital of a singlet carbene with a metal centre.

Reflection on the electron configuration allowed for excitation of carbene carbon (Figure 1.23, A) to facilitate the transition of a d-electron from the metal to empty p-orbital of the carbene carbon (Figure 1.23, B) and the bond polarity was reversed. The electron withdrawing substituents can accommodate delocalization of the negative charge on the carbene carbon⁶⁷.

⁶⁷ L. Lancelotti, R. Tubino, S. Luzzati, E. Licandro, S. Maiorana, A. Papagni, *Synthetic Metals*, **1998**, 93, 27

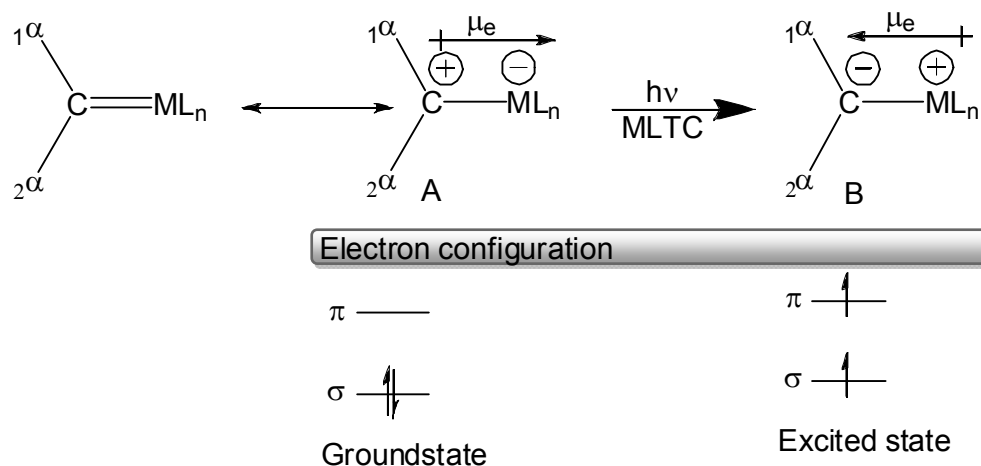


Figure 1.23: Influence of excitation of a carbene complex⁶⁷.

Structure

In most cases the coordinated carbene geometry is described as trigonal planar⁴, thus the metal, carbene atom, and the attached atom of the substituents are coplanar⁶⁸. Sterically the carbonyl groups are above and below the carbene ligand plane (Figure 1.24). The staggered orientation is commonly observed for a pentacarbonyl metal fragment but the type of transition metal complex coordinated to a carbene carbon will influence the geometry of the ligand carbene metal plane. The popular transition metals used for synthesis of Fischer carbene complexes are from group VI to VIII³¹. These do not all consist of hexacarbonyl metals and $Re_2(CO)_{10}$ ⁶⁹ and $MnCp(CO)_3$ ⁵⁰ has been used for the synthesis of Fischer carbene complexes.

⁶⁸ G. Huttner, B. Krieg, *Chem. Ber.*, **1972**, 105, 67

⁶⁹ D.I. Bezuidenhout, MSc Dissertation, *Synthesis and structural investigation of manganese carbene complexes*, **2006**, University of Pretoria

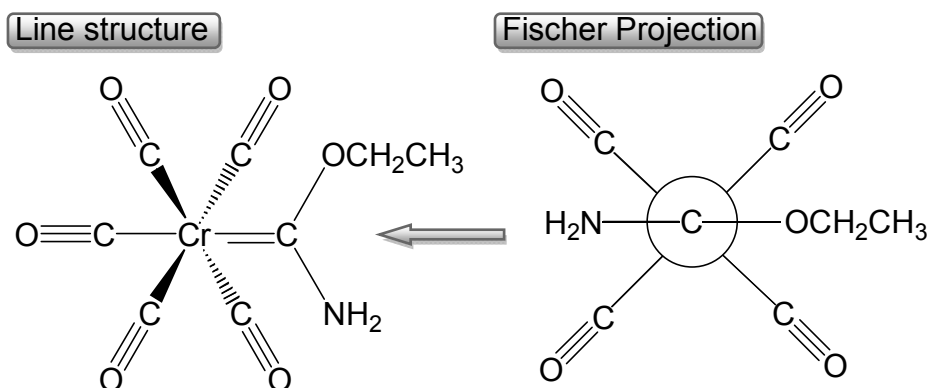


Figure 1.24: A graphical representation of the side and front view of a Fischer carbene complex⁶⁸.

The β -substituents on the carbene carbon atom are able to rotate when the α -substituent is an oxygen atom⁷⁰. Orientation of the β -substituents is relative and is mainly dependent on steric factors (Figure 1.25). These geometric isomers are observed when the rotational barrier of the bond between the carbene carbon atom and the oxygen atom is too high. There is also electronic stabilization between the heteroatom lone pairs and those of the metal carbonyl ligands interaction⁷¹.

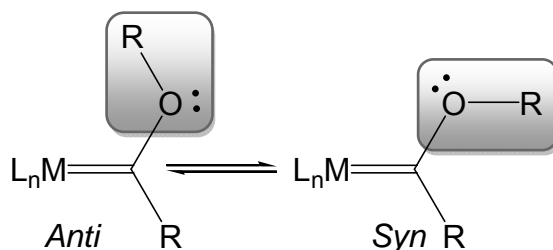


Figure 1.25: Isomers found for a Fischer carbene complex around the carbon-oxygen bond⁴.

⁷⁰ C.G. Kreiter, E.O.Fischer, *Angew. Chem. Int. Ed. Engl.*, **1969**, 8, 761

⁷¹ (a) D.M. Andrada, M.E. Zoloff Michoff, I.Fernández, A.M. Granados, M.A. Sierra, *Organometallics*, **2007**, 26, 5854

(b) I. Fernández, F.P. Cossío, A. Arrieta, B. Lecea, M.J. Mancheño, M.A. Sierra, *Organometallics*, **2004**, 23, 1065

The substitution of the atoms on the α -position of the carbene carbon demonstrated a significant effect on the other metal ligands and the favoured resonance structure. For example a *trans* carbonyl group has two π^* orbitals that can receive back donation from the metal when the carbene carbon atom was sufficiently stabilized by π -interaction from the α -substituents⁷². The resulting effect is an increase of the M-C_{carbene} bond length (Figure 1.26, A), a decrease in the M-(CO)_{trans} bond distance and an increase in the (C-O)_{trans} bond distance. The competition for π -backbonding between a carbene carbon and a carbonyl carbon is shown.

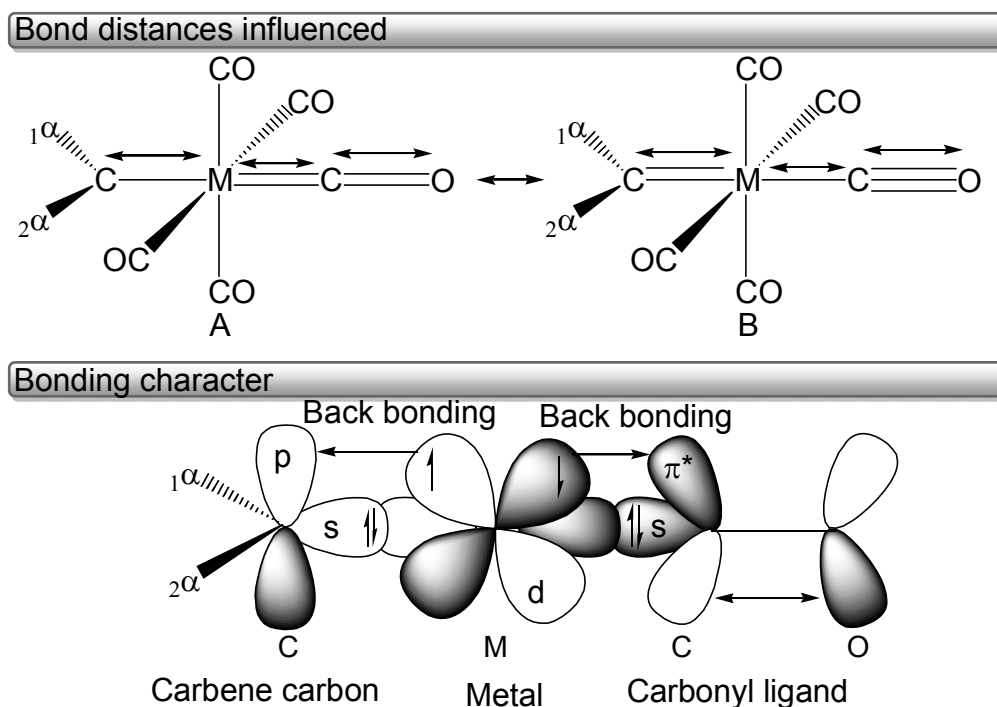


Figure 1.26: Competitive influence of different *trans* ligands for a metal d-orbital⁶⁷.

⁷² S. Maiorana, A. Papagni, E. Licandro, A. Persoons, K. Clay, S. Houbrechts, W. Porzio, *Gazz. Chim. Ital.*, **1995**, 125, 377

A shorter M-C_{carbene} bond length coincides with a longer M-(CO)_{trans} and a corresponding shorter (C-O)_{trans} bond distance (Figure 1.26, B)⁷³ which is more prominent with poorer α -substituents. The partial double bond character of the α -substituent (heteroatom) as seen in the resonance structure of Figure 1.27 shortens the bond and results in a rotational barrier around this bond^{74,75}. For a NHC complex, the π -donor ability of the nitrogen groups is greater than for a carbene containing a phenyl and alkoxy group. From molecular orbital calculations, it is suggested that the rotational barrier around a M-C_{carbene} bond (NHC) is small⁷⁶.

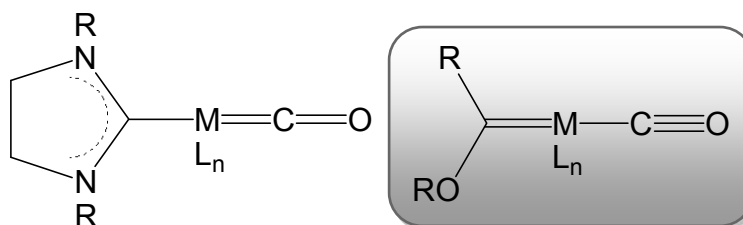


Figure 1.27: Representation of ligand metal interaction due to substituents on the carbene ligand.

Stability and reactivity

As a free carbene, the singlet carbene is nucleophilic³³, but as part of a carbene complex, the carbene carbon is electrophilic⁶⁵ attesting to the electron withdrawing properties of the metal carbonyl fragment. The character of the metal again is influenced by the attached ligands⁶⁵ that play a role in the type of bond formation accessible. The role of the carbene substituents may be the most prominent. Bulky substituents can kinetically stabilize the free carbene carbon atom. As mentioned previously stable free carbenes were isolated and the stability of

⁷³ (a) K. Kitaura, K. Morokuma, *Int. J. Quant. Chem.*, **1976**, 10, 325,

(b) T. Ziegler, A. Rauk, *Theor. Chim.*, **1977**, 46, 1

(c) T. Ziegler, A. Rauk, *Inorg. Chem.*, **1979**, 18, 1558

(d) T. Ziegler, A. Rauk, *Inorg. Chem.*, **1979**, 18, 1755

⁷⁴ D.Y. Myers, G.G. Stroebel, B.R. Ortiz de Montellano, P.D. Gardner, *J. Am. Chem. Soc.*, **1973**, 95, 5833

⁷⁵ C.P. Casey, T.J. Burkhardt, C.A. Bunnell, J.C. Calabrese, *J. Am. Chem. Soc.*, **1976**, 99, 2127

⁷⁶ C. Wang, Y. Wang, H. Lui, K. Lin, L. Chou, K. Chan, *J. Phys. Chem. A*, **1997**, 101, 8887

these carbenes are largely from the substituents and the effects that they infer on the carbene carbon, either in a ring or steric effects³². The reactivity of the carbene carbon was not only charge controlled but also orbital controlled. From molecular orbital calculations, the lowest unoccupied molecular orbital (LUMO) is spatially and energetically localized on the carbene carbon atom⁷⁷. Thus moving from a free carbene to a metal bound carbene carbon, careful consideration must be taken to synthesize an isolable complex. The role of the metal in a carbene complex is mostly that of stabilization of the reactive carbene ligand but not to such an extent that the complex became inert. Stability of Fischer carbene complexes has been listed according to the transition metal to which it was bound: $R_2CMo(CO)_5 < R_2CCr(CO)_5 < R_2CW(CO)_5$ and $R_2CRe_2(CO)_9 < R_2CTc_2(CO)_9 < R_2CMn_2(CO)_9$ ⁷⁸. From the discussion, it was evident that each component of the carbene complex contributes to the overall reactivity and stability of the carbene complex. The π -donor ability of the metal *versus* the heteroatom will determine the favoured resonance structure (Figure 1.28)⁶⁶.

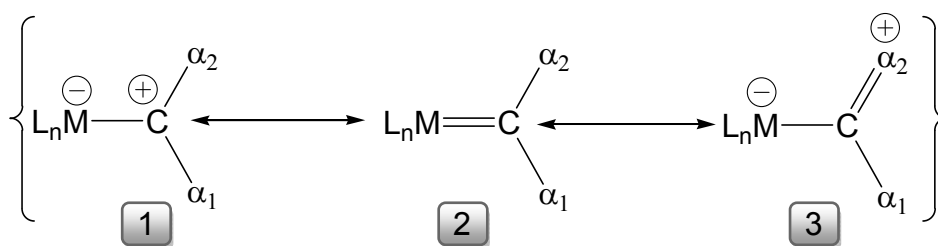


Figure 1.28: Resonance structures of a Fischer carbene complex⁶⁶.

In Figure 1.28, resonance structure 1 represents the σ -bond from the singlet carbene atom to the metal. The π -backbonding from the metal in resonance structure 2 was evident as well as the π -donor ability from one or both α_1 and α_2 in structure 3. Positive charge on the carbene carbon atom in resonance structure 1 is larger when heteroatom has poor π -donor ability⁶⁶. Heteroatoms on the α -position were frequently substituents such as alkoxy, amino or alkylthiol groups that provide the π -donor ability for stabilization of the carbene carbon. The other

⁷⁷ L.M. Toomey, J.D. Atwood, *Organometallics*, **1997**, 16, 490

⁷⁸ H. Fischer, In *The Synthesis of carbene complexes*, **1983**, Verlag Chemie, Weinheim

substituent is commonly an alkyl, aryl vinyl, alkynyl, halogen or a second heteroatom⁷⁹. The reactivity decreases when the methoxy heteroatom is exchanged for an ethoxy group.

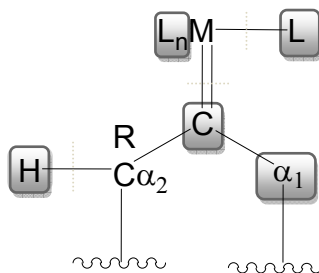


Figure 1.29: The possible sites of reactivity for a Fischer carbene complex⁶⁹.

The resonance structures of the carbene complex also imply different possible sites of reactivity. Figure 1.29 presents the reactivity centres of a classic Fischer carbene complex. The carbene carbon is a site for nucleophilic attack⁶⁹ and results in the acidity of the α -CH. The heteroatom (α_1) will be able to donate an electron pair to a nucleophile. Ligands, such as carbonyls, may be labile or readily substituted¹⁰. The reactivity of a metal carbene complex is thus not only ligand-centered but also metal-centered. Ligand substitution at the carbene carbon position may be a problem during synthesis and result in the formation of an alternative product. The general reactivity profile of the carbene ligand reflects that of an ester with the carbene carbon as the electrophilic centre⁷⁹. As such, it is reactive towards more basic compounds such as primary and secondary amines, thiols and strong nucleophiles such as phenyllithium^{42,80}. Substitution of the heteroatom is easily accomplished by an addition-elimination reaction (Figure 1.30)^{65,66,81}.

⁷⁹ C.F. Bernasconi, *Chem. Soc. Rev.*, **1997**, 26, 299

⁸⁰ E.O. Fischer, M. Leopold, C.G. Kreiter, J. Müller, *Chem. Ber.*, **1972**, 105, 150

⁸¹ J.F. Helling, S.C. Rennison, A. Merijan, *J. Am. Chem. Soc.*, **1967**, 89, 7141

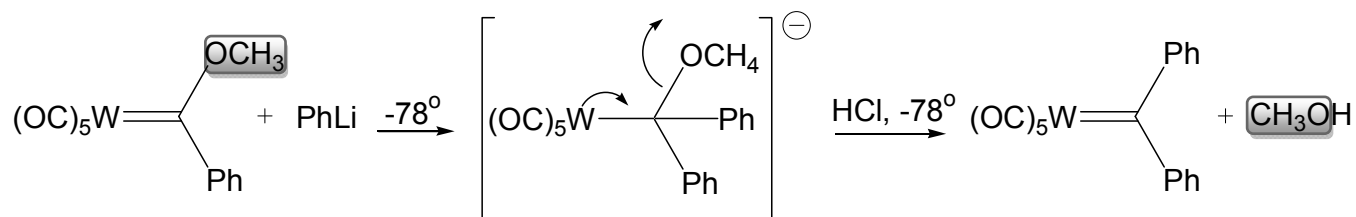


Figure 1.30: Substitution of a heteroatom on the α -position of the carbene carbon⁸².

p-Cyanophenol has a similar acidity to $(\text{CO})_5\text{Cr}=\text{C}(\text{OCH}_3)\text{CH}_3$ in THF attesting to the electrophilic nature of the carbene carbon. A good example of carbene complex reactivity was hydrolysis. The process of hydrolysis is light activated³² and treatment of a carbene with UV radiation results in the same product formation as hydrolysis⁸³. Hydrolysis in this context is the stepwise formation of an aldehyde. Two separate mechanisms can account for the formation of the aldehyde (Figure 1.31)⁷⁹. The specific mechanism used to describe the reaction will be dependent on the results of the kinetic studies but the more general mechanism involves the formation of a tetrahedral intermediate. The tetrahedral intermediate formed during the first step of the reaction is more stable when compared to the similar intermediate for an ester⁷⁹. The intermediate ylide was isolated⁸⁴. Depending on the specific carbene complex, either mechanism can describe the product formation.

⁸² C.P. Casey, T.J. Burkhardt, *J. Am. Chem. Soc.*, **1973**, 95, 5833

⁸³ E.O. Fischer, V. Kiener, *J. Organomet. Chem.*, **1970**, 23, 215

⁸⁴ N. H.T. Huy, E.O. Fischer, H. Guido, K.H. Dötz, *J. Organomet. Chem.*, **1985**, 284, C9

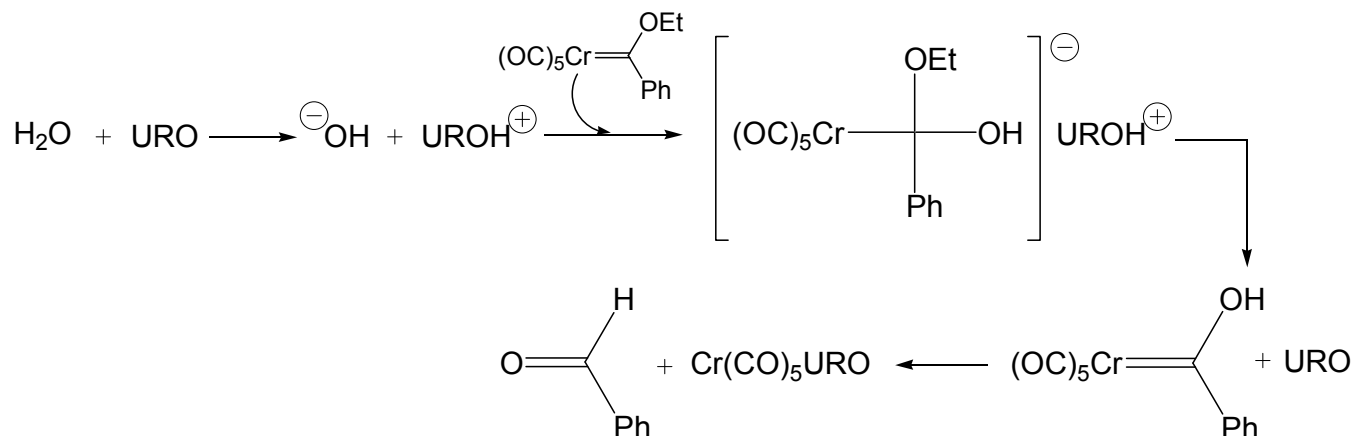


Figure 1.31: General hydrolysis reaction of a Fischer carbene complex⁸⁵.

The metal fragment may also be transferred. A metathesis reaction with a four-member metallocyclic intermediate results in the carbene metal bond transfer, when reacted with nucleophiles such as enol ethers, enamines, diazoalkanes or phosphorous ylids which results in alkene formation (Figure 1.32)⁴².

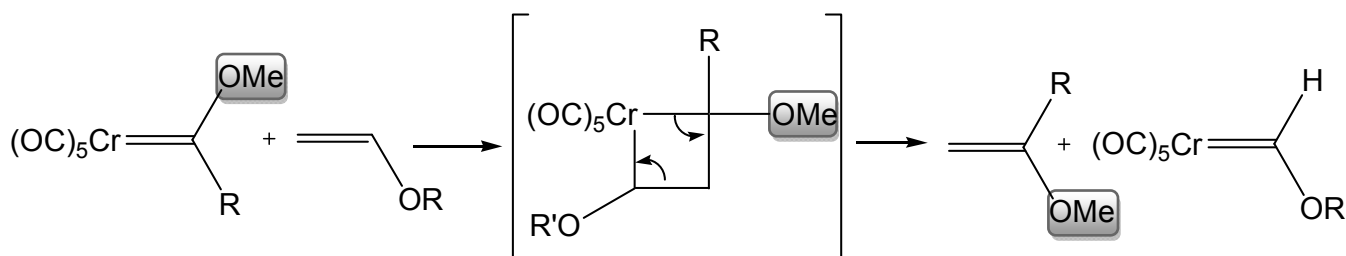


Figure 1.32: Olefin cross metathesis^{86, 75}.

⁸⁵ R. Aumann, P. Hinterding, C. Krüger, R. Goddard, *J. Organomet. Chem.*, **1993**, 459, 145

⁸⁶ (a) E.O. Fischer, K.H.Dötz, S. Walz, G. Krewas, R. Kreißl, *Chem. Ber.*, **1977**, 110, 1651

(b) C.P. Casey, T.J. Burkhardt, *J. Am. Chem. Soc.*, **1972**, 94, 6543

(c) C.P. Casey, H. Bertz, T.J. Burkhardt, *Tetrahedron Lett.*, **1973**, 14, 1421

(d) E.O. Fischer, B. Dorrer, *Chem. Ber.*, **1974**, 100, 1156

Insertion at the carbene moiety affording a modified carbene ligand may also occur with enamines, ynamines and cyanamides and with more electrophilic carbene complexes (Figure 1.33)⁴² via a four-member cyclo-metalobutene intermediate.

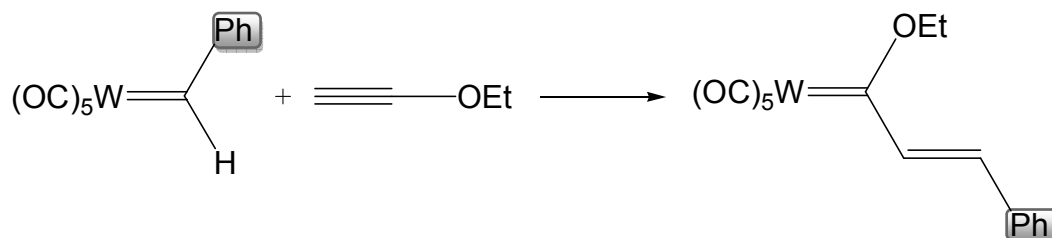


Figure 1.33: Insertion at the carbene centre⁸⁷.

Loss of the carbene moiety could occur via thermal decomposition (Figure 1.34) and results in the formation of the transition metal starting materials and an alkene with exceptions of some alkane formation⁸⁸. Heteroatom substituents with better stabilization property affected the delay of this type of decomposition⁸⁹.

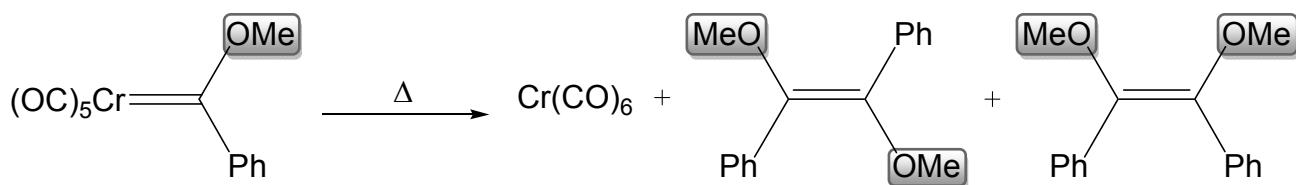


Figure 1.34: Thermal decomposition of a monocarbene complex^{88,89}.

Thermal decomposition of the carbene bond itself commonly leads to dimerization⁴². Thermolysis of the carbonyl group in the presence of a vinyl group resulted in the formation of a saturated cyclopropyl⁴². The metal ligands can also be thermally or photochemically

⁸⁷ C.P. Casey, S.W. Polichnowski, A.J. Shusterman, C.R. Jones, C. Stanley, *J. Am. Chem. Soc.*, **1979**, *101*, 7282

⁸⁸ E.O. Fischer, D. Plabst, *Chem. Ber.*, **1974**, *107*, 3326

⁸⁹ E.O. Fischer, B. Heckl, K.H. Dötz, J.Müller. H. Werner, *J. Organomet. Chem.*, **1969**, *16*, P29

substituted by addition of alkylphosphines, alkylarsanes, alkylstibanes^{90,91}, alkenes, alkynes etc.¹⁰ to a pentacarbonyl carbene complex (Figure 1.35).

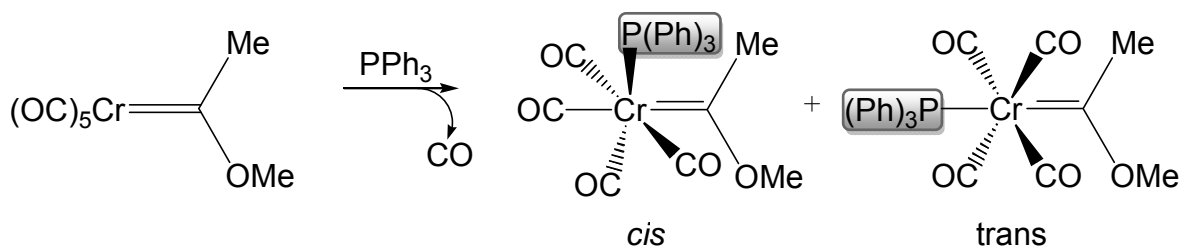


Figure 1.35: Carbonyl substitution of a chromium carbene complex⁹¹.

The reactivity of the carbene complex towards an acid or a base have differing outcomes as compared to hydrolysis. The hydrogens on the α -carbon are especially acidic and may be deprotonated by a base⁹². Basic nitrogen compounds such as pyridine can react with the α -carbon atom hydrogen of a ligand on the carbene carbon to form enol ethers^{88,93}, or in the case of an aromatic group, alkanes(Figure 1.36)⁴². Using a less sterically hindered base resulted in substitution.

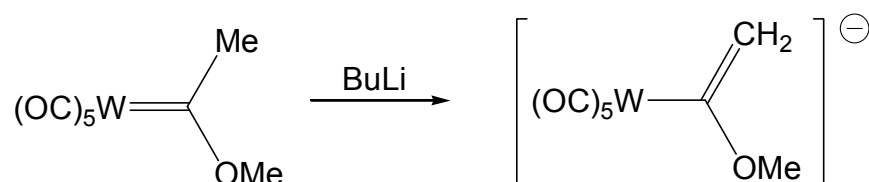


Figure 1.36: Attack of a base occurs at the acidic hydrogen of the β -carbon⁴².

⁹⁰ (a) N.J. Coville, A.M. Stolzenberg, E.L. Muetterties, *J. Am. Chem. Soc.*, **1983**, 105, 2499

(b) W. Fan, R. Zhang, W.K. Leong, Y.K. Yan, *Inorg. Chim. Acta.*, **2004**, 3567, 2441

⁹¹ E.O. Fischer, H. Fischer, H. Werner, *Angew. Chem. Int. Ed. Engl.*, **1972**, 11, 644

⁹² C.G. Kreiter, *Angew. Chem. Int. Ed. Engl.*, **1968**, 7, 390

⁹³ (a) E.O. Fischer, A. Maasböl, *J. Organomet. Chem.*, **1968**, 12, P15

(b) C.P. Casey, *Transition metal organometallics in organic synthesis, Volume 1*, **1976**, Academic Press, New York

(c) C.P. Casey, R.L. Anderson, *J. Chem. Soc. Chem. Commun.*, **1975**, 895

The consequence of oxidation is the cleavage of the metal-carbene bond and the carbene ligand dimerized⁹⁴. Carbene transfer could arise with one of the following groups O₂, S₈, Se_n and pyridine-N-oxide to form a corresponding heteroatom double bond⁵⁰. In some cases, salt formation was observed when a group VI transition metal carbene complex with a cyclic diamino-substitute was reacted with I₂. The formation of a metal(II) carbene complex was afforded when a carbene complex was reacted with a halogen or tin(IV)halide⁹⁴.

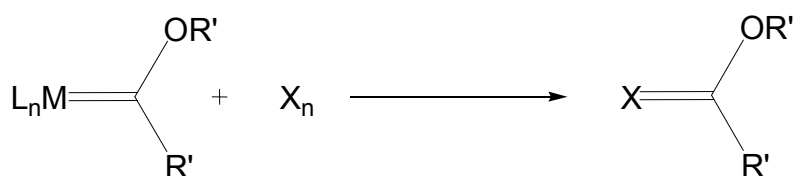


Figure 1.37: Oxidative cleavage of a Fischer carbene complex where X = S, n = 8; X = O, n = 2.

Reductive cleavage of a Fischer carbene complex can occur *via* hydrogenolysis and yields saturated hydrocarbons. Competing dimerization occurred at milder conditions⁴². Hydrogen halides and trihalomethyl mercury will reductively cleave carbene complexes¹⁰. The metal carbene complex is also being reductively demetalated with NaBH₄¹⁰.

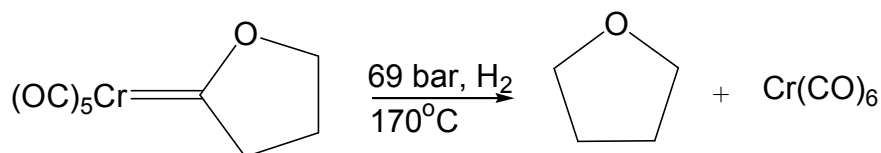
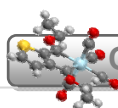


Figure 1.38: Hydride reduction of a metal carbene complex⁹⁵.

⁹⁴ R. Stumpf, M. Jaeger, H. Fischer, *Organometallics*, **2001**, 20, 4040

⁹⁵ E.O. Fischer, A. Frank, *Chem. Ber.*, **1978**, 111, 3740



Application

In recent years group VI Fischer carbene complexes have found application as organic building blocks¹⁰ and stabilization by bonding to a metal allowed for isolation and selective reactivity⁴². Metal carbene complexes are frequent intermediates in metal mediated reactions^{96,97} and were applied in construction of multicomponent and multistep methodologies¹⁰. Popular applications include olefin metathesis, Fischer-Tropsch synthesis⁷⁷ and cycloaddition reactions⁶⁵. The extensive applications are divided into the following categories¹⁰:

- Metal-assisted modification of Fischer carbene complexes
- Cycloaddition reaction
- Metal-template cycloaddition reactions of Fischer carbene complexes
- Benzannulation and cyclopentannulation
- Multistep and multicomponent reactions
- Photo-induced reactions
- Catalytic carbene transfer reactions
- Self-aggregation of carbene complexes

A further reason for the immense interest in metal carbene complexes in organic synthesis is that the carbene moiety can act as a catalyst or increase the reactivity and selectivity of a reaction⁹⁸. The first example of metal carbene complex application was the Diels-Alder

⁹⁶ (a) J. Barluenga, *Pure Appl. Chem.*, **1996**, 68, 543

(b) A. de Meijere, *Pure Appl. Chem.*, **1996**, 68, 61

(c) D.F. Harvey, D.M. Sigano, *Chem. Rev.*, **1996**, 96, 271

(d) R. Aumann, H. Nienaber, *Adv. Organomet. Chem.*, **1997**, 41, 163

(e) J. Barluenga, *Pure Appl. Chem.*, **1999**, 71, 1385

(f) K.H. Dötz, P. Tomuschat, *Chem. Soc. Rev.*, **1999**, 28, 187

(g) M.W. Davies, C.N. Johnson, J.P.A. Harrity, *J. Org. Chem.*, **2001**, 66, 3525

⁹⁷ M Gómez-Gallego, M.J. Mancheño, M.A. Sierra, *Acc. Chem. Rev.*, **2005**, 38, 44

⁹⁸ M. Schlosser, *Organometallics in synthesis: A Manual, 2nd Edition*, **2004**, John Wiley and sons inc., USA

reaction where the C=M bond was compared to the conventional C=O bond (Figure 1.39). The reactivity and selectivity was notably increased and discerning.

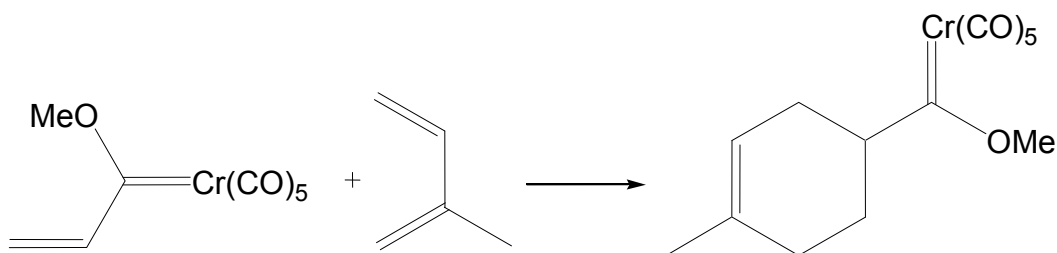


Figure 1.39: Carbene complex showing Diels-Alder reactivity⁹⁸.

The metal activates the Diels-Alder reaction by a factor of 10^4 or more, compared to methyl acrylate of a similar series. The regioselectivity was increased so greatly that it was comparable to that of a Lewis acid catalyst such as AlCl_3 .

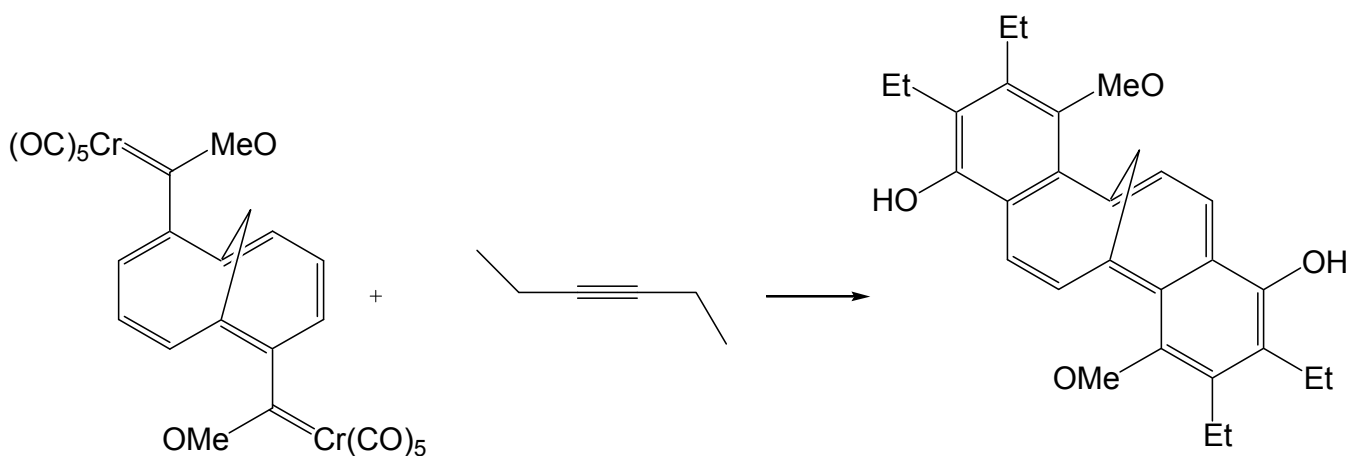


Figure 1.40: Benzannulation of a dinuclear biscarbene complex to produce the bis(phenanthrenehydroquinone) product³¹.

Many of these reactions only utilize monocarbene complexes but introduction of a second metal carbene moiety can allow for greater synthetic possibilities. Biscarbene complex application can include bidirectional organic synthesis of complex molecules²². Biscarbene

complexes were exploited (Figure 1.40) in double benzannulation reaction³¹, synthesis of helicenes, biaryls, unsymmetrical cyclophanes and bis-oxycyclams⁹⁹ but the scope thus far was limited compared to monocarbene complex application³¹.

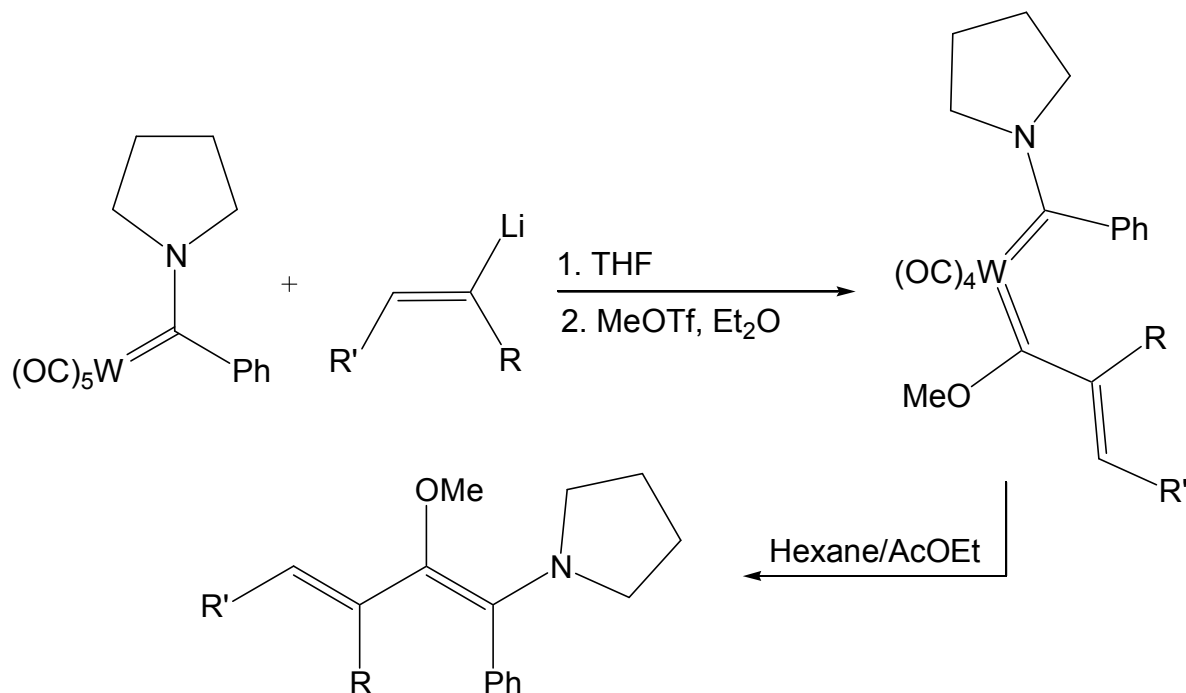


Figure 1.41: Carbene-coupling reaction using a group 6 metal as transfer reagent⁵⁸.

Introduction of a second carbene on the same metal also has vast potential (Figure 1.41). Some of these complexes were studied and isolated by Fischer⁸⁴, Barluenga⁵⁸ and others and were proposed as intermediates in catalysis by Sierra³ and Barluenga⁵⁸. Metathesis

⁹⁹ (a) B. Baeza, L. Casarrubios, P. Ramirez-Lopez, M. Gomez-Gallego, M.A. Sierra, *Organometallics*, **2009**, *28*, 956
(b) P. Tomuschat, L. Kröner, E. Steckhan, M. Nieger, K.H. Dötz, *Chem. Eur. J.*, **1999**, *5*, 700.
(c) J. Bao, W.D. Wulff, M.J. Fumo, E.B. Grant, D.P. Heller, M.C. Whitcomb, S.M. Yeung, *J. Am. Chem. Soc.*, **1996**, *118*, 2166.
(d) H. Wang, W.D. Wulff, *J. Am. Chem. Soc.*, **1998**, *120*, 10573
(e) S. Dumas, E. Lastra, L.S. Hegedus, *J. Am. Chem. Soc.*, **1995**, *117*, 3368.
(f) Y. Hsiao, L.S. Hegedus, *J. Org. Chem.*, **1997**, *62*, 3586.

represents the reaction of a carbene with an olefin whereas these reactions were related to a double coupling of two carbene carbons to give an olefin.

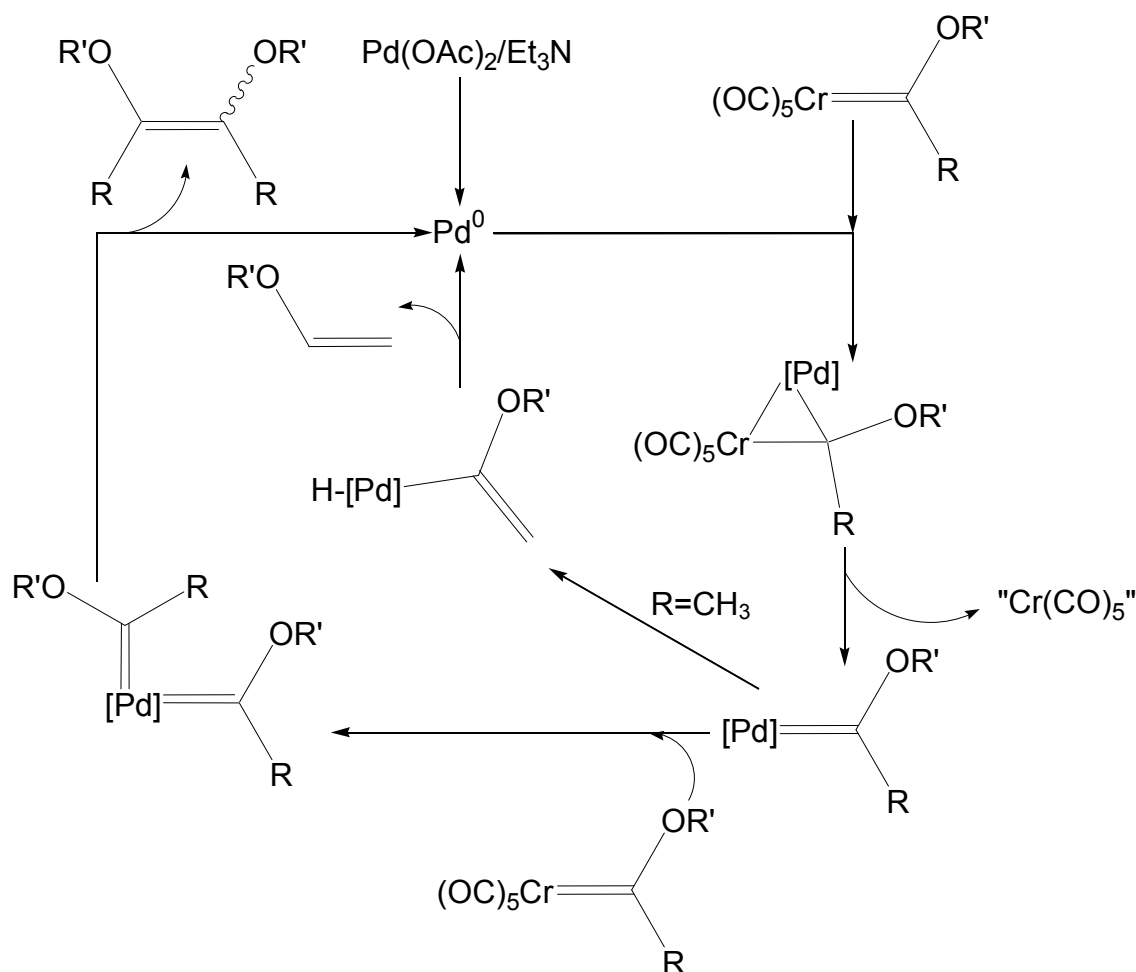


Figure 1.42: Palladium catalyzed reaction showing the formation of a mononuclear bis-carbene intermediate³.

The presence of a mononuclear biscarbene complex was also suggested as an intermediate during palladium catalysis (Figure 1.42). The carbene carbon atom with its substituents were transferred to the catalyst in the first step, which was repeated for a second carbene carbon ligand to give an intermediate with two carbene carbon units in the coordination sphere of palladium.

Characterization

A representation by Hegedus and Hafner⁶ showed the various sites that could be spectroscopically analyzed (Figure 1.43). Position I can provide information on the *cis* and *trans* carbonyl attached to the metal fragment using infrared spectroscopy supplying information on the stretching modes of these ligands. The metal fragment (II) could be analyzed with isotope specific NMR spectroscopy, which was also the case with the carbene ligand and substituents (III and V). UV-visible spectra can provide information about the excitation states of the carbene complex (IV). Spectroscopic techniques combined with computational techniques provide insight into the electronic structure of the complex.

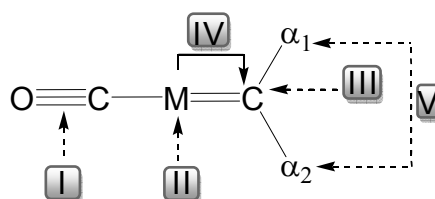


Figure 1.43: Spectroscopically significant sites on a Fischer carbene complex⁶.

The dynamic environment can be elucidated with NMR spectroscopy. X-ray diffraction studies, solid state and mass spectra are techniques that provide insight into the structure and bonding.

Thiophene and thiophene derivatives

General

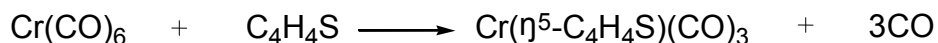
Metal ligands and carbene substituents are of great importance in the design of a metal carbene complex. Of particular interest in this study is thiophene and its derivatives as carbene substituents. Thiophene and many of its derivatives have commercial application especially in electronics. The aromaticity of thiophene is comparable to that of benzene and is one of the most widely studied organosulphur substrates¹⁰⁷. Thiophene and some of its derivatives are products in natural fossil oils and a lot of energy and resources have gone into reducing the sulphur content in petroleum products. The process to degrade and remove sulphur from fossil oil is by way of catalytic hydrodesulfuration processes¹⁰⁷ and is an active area of research. Chemical and physical modulation is effectively achieved by addition of functional groups to a thiophene¹⁰⁰. Coordination chemistry of thiophene is also a hot topic of investigation because of their ability to poison catalysts; the negative influence sulphur has on the environment and their presence in the fossil fuel industry. Metal coordinated derivatives such as $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$ were already synthesized by Baily *et al* in 1965¹⁰¹. Thiophene has a varied range of coordination modes to metals $\eta^1(\text{S})$, $\eta^1(\text{C})$, $\eta^2(\text{C-C})$, $\eta^4(\text{C})$ etc., showing versatility. Thiophene is aromatic and the coordination properties are closer to arenes than thioethers. It is versatile with good stability; it is planar and electron excessive with a partial positive charge on the sulphur atom¹⁰.

¹⁰⁰ G. Raos, A. Famulari, S.V. Meille, M.C. Gallazzi, G. Allegra, *J. Phys. Chem. A*, **2004**, 108, 691

¹⁰¹ M.F. Bailey, L.F. Dahl, *Inorg. Chem.*, **1965**, 4,1306

Synthesis

Synthesis of other thienyl derivatives presents a speckled range of options, from catalytic reactions with palladium and nickel or the use of Grignard reagents. The combinations are limitless and include conjugated thiophenes, thiophene wires, discs and pendants. Synthesis of a conjugated material involves structural organization and electronic considerations¹¹⁶. Thiophene qualifies as a conjugated segment that may be combined by covalent or van der Waals interactions, with a metal fragment or another conjugated molecule. Covalent bonding of multiple thiophene fragments are accomplished by various carbon-carbon coupling techniques. Depending on the desired product, synthesis is non-standard. The synthesis of metal containing thienyl complexes such as η^5 -coordinated thiophene chromium tricarbonyl complex by Fischer and Öfele¹⁰² and altered by Bailey¹⁰¹ is presented below



This synthesis had unsatisfactory yields, which prompted Öfele¹⁰³ to develop an alternate method. This method was also applied successfully to modified thiophenes.



¹⁰² E.O. Fischer, K. Öfele, *Chem. Ber.*, **1987**, 26, 4901

¹⁰³ K. Öfele, *Chem. Ber.*, **1966**, 99, 1732

Characteristics: Electronic structure

Aromatic thiophene is electron excessive and very stable. Thiophene is quite versatile and can change polarity, polarizability and geometry when incorporated into a molecule; it displays a lateral dipole moment, which imparts increased dielectric anisotropy. These electronic properties of this type of complex is dependent on the heteroatom present¹⁰⁴ but there is close relation between aromatic molecules of carbon such as benzene and bivalent sulphur containing heteroaromatic rings such as thiophene. Physical, chemical and spectroscopic similarities are observed such as resonance; first ionization potential and certain chemical behaviours are comparable for thiophene but are not so prominent in furan and pyrrole rings. The resonance structure of thiophene contributes to the dipole moment (Figure 1.44)^{106,108}.

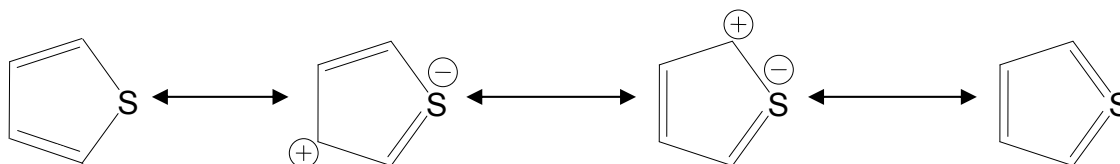
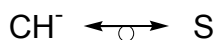


Figure 1.44: Contributing resonance structures of thiophene¹⁰⁶.

Thiophene bonding is rationalized in different ways¹⁰⁵. Comparison of thiophene to a cyclopentadienyl fragment allowed for comparison of the CH^- carbon atom to that of sulphur. They are isolobal.



¹⁰⁴ M. Hwassler, C. Lescop, R. Réau, *J. Organomet. Chem.*, **2005**, 690, 2482

¹⁰⁵ M.J.S. Dewar, N. Trinajtić, *J. Am. Chem. Soc.*, **1970**, 92, 1453

Two of the sp^2 hybrid orbitals are used for the σ -bonds in the ring and the third for the CH-bonds. In the case of the sulphur atom, this orbital has an electron pair. For both Cp and thiophene, six electrons are available for a π -cloud covering the ring (Figure 1.45).



Figure 1.45: Combination of orbitals for CH⁺ in the C₅H₅⁻ fragment.

Alternately, the reasoning was the s and p-orbitals are the only orbitals available to nitrogen and oxygen. Sulphur has d orbitals available for bonding¹⁰⁶ as well as two π electrons. These electrons are donated to the ring creating a π electron sextet cloud similar to that of the benzene or a cyclopentadienyl ring. Thiophene can coordinate to transition metals in a number of different ways¹⁰⁷. Thiophene can utilize the 3d-orbitals of sulphur to reimburse the aromaticity that corresponded to that of benzene and cyclopentadienyl.

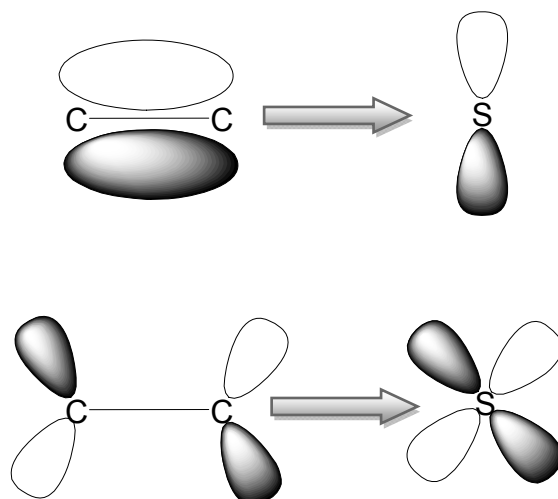


Figure 1.46: Comparison of ethylene orbitals with similar orbitals of sulphur¹⁰⁶.

¹⁰⁶ H.C. Longuet-Higgins, *Trans. Faraday Soc.*, **1949**, 45,173

¹⁰⁷ A.L. Sargent, E.P. Titus, *Organometallics*, **1998**, 17, 65

The hybridized sulphur orbitals have the correct symmetry and energy to bind with the remaining p-orbital not used for the sp^2 hybridized carbon atoms for π -bonding in the ring (Figure 1.46). The hybridized sulphur orbitals are non-orthogonal hybrid π orbitals showing strong overlap with the neighbouring carbon atom p-orbitals (Figure 1.47)¹¹⁴. The third hybridized orbital was vacant in the ground state and directed away from the ring¹⁰⁸.

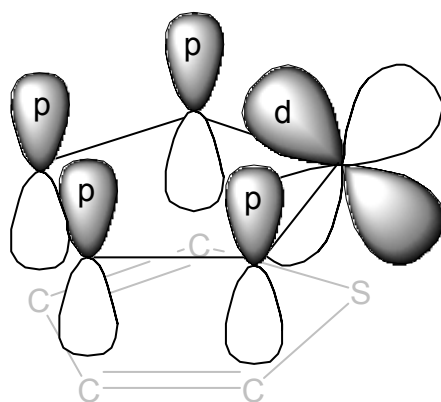


Figure 1.47: Orbital diagram of the carbon and sulphur orbitals¹⁰⁶.

Benzene orbitals are derived from three ethylene molecular orbitals. In Figure 1.47, a thiophene π -molecular orbital of sulphur with similar dimensions, symmetry and bonding energy, represents the same orbital than an ethylene orbital in benzene or a CH^- p-orbital in cyclopentadienyl¹⁰⁶. In the molecular orbital diagram (Figure 1.48) only the s and p-orbitals were exploited, this includes the p_z atomic orbital of a heteroatom, sulphur in this case, and the π molecular orbitals of butadiene¹⁰⁹. The LUMO (ϕ_3) of butadiene interacts with the p_z atomic orbital of sulphur and results in a net stabilization¹⁰⁹. This interaction between these orbitals of thiophene are considered to be greater and the reason for the large difference in properties between thiophene, furan and pyrrole.

¹⁰⁸ G. Cilento, *Chem. Rev.*, **1960**, 60, 147

¹⁰⁹ N.D. Epiotis, W.R. Cherry, F. Bernardi, W.J. Hehre, *J. Am. Chem. Soc.*, **1976**, 98, 4361

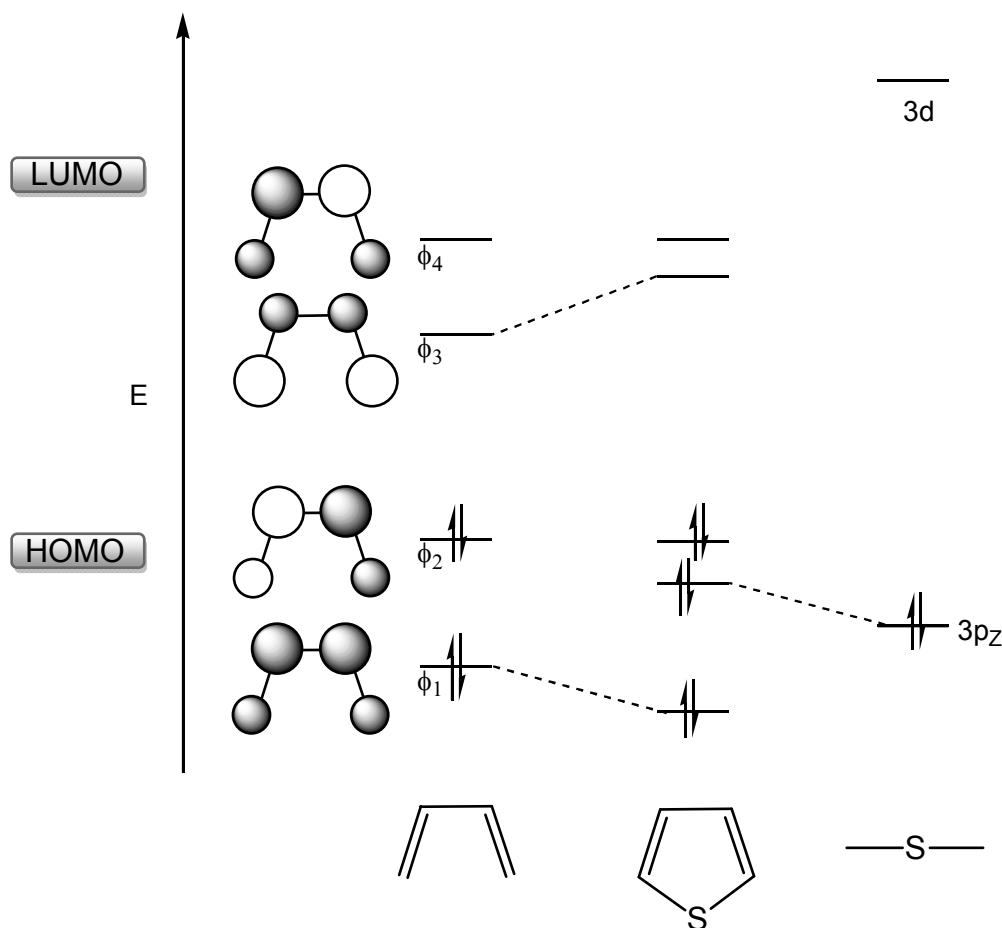


Figure 1.48: Molecular orbital representation of thiophene orbital interaction¹⁰⁹.

Aromatic compounds also have the ability to aggregate due to interaction of the electron density cloud above and below the ring. When the molecules were brought close enough to allow for sufficient overlap an energy band will form. In addition to this, the electronic structure of the energy levels infers conductivity in the condensed phase¹⁰⁸. Moving from thiophene to a thiophene derivatized complex such as a $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$, the bonding can be described either as π -excessive or π -deficient¹¹⁰. The degree to which a heterocycle may bond *via* σ or π -interaction is dependent on this character. Polymers and oligomers of thiophene have been an intense area of investigation¹²⁹. By contrast, studies with metal containing thienyl derivatives are lacking¹¹¹. A significant reason for this is the aptitude of these aromatic

¹¹⁰ A. Albert, *Heterocyclic chemistry*, 1968, Athlone Press, London

aggregates to distribute charge and the addition of a metal fragment causes a disturbance¹¹¹. The aromaticity of a thienyl moiety is altered by addition of an electron-withdrawing metal fragment. A motivation for metal complexation is that it may exaggerate the ability of the heteroatom to impart lateral and/or longitudinal dipoles. Metals prefer σ -bonding to a heteroatom in nitrogen containing heterocycles compared to π -bonding as observed in thiophene¹¹². The metal fragments on a coordinated thiophene, whether it was π -coordinated or σ bound allowed it to be electronically linked to one another because of resonance effects¹¹³.

Structure

Thiophene is a planar molecule with C_{2v} symmetry¹¹⁴. The C-C bond orders of thiophene are similar to that of benzene; this is reflected in the bond lengths of thiophene given below¹⁰⁶. Compared to furan and pyrrole, Epiotis¹⁰⁹ explains that the geometric deviations are due to the interaction of the HOMO of butadiene with the d-orbital of sulphur resulting in removal of electron density from the $C_2=C_3$ bond. This leads to a decline in antibonding density, and a shortening of C_3-C_4 (Figure 1.48). The bond length for a C-C bond in benzene was given as 1.39 Å by Schomaker and Pauling and is similar to those seen in Figure 1.49¹¹⁵ for thiophene.

¹¹¹ M. Landman, H. Görls, S. Lotz, *J. Organomet. Chem.*, **2001**, 617 - 618, 280

¹¹² (a) D.L. Kershner, F. Basolo, *Coord. Chem. Rev.*, **1987**, 19, 279

(b) B.E. Bursten, R.F. Fenske, *Inorg. Chem.*, **1979**, 18, 1760

(c) G.E. Herberich, J. Hengesback, V. Kolle, W. Oschmann, *Angew. Chem. Int. Ed. Engl.*, **1977**, 16, 42.

(d) D.A. Lesch, J.W. Richardson, R.A. Jacobson, R.J. Angelici, *J. Am. Chem. Soc.*, **1984**, 106, 2901

¹¹³ R.D. Thompson, *Acc. Chem. Res.*, **1983**, 19, 292

¹¹⁴ M.H. Palmer, I.C. Walker, M.F. Guest, *Chem. Phys.*, **1999**, 241, 275

¹¹⁵ V. Schomaker, L. Pauling, *J. Am. Chem. Soc.*, **1939**, 61, 1769

Bond angles	Bond lengths	X=N	X=O	X=S
	C ₅ —X ₁	1.39 Å	1.36 Å	1.74 Å
	C ₃ —C ₂	1.38 Å	1.36 Å	1.35 Å
	C ₃ —C ₄	1.41 Å	1.43 Å	1.44 Å
	C ₄ —C ₅	1.38 Å	1.36 Å	1.35 Å
C ₅ —X ₁ —C ₂	92.2°			
X ₁ —C ₂ —C ₃	111.5°			
C ₂ —C ₃ —C ₄	112.5°			

Figure 1.49: The close relationships in bond lengths indicate the aromatic character of thiophene^{106, 109, 118}

Coupling of thiophene at the two and five position by other organic moieties are interesting. The linear and conjugated properties are reserved and strong intermolecular coupling is predicted due to the short interatomic distances¹¹⁶. Oligomers and polymers of thiophene show a herringbone packing which is common for planar compounds. Thiophene can coordinate to transition metals in a number of different ways¹⁰⁷. As with an uncoordinated thiophene, the coordination properties of the thienyl moiety are closer to that of an arene than a thioether^{117,118}. Coordination may occur *via* a single atom (η^1) from thiophene up to a situation where all five-ring atoms (η^5) were employed (Figure 1.50). The η^5 coordination of chromium tricarbonyl is seen as being bonded through the π -electron cloud¹¹⁹. The synthesis of Fischer monocarbene complexes on this system is known¹²⁰ but not expanded¹²¹.

¹¹⁶ F. Garnier, *Acc. Chem. Res.*, **1999**, 32, 209

¹¹⁷ (a) T.B. Rauchfuss, *Prog. Inorg. Chem.*, **1991**, 39, 259

(b) C. Segard, B.R. Roques, C. Prommier, G. Guichon, *J. Organomet. Chem.*, **1974**, 77, 59

(c) C. Segard, B.R. Roques, C. Prommier, G. Guichon, *J. Organomet. Chem.*, **1974**, 77, 49

(d) H. Lumbroso, C. Segard, B.R. Roques, *J. Organomet. Chem.*, **1973**, 61, 249

(e) M. Novi, G. Guanti, C. Dell'Erba, *J. Heterocycl. Chem.*, **1986**, 119, 878

(f) F. Rourke, J.A. Crayston, *J. Chem. Soc. Chem. Comm.*, **1988**, 1264

(g) M.N. Nefedova, V.N. Setkina, D.N. Kursanov, *J. Organomet. Chem.*, **1983**, 244, C21

(h) H. Singer, *J. Organomet. Chem.*, **1967**, 9, 135

¹¹⁸ R.J. Angelici, *Coord. Chem. Rev.*, **1990**, 105, 61

¹¹⁹ A. Mangini, F. Taddei, *Inorg. Chim. Acta.*, **1968**, 2, 12

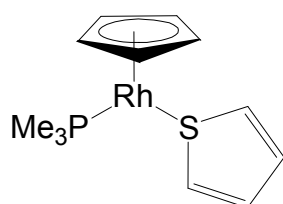
¹²⁰ E.O. Fischer, F.J. Gammel, D. Neugebauer, *Chem. Ber.*, **1980**, 113, 1010

¹²¹ (a) A.P. Sadimenko, A.D. Gamovskii, N. Retta, *Coord. Chem. Rev.*, **1993**, 126, 237

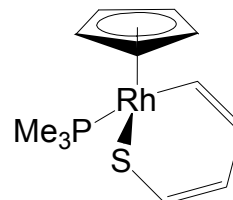
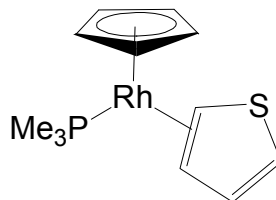
(b) K. Öfele, E.O. Fischer, *Chem. Ber.*, **1958**, 91, 2395

Coordination patterns

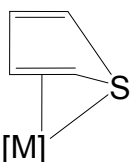
η^1 -bound



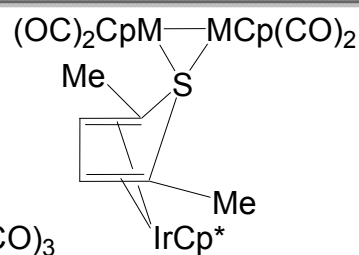
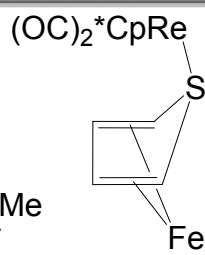
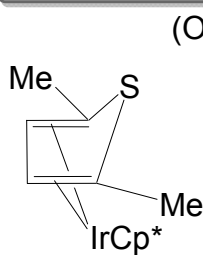
η^2 -bound



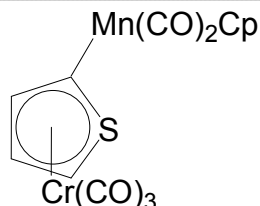
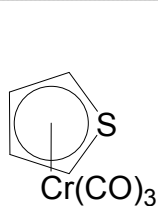
η^3 -bound



η^4 -bound



η^5 -bound



η^6 -bound

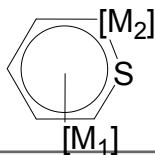


Figure 1.50: A variety of coordination patterns which are available to thiophene ^{107, 122, 50}

- ¹²² (a) R. Angelici, *J. Coord. Chem. Rev.*, **1990**, 105, 61
 (b) J.Chen, R.J. Angelici, *Appl. Organomet. Chem.*, **1992**, 6, 479
 (c) M.G. Choi, R.J. Angelici, *J. Am. Chem. Soc.*, **1989**, 111, 8753
 (d) J.Chen, L.M. Daniels, R.J. Angelici, *J. Am. Chem. Soc.*, **1991**, 113, 5422

The coordinated metal may also insert in the C-S bond to form a metalocycle and the coordinated thiophene still has electronic equivalence between the C=C and S bonds¹¹⁷. The π -coordinated complexes can be seen as a *nido* cage structure similar to that of a half sandwich π -arene complex¹¹⁷. The carbonyl ligands are in a staggered orientation with reference to the ring atoms, viewed through C₃ axis of Cr(CO)₃ (Figure 1.51). Bailey and Dahl¹⁰¹ showed a threefold molecular disorder observed in the solid state, which indicated the rotation of the carbonyl group staying in a staggered conformation. Similarly, the coordinated cyclopentadienyl such as ruthenocene shows a twofold disorder due to the symmetry perpendicular to the ring system.

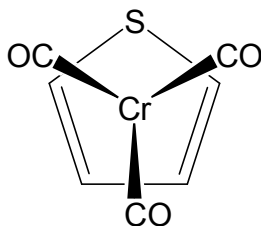


Figure 1.51: Preferred orientation of metal carbonyl groups of a chromium η^5 -thiophene tricarbonyl complex.

Reactivity and stability

Thiophene is more stable than polyenes and distributes electrons better than phenyl derivatives¹²³. The lone pair on the sulphur atom can explain the stability of thiophene interacting with the LUMO of the butadiene fragment and the HOMO of butadiene interacting with the empty d-orbital of sulphur¹⁰⁹. The reactivity of thiophene is rationalized with frontier orbital theory. The degree of electron density in the HOMO of each atomic centre determines the site of attack. During the transition state, the HOMO interaction with the LUMO of an electrophile, show the major contribution to stabilization. In the case of thiophene this is the

¹²³ C.Crause, H. Görls, S. Lotz, *Dalton Trans.*, **2005**, 1649

carbon neighbouring the sulphur atom. Calculated π -electron density also supports this argument¹⁰⁵. As a result, the proton on the carbon neighbouring the sulphur atom is also the most acidic. This argument can also be applied to furan and pyrrole, but to a lesser extent. π -Coordination of transition metal moieties on ring systems has received attention in the past¹²⁴. Arene chromium tricarbonyl systems were well studied. Coordinated thienyls have varying stabilities depending on the coordination number and removal of electron density from the ring. The addition of the $\text{Cr}(\text{CO})_3$ fragment to thiophene withdraws electron density from the aromatic ring resulting in an increase in acidity of the thiophene protons so much so that the protons are acidic enough to be deprotonated by an aqueous base (Figure 1.52 (I))¹²⁵. Because the tricarbonyl metal fragment blocks one side of the planar aromatic moiety, attack on the ring is stereoselective¹²⁶.

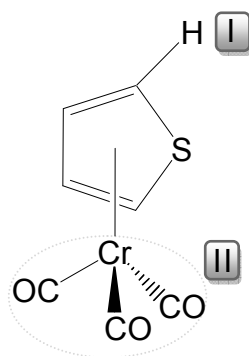


Figure 1.52: Sites of reactivity of chromium η^5 -thiophene tricarbonyl.

Alternate reactions may also be done on the carbonyl ligands but this has not yet been reported and the preferred attack proves to be on the heterocycle. More electron negative atoms in the heterocycle tend to form less stable coordinate complexes. π -Coordinated thiophene chromium is photochemically unstable and formation of the π -coordinated benzene complex is favoured. Hapticities (η^2 - η^4) result in complete loss of aromaticity with the sulphur

¹²⁴ (a) A.D. Hunter, A.B. Szigety, *Organometallics*, **1981**, 8, 1

(b) R. Chukwu, A.D. Hunter, B.D. Santarsiera, S.G. Bott, J.L. Atwood, J. Chassignac, *Organometallics*, **1992**, 11, 589

¹²⁵ T.B. Rauchfuss, *Prog. Inorg. Chem.*, **1991**, 39, 259

¹²⁶ R.J. Card, W.S. Trahanovsky, *J. Org. Chem.*, **1980**, 45, 2560

atom moving out of the plane of the ring¹²⁷. π -Coordinated thiophene is more labile than the π -arene analogue¹¹⁷. The dipole moment of coordinated thiophene is higher than that of the corresponding π -arene complex and the chromium tricarbonyl fragment can be removed from thiophene or other arene compounds by oxidation^{117f}. Bonding of cyclopentadienyl ring to a metal carbonyl is more favourable (stronger bond) than bonding to a neutral heterocyclic complex making it less stable than the former¹¹². Pentacarbonyl metal carbene fragments are strongly electron withdrawing and mimics the reactivity of an activated ester³¹. The electronic and steric factors of coordinated thienyl-metal complexes allowed for unique synthetic possibilities.

Application

Thiophene and its derivatives are widely studied¹²⁸. Thiophene is p-dopable and primarily a p-type semiconductor¹²⁹ of which inorganic semi-conductors are known. Intensive studies on π -conjugated systems were being done to prepare novel polymeric and oligomeric frameworks with enhanced stability and performance¹²⁹. Electrochemically-doped polymers with quaterthiophene pendants have been synthesized for technological application⁶⁷. Thiophene is used as a spacer ligand in molecular wires¹¹¹. The interest is so widespread that this type of research is referred to as polymer electronics¹¹⁶. Desirable properties of conjugated materials include:

- Optical properties: nonlinear optics, LCD's and fluorescence¹²⁸.
- Useful components in electronic materials: light emitting diodes, thin film transistors, batteries¹²⁸ and photovoltaic cells¹²⁹
- Better conduction of electrons than phenyl derivatives¹²⁹

Use of an organometallic system with conjugated structures, allowed for varying oxidation states of a transition metal with different ligand environments. When electrons are polarized it

¹²⁷ D.A. Delafuente, W.H. Myers, M. Sabat, W.D. Harman *Organometallics*, **2005**, 24, 1876

¹²⁸ M. D. Curtis, J.I. Nanos, H. Moon, W.S. Jahng, *J. Am. Chem. Soc.*, **2007**, 129, 15072

¹²⁹ A. Seed, *Chem. Soc. Rev.*, **2007**, 36, 2046

may enhance the nonlinear activity of a conjugated unsaturated system with a transition metal moiety. Specific metal fragments such as Fischer carbene complexes have been known to increase solubility. They have also been proposed in the use of non-linear optics because of their push and pull characteristics¹²⁹. The arene chromium tricarbonyl derivative also has synthetic utility¹³⁰ and the carbene fragment was of interest because of its ability to synthesize organic compounds¹³¹. Arene chromium tricarbonyl derivatives have found application in natural products synthesis¹³², as carbocycles from suitable arene chromium tricarbonyl derivatives¹³³. Desulphurization of thiophene with metals have been studied extensively. By contrast, very few studies have focused on the combination of metals and thiophene in organic synthesis. Although not the aim of this project the complexes prepared in this study will serve as excellent precursors for organic template reactions.

Aims of this study

The scope of this study is to look at the activation of thiophene or thiophene derivatives. Their incorporation as substituents in carbene ligands and the role of the metal fragment to activate or stabilize the carbene ligands. In the study, the role of thiophene as a spacer in multimetal systems as well as the potential of synthesizing multicarbene complexes around a single thiophene were investigated. The information obtained will be used in the future to introduce thiophene units and carbene ligands as important components of larger assemblies such as metal organic frameworks. Ultimately such systems will be studied for possible applications in metal template reactions, organic synthesis and catalysis. The research group at the University of Pretoria has extensively studied various thienyl derivatized carbene complexes with an array of transition metals from group 5, 6 and 7 (Figure 1.53). A deviation to these pure carbene complexes was a π -coordinated thiophene derivative that could be incorporated to create a carbene cluster complex.

¹³⁰ F. Rourke, J.A. Crayston, *J. Chem. Soc., Chem. Commun.*, **1988**, 1264

¹³¹ M.A.H. Alamiry, P. Brennan, A. Coleman, C. Long, M.T. Pryce, *Organometallics*, **2009**, 28, 94

¹³² H.-G. Schmalz, B. Gotov, A. Boettcher, *Top. Organomet. Chem.*, **2004**, 7, 157

¹³³ H. Paramahamsan, A.J. Pearson, A.A. Pinkerton, E.A. Zhurova, *Organometallics*, **2008**, 27, 900

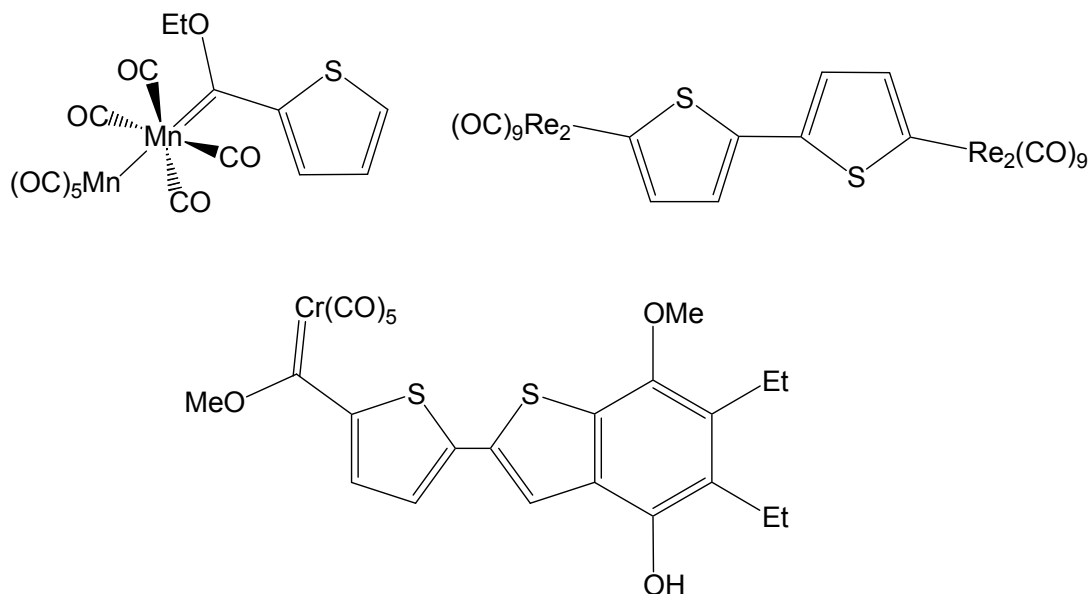


Figure 1.53: Examples of thiophene and other thienyl derivatives synthesized by the organometallic research group at the University of Pretoria^{69,31}.

The π -coordination of a metal to thiophene is attractive. The general activation of the ring protons and especially the 2 and 5 positions is such, that dilithiation can occur at low temperature in a short period of time (Figure 1.54).

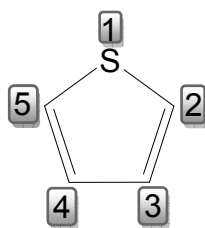


Figure 1.54: IUPAC numbering for thiophene.

Waldbach¹³⁴ and Terblans⁵⁰ have completed the synthesis and characterization of these types of monocarbene complexes but the scope has been limited to single carbene complexes^{50,134}. Addition of a second carbene to the activated position of the π -coordinated thienyl complex¹³⁴ allows for easy incorporation of different metal centres in a carbene cluster complex and an

¹³⁴ T.A. Waldbach, P.H. van Rooyen, S. Lotz, *Angew. Chem. Int. Ed. Engl.*, **1992**, 32, 710

increase in the symmetry of the complex. On the down side it is articulated that the addition of more metal centres will considerably decrease the stability of the complex. Thiophene has four carbon atoms available for addition of a metal centre. The carbon atoms on the 2,5-thiophene position have been extensively exploited but the utilization of the 3,4-thiophene position has not been investigated. The utilization of the unconventional 3,4-thienyl position will be attempted in this study. Fischer reported the first example of such a mononuclear biscarbene complex¹³⁵ on a benzene ring (Figure 1.55). The 1,2-dilithiation of benzene is troublesome and incorporates mercury polymers of benzene and lithium metal¹³⁶.

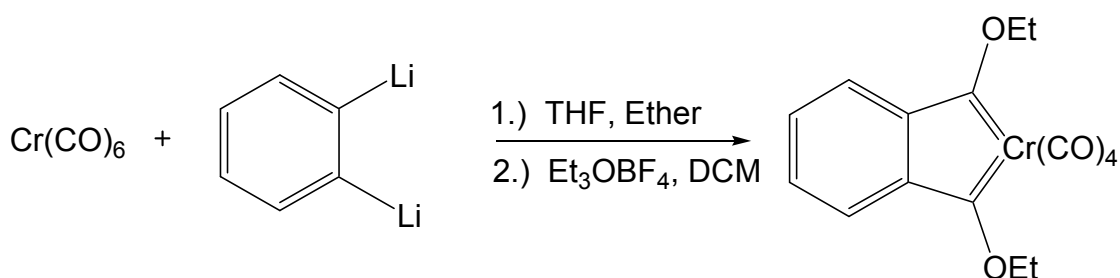


Figure 1.55: The first synthesized mononuclear biscarbene complex¹³⁵.

This was due to the large activation energy difference when moving away from the sulphur atom. If synthetically possible, incorporation of all four positions of the thienyl ligand in the carbene complex opens new scope for synthesizing novel thiophene carbene cluster complexes. The use of bromine atoms can act as an activator for the 3 and 4 positions on the thiophene ring, in the same way as the coordination of the metal centre acts as an activator for the lithiation of both α -positions on the thiophene ring. In addition to the possible formation of mononuclear cluster carbenes on a single aromatic thienyl ring when utilizing position 2 and 3, the method may allow for the formation of mononuclear biscarbene complexes. In essence, forcing the metal centre to form a chelate, to avoid steric interference. Potential applications of these carbene chelate complexes, have not yet been investigated. The thermal reactions of one of these compounds show promising and novel results and acts as an incentive for synthesizing such mononuclear biscarbene complexes (Figure 1.56).

¹³⁵ E.O. Fischer, W. Röhl, N.H.T. Huy, K. Ackermann, *Chem. Ber.*, **1982**, 155, 2051

¹³⁶ G. Wittig, F. Bickelhaupt, *Angew. Chem.*, **1975**, 69, 93

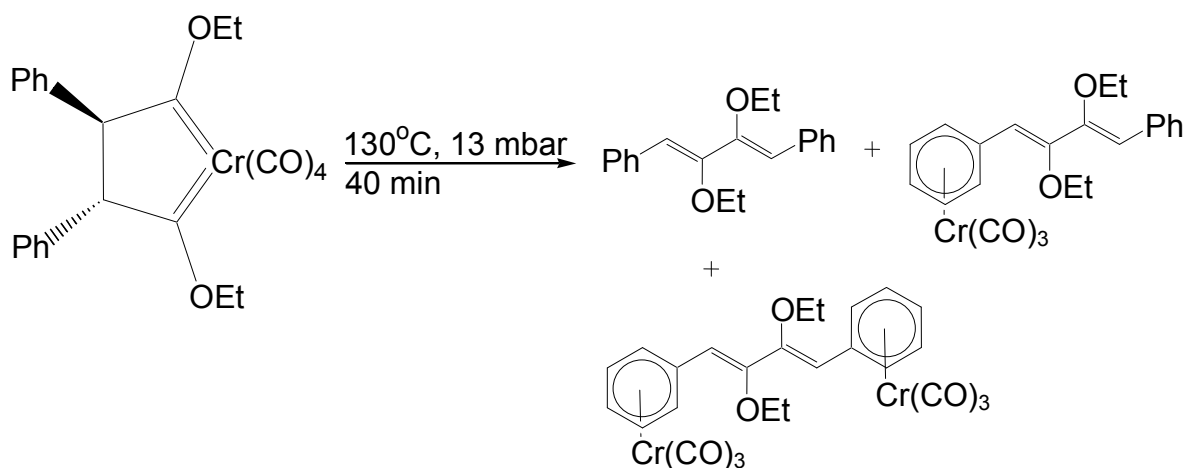


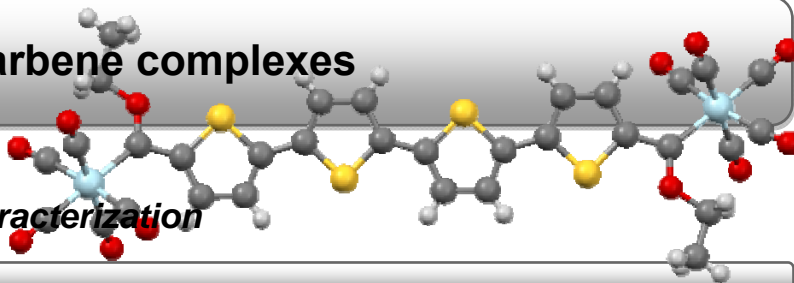
Figure 1.56: Thermal decomposition of a mononuclear biscarbene complex¹³⁷.

Dinuclear complexes containing conjugated spacers were of interest because they may show metal-metal communication which indicates alternative physical and chemical properties. When considering the possibilities allowed by the bromine modified thienyl derivatives, the chelation of the 2 and 3, 3 and 4 all four positions are possible. Results could be significant from a steric and electronic viewpoint. Both types of compounds are considered because of the possible incorporation in a metal organic framework. Since the inception of metal organic frameworks it has become a hot topic because of its possible use as a storage material for gases and other compounds especially hydrogen storage. Not only can a material containing activated centres be used for storage but also for catalytic processes or template reactions, allowing for the synthesis of compounds which have not previously been favoured. Such a system would also allow for a large reactive surface area increasing possible yields and decreasing the time factor. Incorporation of such complexes can either be through covalent bonding *via* the ligand or metal moiety or the use of hydrogen bonding that could allow for a more “breathable” system when considered for application as a storage material.

¹³⁷ N.H.T. Huy, P. Lefloch, J.M. Louis, M. Fetizon, *J. Organomet. Chem.*, **1986**, 311, 79

Chapter 2: Dinuclear biscarbene complexes

Synthesis and spectroscopic characterization



Introductions

General

Huy^{1,2} has reported the formation of biscarbene complexes utilizing benzene and biphenyl as spacer ligands (Figure 2.1). These types of complexes and general synthesis also extend to heteroarenes such as thiophene³, furan⁴ and N-methylpyrrole⁵. As seen with benzene and phenyl derivatives the synthesis of dinuclear biscarbene complexes was extended to larger conjugated systems.

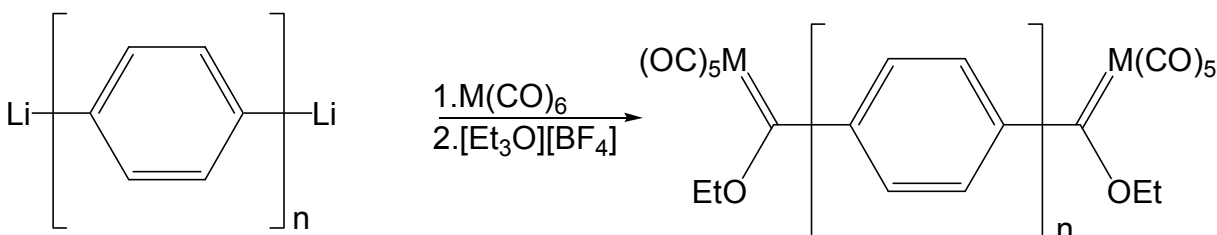


Figure 2.1: Synthesis of dinuclear biscarbene complexes where $M = \text{Cr}$ and W^1 and $n = 1$ and 2 .

¹ E.O. Fischer, W. Roll, N.H.T. Huy, K. Ackermann, *Chem. Ber.*, **1982**, 115, 2951.

² N.H.T. Huy, P. Lefloch, F. Robert, Y. Jeannin, *J. Organomet. Chem.*, **1987**, 327, 211

³ (a) Y.M. Terblans, Phd Thesis, *Thiophene bimetallic carbene complexes*, **1996**, University of Pretoria

(b) S. Maiorano, A. Papagni, E. Licandro, A. Persoons, K. Clay, S. Houbrechts, W. Porsio, *Gazz. Chim. Ital.*, **1995**, 125, 377

⁴ C. Crause, H. Görls, S. Lotz, *Dalton Trans.*, **2005**, 1649

⁵ A.J. Olivier, MSc Dissertation, *Novel carbene complexes with pyrrole ligands*, **2001**, University of Pretoria

Examples of such, is the synthesis of biscarbene complexes on bithiophene^{3b} and terthiophene⁶ with chromium and tungsten pentacarbonyl as metal fragment. Extension of the thienyl spacer beyond three thiophene units by adding another thiophene unit is of interest and is reported in this study. Quaterthiophene is an exceptional candidate for such a complex formation as it has a wide range of application as an organic moiety on its own. Dilithiation of a single thiophene on the 2 and 5 position shows low yields, whereas bithiophene and tetrathiophene has much higher yields due to the ability to distribute the offset of charge in the compound after the first lithiation. The dilithiation of terthiophene, unlike thiophene, was readily achieved with the protons in the 2 and 5 positions being deprotonated. The two thiophene rings on the outside have little interaction and the effect is as if a monolithiation was carried out, proving to be a valuable method to increase the yield of dinuclear biscarbene complexes on a thienyl moiety. The number of thiophene units has structural implications. Three thiophene rings place the carbene substituents on the same side of a line bisecting the interligand bonds of the thiophene units (Figure 2.2). Four thiophene units should place the $M(CO)_5$ fragments of the carbene ligands on opposite sides of such a line.

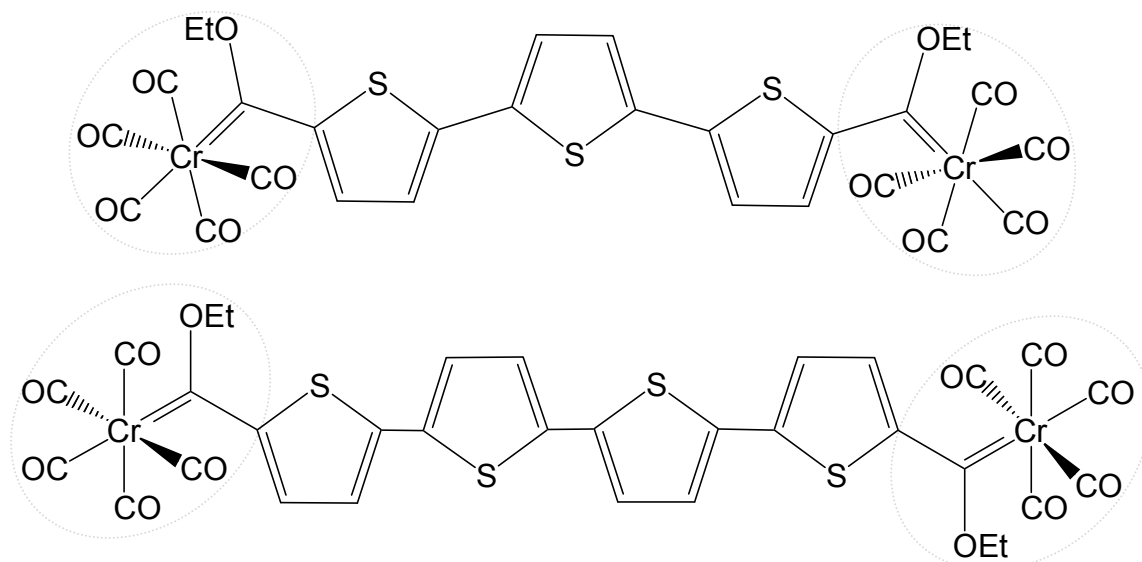


Figure 2.2: Structural differences between terthiophene and quaterthiophene biscarbene complexes⁶.

⁶ M.M. Moeng, MSc dissertation, *Terthienyl carbene complexes*, 2001, University of Pretoria

An alternative method to increase the yield of the synthesis of dinuclear carbene complex with a thiophene spacer is to use π -coordinated thiophene as substrate. Fischer⁷ and co-workers have studied the effects of benzene π -coordinated to group VI transition metals in carbene synthesis (Figure 2.3). π -Coordination of benzene drains electron density from the ring and enhances the acidic character of the protons. π -Coordination localizes the double bonds and hinders π -delocalization. When lithiated, the electron density was localized on the anionic carbon and not delocalized over the ring. This allowed the electron negative carbon to attack the carbon on a metal carbonyl. The π -cloud of benzene was also conjugated to the π -system of the carbene ligand. Hence, the π -bonded metal is in electronic contact with the second metal *via* the carbene carbon atom.

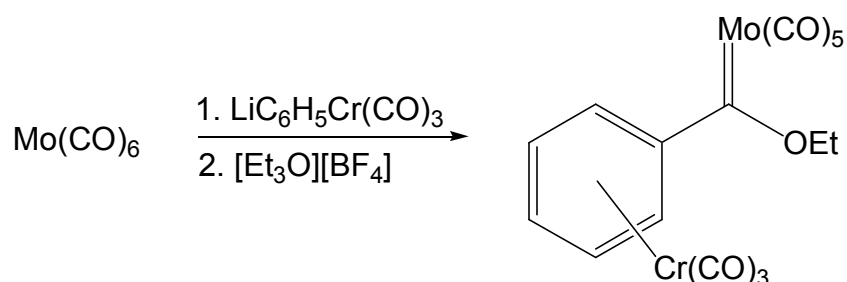


Figure 2.3: Synthesis of π -coordinated benzene monocarbene complex⁷.

Well-studied coordination compounds containing π -bonded ligands include ferrocene, ruthenocene, and titanocene etc.⁸. Lithiation of ferrocene occurs at elevated temperatures with TMEDA coordinated to lithium of butyl lithium in hexane⁸. The lithiated ferrocene was then reacted with a metal carbonyl to form a metal acylate. Synthesis of a heterodimetallic

⁷ E.O. Fischer, F.J. Gammel, D. Neugenbauer, *Chem. Ber.*, **1980**, 113, 1010

⁸ (a) M.A. Sierra, *Chem. Rev.*, **2000**, 100, 3591

(b) J.A. Connor, J.P. Lloyd, *J. Chem. Soc., Dalton Trans.*, **1972**, 1470.

(c) E.O. Fischer, F.J. Gammel, J.O. Besenhard, A. Frank, D. Neugenbauer, *J. Organomet. Chem.*, **1980**, 191, 261

(e) T.A. Waldbach, R. van Eldik, P.H. van Rooyen, S. Lotz, *Organometallics*, **1997**, 16, 4056.

(e) U. Behrendt, R.-M. Pfeifer, R. Wartchow, H. Butenschön, *New J. Chem.*, **1999**, 23, 891.

(f) N.I. Pyshnograeva, V.N. Setkina, V.G. Andrianov, Y.T. Struchkov, D.N. Kursanov, *J. Organomet. Chem.*, **1981**, 206, 169.

(g) Y.-J. Lee, S.-J. Kim, Ch.-H. Kang, J. Ko, S.O. Kang, P.J. Carroll, *Organometallics*, **1998**, 17, 1109.

monocarbene complex utilizing this methodology is shown in Figure 2.4. Ongoing research in our laboratories by Bezuidenhout⁹ afforded dinuclear biscarbene cluster complexes on the 1,1 position of ferrocene containing an additional titandioxy as a metallic linker between the carbene complexes.

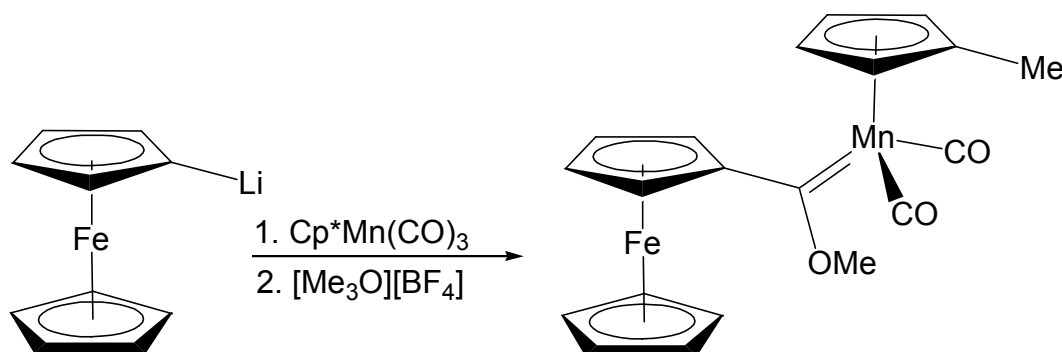


Figure 2.4: Synthesis of a heterodimetallic monocarbene complex^{8(b)}.

An alternative to this is the exploitation of two activated sites on a single heterocycle as done by Lotz and co-workers^{10,11} utilizing the electron withdrawing character of a π -bonded fragment to increase the activation of the protons on the thienyl moiety to afford the monocarbene complex (Figure 2.5)

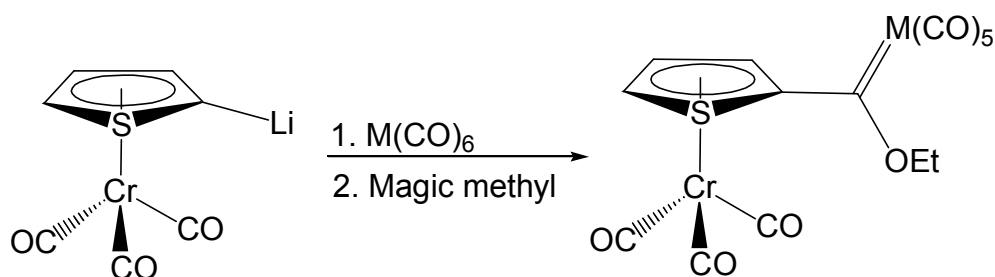


Figure 2.5: Monocarbene synthesis on a π -coordinated thienyl chromium tricarbonyl complex¹⁰, M = Cr and W.

⁹ D.I. Bezuidenhout, D.C. Liles, M. Landman, S. Lotz, *Organometallics*, **2008**, 27, 2447

¹⁰ Y.M. Terblans, S. Lotz, *J. Chem. Soc., Dalton Trans.*, **1997**, 2177

¹¹ T.A. Waldbach, P.H. van Rooyen, S. Lotz, *Angew. Chem. Int. Ed.*, **1992**, 32, 710

This modification of the monocarbene synthesis has proved to be a powerful synthetic method but did have its drawbacks. These complexes tend to be unstable but most carbene complexes were air, light and moisture sensitive resulting in multiple possible side reactions that occur during and after synthesis as with the alkylation procedure. The creation of the π -bonded thiophene monocarbene complexes previously synthesized and isolated (Figure 2.5) was done at -30°C and several fractions were collected. During this reaction it was reported that THF inserted into the ethoxy substituent¹². During this reaction the triethyloxonium tetrafluoroborate interacts with the THF solvent and results in the formation of $[\text{Etthf}]^+$. Ring opening proceeds through attack by the acylate and results in a modified alkoxy carbene complex.

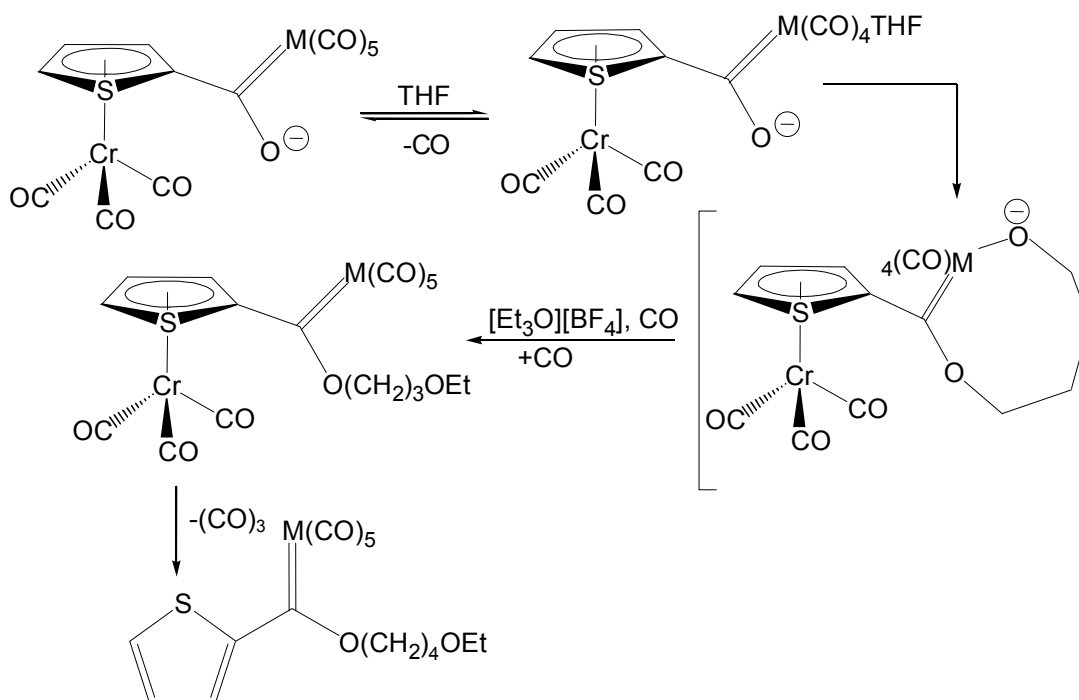
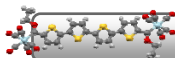


Figure 2.6: Insertion of THF in a carbene complex, $\text{M} = \text{Cr}$ and W ^{10, 12}.

¹² J. Christoffers, K.H. Dötz, *Organometallics*, **1994**, *13*, 4189



The literature of aryl coordinated monocarbene complexes displayed a large number of examples. Multiple carbene ligands on π -coordinated chromium tricarbonyl thiophene have yet to be documented (Figure 2.6). It was possible to reduce the polarization and increase the symmetry of a molecule by synthesizing biscarbene complex rods from thienyl derivatives such as thiophene rods and π -coordinated thiophenes. Such molecules, display synthetic challenges and problems associated with complex stabilities, but could lead to great promise for application in molecular wires and carbene metal frameworks.

Synthesis

Synthesis of A6

The catalytic reaction of $\text{Pd}(\text{PPh}_3)_4$ and 1,3,5-tetrabromobenzene with 2-zinc-bithiophene chloride afforded the unexpected product formation of quaterthiophene (QTP). The synthesis of a dinuclear biscarbene complex on this thienyl derivative was proposed. The use of 1,3,5-tribromobenzene as a source of bromine and $\text{Pd}(\text{PPh}_3)_4$ as catalyst, allowed carbon-carbon linkage to form QTP (Figure 2.7). The carbon-carbon bond formation between two bithienyl derivatives was accomplished by reductive elimination of the quaterthiophene fragment after the bithienyl was oxidatively added to the palladium catalyst. The addition of the 2-zinc-bithiophene chloride to the tribromothiophene to form a 1,3,5-trisubstituted benzene, was in this case not the favourable pathway as with thiophene where a disc type compound was obtained, 1,3,5-trithienylbenzene¹³.

¹³ A. Pelter, I. Jenkins, D.E. Jones, *Tetrahedron*, **1997**, 53, 10357

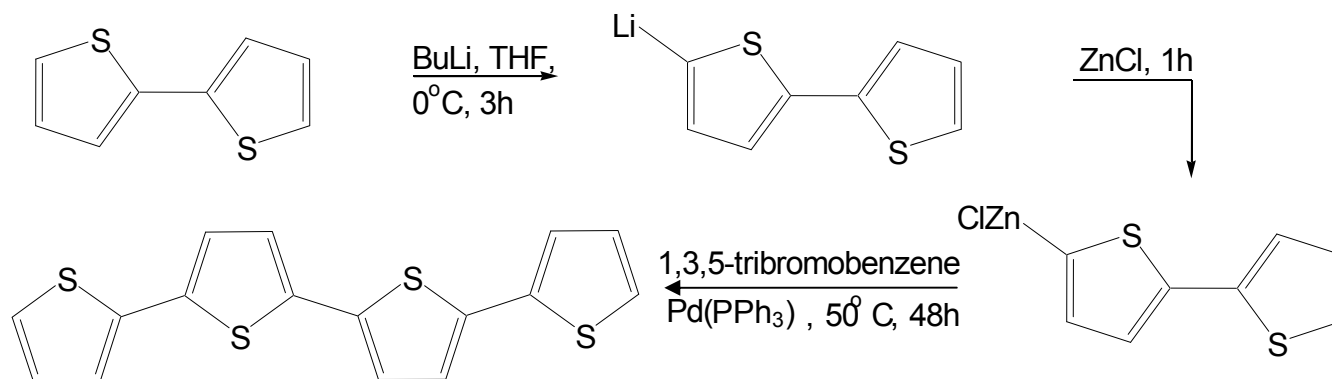


Figure 2.7: Catalytic synthesis of quaterthiophene.

This observation may be due to steric hindrance. Many alternative methods were reported using different metals as catalysts and different lengths of thienyl derivatives linkers¹⁴. Synthesis of a biscarbene complex on thiophene and thienyl derivatives are a prominent area of research in our laboratories. Reported complexes include biscarbene complexes on thienyl spacer ligands from thiophene to terthiophene with a variety of metals from group VI and VII (Figure 2.8). The first step (I) includes dilithiation with appropriate reagents after which (II) the reaction methodology for classic Fischer carbene synthesis with metal carbonyls was applied.

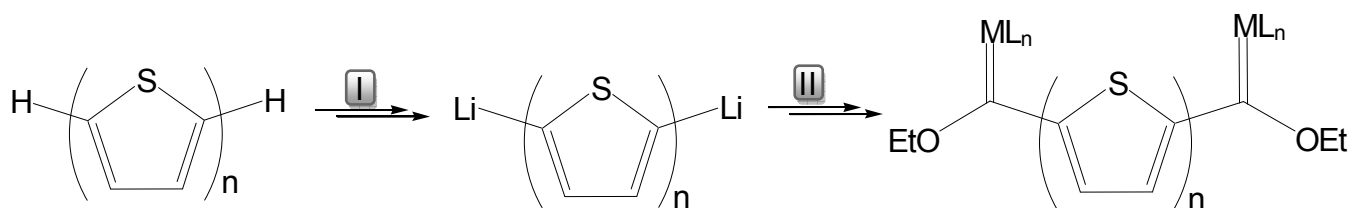


Figure 2.8: General synthesis of thiophene and thiophene derivative biscarbene complexes where $n = 1, 2$ and 3 .

¹⁴ S. Trabattoni, S. Laera, R. Mena, A. Papagni, A. Sassella, *J. Mater. Chem.*, **2004**, *14*, 171

There was a notable increase in the yield over a shorter time period for lithiation of bithiophene compared to thiophene. Considering thiophene, the degree of activation of the protons was dependent on the structure and replacement of one proton with lithium may lower the activation of the other equivalent proton. This was evident in the sequential lithiation of thiophene on the activated 2 and 5 positions (Figure 2.9). Conditions for dilithiation require TMEDA at elevated temperatures, which was problematic during addition of a metal complex, as residual TMEDA may coordinate to the metal fragment¹⁵.

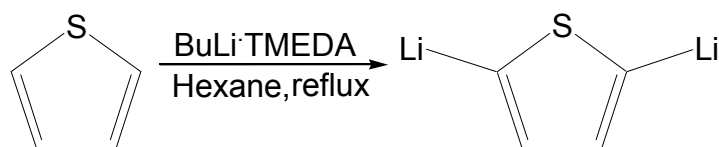


Figure 2.9: Dilithiation of thiophene occurs at elevated temperatures¹⁰.

The position of dilithiation of bithiophene and tetrathiophene was also on the 2 and 5 position of the thienyl derivative. Addition of a second thiophene on the 2 or 5 position to form bithiophene allowed for higher yields in lithiation compared to thiophene because of its ability to distribute the charge imbalance caused by the first lithiation. Increasing the number of thienyl linkers to 4 (quaterthiophene) also shows similar results. Dilithiation of QTP was accomplished at -78°C after 30 minutes in THF at which a notable colour change from yellow to turquoise was observed (Figure 2.8 step I). Lithiation was followed by the addition of two equivalents of chromium hexacarbonyl at -70°C and allowed to react further for approximately an hour and a half. Alkylation with $[\text{Et}_3\text{O}][\text{BF}_4]$ in DCM at -35°C (Figure 2.7 step II) afforded the 2,5-quaterthiophene biscarbene complex (20% yield). From the reaction mixture, three distinctly coloured products could be observed. A yellow fluorescent starting material (QTP), a second pink-purple product with low stability and a third purple product that was determined to be the biscarbene complex (**A6**).

¹⁵ R. Gräffing, L. Brandsma, *Recl. Trav. Chem. Pays-Bas*, **1970**, 95, 264

Synthesis of A1-5

A surrogate for thiophene, which allowed for ease of lithiation was $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$. The increase in acidity¹⁶ of the thiophene hydrogens on the 2 and 5 position by the metal fragment allowed for easy removal of both hydrogens, compared to non-coordinated thiophene. The efficiency of activation was so prominent that these protons were removed with an aqueous base¹⁷. Synthesis of the $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$ was done *via* a method by Rausch¹⁷ and Novi¹⁸. The method relies on the acid and base properties of the respective complexes and the lability of specific ligands (Figure 2.10).

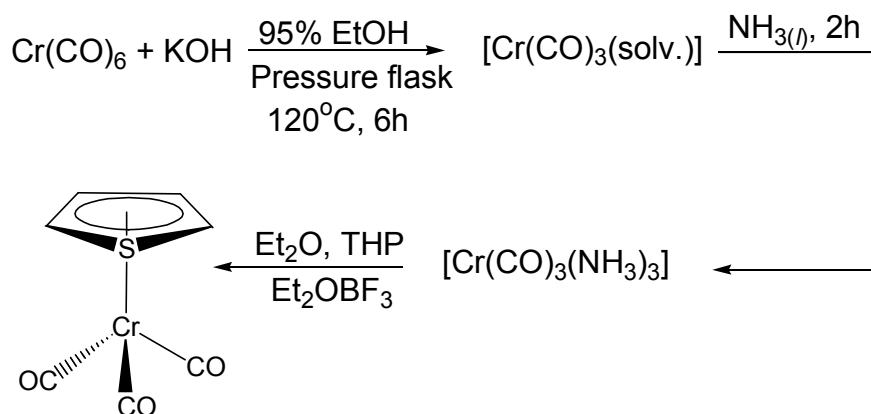


Figure 2.10: Synthesis of chromium (η^5 -thiophene) tricarbonyl^{17, 18}.

Synthetic requirements were met by up scaling the reaction and approximately three carbene reactions were done from one synthesis. Unsatisfactory yield were obtained by this method due to the reactivity of the intermediates. To stop oxidation from occurring, the reaction solution and liquid reagents were degassed with N_2 after each reaction step. Storage of the

¹⁶ M.N. Nefedova, V.N. Setkina, D.N. Kursanov, *J. Organomet. Chem.*, **1983**, 244, C21

¹⁷ M.D. Rausch, G.A. Mosser, E.J. Zaiko, A.L. Lipman, *J. Organomet. Chem.*, **1970**, 23, 185

¹⁸ M. Novi, G. Guanti, C. Dell'Erba, *J. Heterocycl. Chem.*, **1975**, 12, 1055

triamine chromium tricarbonyl precursor was not recommended and immediate completion of the synthetic procedure tends to generate optimum yields. The final π -coordinated chromium tricarbonyl product shows much higher stability towards moisture than the reaction intermediates, as it is separated from other reaction byproducts in degassed water. The dry product can also be stored for prolonged periods with minimal decomposition. The stability of other π -coordinated chromium tricarbonyl derivatives containing N-methylpyrrole and 2-methylthiophene, 3-bromothiophene showed higher decomposition rates in solution and much lower yields utilizing the same synthetic methodology. The method presented by Terblans¹⁰ for monolithiation of π -coordinated chromium tricarbonyl was achieved in THF at -50°C for 30 minutes¹⁰ and Waldbach¹¹ at -90°C for the dilithiation of $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$ in sequential steps with a relatively high yield (Figure 2.11). Upon reacting the π -coordinated chromium tricarbonyl with BuLi, a notable colour change was observed from red to light yellow and during the second lithiation, the solution turned yellow-brown.

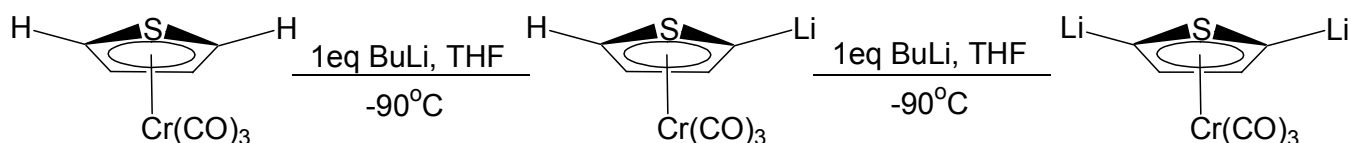


Figure 2.11: Dilithiation of coordinated thiophene occurs in a stepwise fashion¹¹.

Only activated protons were accessible with $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$ and the protons on the 3 and 4 position were unreactive towards basic BuLi. Sequential lithiation was necessary, as addition of two equivalents at -90°C did not yield the desired product. The reason for this was unknown, and attempts at alternative lithiation sequences failed. In between lithiations, the temperature was not raised above -78°C . Lithiation was performed with a 10% excess BuLi. After lithiation, the addition of two equivalents of metal carbonyl at -78°C to afford the bismetal bisacrylate, was followed by removal of THF and the reaction mixture was suspended in DCM (Figure 2.12). On completion of the reaction, the dark red metal complex anion was alkylated with triethyloxonium tetrafluoroborate to form a dark purple solution. The chronological

completion of lithiation, metalation and alkylation procedure in these cases resulted in many compounds forming in varying amounts. The metal carbonyls utilized were $\text{Cr}(\text{CO})_6$ (**A1**, 30%), $\text{W}(\text{CO})_6$ (**A2**, 20%), $\text{Mo}(\text{CO})_6$ (**A3**, 35%), $\text{MnCp}(\text{CO})_3$ (**A4**, 10%) and $\text{Re}_2(\text{CO})_{10}$ (**A5**, 10%). Because of the low yields and stability, only the target compounds were isolated and purified.

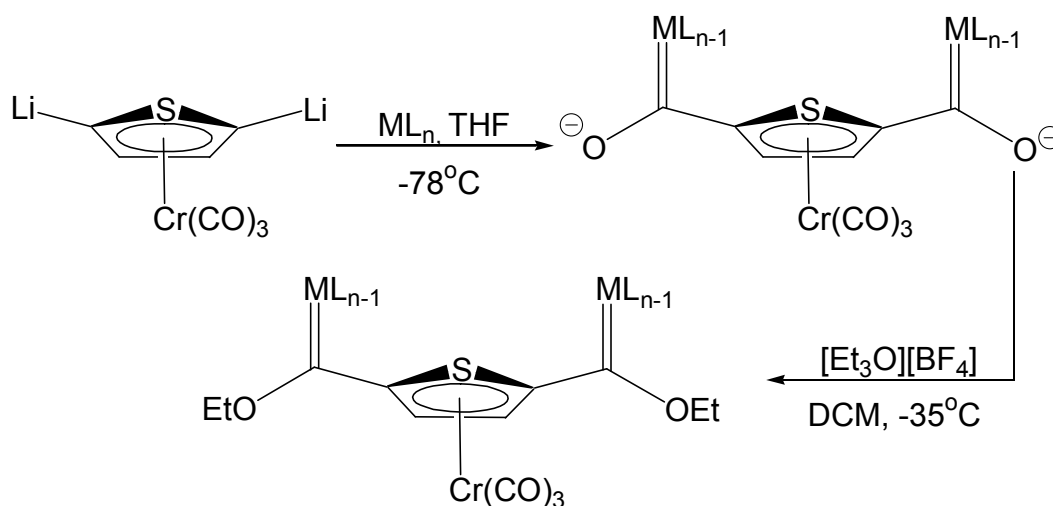


Figure 2.12: Fischer biscarbene complex formation $[\text{ML}_n\{\text{C}(\text{OEt})\eta^5\text{-2,5-C}_4\text{H}_2\text{SC}(\text{OEt})\}\text{ML}_n(\text{Cr}(\text{CO})_3)]$ $\text{ML}_n = \text{Cr}(\text{CO})_6$ (A1**), $\text{W}(\text{CO})_6$ (**A2**), $\text{Mo}(\text{CO})_6$ (**A3**), $\text{MnCp}(\text{CO})_3$ (**A4**) and $\text{Re}_2(\text{CO})_{10}$ (**A5**).**

During the classic Fischer carbene synthesis, BuLi reacts as a strong base with the acidic protons on position 2 and 5 of the thienyl moiety (Figure 2.13, I) to form a dilithium intermediate II. The intermediate was stabilized by the removal of electron density from the thiophene ring by the $\text{Cr}(\text{CO})_3$ fragment. This intermediate complex reacts with an electron deficient carbon atom of a carbonyl ligand on the metal to afford the metal acylate. There were two possible types of resonance structures, the metalate (III) or acylate (IV) of which the latter reacts with the triethyloxonium tetrafluoroborate to form the desired product. The stability was expected to increase because it is suggested that a more ionic interaction between the ring and the metal fragment or less electron negative heterocyclic ring results in a more stable

complex¹⁹. Substitution also played a role in the stability. The complex **A1-5** is unstable even at 0°C and can only be stored for longer periods as solids, at -15°C.

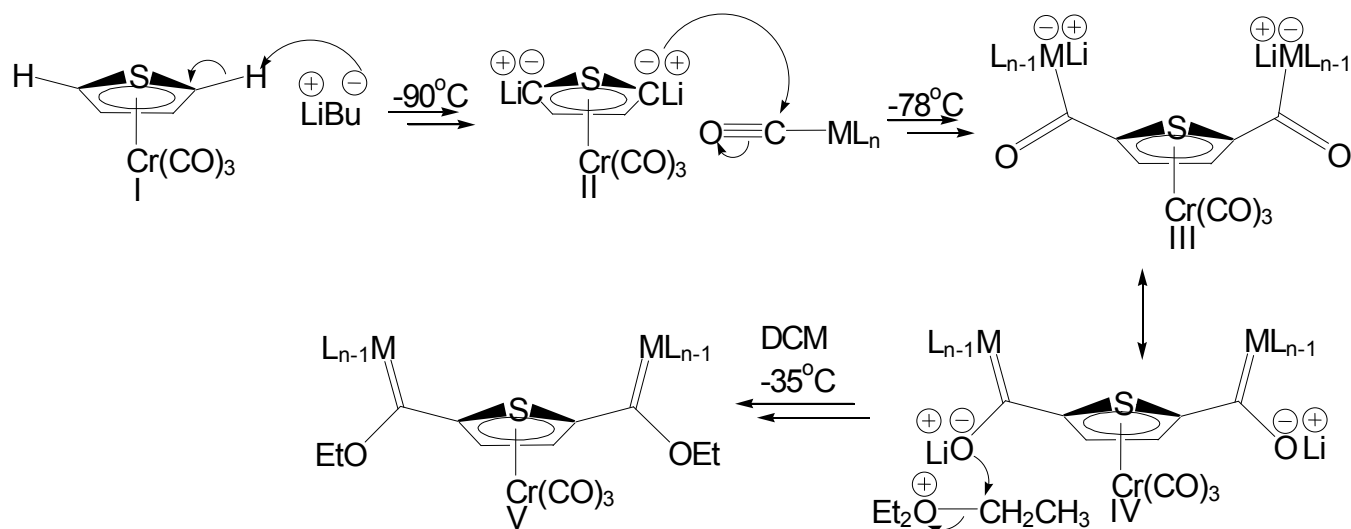


Figure 2.13: Mechanism for biscarbene complex formation $[\text{ML}_n\{\text{C}(\text{OEt})\eta^5\text{-2,5-C}_4\text{H}_2\text{SC}(\text{OEt})\}\text{ML}_n(\text{Cr}(\text{CO})_3)]$, $\text{ML}_n = \text{Cr}(\text{CO})_6$ (A1), $\text{W}(\text{CO})_6$ (A2), $\text{Mo}(\text{CO})_6$ (A3), $\text{MnCp}(\text{CO})_3$ (A4) and $\text{Re}_2(\text{CO})_{10}$ (A5).

All reactions, barring that of rhenium decacarbonyl, resulted in three major products forming. The rhenium reaction contained six purple fractions, which were suspected to be structural isomers and biscarbene modified products but could not be successfully isolated for characterization due to decomposition. Byproducts of this reaction were a butyl carbene, unreacted starting material and a π -bonded monocarbene complex and both mono- and biscarbene complexes of which the chromium tricarbonyl fragment was lost by oxidation.

¹⁹ D.L. Kershner, F. Basolo, *Coord. Chem. Rev.*, **1987**, 19, 279

Characterization

^1H – NMR Spectroscopy

Elucidation of A6

The magnitude of J was only dependent on the number and types of bonds to the specific nuclei. The number of nuclei bound will result in additional splitting. Magnetically equivalent protons do not have this effect. A strong coupling exist between nuclei where the chemical shift and the coupling constant is comparable. A weak coupling exist when the chemical shift is much larger than that of the coupling constant of which this is not influential. Because of the point of inversion in the quaterthiophene dichromium biscarbene complex the proton spectrum was simplified (Figure 2.14).

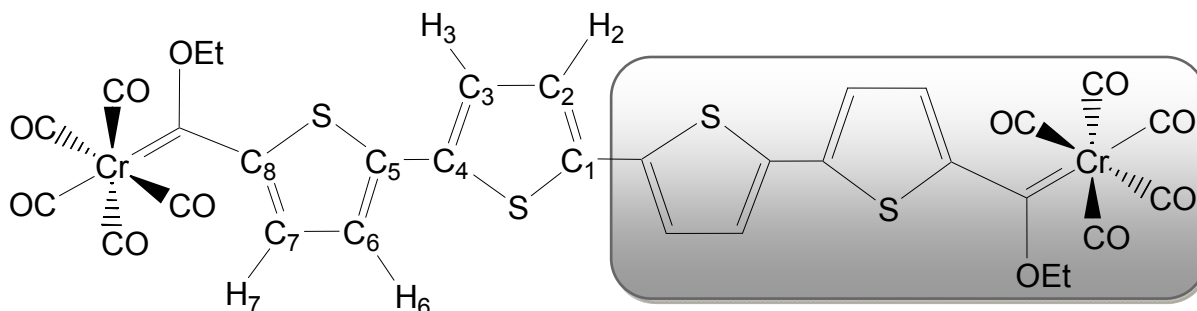
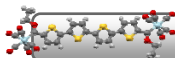


Figure 2.14: Representation of the point of inversion observed in A6.

The chemical shift is characteristic because it is dependent on the electronic environment,. This may not always be seen with dynamic environments (chemical exchange), a chemical



shift may be observed as a single resonance or give rise to two resonance lines due to the exchange rate.

Table 2.1: $^1\text{H-NMR}$ data of **A6**.

Assignments	Complexes	
	Chemical shift (δ) and coupling constant (J , Hz)	
Proton	A6 (CDCl₃)	
	δ	J
H2	7.17 (d)	3.6
H3	7.29 (d)	4.2
H6	7.33 (d)	4.0
H7	8.16 (d)	4.2
OCH ₂ CH ₃	5.14 (q)	6.9
OCH ₂ CH ₃	1.66 (t)	6.7

From the observed spectrum of complex **A6**, the strong influence of the carbene moiety was observed. The chemical shift, when moving away from the centre proton H2, to the proton closest to the carbene substituent H7, are shifted downfield. The difference is almost 1 ppm between H7 and H2. The splitting pattern observed for QTP protons is rationalized by the slight variation in environment for each of these protons due to the presence of the electron withdrawing carbene metal substituent. There was only one quartet and triplet observed for the ethoxy fragments that implies that these two groups of protons are in an identical electronic environment respectively. Moving away from the carbene metal fragment, to the centre of the complex, the coupling constant of the QTP proton resonance resembles that of thiophene ($J = 3.6$ Hz) and moving towards the metal fragment the coupling constant increases ($J = 4.2$). This value still resembles that of thiophene but was more prominent due to the electron withdrawal from the carbene metal substituent. The coupling constant observed for the ethoxy group ($J = 6.9$ Hz) was also characteristic to those of carbene complexes (Figure 1.1).

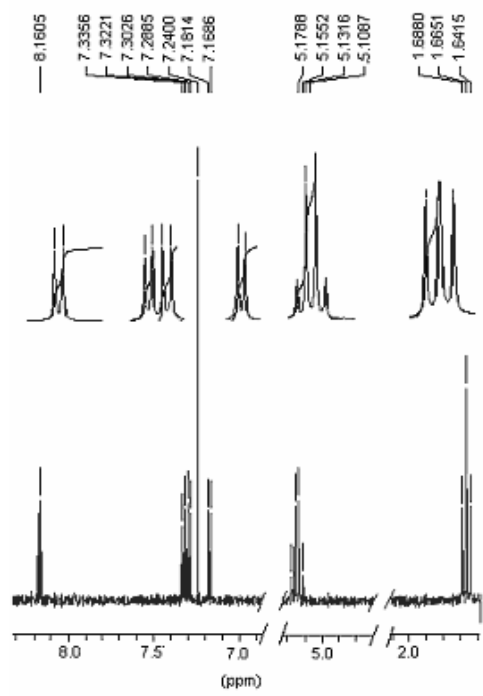
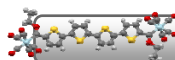
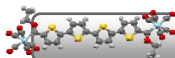


Figure 2.15: $^1\text{H-NMR}$ spectrum of **A6**.

Elucidation of **A1-5**

Similar values were observed for complex **A1-5** and are summarized in the table below. The chemical shifts for the ring protons (**A1**, δ 6.21, **A2**, δ 6.51, **A3**, δ 6.0, **A4**, δ 5.69 and **A5**, δ 6.39) were upfield to the thiophene chemical shift in the corresponding biscarbene complexes without a π -bonded $\text{Cr}(\text{CO})_3$ fragment, $[\text{M}(\text{CO})_5\{\text{C}(\text{OEt})\text{C}_4\text{H}_2\text{SC}(\text{OEt})\}\text{M}(\text{CO})_5]$, δ 8.06 (Cr) and δ 7.95 (W) respectively³. The shielding of protons was usually associated with increased charge density on these protons²⁰.

²⁰ C. Segard, B.R. Roques, C. Prommier, G. Guichon, *J. Organomet. Chem.*, **1974**, 77, 59


 Table 2.2: $^1\text{H-NMR}$ data of **A1-5**.

Assignments	Complexes									
	Chemical shift (δ) and coupling constant (J , Hz)									
	A1 (C_6D_6)		A2 (CDCl_3)		A3 (CDCl_3)		A4 (CDCl_3)		A5 (C_6D_6)	
Proton	δ	J	δ	J	δ	J	δ	J	δ	J
H3, H4	6.21 (d)	3.6	6.51 (2s)	3.5	6.00 (d)	3.5	5.69(s)		6.39 (2s)	3.5
	6.06 (d)	3.6								
$\text{OCH}_a\text{H}_b\text{CH}_3$	4.68 (q)	7.1	4.88 (br)		4.50 (m)	7.1	5.10 (br)		4.13 (q)	6.8
$\text{OCH}_a\text{H}_b\text{CH}_3$	4.73 (q)	7.0								
Cp							4.85(s)			
OCH_2CH_3	0.95(t)	7.1	1.50 (br)		0.90 (m)	7.0	1.69 (br)		1.1 (br)	

Instead, the influence of the chromium tricarbonyl fragment on the thienyl ring is localized to the double bonds and pull electron density away from the ring and deshielding the protons. The upfield change in the resonances of the thienyl ring in the complexes **A1-5** compared to free thiophene is attributed to the loss of ring current aromaticity of the thienyl moiety due to this localization of the double bonds²¹. $^1\text{H-NMR}$ signals of thiophene π -coordinated to chromium tricarbonyl were assigned to the signals at δ 5.58 (m, 2H) and 5.36 (m, 2H) in chloroform²². Experimentally the values have been redetermined to take into account the solvent and are δ 4.77 – 4.72 (m, 2H), 4.30 – 4.24 (m, 2H) in deuterated benzene and δ 5.84 (s, 2H), 5.61 (s, 2H) in deuterated chloroform. The chemical shift, which showed a difference of approximately 1ppm, is dependent on the solvent used. Hence, comparing the resonances of analogous compounds the use of different deuterated solvents must be taken into account. In addition, the chemical shifts for **A1-5** are downfield compared to those of thiophene in $\text{M}(\eta^5-$

²¹ Ch. Elschenbroich, A. Salzer, *Organometallics: a concise introduction 2nd edition*. 1992, Verlagsgesellschaft, New York

²² (a) P. Mills, S. Korlann, M.E. Bussell, M.A. Reynolds, M.V. Ovchinnikov, R.J. Angelici, C. Stinner, T. Weber, R. Prins, *J. Phys. Chem. A*, **2001**, 105, 4418

(b) A. Mangini, F. Taddei, *Inorg. Chim. Acta*, **1968**, 2, 12

$C_4H_4S(CO)_3$. For symmetrical π -coordinated biscarbene complexes, a specific pattern was expected. The two protons on the thiophene ring were influenced by both types of functional groups. The electron withdrawing carbene fragments result in a downfield shift from that of the π -coordinated chromium tricarbonyl thiophene. Other proton resonances on the complex were produced by the ethoxy group. The chemical shifts for these protons were well documented and expected at characteristic chemical shift values. The CH_2 group was expected to have resonances between δ 4.50 and δ 5.30 in $CDCl_3$ and was observed experimentally at δ 4.88(**A2**), δ 4.50(**A3**) and δ 5.10(**A4**). These chemical shifts were dependent on the metal fragment of the carbene moiety. If exchanged with oxygen, a weaker electron withdrawing group, the shift was more upfield thus the polarity of the ester group was not as prominent as that of the metal carbene complex. Moving three bonds away the influence of the metal carbene moiety on the CH_3 group was not as prominent and found between δ 1.50 to δ 1.90 in $CDCl_3$.

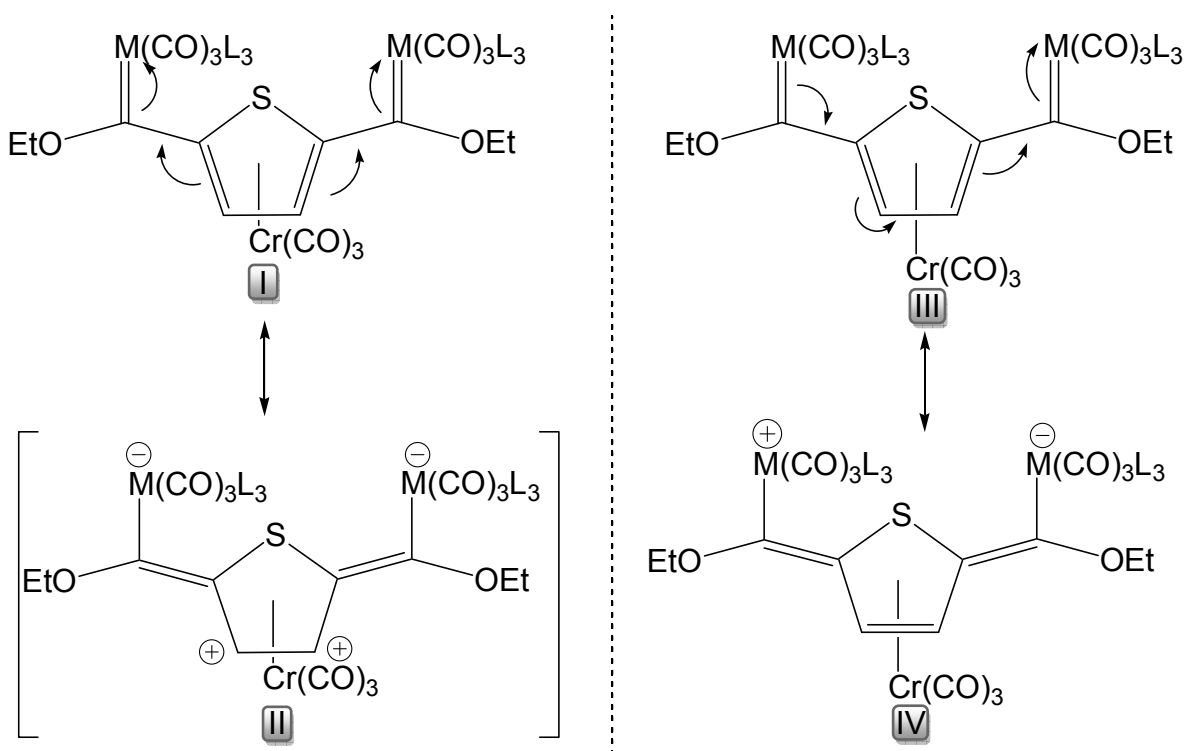
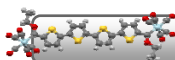


Figure 2.16: Possible structures showing electron delocalization pathways.



From the resonance structure presented (Figure 2.16), the thienyl ring proton chemical shifts will be influenced, because the carbene carbon is electrophilic, it will withdraw electron density from the thiophene ring. In this case, both carbenes are identical and the effect will be the same. The protons displayed the same chemical shift at a downfield value compared to the chemical shift of the protons in position 4 of $\text{Cr}(\eta^5\text{-C}_4\text{H}_4\text{S})(\text{CO})_3$. The resonance structure II is less relevant, as adjacent carbons will not both carry a positive charge. Structure IV shows a π -delocalization pathway from the metal on the 2 position to the metal on the 5 position. Again, the structure is meaningless as there is no driving force (push-pull effect) and there is an equilibrium due to the symmetry. Because the $^1\text{H-NMR}$ was measured in solution, the signal observed should be an average of all the conformations, except if a barrier of rotation is too high. The resonance structures indicates such energy barriers²³. The spectra of complex **A1-5** showed unexpected splitting patterns for the thienyl protons and multiplets for the ethoxy proton resonances. With the two same substituents in the same position inflicting the same electronic effect on the ring. The 3 and 4 proton signals were expected to be singlets and the ethoxy CH_2 and CH_3 were expected to show a quartet and triplet resonance respectively.

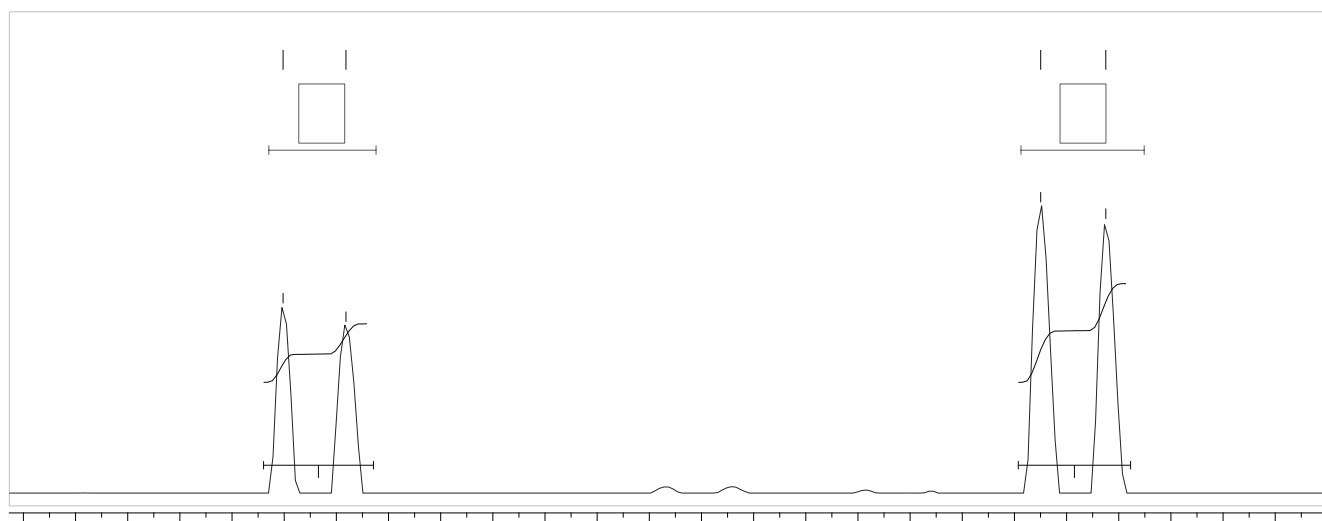


Figure 2.17: Proton splitting of A1.

²³ H. Fischer, In *The Synthesis of carbene complexes*, 1983, Verlag Chemie, Weinheim

Considering spin coupling for a symmetric complex **A1** the spectrum displayed two doublets in the expected chemical shift range of the thienyl moiety with two strong electron withdrawing groups (Figure 2.17). The ratio of the two doublets is 2:3. This indicated the presence of two individual isomers in the solution because of constrained geometry²⁴ due to the size and positioning of the three metal fragments.

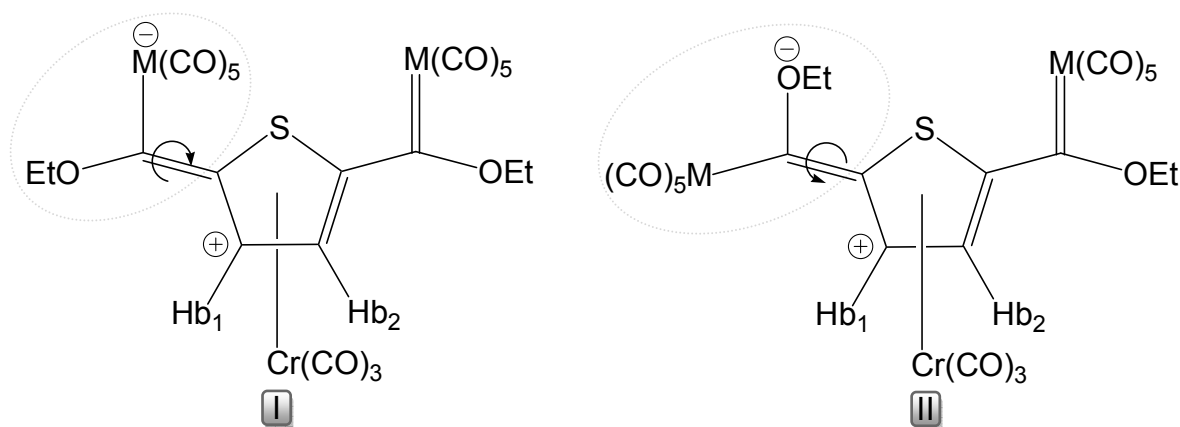
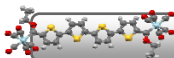


Figure 2.18: Restricted rotation around the $C_{\text{carbene}}-C_{2\text{thiophene}}$ bond.

Because of the large metal fragments, restriction around the ring carbon and carbene carbon bond results in alternate positioning of the metal carbene fragment to the ring protons. Each proton signal was further split into a doublet, where only a single chemical shift was expected. This observation further supports the presence of isomers with restricted rotation (Figure 2.18) shows restricted rotation around the $C_{\text{carbene}}-C_{\text{thienyl}}$ bond.

²⁴ H. Braunschweig, F.M. Breitling, *Coord. Chem. Rev.*, **2006**, 250, 2691



The coupling constant between these two signals correspond to recorded literature values of the thienyl protons in π -coordinated monocarbene complex analogue of chromium ($J = 3.7$ Hz). The asymmetrically substituted thiophene ring, π -coordinated to $\text{Cr}(\text{CO})_3$ resulted in two stereoisomers known as planar chiral diastereomers. The coupling constant indicated that the individual isomers has the protons in chemically differing environments. The chemical environment of each ring proton differs significantly. In addition both structures show planar chirality along the $\text{C}_{\text{thienyl}}-\text{C}_{\text{carbene}}$ bond because of the chromium tricarbonyl fragment. The planar chirality was not observed in the thienyl bis-carbene complexes of chromium and tungsten^{3a}. The isomers of complex **A1** were not present in equal amounts indicated by the height ratio of signals. The possible isomers influenced not only the ring protons but also the methylene protons such that the observed splitting pattern of the ethoxy CH_2 was duplicated at δ 4.68 and δ 4.73 for complex **A1**. Two individual quartets were positively assigned with a coupling constant ($J = 7.0$ Hz) similar to that of the π -coordinated monocarbene complex analogue ($J = 7.2$ Hz). No such duplication was observed for the CH_3 fragment on the ethoxy group. These protons were too far away and mobile thus presenting a single triplet at 0.95 ppm. From spectral data for complex **A2** and **A3**, there was a clear difference in the observed spectrum compared to **A1**. There was a single split resonance. Three possible isomers may contribute to the splitting pattern. The ring proton resonance appears at δ 6.51 and 6.00 in that order. The splitting of the thienyl resonance coincides with the presence of two isomers in the solution. The duplication of the methylene protons in contrast, was extensive with prominent overlap. The rotation about one of the carbene carbon and oxygen bond allowed for two diastereomer possibilities (Figure 2.19). The triplet signal of the CH_3 group was slightly more upfield than expected (**A2**, δ 1.5 and **A3**, 0.9) and the ethoxy groups on either metal carbene fragment may be restricted geometrically. From the broad signals obtained there seemed to be a number of geometrical isomers. This coincided with the size of the metal. The smaller chromium analogue (**A1**) shows distinct splitting pattern and the molecule seems to be locked in certain geometries.

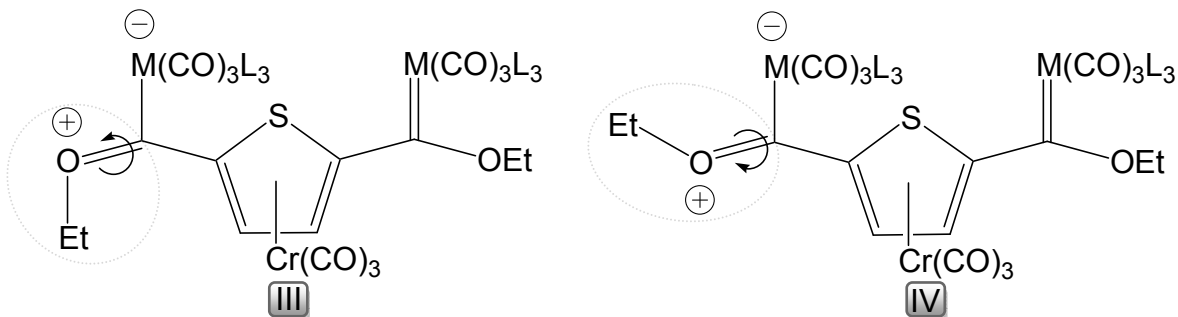


Figure 2.19: Restricted rotation around the $O_{\text{ethoxy}}-C_{\text{carbene}}$ bond.

The rotation of the carbene metal double bond was not considered when the ligands on the metal was only carbonyls as for the case of a carbene with a metal pentacarbonyl fragment. Because all the ligands are similar the environment is unchanged with no influence on the ring (δ 5.69) or ethoxy (δ 5.10 (CH_2) and δ 1.69 (CH_3)) protons. When some carbonyl ligands were substituted for a cyclopentadienyl ring, the M-Cp rotation was constrained and only one resonance was observed for the ring protons. Not only did the Cp ring contribute to chemical shift environment, it resulted in a change in the carbene bond character. The Cp ring was electron donating which resulted in less electron withdrawal from the thienyl moiety placing the resonances of the ring protons at more upfield shift. Complex **A5** also showed a single identifiable quartet signal, which was attributed to restricted rotation due to the size of the $\text{Re}_2(\text{CO})_9$ metal fragment.

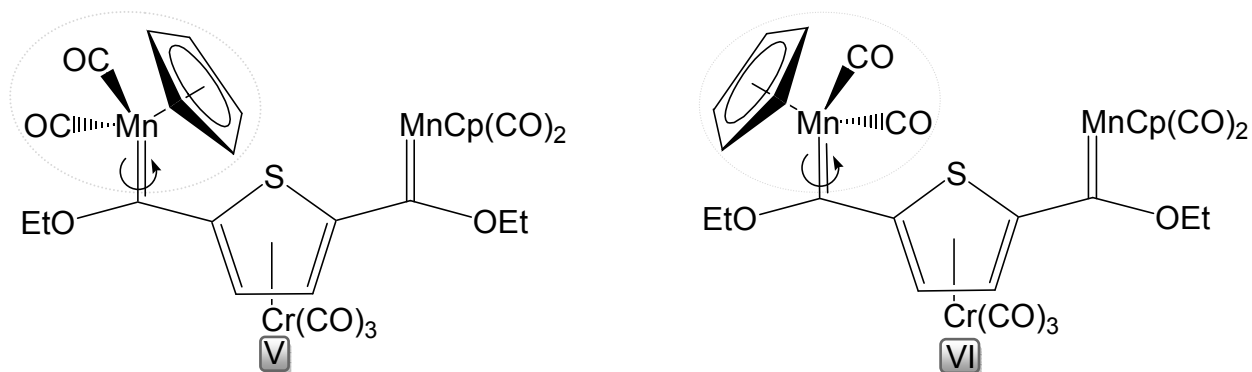


Figure 2.20: Restricted rotation around the $C_{\text{carbene}} - \text{Metal}$ bond.

There are two possible orientations for the chromium tricarbonyl fragment. A staggered and eclipsed conformation (Figure 2.21 (I) and (II)). These conformations do not show significant splitting patterns unless measured at low temperatures because of the small rotational barrier. The contribution of either staggered or eclipsed must be considered equal at room temperature in solution but a favoured configuration may exist in the solid state.

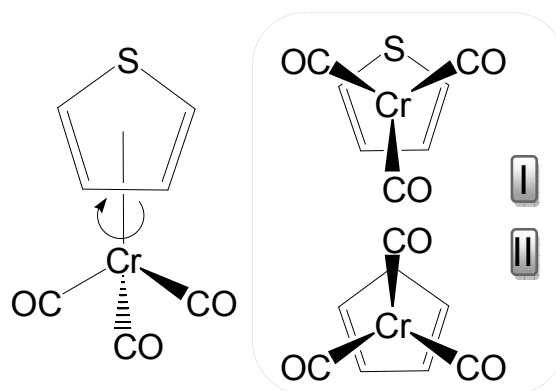


Figure 2.21: Restricted rotation of the $\text{Cr}(\text{CO})_3$ fragment.

In contrast with the metal pentacarbonyl biscarbene complexes (**A1-3**), the rhenium and manganese biscarbene complexes show only single isomers. The nature of these metal fragments did not allow for a varied number of rotations due to steric hindrance. The large metal fragments will prefer the orientation with the lowest energy and it may be assumed that rotation of the carbene carbon metal bond was restricted (Figure 2.18). Steric consideration suggests that the metal fragments positioning was at the lowest possible energy configuration. Rotation about this bond may be observed using NMR but not assigned to a specific orientation (Figure 2.22). The polarity of the metal carbene complex caused by the orientation of the ligands on the ring results in a difference in the molecular electron distribution.

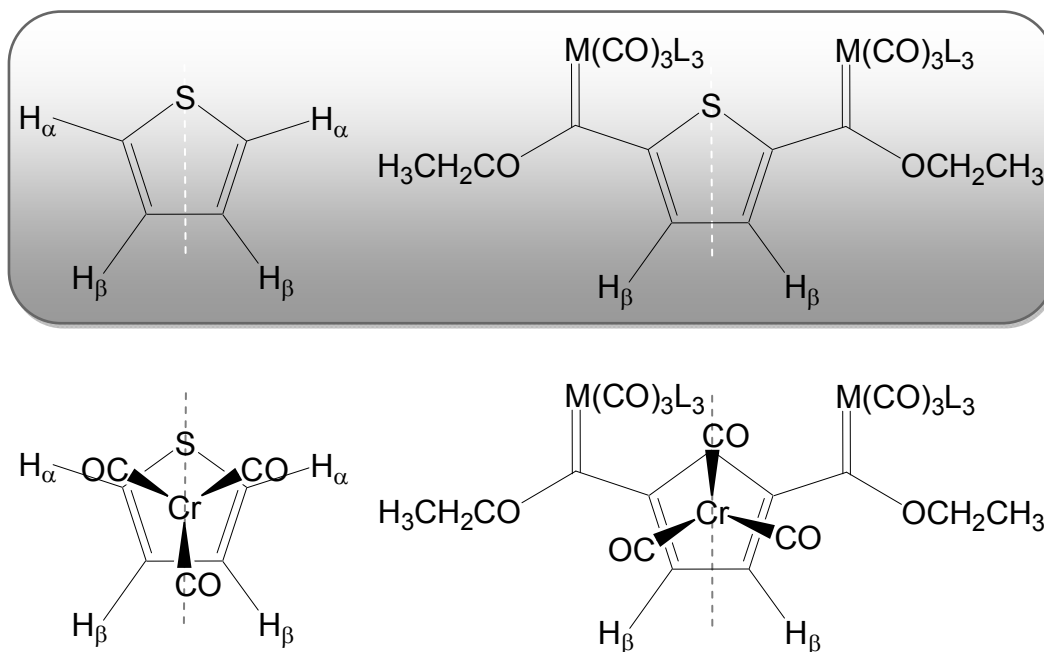
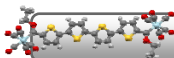


Figure 2.22: Equivalent protons for thiophene and thienyl derivatives²⁵.

Line broadening was significant for the proton spectrum of **A4** due to the paramagnetism of the Mn metal fragment, but not the case for **A5**. Considering thiophene symmetry (Figure 2.22), the only signals observed were two singlets at δ 7.20 H_α and δ 6.96 H_β ²⁶, which were due to the magnetic anisotropy of the neighbouring atoms resulting in a ring current. Symmetrical substitution of the ring protons 2 and 5 leads to the formation of a single resonance. If these substituents were metal carbene complexes the ring protons will be deshielded. Deshielding of these protons were attributed to diamagnetism.

²⁵ M.F. Bailey, L.F. Dahl, *Inorg. Chem.*, **1965**, 4,1306

²⁶ R.J. Abraham, J. Fischer, P. Loftus, *Introduction to NMR Spectroscopy*, **1988**, John Wiley and Sons



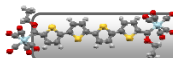
^{13}C – NMR spectroscopy

The ^{13}C -NMR spectra were recorded in CDCl_3 and in some instances in C_6D_6 when decomposition proved to be significant over the time of the recording. This was especially important for **A5** and **A3**. Complex **A6** is the most stable against decomposition in solution.

For complexes **A1-5** the following observations are of a general nature. Carbon spectra resonance showed characteristic regions for specific types of functional groups and were less sensitive to variation with similar atoms. This observation was prominent when considering the pentacarbonyl metal fragments, $\text{W}(\text{CO})_5$, $\text{Cr}(\text{CO})_5$ and $\text{Mo}(\text{CO})_5$. The range in which the carbon signals of these carbonyl groups are present, is limited (CDCl_3 : δ 190 – δ 220). The uncoordinated hexacarbonyl metal fragments also fall in this range but the deviation from this value was minimal. In CDCl_3 the recorded values were the following: $\text{W}(\text{CO})_6$ δ 192, $\text{Cr}(\text{CO})_6$ δ 212 and $\text{Mo}(\text{CO})_6$ δ 202²¹. A similar observation was made for the carbene carbon (CDCl_3 : δ 310 – 320), thienyl moiety (CDCl_3 : δ 80 – 95) and ethoxy group (CDCl_3 : CH_2 δ 75 – 79 , CH_3 δ 13 - 17). Experimentally observed values of uncoordinated thiophene are typically found around CDCl_3 : δ 126 and that of the π -coordinated thiophene carbons in CDCl_3 : δ 91 and δ 86 for C_2 - C_5 and δ 233 for the chromium tricarbonyl carbons.

Elucidation of **A6**

The observed range for the ring carbon chemical shifts in the ^{13}C -NMR spectrum of the QTP fragment in complex **A6** falls between 154 and 125 ppm as expected. The wide range of these chemical shifts attests to the electron withdrawing character of a carbene metal substituent.

Table 2.3: ^{13}C -NMR data of **A6**.

Assignments	Complexes
	Chemical Shift (δ)
Carbon atom	A6 (CDCl_3)
$\text{C}_{\text{carbene}}$	331.3
$\text{M}(\text{CO})_5$ <i>trans</i>	223.7
$\text{M}(\text{CO})_5$ <i>cis</i>	217.5
C1	138.4
C2	125.3
C3	127.3
C4	135.6
C5	145.9
C6	135.6
C7	142.7
C8 <i>ipso</i>	154.7
OCH_2CH_3	75.7
OCH_2CH_3	15.2

From the NMR spectrum the QTP carbon shifts is assigned. The signals also coincide with the withdrawal of electron density from the conjugated system. The *ipso* carbon has a significant downfield shift compared to that of C2 and C3. The carbonyl resonances of complex **A6** was similar to that observed for complex **A1** presented in the table below (Table 2.4). The *cis* and *trans* carbonyl and ethoxy shifts of complex **A6** and **A1** differ by 1 ppm respectively. In contrast, the carbene resonance of complex **A6** was shifted downfield by ± 15 ppm. This observation may indicate the ability of the spacer ligand to stabilize the carbene carbon.

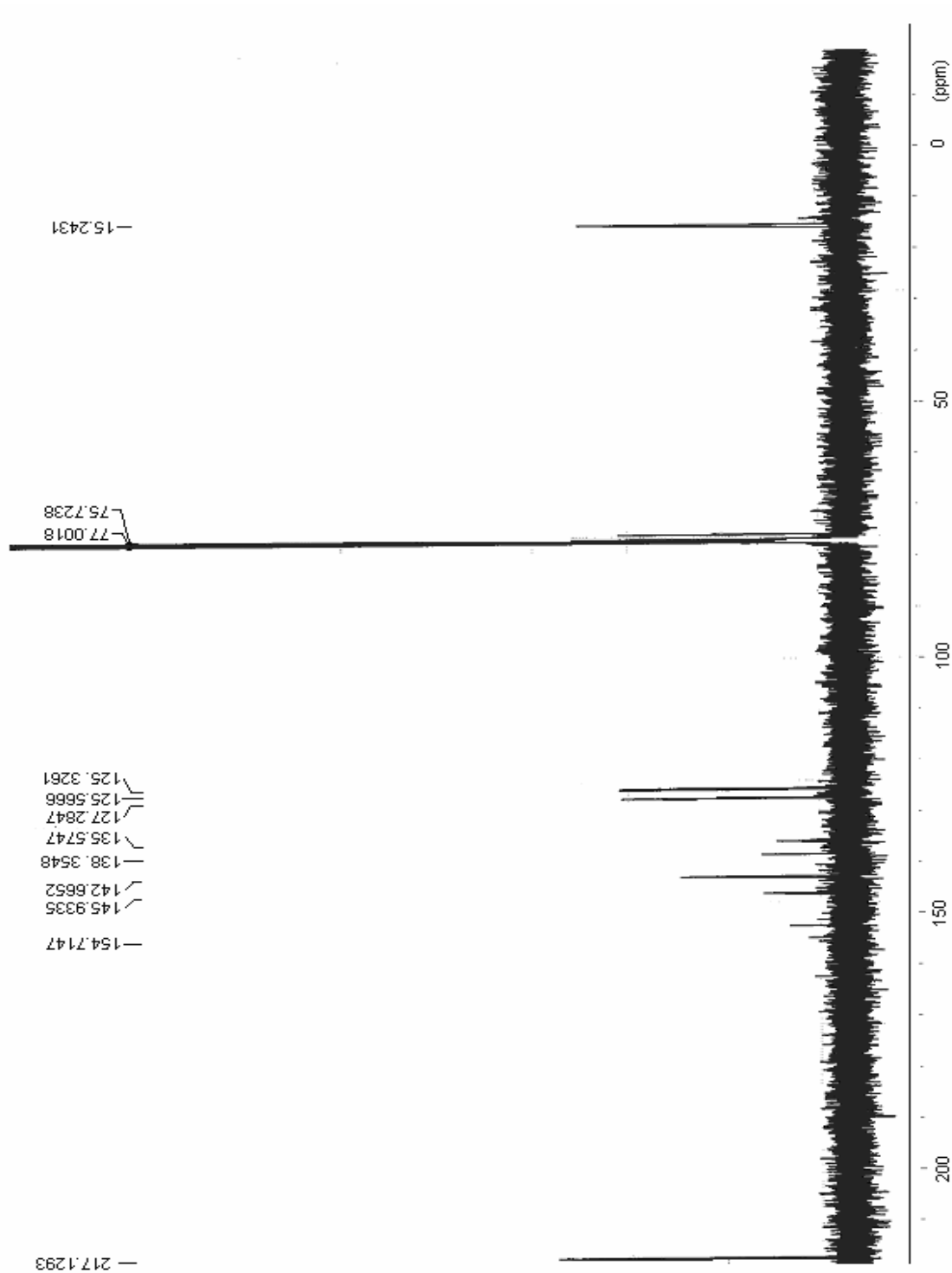
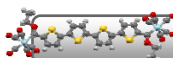
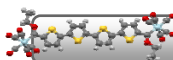


Figure 2.23: A section of the ^{13}C -NMR spectrum of A6.



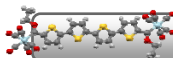
Elucidation of A1-5

The ^{13}C -NMR data of **A1-3** is shown in Table 2.4 below. The resonances of the carbene carbon were not observed for **A2** and **A3**, but the metal carbonyl carbons are in the expected range given.

Table 2.4: ^{13}C -NMR data of A1-3.

Assignments	Complexes		
	Chemical Shift (δ)		
Carbon atom	A1 (C_6D_6)	A2 (CDCl_3)	A3 (C_6D_6)
$\text{C}_{\text{carbene}}$	311.1		
$\text{Cr}(\text{CO})_3$	233.4	232.7	233.1
$\text{M}(\text{CO})_5$ <i>trans</i>	222.7	211.4	213.8
$\text{M}(\text{CO})_5$ <i>cis</i>	216.6	205.2	197.0
C2,5 <i>ipso</i>	115.4	117.0	115.9
	109.0		
C3,4	92.4	92.9	92.4
	93.2	92.1	92.8
OCH_2CH_3	76.0	76.5	78.3
OCH_2CH_3	14.6	14.9	14.3

The chemical shift of C2 is expected to be further downfield (effect of two carbene groups) compared to that of the *ipso* carbon on the thienyl moiety of the metal monocarbene complex $[\text{M}(\text{CO})_5\{\eta^5\text{-C}_4\text{H}_3\text{SC}(\text{OEt})\}(\text{Cr}(\text{CO})_3)]$ (Table 2.4)¹⁰. This value was recorded at CDCl_3 : δ 108.8 compared to 116 ppm for **A1** and **A3**.

Table 2.5: Thiophene ^{13}C -NMR data of $(\eta^1\text{-}\eta^5\text{-C}_4\text{H}_2\text{SC(OEt)Cr(CO)}_5\text{Cr(CO)}_3)$ where $M = \text{Cr}$ and W .

Assignments	Complexes	
	Chemical Shift (δ)	
Carbon atom	$(\eta^1\text{-}\eta^5\text{-C}_4\text{H}_2\text{SC(OEt)Cr(CO)}_5\text{Cr(CO)}_3)$	$(\eta^1\text{-}\eta^5\text{-C}_4\text{H}_2\text{SC(OEt)W(CO)}_5\text{Cr(CO)}_3)$
	(CDCl_3)	(CDCl_3)
C2 <i>ipso</i>	108.8	111.8
C3	93.5	93.1
C4	88.1	88.4
C5	96.8	97.8

A difference in the signals of the metal monocarbene analogue is observed when this range is compared with the resonances in the experimental spectra of **A1-3**. The latter was shifted more than those of the monocarbene analogues (Table 2.5). Considering the difference in the deuterated solvent used, the values of the carbene carbon atom, tricarbonyl metal fragment and pentacarbonyl metal fragment deviates minimally. The shift in thienyl resonances indicate deshielding because of electron withdrawing carbene carbons and shielding because of the loss of ring current. From the spectral information for complex **A1** the existence of two isomers was again evident (Figure 2.23, p78). Almost all signals were duplicated and the presence of four individual carbon chemical shifts for the thienyl moiety strengthens the argument that the carbons are not equivalent. The presence of geometrical isomers is confirmed on the spectrum depicted in Figure 2.24. From the intensities in the spectrum it is clear that there are two geometrical isomers present. The same duplication of signals were identified in the spectra of complex **A2** and **A3**.

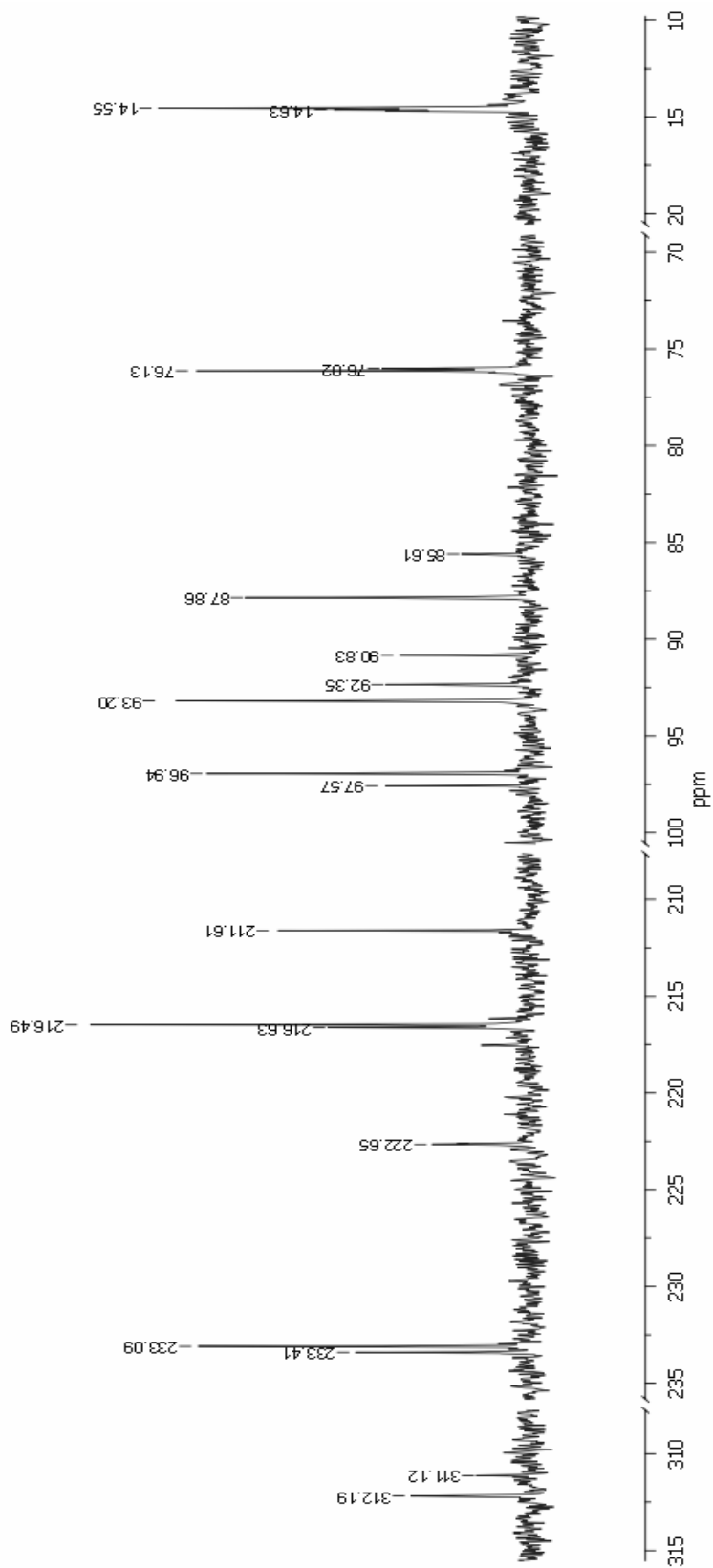
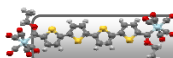
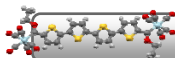


Figure 2.24: ^{13}C - NMR spectrum of A1.



The rhenium and manganese metal fragments differed with respect to characteristic regions of chemical shifts of the metal carbonyl and carbene carbons. The rhenium resonance of the carbonyls is expected between δ 188 and 195 and is observed as a broad peak. Peak broadening in $\text{Re}_2(\text{CO})_9$ is the result of carbonyl scrambling. The chemical shifts of carbonyl ligands in the ^{13}C -NMR spectrum of **A4** is expected to give signals for $\text{MnCp}(\text{CO})_2$ between 230-220 ppm. There was a broad peak observed between 220 and 224 ppm and a sharp singlet at 230.6 ppm. The peak at 230 ppm was assigned to the chromium tricarbonyl fragment and was shifted upfield presumably due to the influence of a donating Cp group on the manganese fragment. In the ^{13}C -NMR spectra of **A4** and **A5**, a significant difference in the chemical shifts of not only the metal carbonyl but also the carbene carbon resonances were observed. The same argument was applied for duplicated signals observed in **A5** as for those of **A1-3**. For **A4**, the electron donating ability of the Cp ligand was clear and thienyl carbon resonances were more shielded.

Table 2.6: ^{13}C -NMR data of **A4** and **A5**.

Assignments	Complexes	
	Chemical Shift (δ)	
Carbon atom	A4 (CDCl₃)	A5 (C₆D₆)
C _{carbene}	316.9	294.7
Cr(CO) ₃	230.6	232.9
M(CO)	224.2 -222.9(br)	193.7 (Re(CO) ₄) 192.9 (Re(CO) ₅) 198.0
C _{2,5 ipso}		95.4
C _{3,4}	86.4	90.8
	87.3	89.6
OCH ₂ CH ₃	73.9	78.0
OCH ₂ CH ₃	14.0	15.5
Cp	83.6	

IR-Spectroscopy

Assignments of A5 and A6

Complexes **A1-3** should show the typical patterns for a $M(CO)_5$ and a $M(CO)_3$ metal carbonyl fragment. The $M(CO)_5$ fragment (C_{4v} symmetry) typically gives the $A_1^{(1)}$, B_1 (infrared inactive), $A_1^{(2)}$ and E-bands with the $A_1^{(1)}$ band of highest and the E-band of lowest wavenumber²⁷. The $M(CO)_3$ (C_{3v} symmetry) displays an A and E band. Only three bands could be assigned from the IR spectra of **A1-3** because of extensive overlapping of the bands in the carbonyl regions of their infrared spectra. The first band, A_1 (sharp) is weak and found between 2050 – 2070 cm^{-1} , the second, a strong band between 1990 to 1940 cm^{-1} and the third a second strong band between 1920 – 1880 cm^{-1} . The first region belong to the $A_1^{(1)}$ ($M(CO)_5$) vibration, the second to the $A_1^{(2)}$ ($M(CO)_5$), E ($M(CO)_5$), A_1 ($M(CO)_3$) vibrations and the third to the E ($M(CO)_3$) vibration. Complex **A4** displayed three bands with some overlapping of the lower wavenumber band of $Mn(CO)_2$ and the A-band of the $M(CO)_3$ fragment. This spectrum was further complicated as it contained bands of the biscarbene without the π -bonded $Cr(CO)_3$ fragment.

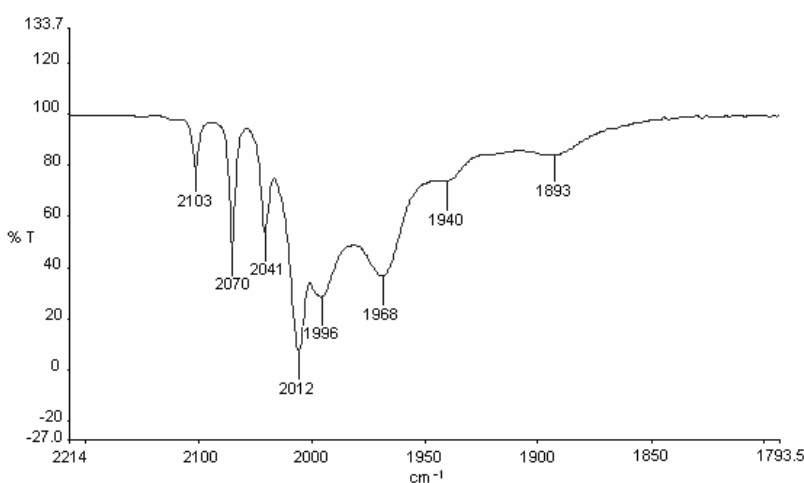
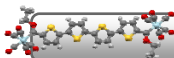


Figure 2.25: IR spectrum obtained of A5 in hexane.

²⁷ P.S. Braterman, *Metal carbonyl spectra*, 1975, Academic Press, New York, USA

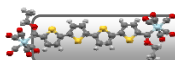


The IR spectrum of **A5** is shown in Figure 2.25 (Table 2.7) and displays seven of the nine expected bands for equatorial substituted $\text{Re}_2(\text{CO})_9\text{L}$ complex. The complex e.g. $[\text{Re}_2\{\text{C}(\text{OEt})\text{C}_4\text{H}_3\text{O}\}(\text{CO})_9]^{28}$ displays bands at 2102 (w), 2045 (m), 2016 (s), 2002 (vs), 1992 (s), 1974 (m), 1955 (m), 1945 (m) and 1923 (w) cm^{-1} and from Figure 2.25 it is clear that the unobserved bands probably fall between 1940 and 1893 cm^{-1} (a very weak band is indicated) and below the strong band 1968 cm^{-1} . A complex with only five bands would have been representative of an axial substituted $[\text{Re}_2(\text{CO})_9\text{L}]$. The two remaining bands at the lowest wave numbers 1940 and 1893 cm^{-1} was assigned to the vibration frequencies of the $\text{Cr}(\text{CO})_3$ fragment. These bands are of much lower intensity as expected for fewer carbonyl ligands and more restricted vibrations.

Table 2.7: Selected infrared data of A5.

Assignments		Complex
Stretching vibrational Frequency (νCO , cm^{-1})		
A5		
$\text{M}(\text{CO})_9$	A_1	2103 (s)
	$\text{A}_1^{(2)}$	2070 (s)
	$\text{A}_2^{(1)}$	2041 (s)
	$\text{A}_1^{(3)}$	2011 (vs)
	$\text{A}_1^{(4)}$	1996 (vs)
	$\text{A}_2^{(2)}$	1868 (s)
	$\text{A}_1^{(5)}$	1955 (w)
	$\text{A}_1^{(1)}$	1940 (s)
	$\text{A}_2^{(3)}$	1892 (s)
$\text{M}(\text{CO})_3$	A_1	1940 (s)
	$\text{E}(\text{A}', \text{A}'')$	1892 (s)

²⁸ D.I. Bezuidenhout, D.C. Lilies, P.H. van Rooyen, S. Lotz, *J. Organomet. Chem.*, **2007**, 692, 774

Table 2.8: Selected infrared data of **A6**.

Assignments	Complex
Stretching vibrational Frequency (ν_{CO} , cm^{-1})	
A6	
$\text{M}(\text{CO})_5$	$\text{A}_1^{(1)}$ 2054 (vs)
	B_1 1983 (w)
	$\text{A}_1^{(2)}$ 1931 (s)
	E 1926 (vs)

The pentacarbonyl fragment of complex **A6** showed no overlapping of the bands with the expected pattern. For C_{4v} symmetry, degeneration of the E band was lifted and the B_1 band gained intensity probably due to the same distortion of the C_{4v} symmetry of the molecule affecting the carbonyl ligands in the equatorial plane.

X-ray diffraction

Selected data of **A6**

The structure of complex **A6** was obtained from single crystal X-ray diffraction studies and confirmed the structure proposed by spectroscopy. The structure is presented and numbered below as an ORTEP²⁹+POV³⁰-Ray picture. Hydrogens are subjectively assigned as round spheres whereas the other atoms were displayed as ellipsoids showing the anisotropic displacement. Other graphical representations of the crystal structure were obtained using Mercury software³¹.

²⁹ L.J. Farrugia, *J. Appl. Crystallogr.* **1997**, 30, 565

³⁰ The POV-Ray Team 2004, <<http://www.pov-ray.org/download/>>

³¹ (a) F.H. Allen, *Acta Cryst.*, **2002**, 380, Mercury CSD 2.0 2002

(b) J. van de Streek, *Acta Cryst.*, **2006**, 567, Mercury visualization 2006

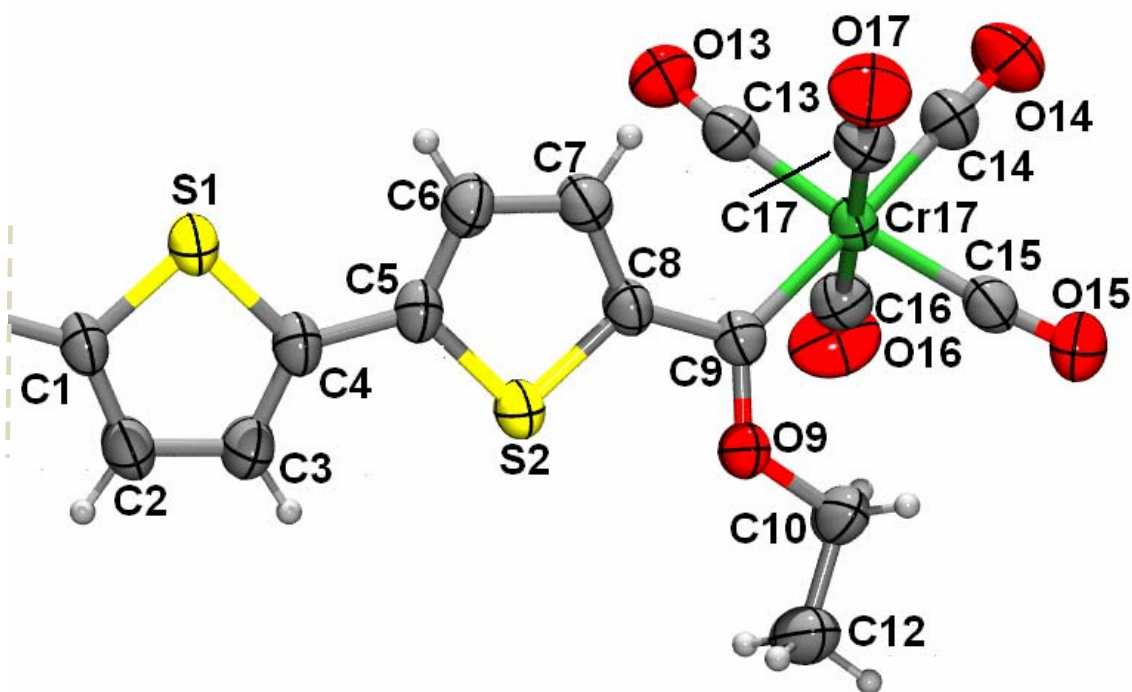
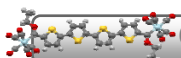


Figure 2.26: ORTEP+ POV-Ray representation of **A6**.

The structure of complexes **A1-5** could not be determined by means of this method as these complexes coated crystallized metal starting material. This was observed for complex **A1**, **A2** and **A5** respectively. The stability of complexes **A3** and **A4** proved to be too problematic to produce crystals and the complex decomposed in solution. The crystal structure was refined with an R_{factor} of 4.49%. From the crystal structure of complex **A6** the space group (P1) was obtained where $a = 6.8359(10)$ Å, $b = 9.2417(14)$ Å and $c = 14.740(2)$ Å triclinic system.

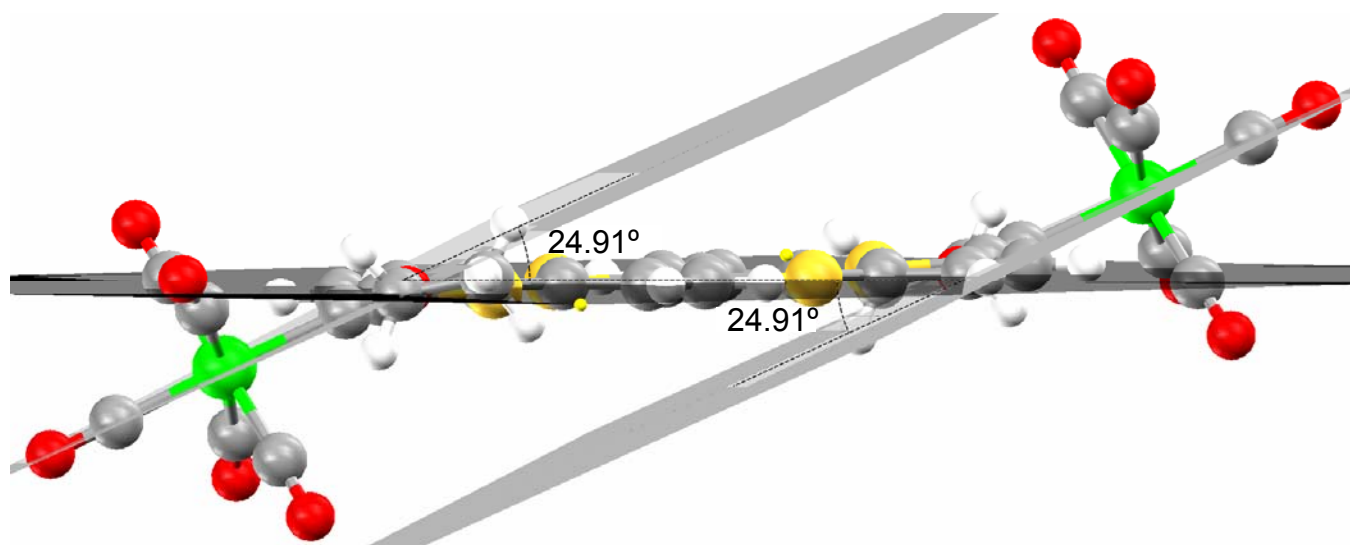
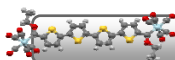


Figure 2.27: Ball and stick representation illustrating deviation from planarity of the biscarbene complex.

Selectively chosen bond distance and bond angles are given below (Table 2.9 and Table 2.10). The same numbering applied as was used for NMR spectroscopy. The metal fragments showed octahedral geometry and the thienyl rings are coplanar with the metal fragment protruding above and below the thienyl plane. The orientation of the ethoxy substituents are eclipsed with respect to the 'carbonyl wall' of the equatorial carbonyl ligands and in plane with the thienyl linker. The 'carbonyl wall' excludes the carbonyl situated in the *trans* position with respect to the carbene carbon. From the geometry of the structure, the metal fragment deviated from planarity with four coplanar thienyl rings with an angle to the plane of 24.91° (Figure 2.27). The structure indicated that the conjugation and ability of the thienyl linker to transfer charge was still intact. The observed bond angles and bond distances were exact duplicates at the plane of symmetry in the molecule.

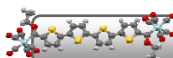


Table 2.9: Selected bond distances of A6.

Bond		Space Group
		P1
		Bond distance (Å)
		A6
	C _{carbene} -M	2.073(3)
	C _{carbene} -C _{thp}	1.446(4)
	C _{carbene} -OEt	1.323(4)
	M-CO _{trans}	1.875(4)
Thiophene	C ₁ -C _{1'}	1.438(6)
	S ₁ -C ₁	1.719(3)
	C ₁ -C ₂	1.360(5)
	C ₂ -C ₃	1.392(5)
	C ₃ -C ₄	1.358(5)
	C ₄ -S ₁	1.718(3)
	C ₄ -C ₅	1.456(5)
	S ₂ -C ₅	1.717(3)
	C ₅ -C ₆	1.367(5)
	C ₆ -C ₇	1.389(5)
	C ₇ -C ₈	1.379(5)
	C ₇ -S ₂	1.740(3)

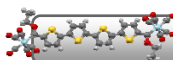


Table 2.10: Selected bond angles for A6.

Bond Angles		Space Group
		P1
		Bond angle (°)
		A6
	M-C _{carbene} -C _{thp}	123.9(2)
	EtO- C _{carbene} -C _{thp}	106.0(3)
	M-C _{carbene} -OEt	129.8(2)
Thiophene	C ₁ -C ₁ '-S	120.3(4)
	S-C ₁ -C ₂	110.0(2)
	C ₁ -C ₂ -C ₃	113.8(3)
	C ₂ -C ₃ -C ₄	113.4(3)
	C ₃ -C ₄ -S ₁	120.4(3)
	C ₄ -S ₁ -C ₁	92.36(17)
	C ₄ -C ₅ -S ₁	120.4(3)
	S ₂ -C ₅ -C ₆	111.2(2)
	C ₅ -C ₆ -C ₇	113.2(3)
	C ₆ -C ₇ -C ₈	114.0(3)
	C ₇ -C ₈ -S ₂	109.5(2)
	C ₉ -S ₂ -C ₅	92.05(16)
	S ₂ -C ₉ -C _{carbene}	119.3(2)

The carbene-thienyl bond distances is not the same as that of a similar type of carbene structure by Fischer², *p*-biphenyl chromium biscarbene complex (Figure 2.28). The *p*-biphenyl biscarbene complex was also coplanar and centrosymmetric with an inversion centre in the middle of the complex. Comparison of respective bond lengths and angles to known complexes gave insight into geometry and bonding of the synthesized complex (**A6**).

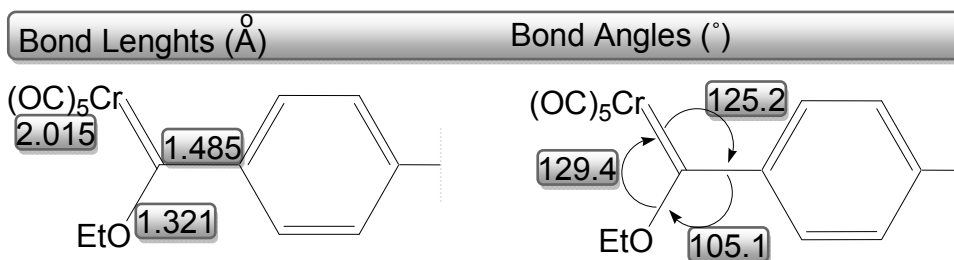
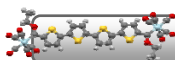
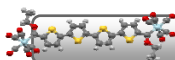


Figure 2.28: Selected X-Ray data of *p*-biphenyl chromium biscarbene complex^{2*}.

The $C_{\text{carbene}}\text{-O}$ bond length 1.323(4) Å indicated the contribution of the heteroatom substituent to assist in stabilizing the electrophilic carbene carbon. This value is the same as that recorded for the *p*-biphenyl chromium biscarbene complex². The $C_8\text{-}C_{\text{carbene}}$ bond distance of 1.446(4) Å is much shorter than the corresponding $C_{\text{Ph}}\text{-}C_{\text{carbene}}$ distance of the phenyl carbene derivative in Figure 2.28 and the $C_{\text{carbene}}\text{-M}$ bond of **A6** of 2.073(3) Å is much shorter than this distance in the biphenyl carbene. It is clear from this comparison that the phenyl substituent does not alleviate the electron shortage at the carbene carbon as efficiently as the thienyl substituent. By comparison, one could say that the thienyl is an electron donor whereas the phenyl is electron withdrawing or electron-withholding. This short fall of electron density for the biphenyl complex is compensated by storage π -backbonding from the chromium while less of this bonding is required in the case of the thienyl carbene. The bond distances of $C_6\text{-}C_7$ and $C_7\text{-}C_8$ are the same, 1.389(5) and 1.379(5) Å respectively. The $C_8\text{-}C_7$ distance is longer than a C-C double and the $C_7\text{-}C_6$ distance is shorter than a single bond, indicating electron delocalization in the thienyl ring closest to the carbene carbon. The bond angles around the carbene carbon, $C_{\text{thp}}\text{-}C_{\text{carbene}}\text{-M}$, 123.9(2)° and $\text{M}\text{-}C_{\text{carbene}}\text{-O}$, 129.8(2)° exclude any effect related to the size of the substituent. In comparison with the phenyl carbene the thienyl derivative showed a greater deviation from planarity (Figure 2.28). The reported deviation for *p*-phenyl biscarbene complex was 37° and **A6** was 24.91°. The deviations from the plane suggested that conjugation between the carbene metal substituent and aromatic substituent is disrupted and more so for biphenyl than thiophene. Computational chemistry was employed to determine whether there was a path of conjugation in the spacer ligand to allow for communication between the metal fragments. Computation of the structure and other



electronic characteristics was done using the Gaussian package³² version 04 with Gaussview 3. Below is the graphic representation of the highest occupied molecular (HOMO) and the lowest occupied molecular orbitals (LUMO) (Figure 2.29).

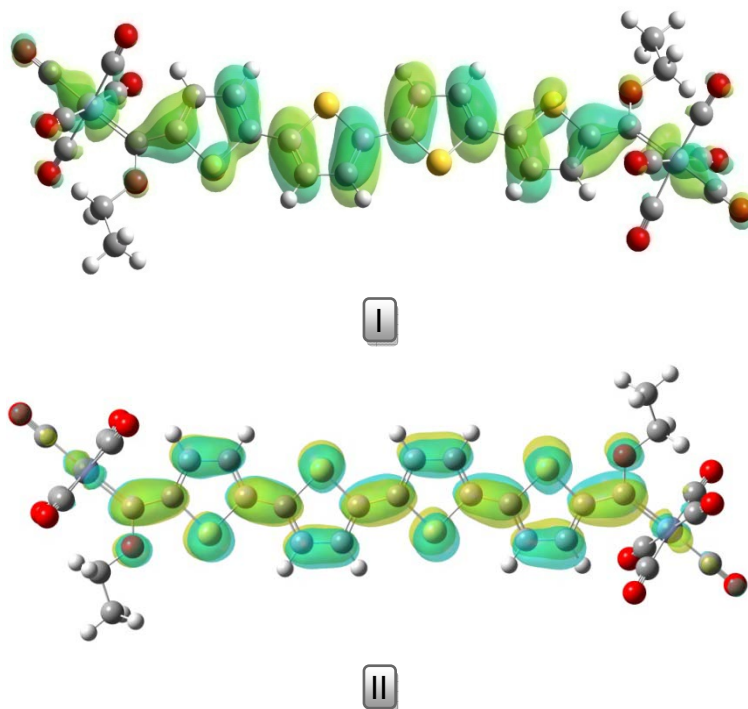


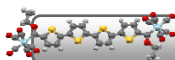
Figure 2.29: Orbital occupation I, HOMO and II LUMO obtained from computation for A6 using Gaussview 3 package³².

The localization of orbital occupation was indicative of the confinement of electronic charge to specific sites in contrast to the continuous orbital occupation (LUMO) observed in other polythiophenes³³. The HOMO (I) clearly shows higher electron density on the carbon double bonds as expected and backbonding was evident from the distribution of charge from the C₇ atom towards the carbene metal substituent. The large contribution of the LUMO (II) on the carbene carbon atom was characteristic, as this was the reason attributed to the

³² M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *Gaussian 94*, **1995**, Revision D1, Gaussian, Inc., Pittsburgh, PA,

* standard deviations not reported in article

³³ A.G. MacDiarmid, *Rev. Mod. Phys.*, **2001**, 73, 701



electrophilicity of the carbene carbon atom. The respective HOMO's showed that the orbitals have an even alternating phase contribution in the centre of the molecule away from the carbene metal substituents. This demonstrated that the electron distribution throughout the molecule was fragmented and the molecule would not be able to conduct charge. The deviation of the carbene metal substituents from the coplanar QTP spacer ligand also suggested the contribution of the electronic character of the molecule and supported this trend.

Packing

There are six different hydrogen interactions to six bordering molecules observed in the crystal structure. Overall, twelve interactions are found for a single molecule which interacts with two bordering molecules. Interaction between adjacent molecules is illustrated in Figure 2.30 and demonstrates the hydrogen bonding and packing pattern. As was seen from this Figure 2.31 the interaction from one molecule to the neighbouring six molecules and packing of these molecules coincides.

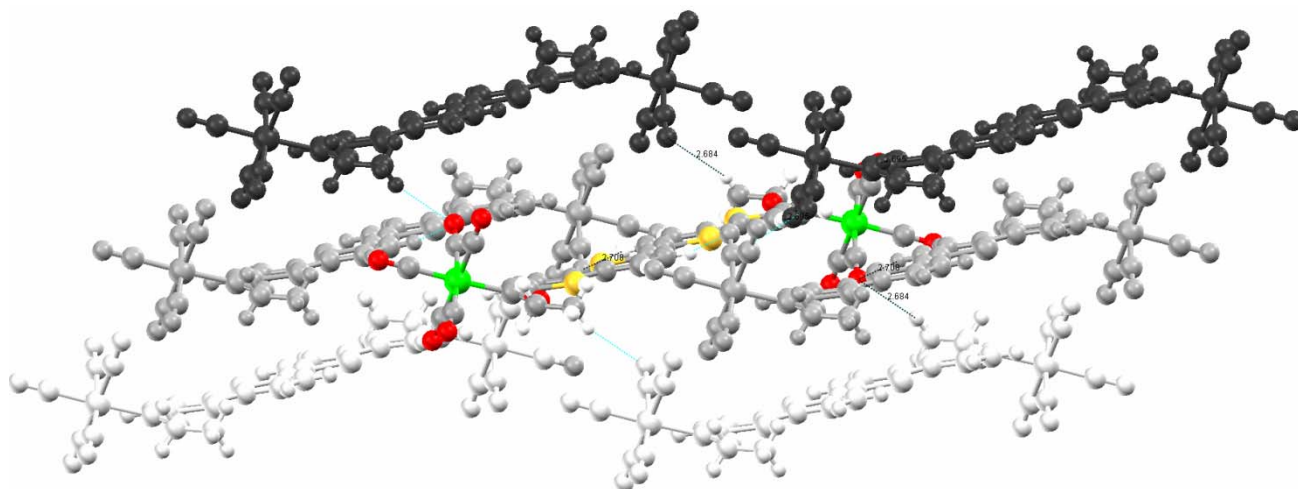


Figure 2.30: Illustrated hydrogen bonding and packing pattern of A6.

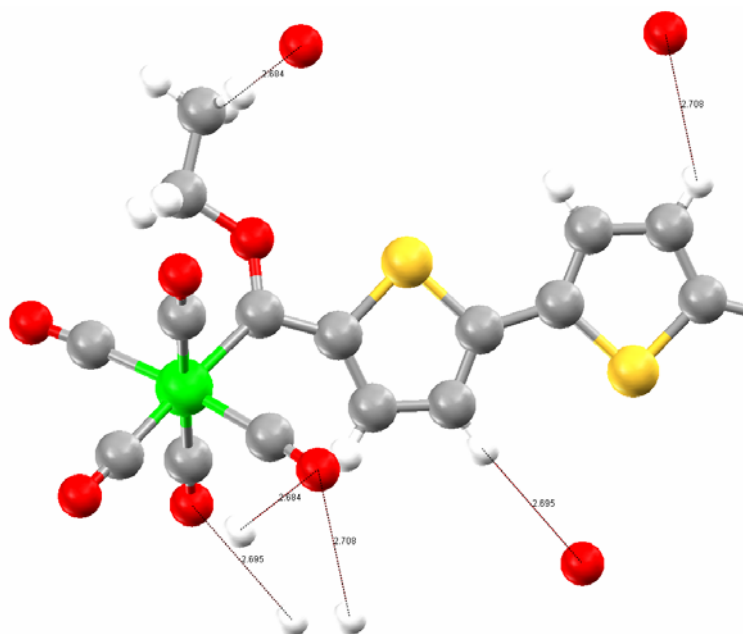
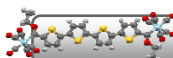


Figure 2.31: Hydrogen interaction involved in one QTP biscarbene complex.

The sulphur atoms on the QTP spacer ligand lie in an alternate shifted pattern or slide to accommodate the larger carbonyl ligands on the metal (Figure 2.32) that bridges the next molecule. There was no overlap of the thienyl rings and packing is mainly supported by hydrogen interactions.

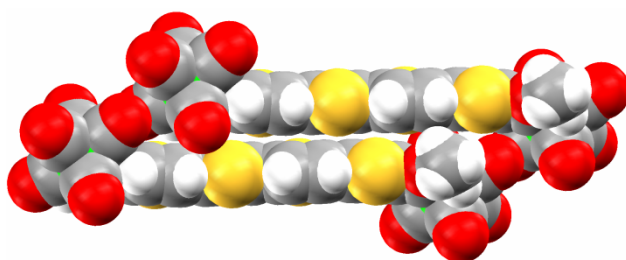


Figure 2.32: Space filled model of A6.

From Figure 3.31, a small space between the thienyl rings is observed as a further indication that there was no interaction between the electron densities of the thienyl moieties between adjacent molecules.