Biscarbene Complexes of Bithiophene

by

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Summary

Binuclear mixed biscarbene complexes of bithiophene were synthesized *via* the classical Fischer method of synthesis. The metal carbonyls, $Mo(CO)_6$, $Cr(CO)_6$, $W(CO)_6$ and $Mn(MeCp)(CO)_3$ were reacted with dilithiated bithiophene to afford complexes of the formula, $[M(CO)_5\{C(OEt)C_4H_2S\text{-}C_4H_2SC(OEt)\})M'(CO)_5]$ (in case of manganese, $M(CO)_5$ is replaced with $MMeCp(CO)_2$), where [M] and [M'] are the metal carbonyls in different combinations. Quenching was achieved with triethyl oxonium tetrafluoroborate. In all the reactions the products included monocarbene complexes, biscarbene complexes and the decomposition products. C-C coupling reactions produced unexpected biscarbene complexes of Cr, W, and Mo having extended bithiophene spacers. The complexes were of the formula,

$[M(CO)_5\{C(OEt)C_4H_2S\text{-}C_4H_2SC(R)\text{-}C(R)C_4H_2S\text{-}C_4H_2SC(OEt)\})M'(CO)_5]$ (R = O, OH or OEt).

These complexes were characterized with NMR, infrared spectroscopy and some with mass spectrometry. Furthermore, three biscarbene complexes of the metal combinations $Mo(CO)_6$ and $Cr(CO)_6$, $W(CO)_6$ and $Cr(CO)_6$, and $Mn(MeCp)(CO)_3$ and $Cr(CO)_6$ were all reacted with 3-hexyne. The result was the benzannulation or the Dötz products.

Keywords: Manganese; Chromium; Molybdenum; Tungsten, Biscarbene complexes, Bithiophene and Dötz products.

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I would like to express my sincerest gratitude to the following people as they have contributed much to this study:

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Table of Contents

Summary

List of abbreviations

List of Compounds

Chapter 1

General introduction

Chapter 2

Bithiophene

Chapter 3

Carbene complexes of bithiophene

Chapter 4

Reactions of selected biscarbene complexes with alkynes

Chapter 5

Conclusion

Chapter 6

Experimental

List of abbreviations

br	:	broad
BT	:	Bithiophene
$CDCl_3$	:	Deuterated chloroform
CO	:	Carbonyl
CPs	:	conducting polymers
Cps	:	Cyclopentadienyl
dd	:	doublet of doublets
IR	:	Infrared
LDA	:	Lithium Diisopropyl Amine
Me	:	Methyl
MS	:	Mass spectroscopy
n.o	:	not observed
n-BuLi	:	n-Butyllithium
NMR	:	Nuclear magnetic resonance
Ph	:	Phenyl
ppm	:	parts per million
PT	:	Polythiophenes
q	:	quartet
s	:	singlet
t	:	triplet
THF	:	Tetrahydrofuran
TLC	:	Thin layer chromatography
η^n	:	number, n, of ring atoms bonded to the metal.

LIST OF COMPOUNDS

[Cr(CO)₅{C(OEt)C₄H₂S-C₄H₂SC(OEt)}W(CO)₅]

A

[Cr(CO)₅{C(OEt)C₄H₂S-C₄H₂SC(OEt)}MeCpMn(CO)₂]

1

[Mo(CO)₅{C(OEt)C₄H₂S-C₄H₂SC(OEt)}MeCpMn(CO)₂]
2

[W(CO)₅{C(OEt)C₄H₂S-C₄H₂SC(OEt)}MeCpMn(CO)₂]

3

[Cr(CO)₅{C(OEt)C₄H₂S-C₄H₂SC(OEt)}Mo(CO)₅]
4

LIST OF COMPOUNDS

[Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)C(O)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}Mo(CO)$_5$]

5

[W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)C(O)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}]W(CO)$_5$]

6

[Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OH)C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt}]Cr(CO)$_5$]

7

MnMeCp(CO)$_2${C(OEt)C$_4$H$_2$SCCHCC(OH)C(Et)C(Et)C(OEt)CS}

8

LIST OF COMPOUNDS

W(CO)₅{C(OEt)C₄H₂SCCHCC(OH)C(Et)C(Et)C(OEt)CS}

9

Mo(CO)₅{C(OEt)C₄H₂SCCHCC(OH)C(Et)C(Et)C(OEt)CS}

10

Chapter 1

General Introduction

1.1 The background of organometallics and application in organometallic chemistry.

When a metal forms a direct bond with carbon[1], the resulting compound is called an organometallic compound. Extensive research in organometallic chemistry has been influenced by industrial applications in catalytic reactions[2]. Since the industrial approach is driven by productivity, new materials with great processability are needed. New and efficient methodologies are being developed. Numerous organometallic compounds have been synthesized earlier e.g. Grignard reagents (produced from the reaction of magnesium with aryl or alkyl halides in ether and in the form of [RMgX], where R=alkyl/aryl and X=halide) and these are used vastly in synthetic reactions[3] as alkylating agents. Other organometallic compounds are produced from alkylation reactions by the use of organolithium reagents[3] e.g. n-butyllithium. Over the past two decades, the barrier between inorganic and organic chemistry has been bridged. This has opened a path for the application of organometallic complexes in stoichiometric organic synthesis[4].

1. (a) M. Bochman, *Organometallics 1, Complexes with Transition Metal-Carbon σ-bond*, Oxford, New York, **1994**.

   (b) C. Elschenbroich, A. Salzer*, Organometallics: A Concise introduction,* VCH Verlagsgesellschaft, Weinheim, Germany, **1992**, 227.

2. (a) G. Süss-Fink, G. Meister*, Adv. Organomet. Chem.*, 35, **1993**, 45.

   (b) D.M. Roundhill*, Adv. Organomet. Chem.*, 38, **1995**, 38.

3. (a) J.P. Collman, L.S. Hedges, J.R. Norton, R.G. Finke, Principles and Applications of Organo-transition Metal Chemistry, University Science Books, California, **1987**.

   (b) F.A. Cotton, G. Wilkinson, P.L. Gauss, Basic Inorganic Chemistry, 2nd Edition John Wiley & Sons, New York, **1987**.

4. C.M. Lukehart, Fundamental Transition Metal Organometallic Chemistry, Brooks/Cole, California**, 1985**.

An example is shown in fig 1.1, where alkylidene complex transfer alkylidene ligands to unactivated alkenes.
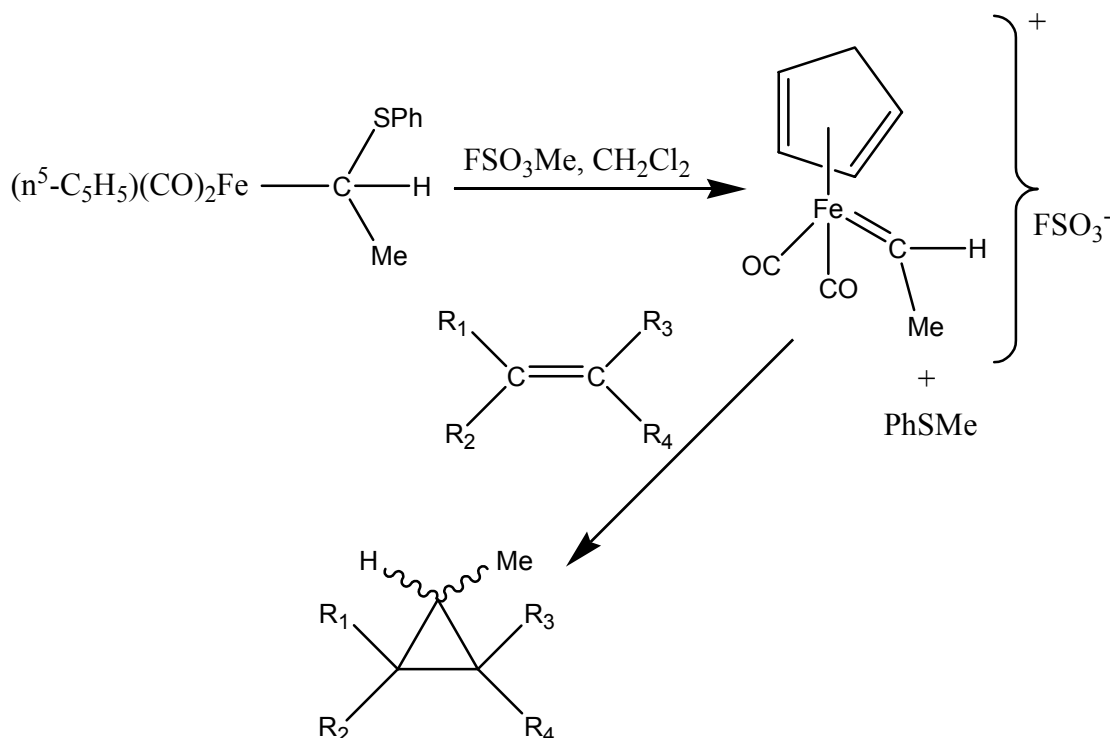
Fig 1.1 Alkylidene complex transfer alkylidene ligands to unactivated alkenes.

Some stable organometallic compounds can be used as protecting groups during organic synthesis, thus isomerism can be controlled because these complexes are extremely good stereo- and regio-selective[4]. Other organometallic compounds also play a role as intermediates in olefin metathesis[5].

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5. (a) R.H. Grubbs, S. Chang, *Tetrahedron*, 54, **1998**, 4413.

   (b) K.J. Irvin, J.C. Mol, Olefin Metathesis and Metathesis Polymerization, Academic Press, San Diego, CA, **1997**. Alkene metathesis in organic Synthesis, A. Fuerstner (Ed), Springer, Berlin, **1998**.

1.2 Complexes with unsaturated metal-carbon double bonds

Recently, the Royal Swedish Academy of Sciences awarded Richard R. Schrock, Robert H. Grubbs along with Yves Chauvin the 2005 Nobel Prize in Chemistry. These chemists have developed metal-containing molecules that are used in pharmaceutical and chemical industries to make important compounds. In the early 1990s, Schrock and Grubbs developed ruthenium carbene catalysts that facilitate metathesis[5] which then led to the making of medicines and bullet proof materials to name few. Schrock carbenes are nucleophilic.

It should be noted their catalysts are environmentally friendly and had a great impact on the development of advanced materials.

1.2.1 Carbene complexes

The first stable transition metal carbene complex was synthesized and characterized in 1964 by Fischer and Maasböl[6]. These complexes contain a formal metal to carbon double bond. Since their discovery, various synthetic paths have been developed for their preparation and other similar complexes. The compounds that are without a heteroatom bonded directly to the carbene carbon atom are named metal-alkylidene complexes.

There are two distinguished bonding extremes presently[7]. The first is the Fischer-type carbene complexes, which are electrophilic carbene complexes. These are prepared by the reaction of metal carbonyls of transition metals such as manganese, ruthenium, chromium, iron, molybdenum, tungsten and rhenium with various organolithium reagents. They undergo reactions at a number of sites[8] and have a very rich chemistry. The bonding is similar to that of carbon monoxide and is resonance stabilized (depicted in fig1.2).
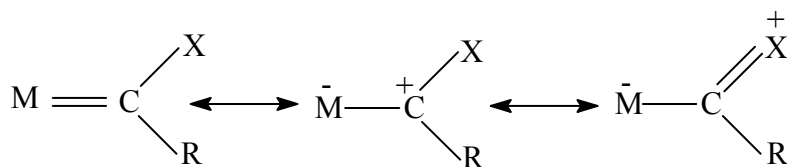
Fig 1.2 Resonance structures showing the role of the metal and the
heteroatom substituent as electron donors.

6. E.O. Fischer, A. Maasböl, *Angew. Chem.*, 76, **1964**, 645.

7. L.S. Hegedus, Transition Metals in the Synthesis of Complex Organic Molecules, University Science Books, Mill Valley, California**, 1994**.

8. K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kriessl, U. Schubert, K. Weiss, Transition Metal Carbene Complexes, VCH Verlag, Weinheim**, 1983**, 218.

An example of a Fischer carbene complex is shown below,
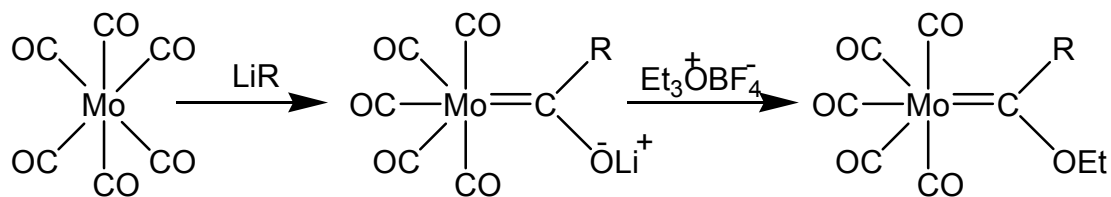
Fig 1.3 A Fischer-type carbene complex.

The second type is the Schrock-type carbene complexes. These have a nucleophilic carbene carbon atom and show an ylide like reactivity, Fig1.4. They are afforded using metals in high oxidation states with strong donor ligands and weak acceptor ligands. These complexes are derived from coordination of a methylene or alkylidene substituted methylene ($:CR_2$) ligand to a metal center.
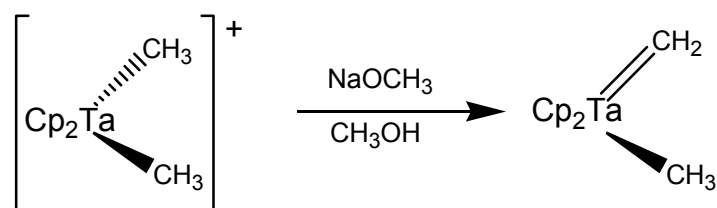
Fig 1.4 A Schrock-type carbene complex.

Taylor and Hall[9] reported that the Fischer-type metal-to-carbon bond comprises a dative bond between two singlet fragments, whereas the Schrock-type metal to carbon bond is seen as a covalent bond between two triplet fragments as shown in figure 1.5.

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9. T.E Taylor, M.B. Hall, *J. Am. Chem. Soc.,* 106, **1984**, 1576.

In other words, Fischer-type complexes may be viewed as a singlet-state carbene donating to the metal from its "sp^2 hybrid" orbital, with a corresponding amount of back-donation from the metal to the empty π orbital, **1**. Conversely, Schrock carbenes may be viewed as a triplet-state carbene spin-coupled to two electrons on the tantalum center, **2**.
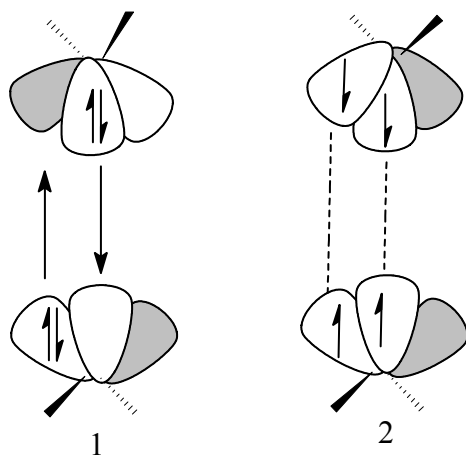
Fig 1.5 Metal to carbon bonding in Fischer (1) and Schrock (2) carbene complexes.

In the Fischer-type complex the π electrons would be polarized toward the metal, while in the tantalum complex the π electrons would be nearly equally distributed. Transition metal carbene complexes are used as starting materials for the synthesis of organic compounds or as precursors for new organometallic compounds[2a]. These are known to undergo a number of reactions; (a) reactions with transition metal nucleophiles, (b) substitution reactions (e.g. substitution of a non-carbene or carbene ligand), (c) reactions with electrophilic reagents (synthesis of neutral and cationic transition metal carbene complexes, rearrangement to carbene complexes), (d) reactions with nucleophiles (e.g. aminolysis and related reactions, formation of ylide complexes, addition of carbon and transition metal nucleophiles), (e) addition-rearrangement reactions (e.g. metal-heteroatom bond formation, modification of the carbene side chain, formation of metal π complexes), (f) carbene transfer reactions (inter-metallic transfer, cyclopropanation, synthesis of heterocycles, insertion reactions and (g) oxidation reactions.

Carbene complexes also play an important role as intermediates in olefin metathesis[10]. Carbene complexes of the type trans-[Ru=CHCH=CPh$_2$(PPh$_3$)$_2$Cl$_2$] have been prepared to catalyze the polymerization of highly strained cyclic olefins.

1.2.2 Cumulene and related compounds

The M=C of metallacumulenes offers useful applications in the field of organometallic as well as organic synthesis. These compounds encompass a new class of organometallic compounds containing a metal moiety coordinated to a carbon-rich unsaturated chain and are of the form M=(C)$_n$R$_2$. Metalacumulenes have the potential for access to metal containing copolymers exhibiting useful material properties[11]. Linear, unsaturated carbon chain complexes have recently attracted considerable interest due to their physical and chemical properties[12]. Transition metal complexes of this structural type have been proposed as one-dimensional molecular wires[13]

10. C.P. Casey, *J. Am. Chem. Soc.*, 96, **1974**, 7808.

11. D. Touchard, N. Pirio, L. Toupert, M. Fettouhi, L. Ouahab, P.H. Dixneuf, *Organometallics.*, 14, **1995**, 5263.

12. H. Lang, *Angew. Chem. Int. Ed. Engl.*, 33, **1994**, 547.

13. (a) J.S. Schumm, D.L. Pearson, J.M. Tour, *Angew. Chem. Int. Ed. Engl.*, 33, **1994**, 1360.

   (b) M.D Ward*, Chem. Soc. Rev.**, 1995**, 121.

and exhibit both liquid crystalline[14] and nonlinear optical properties[15]. The simplest unsaturated carbene complexes of this class, vinylidene complexes (R=H) contain one carbon-to-carbon double bond, $MCCR_2$, in addition to a metal to carbon double bond. Vinylidene complexes are prepared from metal acetylides, olefins, 1-alkynes, disubstituted alkynes, modification of vinylidene ligand, deprotonation of carbene complexes, vinylidene ligand transfer, vinyl and acyl complexes.

Articles on vinylidene complexes[16] are available. Other complexes are allenylidene complexes (fig1.6), that consist of two carbon to carbon double bonds in addition to the metal to carbon bond, $MCCCR_2$[17, 18] compared to vinylidene complexes.

These have been known since 1976[19]. Though their use is limited by the lack of general preparation methods, they are obtained through (i) transformation of

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14. (a) A.M. Giroud-Godquin, P.M. Maitlis, *Angew. Chem. Int. Ed. Engl*., 30, **1991**, 375.

   (b) M. Altman, U.H.F. Bunz, *Angew. Chem. Int. Ed. Engl*., 34, **1995**, 569.

   (c) L.Oriol, J.L. Serrano, *Adv. Mater*., 7**, 1995**, 248.

15. (a) D.W. Bruce, D.O' Hare*, Inorganic materials*, Wiley: Chichester, UK**, 1992**.

   (b) I.R. Whittall, M.G. Humphrey, A. Persoons, S. Houbrechts, *Organometallics*., 15, **1996**, 1935.

   (c) W.J. Blau, H.J. Byrne, D.J. Cardin, A.P. Davey*, J. Mater. Chem*., 1, **1991**, 245.

16. M.I. Bruce*, Chem. Rev*., 91, 1991, 197.

17. D. Peron, A. Romero, P.H. Dixneuf, *Organometallics*, 19, **1995**, 3319.

18. D. Touchard, N. Pirio, P.H. Dixneuf, *Organometallics*., 14, **1995**, 4920.

19. (a) H. Berke, *Angew. Chem. Int. Ed. Engl*., 15, **1976**, 624.

   (b) E.O. Fischer, H.J. Kalder, A. Frank, F.H. Köhler, G. Huttner, *Angew. Chem. Int. Ed. Engl*.,15, **1976**, 623.

alkenyl and alkynylcarbene complexes[19b, 20] and (ii) coordination of C_3 skeleton dianion, either $[C{\equiv}CC(R)O]^{2-}$ or $Li_2C_3Ph_2$[21].

M=C=CR$_2$ M=C=C=CR$_2$ M=C=C=C$_n$R$_2$

Vinylidene complex (a)   Allenylidene complex (b)   Metalacumulene
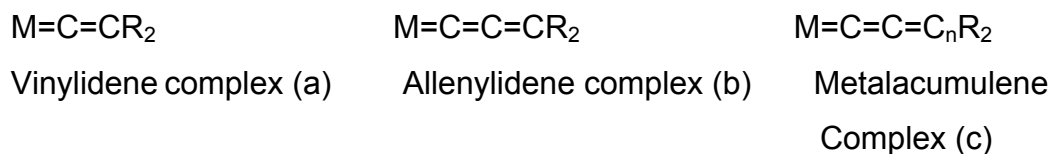
                                                            Complex (c)

Fig 1.6 Cumulene complexes.

Selegue and co-workers[22] recently employed a straight forward method which comprises the reactions of alkyne-3-ols with metal complexes e.g. [RuCpCl(PR$_3$)$_2$] in polar media that lead to the formation of hydroxy vinylidene intermediates, which spontaneously dehydrate *in situ* to yield allenylidene complexes. This method is now directed towards the building of bimetallic systems with allenylidene ligands[23] and bridges[24].

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20. F. Stein, M. Deusch, M. Noltemeyer, A. de Meijere, *Synlett*., **1993**, 486.

21. (a) S. Takahashi, Y. Takai, H. Moromoto, K. Sonogashira, J. Chem. Soc., Chem. Commun., 3, **1984**.

   (b) K. Sonogashira, Y. Fujikura, T. Yatake, N. Toyoshima, S. Takahashi, N. Hagihara*, J. Organomet. Chem*., 145, **1978**, 101.

    (c) Y. Wakatsuki, H. Yamazaki, N. Kumegawa, T. Satoh, *J. Am. Chem. Soc*., 113,**1991**, 9604.

22. J.P. Selegue, B. A. Young, S.L. Logan, *Organometallics*., 10, **1990**,1972.

23. D. Touchard, S. Guesmi, M. Bouchaib, P. Haquette, A. Daridor, P.H. Dixneuf, *Organometallics*., 15, **1996**,2579.

24. H.P. Xia, G. Jia, *Organometallics*., 16, **1997**, 1.

1.3 Binuclear Complexes with unsaturated Metal-to-Carbon Double Bonds.

1.3.1 Conjugated Bridging Ligands

Binuclear complexes containing bridges composed of different organic units have been reported[25].These complexes are widely recognized for their ability to allow long distance electronic coupling through π delocalization. The most common bridges are those bound through nitrogen, for example pyrazine and related heteroaromatic groups[26]. Linear π –conjugated systems represent the simplest models of molecular wires[27], which together with their complimentary functions such as molecular switches, or logical gates, have contributed to the emergence of the concepts of molecular electronics and logic[28, 29]. Their electronic properties have acquired a growing importance in many areas of modern chemistry and physics of condensed matter. Until recently, conjugated polymers represented the best-known prototypes of linear π – conjugated systems. The discovery of metallic electrical conductivity in oxidatively doped polyacetylene $(CH)_x$, Fig1.7, in the 1970s started the interest in conjugated polymers.
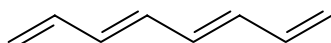
Fig 1.7 Polyacetylene

26. S. Boyde, C. Lapinte, *Coord. Chem. Rev.*, 178-180, **1998**,431.

27. J.M. Lehn, *Angew. Chem. Int. Ed. Engl.*, 27, **1988**, 90.

28. F.C. Carter, *Molecular Electronic devices*; Ed., Marcel Dekker: New York, **1982**.

29. A. Aviram, *J. Am. Chem.Soc.*,12, **1988**,171.

New classes of conjugated polymers based on aromatic precursors such as pyrrole[30], benzene[31], aniline[32] or thiophene[33] have been developed. They differ from $(CH)_x$ by (a) their non degenerate ground state, which has important consequences regarding the nature of charged species involved in the mechanisms of charge transport[34] and (b) by their electrochemical synthesis which leads in one step to a doped conducting polymer, thus contributing to extending their potential applications.

Among the number of linear π –conjugated systems discovered during the past two decades, polythiophenes have become the focus of considerable interest due to their unique combination of original electronic properties, environmental stability, and structural versatility[34]. They are synthesized chemically and electrochemically[35].

Polythiophenes (Fig1.8) can be viewed as sp^2 carbon chains that are structurally similar to that of *trans* $(CH)_x$ connected units which is stabilized by sulfur.
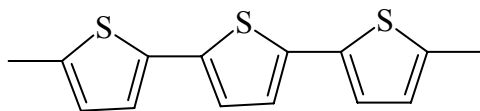
Fig 1.8 Polythiophenes

30. A.F. Diaz, J.C. Lacroix, *New. J. Chem.*, 12,**1988**,171.

31. P. Kovacic, M.P. Jones, *Chem. Rev.*,87,**1987**, 357.

32. E.M. Genies*, New. J. Chem.*, **1989**.

33. J. Roncali*, Chem. Rev.,* 92, 1992, 711.

34. J.W.P. Lin, Z.P. Dudek*, J. Polym. Sci.*, 18,**1980**, 2869.

35. (a) H.S. Nalwa*, Appl. Organomet. Chem.*,5, **1991**, 711.

    (b) M.H. Chisholm, *Angew. Chem. Int. Ed. Engl.*, 30, **1991**, 673.

    (c) Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, J.A. Gladysz*, J. Am. Chem. Soc.*,115, **1993**, 8509.

The essential structural feature of polythiophene is the conjugated π -systems extending over a large number of recurrent monomeric units.

1.3.2 Dinuclear Transition Metal Complexes with a Conjugate Ligand System.

Metal complexes have now become a part of the tools available to the organic chemists for designing and accomplishing the synthesis of target compounds. Attention has shifted to the activation of simple unsaturated organic substrates by transition metals and the resulting electronic and steric properties are being exploited to facilitate unique conversions and to synthesize novel compounds. A wide range of dinuclear transition metal complexes with σ- and π-bonded hydrocarbon bridges/spacers have been synthesized[36] and sufficient information about these complexes and their synthesis is available, hence closer investigation into their reactivity and their potential application in materials are important for future research.

Organometallic compounds in which two metal-containing fragments are bridged by arene[37] or heteroarene ligands[38] have enjoyed considerable attention recently since they serve as models for repeating units in related organometallic polymers[39].

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36. W. Beck, B. Niemer, M. Weiser, *Angew. Chem. Int. Ed. Engl*., 21, **1993**, 923.

37. Y. Kim, S. Song, S. Lee, S.W. Lee, K. Osakada, T. Yamamoto*, J. Chem. Soc., Dalton Trans*., **1998**, 1775.

38. R. Chukwu, A.D. Hunter, B.D. Santarsiero, *Organometallics*.,10**, 1991**,2141.

39. R. McDonald, K.C. Sturge, A.D. Hunter, L. Shiliday, *Organometallics*., 11, **1992**, 893.

It was discovered that increasing the number of fused aromatic rings in the bridging groups of such materials, increased the degree of intermetallic conjugation in complexes having two metal centers directly joined to the aromatic core by metal-carbon σ bonds, and has been demonstrated for conjugated organic polymers[40].

1.4 Thiophene Derivatives and related compounds

The coordination and reactivity of thiophenes on transition metal centers continues to attract considerable attention as model chemistry for the species and reactions that occur during heterogeneous hydrodesulfurization of petroleum and other fossil fuels[41]. During the hydrodesulfurization process, sulfur is removed from organosulfur compounds in petroleum-based feedstocks by treatment with H_2 at roughly 400^0 C over a Co- or Ni-promoted Mo or W catalyst supported on Al_2O_3.

$$C_xH_yS + 2H_2 \xrightarrow{\text{catalyst}} C_xH_{y+2} + H_2S$$

Thiophene is the heteroaromatic unit that displays the strongest conductive properties known today[42], because of the extensive delocalization of electrons within the ring(s).

40. A.D. Hunter, D. Ristic-Petrovic, J.L. McLernon, *Organometallics*., 11,**1992**, 864.

41. (a) R.J. Angelici, *Coord. Chem. Rev.*, 105, **1990**, 65.

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

(c) R.A.J. Sanchez-Delgado, *Mol. Cat*., in press.

42. H. Wynberg, J. Metselaar, *Synth. Commun*., 14, **1984**, 1.

Thiophenes fall into the category of 5-membered heteroarene compounds, but are more nucleophilic than benzene[41b]. They are produced by the action of sulfur on hydrocarbons in fossil fuels. Other synthetic routes have been investigated including the direct reaction of the elemental sulfur with alkanes, alkenes or butadienes at elevated temperatures[43].

Thiophene is readily metallated even at low temperatures and can result in single or double metallated products and therefore it is ideally suitable for the synthesis of Fisher-type mono- and biscarbene complexes. A number of different reactions and conductivity modes for thiophene have been reported in various metal systems[44] and proposed as molecular analogues for the chemisorption of such sulfur heterocycles onto active metal sites in catalytic surfaces. These include η^1-S, η^2-C=C, η^4 and η^5 as well as some bridging modes in dinuclear or cluster compounds, Fig1.9.

S-Coordination η^2-Coordination

η^4-Coordination η^5-coordination
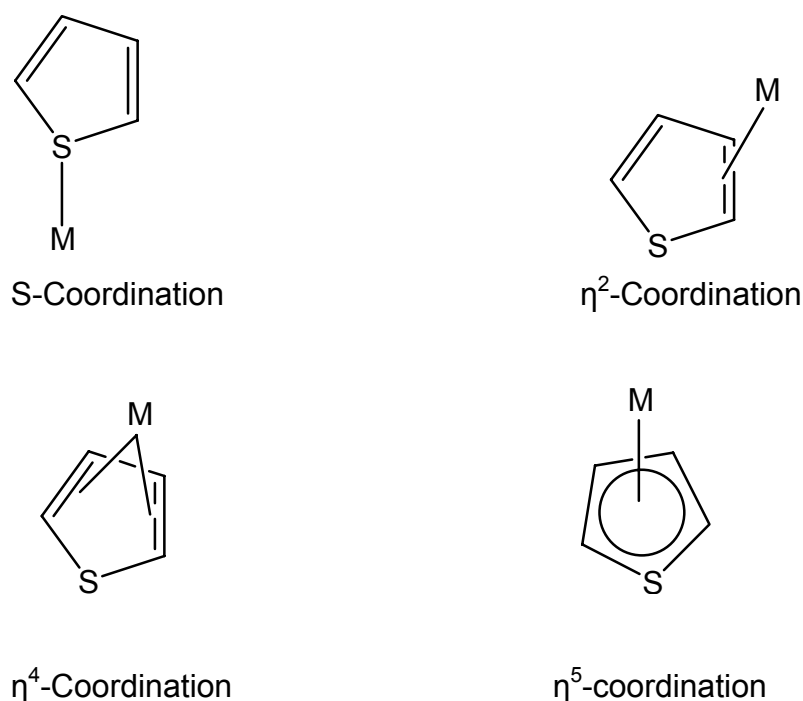
Fig 1.9 Coordination modes of thiophene to a metal

43. S.Gronowitz, Thiophene and its derivatives, Vol. 1, Wiley, New York, **1985-1986.**

44. M.G. Choi, M.J. Robertson, R.J. Angelici, *J. Am. Chem. Soc.*,113,**1991**,4005.

Oligomers of thiophenes are also of current interest, since many of them show photo-enhanced biological activities[45], while α-polymerization of thiophene produces crystalline electroconductive polythiophenes[46].

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45. S.W. Lai, M.C.W. Chan, K.K. Cheung, S.M. Peng, C.M. Chi, *Organometallics*., 18, **1999**, 3991.

46. J. Nakayama, T. Konishi, *Heterocycles*, 27, **1988**, 1731.

1.5 Aim of this study

It is well known that thiophene can be either singly or doubly lithiated with relative ease at low temperatures, thus Fischer-type mono- or biscarbene complexes could be produced. Biscarbene complexes of thiophene have been prepared[47]. Van Staden[48] has synthesized Fischer-type mono- and biscarbene complexes using metal carbonyls of Mn, W, Mo and Cr with bithiophene as a spacer unit.

In this study we extended these promising results by synthesizing binuclear mixed biscarbene complexes, Fig1.10, still using bithiophene as a spacer unit and the metal carbonyls.

The effect of different metal carbonyls on the bridging ligand, stability of the complexes, possible communication through the spacer were studied. Dötz/benzannulation reactions, Fig1.11, were also performed on selected complexes and the results were reported in chapters 3 and 4.

M/M' = W, Mo, Cr
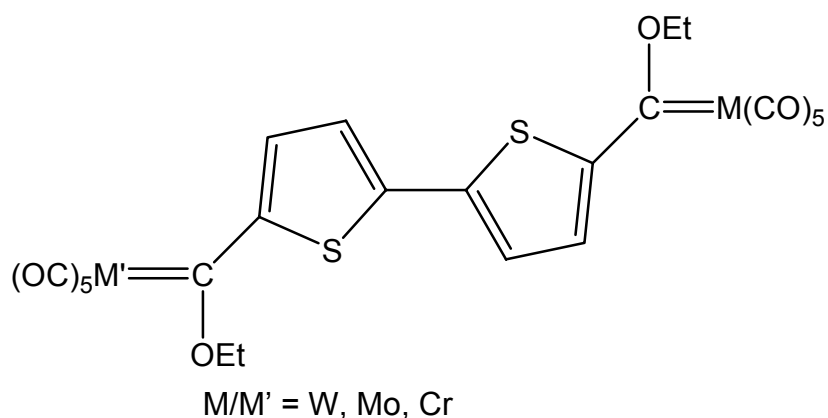
Fig 1.10 Ethoxy(bithiophene)carbene complex

47. (a) M. Landman, H. Görls, S. Lotz, *J. Organomet. Chem*., 285, **2001**, 617.
    (b) M. Landman, H. Görls, S. Lotz*, Eur. J. Inorg. Chem*., **2001**, 233.
    (c) Y.M. Terblans, S. Lotz*, J. Chem, Soc*., Dalton Trans,**1997**, 2177.
    (d) Y.M. Terblans, H.M. Roos, S. Lotz, *J. Organomet. Chem*., 566, **1998**, 133
48. M. van Staden, MSc dissertation, Binuclear Bithiophene Biscarbene Complexes (unpublished results), University of Pretoria, **2001**.

M= W, Mo, Cr
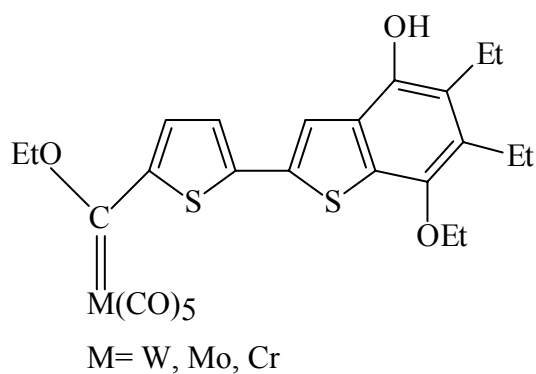
Fig 1.11 An example of Dötz Product

1.6 Future Prospects

Future work will focus on:

(i) The role of the ancillary ligands in stabilizing or activating the carbene ligands (ligands other than carbonyls will be introduced i.e. PR_3);

(i) The effect of energy (thermal, radiation) on activating the carbene and other ligands;

(ii) The reactivity of the carbene ligand towards different alkenes (Grubbs/Sierra) with or without additional catalysts.

Chapter 2

Bithiophene

2.1 Introduction

Bithiophenes and their derivatives are important compounds, in view of their numerous applications[1]. Bithiophene is of interest as a model system for conjugated polymers, in particular polythiophene[2]. The interest arises from the long-range delocalization of the π-systems on neighboring rings that gives rise to a small HOMO/LUMO gap that can be tuned for conducting/semiconducting purposes. The influence of the torsion angle along the chains on the electronic rings is very important[3, 4]. Some bithiophene derivatives have the ability to inhibit seed germination[5] and others e.g. 5-(3-buten-1-ynyl)-2,2'-bithienyl, have nematacidal and photo-induced anti-fungal properties[6].

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1. (a) J. Roncali*, Chem. Rev*., **1997**, 97, 173-205.

    (b) P. Bäuerle*, Sulfur-containing Oligomers*, K. Mullern and G. Wegner.,

    Electronic Materials: The Oligomer Approach; Weinheim; New York; Chichester Brisbarne; Singapore; Toronto: Wiley-VCH, **1998**,105-197.

2. Z.G. Yu, D.L Smith, A. Saxena, R.L. Martin, A.R. Bishop*, Phys. Rev. Lett., **2000**, 84.

3. C. Alemán, L. Julia, *J. Phys. Chem*., **1996**, 100, 1524 and the references therein.

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5. G. Campbell, J.D.H. Lambert, T. Arnason, G.H.N. Towers*, J. Chem. Ecol*., **1982**, 8, 961.

6. R. Rossi, A. Carpita, A. Lezzi, *Tetrahedron*, **1984**, 40, 2773.

2.2 Synthesis

Bithiophene was synthesized as early as 1956[7]. Pelter[8] used a two-phase system of CH_2Cl_2, methanol, N-borosuccinamide and a borane buffer at pH = 9 to produce 90% yield of bithiophene and a recovery of about 82%. This was the modification of the work done by Kagan and co-workers[9] who reported an 81% yield, which was later discovered that almost half the residues were recovered as thiophene, not bithiophene. Other early methods of synthesis included the coupling of halothiophenes with Grignard reagents derived from halothiophenes using palladium[5] or nickel[10] as catalysts. But this method was restricted to functional groups which did not react with organomagnesium reagents. Several other attempts were also made and reported in literature[11]. The reaction of $[RhCl(CO)_2]_2$ and thienylmercuric chloride in the presence of hexamethylphosphoramide and LiCl for 24 hours at 80 ^{o}C produced a 96% yield of bithiophene as a greenish oil which solidified on standing. This was the synthetic route reported by Larock and co-workers[12]. With this, bithiophene was reported to have a melting point of 32-33 ^{o}C. Recently, it has been shown that $Pd(OAc)_2$/n-Bu$_4$NBr is efficient as a catalyst for the direct arylation of activated thiophenes by iodoaryl[13] in a Heck type reaction.

7. H. Wynberg, A.J. Logothesis, *J. Am. Chem. Soc.*, **1956**, 78, 1958.
8. A. Pelter, H. Williamson, G.M. Davies, *Tetrahedron Lett.*, **1984**, 25, 453.
9. J. Kagan, S.K. Arora, *Tetrahedron Lett.*, **1983**, 24, 4043.
10. R. Rossi, A. Carpita, *Gaz. Chim. Ital.*, **1985**, 115, 575.
11. M.D' Auria, D. Mico, F.D' Onofrio, G. Piancatlli, *J. Org. Chem.*, **1987**, 52, 5234.
12. R.C. Larock, J.C. Bernhardt, *J. Org. Chem.*, **1977**, 42, 1680.
13. C. Gozzi, L. Lavenot, K. Ilg, V. Penalva, M. Lemaire, *Tetrahedron Lett.*, **1997**, 38, 8867-8870.

This catalyst has been proved to be efficient for the synthesis of symmetrical biaryls via homocoupling of arylhalides[14, 15]. Thiophene halides bearing various activating groups coupled, using $Pd(Oac)_2$ as a catalyst to synthesize symmetrical functionalized bithiophenes in good to excellent yields[16], Fig 2.1

X = I, Br, Cl
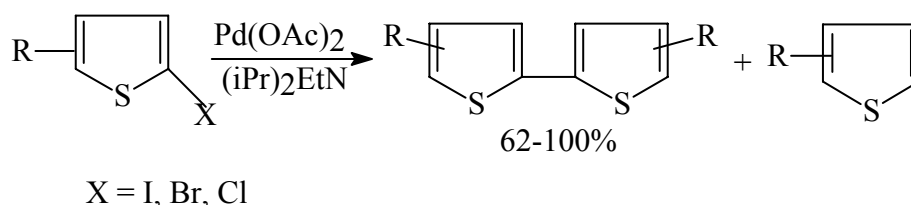
Fig 2.1 Homocoupling of thiophene halides catalyzed by palladium.

A more general method of synthesis of bithiophene and its derivatives as intermediates in the synthesis of biologically active molecules was developed[17]. This method involved the coupling of iodothiophenes and stamylthiophenes using palladium as a catalyst.

2.3 Structure of Bithiophene

The structure of 2,2'-bithiophene is well-known in the vapor phase[18] (anti-gauche conformation with a torsional angle of 146^0 and in solid phase[19] (anti-planar Conformation), fig 2.2 a and b.

14. V. Penalva, J. Hassan, L. Lavenot, C. Gozzi, M. Lemaire, *Tetrahedron Lett.*, **1998**, 39, 2559-2560.

15. V. Penalva, J. Hassan, L. Lavenot, C. Gozzi, M. Lemaire, *Tetrahedron.*, **1998**, 54, 13793-13804.

16. J. Hassan, L. Lavenot, C. Gozzi, M. Lemaire, *Tetrahedron Lett.*, **1999**, 40, 857-858.

17. G.T. Crisp, *Synth. Commun.*, **1989**, 19, 307.

18. A. Almenningen, O. Gastiansen and P. Suendsas, *Acta Chem. Scand.*, **12** (**1958**), 1671.

a. trans/anti-planar   b. Syn/cis-planar

Fig 2.2 (a) Trans/anti-planar conformation and (b) Syn/cis-planar
conformation of 2,2'-bithiophene.

NMR spectroscopy experiments show that both syn and anti conformations
co-exist at room temperature[20] with energy difference of ca. 0.2kcal/mol (0
0032a.u.). The main features of torsion energy profile of bithiophene have
been known for at least a decade[21-29]. A number of semi-empirical and ab
initio calculations of the torsion potential of bithiophene were carried out in the
late 1980s and the first half of the 1990s.

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20. P. Bucci, M. Longeri, C.A. Veracini and L. Lunazzi, *J. Am. Chem. Soc.* 96 (**1974**), 1305.

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29. R. Berardi, F. Spinozzi, C. Zannoni, *Liq, Cryst.*, **1994**, 16, 381.

Orti *et al*[21] have provided a useful summary of these early attempts, together with an extensive compilation and discussion of experimental studies (including gas-phase electron diffraction[25], high-resolution spectroscopy[26, 27] or NMR in liquid crystalline solvents[28, 29]). Visser[19] showed that in the solid phase, the molecules are planar and have *trans*-conformation with respect to the sulfur atoms. Whereas Almenningen *et al*[18] showed that, in the gas phase, the molecule is flexible with rotations of up to 80^0 possible. Bucci and co-workers[20] concluded that nematic phase spectra could not give very accurate results concerning conformational analysis because the symmetry of bithiophene results in insufficient observable parameters. The Electron Spin Resonance (ESR) and the theoretical studies of Cavalieri d'Oro[30] and, Dewan and Trinajstic[31] respectively confirm the planar structure of 2,2'-bithiophene, which plays a role in the potential use of these molecules in conducting materials as it facilitates charge transfer across the rings. Aleman[32] has recently applied molecular modeling computational methods in order to study conformational preferences of 2,2'-bithiophene. Their results concur with those of Almenningen *et al*[18]. They reported two minimum energy conformations, *anti*-gauche and *syn*-gauche conformations for which $\theta = 43^0$. The latter is less favored than the *anti*-gauche by ca 2.17KJ/mol.

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30. P. Cavalieri d' Oro, A. Mangini, G.F. Pdulli, P. Spagnolo, M. Tiecco, *Tetrahedron Lett.*, **1967**, 4179.

31. M.J.S. Dewar, N. Trinajstic, *J. Am. Chem. Soc.*, **1970**, 92, 1453.

32. C. Aleman, V.M. Domingo, L. Fajari, L. Julia, A. Karpfen, *J. Org. Chem.*, **1998**, 63, 1041.

2.4 Applications of bithiophene and its derivatives

Bithiophene serves as a starting material for polythiophene synthesis (PT)[33], it offers advantage over corresponding thiophenes in that polymerization proceeds at lower oxidation potentials and lower monomer concentration and gives polymers with higher yield and better regularity as shown by cyclic voltametry and ^{1}H NMR spectroscopy[34]. It can also be used as a model[35] for adjustments to the properties of conducting polymers. These substances (conducting polymers) have the properties of inorganic semiconductors combined with processibility, resistance to corrosion and light weight of organic polymers and are highly desirable in the world of electronics today. They (CPs) have applications ranging from bulk applications such as antistatic coatings to sophisticated molecular devices such as electronic components or selective or modified electrodes. Bithiophene (BT), which was the first thiophene derivative to be electropolymerized[36], remains an interesting precursor combining good film-forming properties with a moderate oxidation potential (1.30V/SCE).

CP's are synthesized by two main routes: - (A) Chemical synthesis: Since their first synthesis in 1986[37, 38], poly(3-alkylthiophene) (PATs) have attracted increasing interest owing to the significant improvement in solubility resulting from the grafting of flexible hydrocarbon chains onto the PT-backbone. This processability and the prospect of industrial applications have triggered a strong renewal of interest in chemical synthesis.

33. A. Berlin, G.A. Pagani, F. Sannicolo, *J. Chem Soc., Chem. Commun.*, **1986**, 1663.

34. B. Krische, M. Zagorska, J. Hellberg, *Synth. Met.*, **1993**, 58, 295-307.

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36. A.F. Diaz, *Chem. Scr.*, **1981**, 17, 142.

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38. K.Y. Jen, G.G. Miller, R.L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, **1986**, 1346.

Thus, polymerization of 3-alkylthiophenes using $FeCl_3$ as oxidant acquired a growing importance[39]. However, polymers produced by this method proved to have contained a significant amount of regiochemical defects. McCullough[40] *et al* have developed a synthesis based on the lithiation of 2-bromo-3-alkylthiophenes at the 5-position followed by metal exchange to obtain a Grignard compound which is then polymerized by cross coupling using $Ni(dppp)Cl_2$ as a catalyst. Rieke *et al* came with another approach that involved the regiospecific formation of an organozinc compound by the reaction of dibromo-3-alkylthiophenes with highly reactive zinc, and subsequent nickel-catalyzed polymerization[41].

(B) Electrochemical synthesis: Polythiophene derivatives (PTs) have become the focus of considerable interest due to a unique combination of original electronic properties, environmental stability, and structural versatility[35, 36, 42]. Two main routes are known (1) anodic and (2) cathodic.

Anodic route[35] is most widely used. With this method, no catalyst is needed; direct grafting of the doped conducting polymer onto the electrode surface; easy control of the film thickness by the deposition charge and the ability to perform the first *in situ* characterization of the growth process by electrochemical and/or spectroscopic techniques. The cathodic route[43] has the disadvantage that the polymer is produced in a neutral form, which lead to rapid passivation of the electrode and limited thickening of the film. However, the advantage of this method is that it is suitable for use on materials which are subject to anodic corrosion, such as small band gap semi-conductors[44].

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39. R. Sugimoto, S. Takeda, H.B. Gu, K. Yoshino, *Chem. Express.*, **1986**, 1, 635.

40. (a) R.D. McCullough, R.S. Lowe, *J. Chem, Chem Commun.*, **1992**, 1, 70.

    (b) R.D. McCullough, R.S. Lowe, M. Jayaraman, D.L. Anderson, *J. Org, Chem.*, **1993**, 58, 904.

    (c) K. Tamao, S. Odama, I. Nakasima, M. Kumada, A. Minato, K. Suzuki, *Tetrahedron.*, **1982**, 8, 3347.

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42. J.W.P. Lin, L.P. Dudek, *J. Polym. Sci.*, **1980**, 18, 2869.

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44. Z. Xu, G. Horowitz, F.J. Garnier, *J. Electroanal. Chem.*, **1988**, 246, 467.

Chapter 3

Carbene complexes of bithiophene

3.1 Introduction

3.1.1 Monocarbene complexes

It is since the synthesis of [W(CO)$_5$C(OMe)Ph] by Fischer and Maasböl[1] that the Fischer carbene complexes have received much attention. The structural data of the complexes [W(CO)$_5$C(OMe)Ph] and [Cr(CO)$_5$C(OMe)Ph][2] published, clearly showed the sp^2-character of the carbene carbon. Later studies[3] indicated the d(t$_{2g}$)-p π-interaction of the transition metal with the carbene carbon and that the important role of the heteroatom (X) lone-pair in p$_c$-p$_x$ π-bonding is to stabilize the "singlet" carbene carbon (figure3.1).
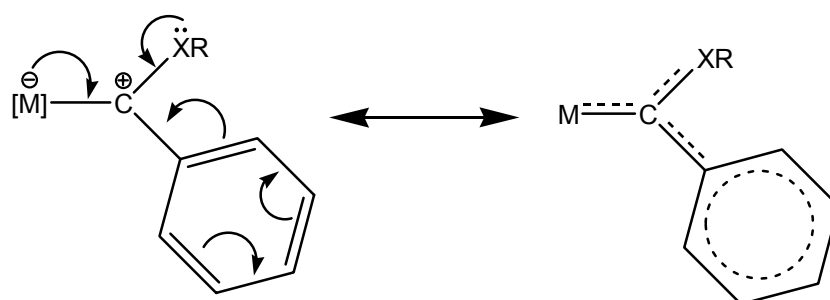
Fig 3.1 π-delocalization around carbene carbon in arene carbene complex.

When a phenyl or heteroarene substituent is incorporated into the π-delocalized network surrounding the carbene carbon, it may act as electron donating or electron withdrawing substituent. The aromatic groups act as electron-donating groups in complexes such as [W(CO)$_5$C(Ph)Ph], synthesized from [W(CO)$_5$C(OEt)Ph][4] whereas, the cabonyl ligands have

1.   E.O. Fischer, A. Maasböl, *Angew. Chem.*, 76, **1964**, 645.

2.   O.S. Mills, A.D. Redhouse, *J. Chem. Soc.* A, **1968**, 642.

3.   (a) E.O. Fischer, *Angew. Chem. Int. Ed.Engl.*, 13, **1974**, 651.

     (b) F.A. Cotton, C.M. Lukehart, *Prog. Inorg. Chem.*, 16, **1972**, 487.

some electrophilic influence in complexes such as [Cr(CO)$_5$C(OEt)Ph], [MnCp(CO)$_2$C(OMe)Ph] and [W(CO)$_5$C(OEt)Ph]. Further investigations by Fischer and co-workers[5] on whether carbene complexes can accommodate dinuclear metal carbonyl complexes have been determined by synthesizing the dinuclear Mn$_2$(CO)$_9$ carbene complex [Mn$_2$(CO)$_9$C(OEt)Ph]. Cardin *et al* [6] have synthesized the iron carbene complex [Fe(CO)$_4$C(OEt)Ph], since Fischer-type carbene complexes of iron containing carbonyl ligands are not readily accessible due to the preferred alkylation of the metal center rather than of the oxygen[7]. The synthesis of carbene complexes of iron by the addition of thiazolyl- or isothiazolyl-lithium to [FeCp(CO)$_2$Cl] was reported by Toerien and co-workers[8], followed by alkylation or protonation of products. Hence, in the thiazolylidene complexes, the N-atom is in an α-position with respect to the coordinated carbene carbon, while the isothiazolylidene complexes have the nucleophilic heteroatom situated γ to the coordinated carbon atom. Monocarbene complexes of chromium of the type [Cr(CO)$_5$C(OR)R'] where R' = 2-thienyl and 2-furyl were synthesized by Connor and Jones[9] in order to investigate the effect of different R-groups on the stability of the empty P$_z$-orbital on the carbene carbon. Aoki and co-workers[10] synthesized the tungsten thienyl carbene complex. A complex formed by C-H bond activation in an S-thiophene was synthesized by Angelici *et al*[11].

This was a cationic 2-thienylidene carbene complex of rhenium. The 2-thienyl complex [ReCp(NO)(PPh$_3$)(2-thienyl)] is produced from the deprotonation of

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4. C.P. Casey, *J. Am. Chem. Soc.*, 95, **1973**, 5833.

5. E.O. Fischer, E. Offhaus, *Chem. Ber.*, 102, **1969**, 2549.

6. D.J. Cardin, B. Centinkaya, M.F. Lappert, *Chem. Rev.*, 72, **1972**, 545.

7. (a) M.F. Semmelhack, R. Tamuar, *J. Am. Chem. Soc.*, 105, **1983**, 4099.

    (b) S. Lotz, J.L.M. Dillen, M.M. van Dyk, *J. Organomet. Chem.*, 371, **1989**, 371.

8. J.G. Toerien, M. Desmet, G.J. Kruger, H.G. Raubenheimer, *J. Organomet. Chem.*, 479, **1994**, C12.

9. J.A. Connor, E.M. Jones, *J. Chem. Soc.* A, **1971**, 1974.

10. S. Aoki, T. Fujimura, E. Nakamura, *J. Am. Chem. Soc.*, 114, **1992**, 2985.

11. M.J. Robertson, C.J. White, R.J. Angelici, *J. Am. Chem. Soc.*, 116, **1994**, 5190.

[ReCp(NO)(PPh$_3$)(thiophene)]$^+$ by a strong base and the reprotonation with triflic acid occurs at the 3-position to form a thielydene carbene product instead of generating the S-thiophene complex. Maiorana *et al*[12] recently reported the synthesis of monocarbene complexes of 2,2'-bithiophene (including **A**) in order to establish the influence of a "push-pull" electronic system set up along the carbene, by placing transition metals with multiple electron-withdrawing carbonyls on one side of a thiophene ring, and with the other thiophene ring as an electron donor. Measurements to evaluate the non-linear optical responses of these systems were done, and it was concluded that the preliminary evaluation looks promising but the work was not investigated further since. Heterocyclic carbenes produced from imidazolium and pyrazolium salts discovered by Wanzlick[13] and Öfele[14], form very stable complexes with certain transition metals. The complexes pentacarbonyl(1,3-dimethylimidazoline-2-ylidene)chromium(0) **I** and bis(1,3-diphenylimidazoline-2-ylidine)mercury(II)diperchlorate **II** were synthesized[13,14], Fig3.2. However, free carbenes could not be isolated. In 1991, Arduengo[15] discovered a way to produce isolable N-heterocyclic carbenes, in which the metal-carbon bond is more stable than in the Fischer and Schrock carbenes.
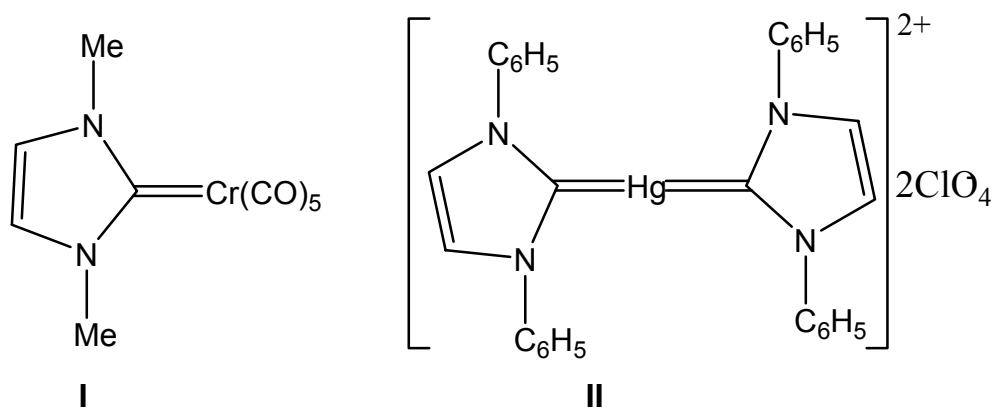
Fig 3.2 Early N-heterocyclic carbene complexes

12. S. Maiorana, A. Papagni, E. Licandro, A. Persoons, K. Clay, S. Houbrechts, W. Porzio, *Gazz. Chim. Ital.*, 479, **1994**, C.12.

13. H.W. Wanzlick, H.J. Schönherr, *Angew. Chem. Int. Ed. Engl.*, 7, **1968**, 141.

14. K. Öfele, *J. Organomet. Chem.*, 12, **1968**, 42.

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

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

3.1.2 Biscarbene complexes

Dinuclear biscarbene complexes were first synthesized from the reaction of dilithiated *o*- and *p*-phenylene and metal carbonyl complexes of transition metals like molybdenum, cobalt, manganese, tungsten, iron chromium etc. by Fischer[16]. Bisacylate anions are quenched with Meerwein-type oxonium salts[17]. Hoa Tran Huy and co-workers[18] continued this carbene study by including biphenylene ligand to produce dinuclear tungsten and chromium biscarbene complexes. The study of the X-ray diffraction of chromium complex proved that the molecule was centrosymmetric and that the rings are strictly coplanar[19], see fig.3.3.
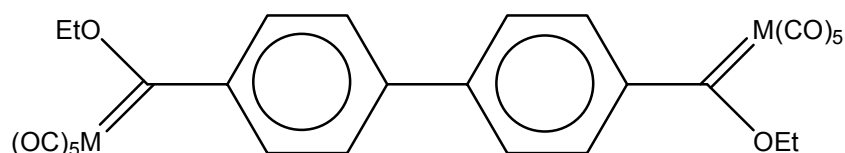
Fig 3.3 An example of phenylene complex.

Other bimetallic biscarbene complexes such as μ-9,10-anthracenediyl{bis(methoxycarbene)pentacarbonyltungsten}, figure 3.4, have been synthesized[20] in order to see if the functional group $W(CO)_5C(OMe)$ could withdraw electron density from dienes and thus assist in inverse Diels-Alder reactions.
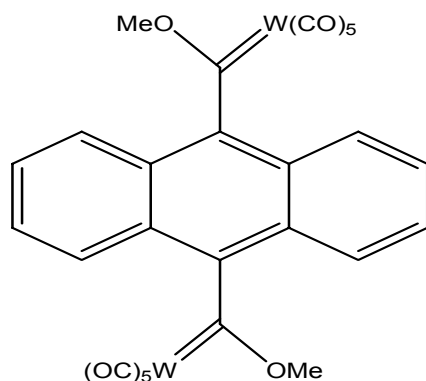
Fig 3.4 μ-9,10-anthracenediyl{bis(methoxycarbene)pentacarbonyltungsten}

Because these complexes have interesting properties, C_n carbon rich[21], aromatic[18] and heteroaromatic[22]carbene complexes triggered further investigation.

Recently in our laboratories, mono- and biscarbene complexes, together with their decomposition products have been synthesized and studied extensively using various spacers[22] (thiophene, 2,2-bithiophene, dithieno[3,2-b:2',3'-d]thiophene, terthienyl and 3,6-dimethylthieno[3,2-b]thiophene). All the systems are conjugated and they have delocalized moieties capable of distributing electron density from one end of the molecule to the other. Recent electrochemical studies have shown that metal-metal communication in thiophene bridged complexes is weak but greater in the corresponding phenylene analogues[23].

The importance of thiophene in electronic and non-linear optical properties prompted the investigation into the use of longer spacer groups metal centres. Maiorana *et al*[12] are the first to synthesize the first mixed metal biscarbene complex of bithiophene, but could not purify it due to unavailability of feasible purification method at that time.

16. L.S. Hegedus, "Transition Metals in the Synthesis of Complex Organic Molecules", p.151, University Science Books, Mill Valley California, 1994.

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21. H. Lang, *Angew. Chem. Int. Ed. Engl*., 34, **1994**, 547.

22. (a) Y.M. Terblans, H.M. Roos, S. Lotz, *J. Organomet. Chem.*, 566, **1998**, 133

    (b) M. Landman, H. Görls, S. Lotz, *J. Organomet. Chem.*, 617-618, **2001**, 285-287.

    (c) M. Landman, H. Görls, S. Lotz*, Eur. J. Iorg. Chem.*, **2001**, 233.

    (d) Y.M. Terblans, S. Lotz*, J. Chem, Soc.*, Dalton Trans,**1997**, 2177.

    (e) M. van Staden, MSc dissertation, Binuclear Bithiophene Biscarbene Complexes (unpublished results), University of Pretoria, 2001.

    (f) M.M. Moeng, MSc dissertation, Terthienyl Carbene Complexes (unpublished results), University of Pretoria, 2001.

3.2 Synthesis

The procedure for the synthesis of bimetallic bithiophene mixed biscarbene complexes **A**,**1**-**4** involves classical Fischer carbene synthesis. The general procedure for the synthesis is outlined in figure 3.5.

Thiophene is readily metallated by butyllithium in diethyl ether or THF. The dimetallation of thiophene is done in hexane rather in ether or THF solvents, since it was discovered that these solvents are attacked under forcing conditions. The experiences are quite different with bithiophene, as the dilithiation of bithiophene is achieved at very low temperatures (-10 or lower) in THF. The explanation to this observation could be due to increased stabilization of the negative charge over the two rings relative to that over one ring, causing the abstraction of the second proton being more difficult in the case of thiophene.

The biscarbene and the mixed biscarbene complexes of bithiophene were synthesized following the classical Fischer method, using THF as a solvent. Both protons 5- and 5'- were abstracted at low temperatures by n-butyllithium (n-BuLi) and lithium diisopropylamine (LDA) respectively. The second proton (5') is abstracted after the addition of the first metal carbonyl. The second metal is added , at which point nucleophilic attack by the dianion of the bithienylene takes place at the carbonyl carbons to form the dilithium diacylmetallated salt. Quenching is achieved by the addition of $Et_3O^+BF_4^-$ to afford the desired dinuclear mixed biscarbene complex. In addition to this five other products were produced as represented in figure 3.6.

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23. K.R. Justin Thomas, J.T. Lin, Yu S. Wen, *Organometallics*, 2000, 19, 1008.

Fig 3.5 General procedure for the synthesis.
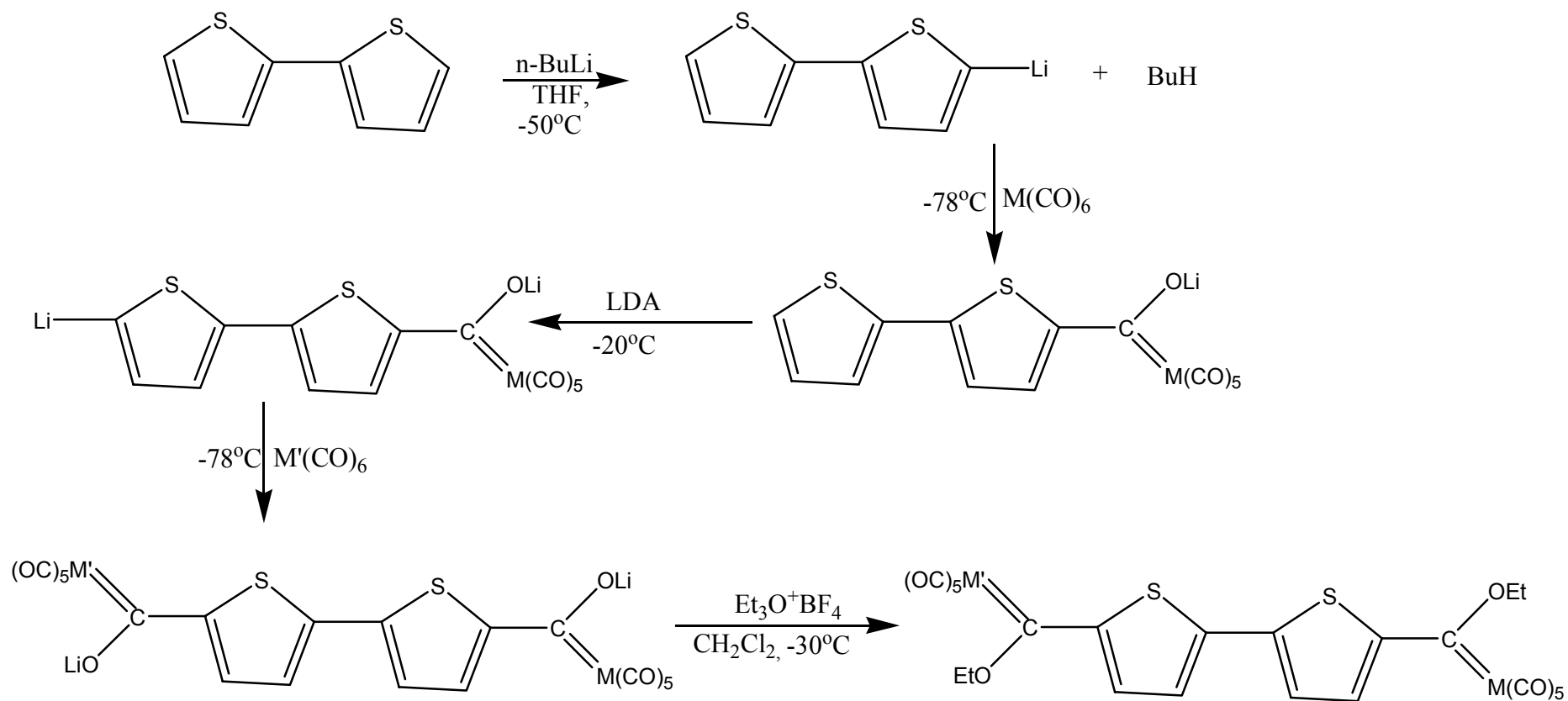
1: M and M' = Mn, Cr; **2**: M and M' = Mn, Mo;

3: M and M' = Mn, W; **A**: M and M' = Cr, W;

4: M and M' = Cr, Mo

M = Cr, Mo, W

+

M' = Cr, Mo, W,

+

5: M' = Mo, **6**: M' = W, **7**: M' = Cr

+

M' = Cr, W, Mo

+

M = Mn, Cr
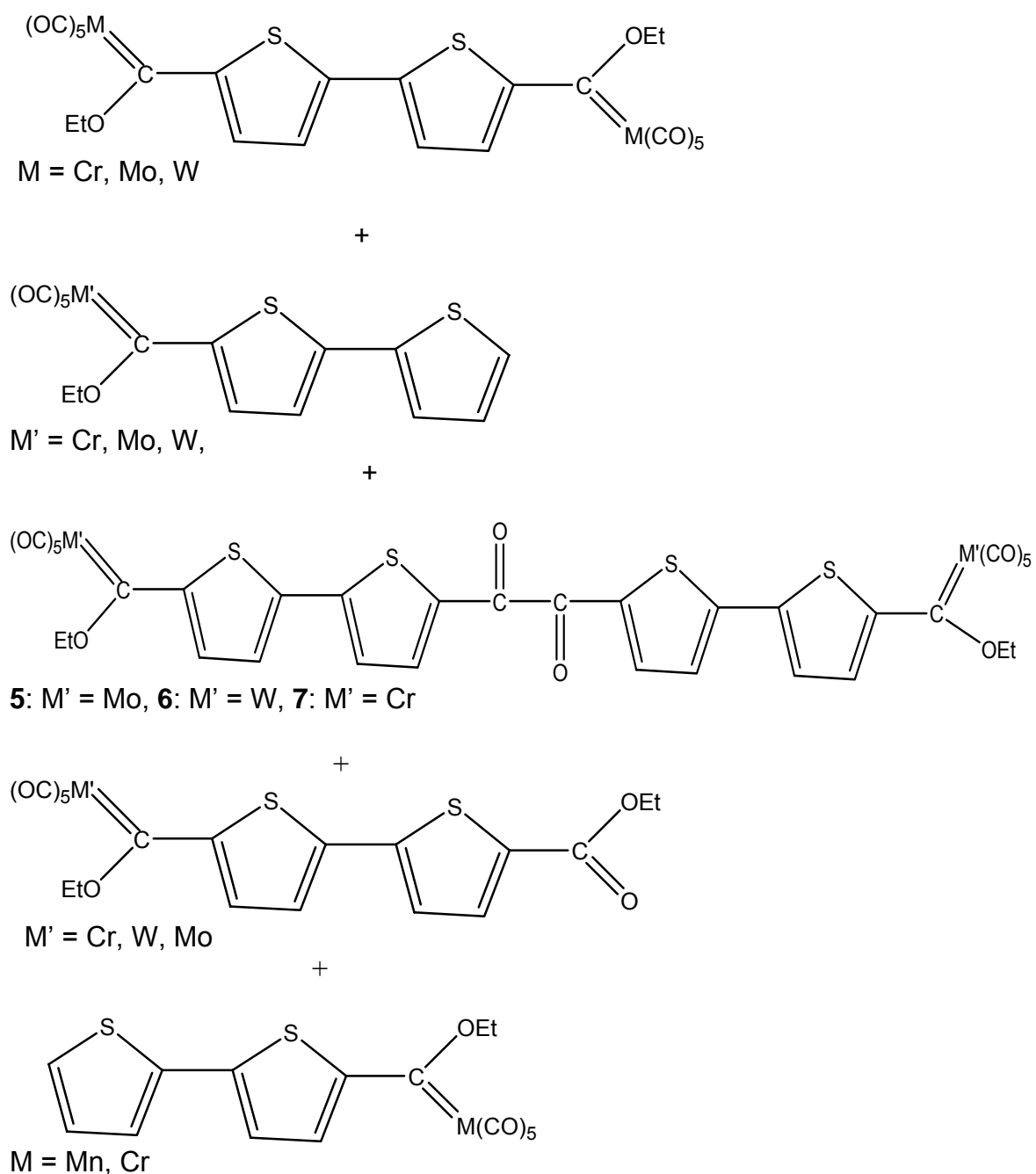
Fig 3.6 Additional products obtained in the synthesis of mixed biscarbene complexes

Although all complexes (**A**, **1-4**) were produced in the same way, complexes **1**, **2**, and **3** show very similar characteristics, they are all isolated together with five other products. For instance in the production of **1**, the first product was isolated as a red monocarbene complex of chromium, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}], the second was a deep purple biscarbene complex of chromium, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})Cr(CO)$_5$], the third purple band was identified as a chromium biscarbene complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-

$C_4H_2SC(OH)C(OEt)C_4H_2S-C_4H_2SC(OEt)\}Cr(CO)_5]$ (**7**), the fourth orange-red product was found to be the monocarbene complex, $[MeCpMn(CO)_2\{C(OEt)C_4H_3S\}]$, the fifth purple blue product was identified as a mixed biscarbene complex, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_2SC(OEt)\}MeCpMn(CO)_2]$ (**1**) and the sixth reddish blue compound was found to be a decomposition product, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_2SC(O)OEt\}]$. Bands 1, 2, 4, and 6 were characterized by NMR spectroscopy only and were found to be all known products as synthesized by van Staden *et al* [22(e)]. Some of these products were also observed in the production of complexes **A** and **4**, except that tungsten and molybdenum respectively were used instead of manganese. The third products will be discussed together later in this chapter. Complexes **1-3** seemed to have undergone similar reaction mode. Only four products could be observed in the synthesis of these products. In each case product one was a combination of two red monocarbene complexes eluted at the same time, the second was found to be a purple dinuclear mixed biscarbene complex and the third was identified as reddish-blue decomposition product.

3.3 Mixed biscarbene complexes

3.3.1 Spectroscopic characterization of dinuclear mixed biscarbene complexes **A**,**1**-**4**.

The complexes **A**, **1-4** were characterized using NMR-, infrared- and mass spectrosmetry. All molecular formulations were based on this data, as the crystal structures could not be obtained. All NMR spectra were recorded in deuterated chloroform, $CDCl_3$. The system of numbering used for the protons and carbon atoms of bithienylene fragment is shown in figure 3.7 and will be used consistently in the discussions, unless otherwise stated.
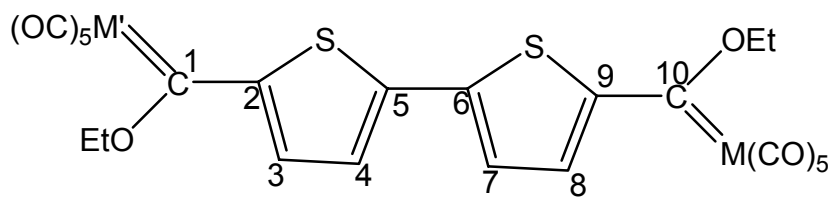
Fig 3.7 The labelling system used in the discussion of spectroscopic data of **A**, **1-4**

3.3.1.1 ^{1}H NMR spectroscopy

All NMR samples were prepared under the inert atmosphere of nitrogen and recorded in deuterated chloroform. The ^{1}H NMR data for the binuclear mixed biscarbene complexes **A**,**1-4** is summarized in table 3.

Table 3.1 ^{1}H NMR data of complexes A,1-4

Proton	Complexes Chemical shifts (δ, ppm) and coupling constants (J, Hz)									
	1		**2**		**3**		**A**		**4**	
	[M']=Cr, [M]=Mn		[M']=Mo, [M]=Mn		[M']=W, [M]=Mn		[M']=Cr, [M]=W		[M']=Cr, [M]=Mo	
	δ	J	δ	J	δ	J	δ	J	δ	J
H_3	8.15(s;br)	-	8.11(s;br)	-	8.07(s;br)	-	8.16 (d), 8.15(d)	4.4	8.16(d)	4.4
H_4	7.39(s;br)	-	7.38(s;br)	-	7.36(s;br)	-	7.47 (d)	4.1	7.47(d)	4.1
H_7	7.32(s;br)	-	7.34(s;br)	-	7.24(s;br)	-	7.45(d)	4.4	7.45(d)	4.4
H_8	7.77(s;br)	-	7.76(s;br)	-	7.76(s;br)	-	8.08 (d), 8.07 (d)	4.1	8.12(d)	4.4
O**CH₂**CH₃M'	5.15(s;br)	-	5.03(s;br)	-	4.97(s;br)	-	5.17 (q)	7.0	5.18(q)	7.1
OCH₂**CH₃**M'	1.67(s;br)	-	1.60(s;br)	-	1.67(t)	-	1.68 (t)	7.0	1.68(t)	6.6
O**CH₂**CH₃M	5.02(s;br)	-	5.03(s;br)	-	5.02(s;br)	-	4.98 (q)	7.1	5.06(q)	7.1
OCH₂**CH₃**M	1.59(s;br)	-	1.60(s;br)	-	1.59(s;br)	-	1.66 (t)	6.6	1.64(t)	6.6
C₅H₄CH₃	4.49(s;br) 4.37(s;br)	-	4.49(s;br) 4.38(s;br)	-	4.50(s;br) 4.38(s;br)	-	-	-	-	-
C₅H₄**CH₃**	1.79(s;br)		1.80(s;br)	-	1.80(s;br)	-	-	-	-	-

The data supports the molecular structures of the complexes. Wynberg[24] has estimated the proton spectrum of bithiophene to exist in the range 7.01-7.20 ppm, but could not elaborate further due to lack of good instruments. Kagan[25] has as well reported a proton spectrum of bithiophene to be a multiplet in the range 7.0-7.25ppm. A good proton spectrum was obtained by van Staden *et al* [22(e)] using modern techniques, where all the protons could be accounted for. However, these values are sightly different from those in the complexes. This is explained by the fact that the strongly electrophilic carbene moieties are draining an electron density from the double bonds in the rings. So, this causes the values of the protons to shift further downfield with respect to those in uncoordinated bithiophene ligand. Since there is competitive electron drainage, Figure 3.8, H_3 and H_8 were observed further downfield than H_4 and H_7 as they are highly deshielded.
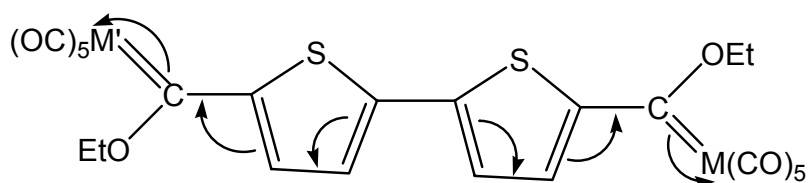
Fig 3.8 A competitive drainage of electron density from bithiophene rings by the biscarbene moieties.

24. H. Wynberg, A.J. Logothesis, *J. Am. Chem. Soc.*, 78, **1956**, 1958.
25. J. Kagan, S.K. Arora, *Tetrahedron Lett.*, 24, **1983**, 4043.

All these complexes have ethoxy groups of similar electronic environment of the methylene and methyl groups and therefore display the same properties. The signals for cyclopentadienyl ring attached to the metal in the manganese-containing complexes **1**, **2**, and **3** are observed at around 4.5 ppm and the methyl groups attached to the cyclopentadienyl ring are observed at around 1.78 ppm. Due to the paramagnetic nature of manganese, the coupling constants could not be calculated because of poor resolution of spectra.

All the signals (exceprt for methyls) were observed as broad singlets for **1**, **2**, and **3**. In complex **4 (**see figure 3.9), all the signals can easily be assigned as all the splitting patterns are as expected. H_3 and H_8 are observed as doublets further downfield at 8.16 and 8.12 ppm, respectively, than H_4 and H_7 which appears at 7.47 and 7.45 ppm, respectively, as doublets as well. This is of course due to the withdrawing of electron density from the biethienylene rings by the two different metal carbonyls and ethoxy groups. The two methyl groups are observed as triplets at 1.68 and 1.64 ppm, whereas the methylene (CH_2-) protons are observed as quartets at 5.18 and 5.06 ppm.

Although complex **A** was synthesized and characterized[12], we have obtained different interesting results with regard to it. Looking at the spectrum of this, one would think of possible isomers or mixture of two biscarbene complexes because protons, H_3 and H_8 each appear as two doublets at 8.16 and 8.15 ppm, and 8.08 and 8.07 ppm, respectively. Other signals, however are as expected, e.g. H_4 and H_7 appear as doublets at 7.47 and 7.45 ppm, respectively as in **4.** Methylene protons are quite clear with the same intensities as quartets at 5.17 and 4.98 ppm, with the methyl groups as triplets at 1.68 and 1.66 ppm (also with almost equal intensities).
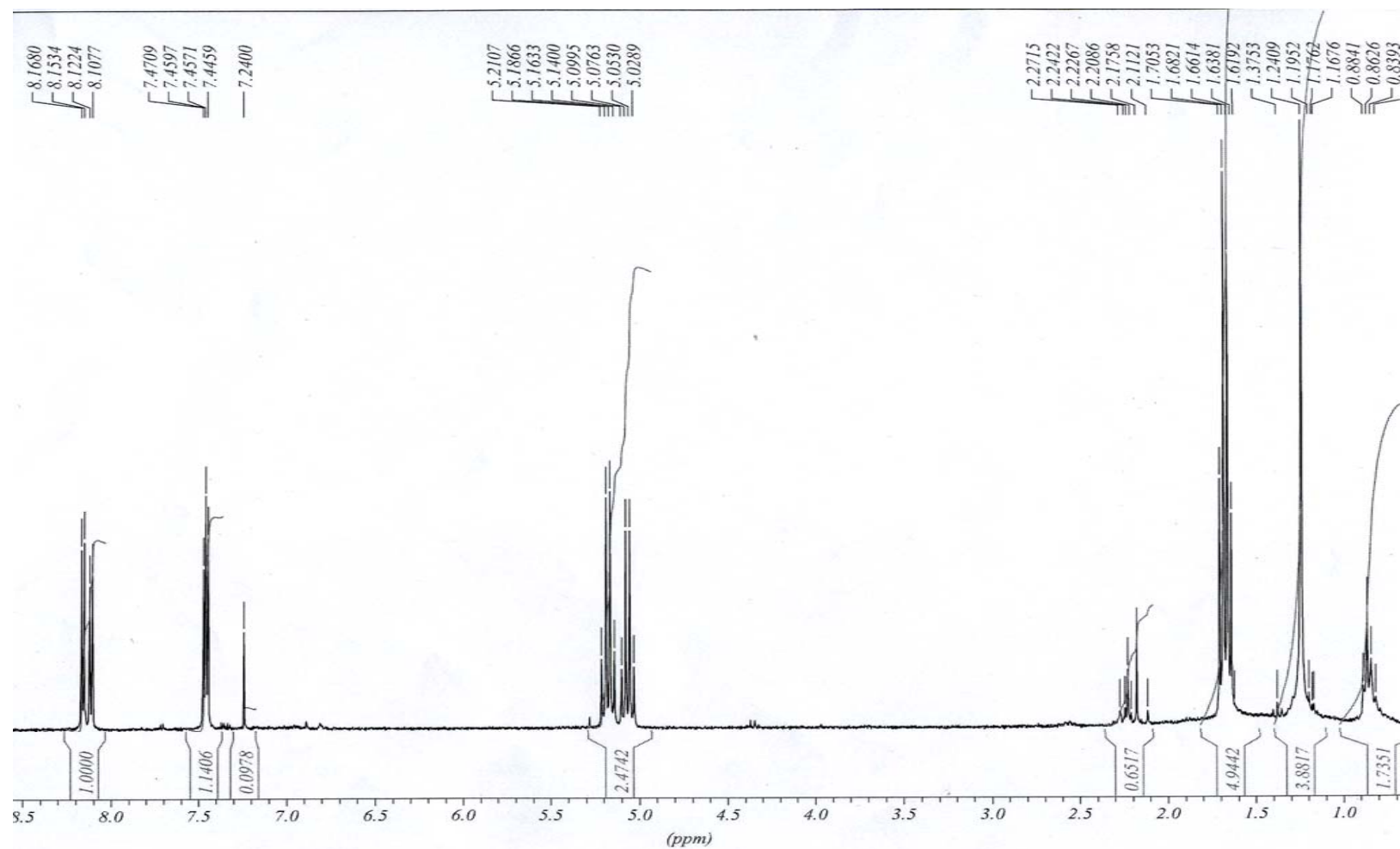
Fig 3.**9** The proton spectrum of **4**

1.2 ^{13}C NMR spectroscopy

Table 3.2 ^{13}C NMR data of complexes A,1-4

	Chemical shifts (δ, ppm)				
	1	**2**	**3**	**A**	**4**
	M'=Cr, M=Mn	M'=Mo, M=Mn	M'=W, M=Mn	M'=Cr, M=W	M'=Cr, M=Mo
Carbenes	C_1 = 316.5 C_{10} = 313.0	C_1 = 308.7 C_{10} = 316.5	C_1 = 287.3 C_{10} = 313.0	C_1 = 314.6 C_{10} = n.o	C_1 = 314.5 C_{10} = 305.1
C_2	155.5	155.6	n.o	154.5	154.5
C_3	142.2	143.0	143.1	142.5	144.4
C_4	126.7	126.1	126.1	127.3	127.1
C_5	142.2	142.9	n.o	141.6	141.7
C_6	146.2	147.2	147.2	145.4	145.4
C_7	128.2	126.5	126.4	127.1	127.0
C_8	136.4	136.3	136.4	141.7	144.3
C_9	n.o	n.o	n.o	n.o	154.4
O**CH$_2$**CH$_3$M'	75.9	77.6	78.3	76.1	76.7
OCH$_2$**CH$_3$**M'	15.3	15.1	15.0	15.2	15.2
O**CH$_2$**CH$_3$M	73.9	74.0	74.0	78.5	77.8
OCH$_2$**CH$_3$**M	13.6	15.3	15.3	14.9	15.1
M(**C**O)$_2$	230.6	230.6	230.6	-	-
M(**C**O)$_5$	-	-	-	202.5 (trans) 197.4 (cis)	212.3(trans) 206.0 (cis)
M'(**C**O)$_5$	223.3 (trans) 217.1 (cis)	212.8 (trans) 206.1 (cis)	202.5 (trans) 197.6 (cis)	223.4 (trans) 216.9 (cis)	223.3 (trans) 216.9 (cis)
C$_5$H$_4$CH$_3$	83.6, 82.3	83.8, 82.6	83.8, 82.7	-	-
C$_5$H$_4$**CH$_3$**	13.5	13.5	13.5	-	-

† n.o = not observed.

The chemical shifts of carbene carbon atoms in spectra for certain silicon complexes[26] and aminocarbene complexes[27], range from 400 – 200 ppm. The metal plays an important role in the chemical shift of the carbene carbon due to the interaction of the metal d-orbitals with the p_z-orbital of the carbene carbon.

The deshielding of the carbenium carbon on bonding causes a significant positive charge on carbene carbons in metal complexes. With a group of metals shielding of carbon nucleus bonded to the metal atom increases with an

increasing atomic number of the metal e.g. $W(CO)_6$ 197 ppm, $Mo(CO)_6$ 202 ppm and $Cr(CO)_6$ 206 ppm.

Carbene carbon atoms in complexes, **A** and **1-4** have chemical shifts of between 280 and 320 ppm. Almost all the signals were observed and were found to be somehow consistent in comparison with the literature. Signals that could not be accounted for are quaternary carbon atoms, especially C_9. As expected the observed signals for C_2 and C_9 are found further downfield due to a strong deshielding by the two carbene moieties and ethoxy groups on either side of the complexes. This is followed by C_3 and C_8, then C_4 and C_7 which have very close values and then C_5 and C_6. Interestingly, the carbonyl carbons of the manganese all have the same signals in all complexes containing manganese metal. They are all observed at 230.6 ppm. Methyl groups of the ethoxy moieties are also well characterized for all these complexes, all observed at around 15 ppm as in literature[28]. The *cis* and *trans* carbonyls for individual metal carbonyls as well are observed at expected regions as compared with the literature values[29]. Methyl groups of Cp ring all appear at 13.5 ppm, Cp ring signals all appear at around 82-83 ppm. Carbenes are observed furtherst downfield, as separate signals (figure 3.10).
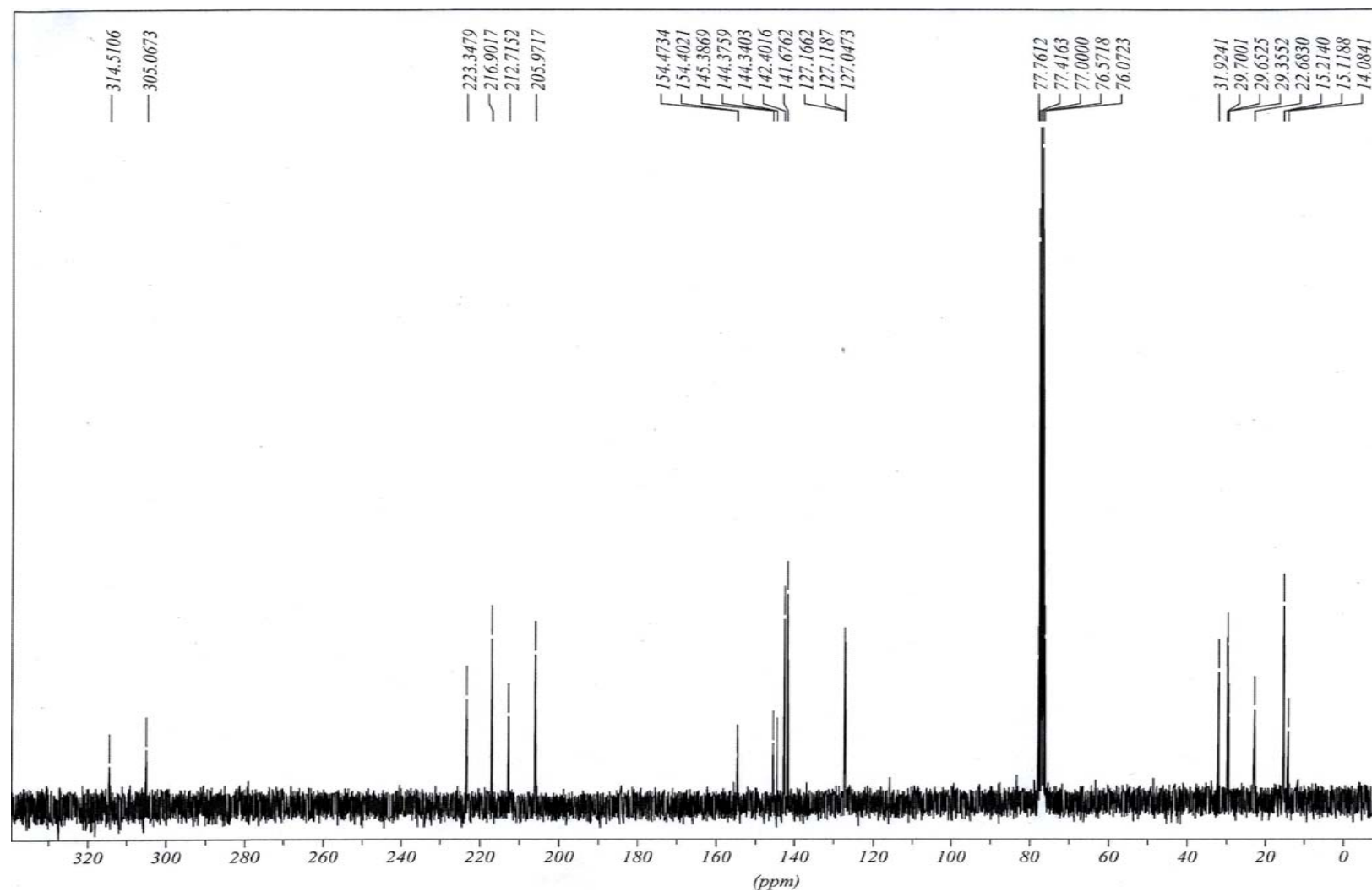
26. E.O. Fisher, T. Selmayr, F.R. Kreissl, U. Shubert, *Chem. Ber.*, 110, **1977**, 574.

27. B.A. Anderson, W.D. Wulff, A. Rahm, *J. Am. Chem. Soc.*, 115, **1993**, 4602.

28. J.A. Connor, E.M. Jones, E.W. Randall, E. Rosenberg, *J. Chem. Soc., Dalton Trans*., **1972,** 2419.

29. B.E. Mann, *Adv. Organomet. Chem.*, **1974,** 12, 135.

Fig 3.10 The ^{13}C NMR Spectrum of **4**

3.3.1.3 Infrared spectroscopy

The carbonyl stretching vibrational frequencies can be regarded as independent from other vibrations in the molecule when compared with the M-C stretching frequencies.

The stretching vibrational frequency for a free CO group is 2143 cm^{-1}, whereas it lies between 1850 and 2120 cm^{-1} for terminal carbonyl ligands[30].

The infrared spectroscopic data for the bimetallic bithienylene biscarbene complexes **A** and **1-4** are summarized in table 3.3.

Table 3.3 Infrared data of the bimetallic bithienylene complexes A and 1-4.

Stretching vibrational frequency (v_{co}, cm^{-1})									
Band	**1**		**2**		**3**		**A**		**4**	
M	Cr	Mn	Mo	Mn	W	Mn	Cr	W	Cr	Mo
$A_1^{(1)}$	2056	1939	2064	1942	2064	1936	2056	2066	2056	2066
B	1981	-	1980	-	1981	-	1981	1981	1980	1980
E	-	-	-	-	-	-	-	-	-	-
$A_1^{(2)}$	1939	1872	1942	1868	1936	1872	1967	1936	1944	1944

$A_1^{(2)}$ and E bands overlap in dichloromethane as solvent resulting in low values for E.

The wavenumbers of the carbonyl bands for **A** and **1-4** lie between 1870 and 2080 cm^{-1}, which clearly shows the presence of terminal carbonyl groups, only. The stretching frequencies and the pattern of the absoption bands shows that all the complexes have either $M(CO)_5$ or $M(CO)_2$ fragment. Complexes **1**, **2**, and **3** have $M(CO)_2$ fragment. Characteristic for the pentacarbonyl carbene complexes is the appearance of the $A_1^{(2)}$ band as a shoulder on the higher wavenumber side of the E band if hexane is the solvent.

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30. Ch.Elschenbroich, A Salzer "Organometallics, A Concise Introduction", VHC
    Verlagsgesellschaft mbH, Weinheim And VCH Publishers Inc, New York, 2nd. 1992.

Due to poor solubility of these complexes in hexane, the E and the $A_1^{(2)}$ bands overlap as dichloromethane was used as a solvent. Otherwise all the values are reasonably good compared with the literature values[22e].
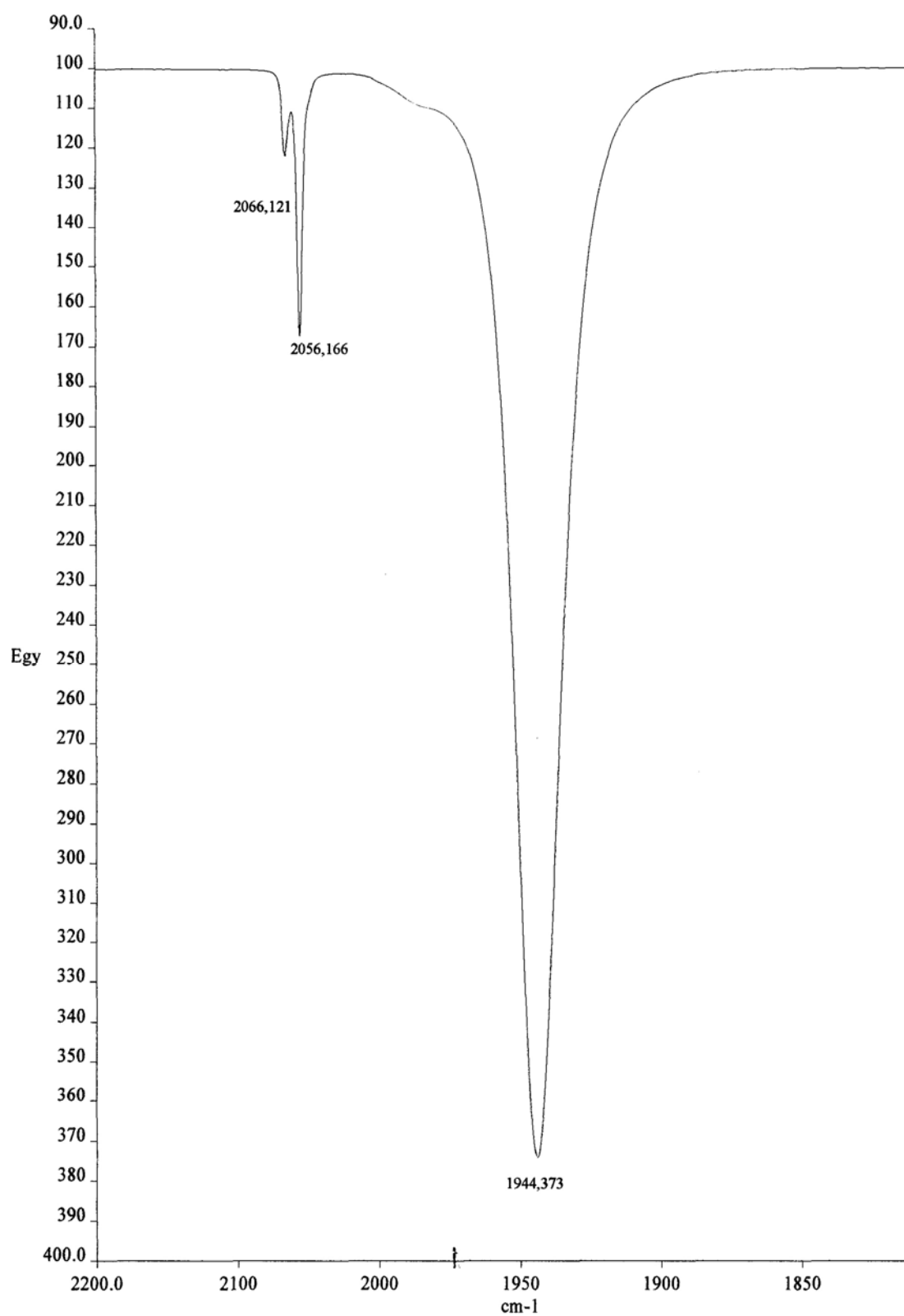
Fig 3.11 The Infrared spectrum of **4**.

3.3.1.4 Mass spectrometry.

Fragmentation data of **A**, **1** and **4** is summarized in table 3.4.

Table 3.4 Mass spectroscopy data of the bimetallic bithienylene complexes A and 1 and 4.

Fragment	A		1		4	
	m/z	I/%	*m/z*	I/%	*m/z*	I/%
M^+	n.o	n.o	659.7	25	713.6	22.0
M^+-CO	762.0	3.9	n.o	n.o	685.5	10
M^+-2CO	n.o	n.o	603.8	20	n.o	n.o
M^+-4CO	681.7	11.0	547.7	13.0	n.o	n.o
M^+-5CO	n.o	n.o	519.8	15.0	n.o	n.o
M^+-8CO	577.0	17.0	-	-	n.o	n.o
M^+-10CO	515.1	14.1	-	-	441.9	5.9
M^+-2OEt	594.9	18.8	n.o	n.o	n.o	n.o

† n.o = not observed

The spectra of **1** and **4** show a molecular ion peak, M^+, and a general fragmentation pattern in which the carbonyls are lost first, followed by the loss of the C(OEt) fragment. For **A**, a molecular ion peak could not be observed, but the fragmentation pattern is similar to the one in **1** and **4**.

3.3.2 Spectroscopic characterization of dinuclear biscarbene complexes **5-7**.

The complexes **5-7** were characterized using NMR-, infrared- and mass spectroscopy. All molecular formulations were based on this data, as crystal structures could not be obtained. The system of numbering used for the protons and carbon atoms of bithienylene fragment is shown in figure 3.12 and will be used consistently in the discussions, unless otherwise stated.
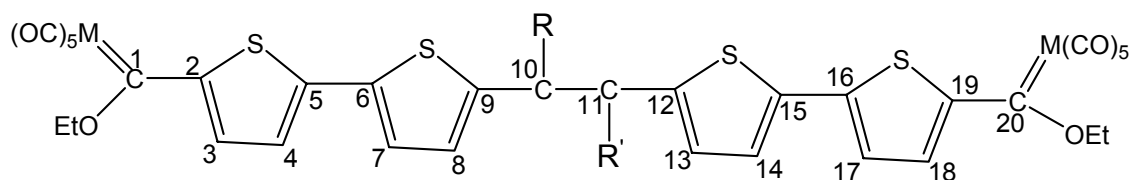
Fig 3.12 The labelling system used in the discussion of spectroscopic data of **5-7**

3.3.2.1 ^{1}H NMR spectroscopy

All NMR samples were prepared under the inert atmosphere of nitrogen and recorded in deuterated chloroform. The ^{1}H NMR data for the binuclear mixed biscarbene complexes **5-7** is summarized in table 3.5.

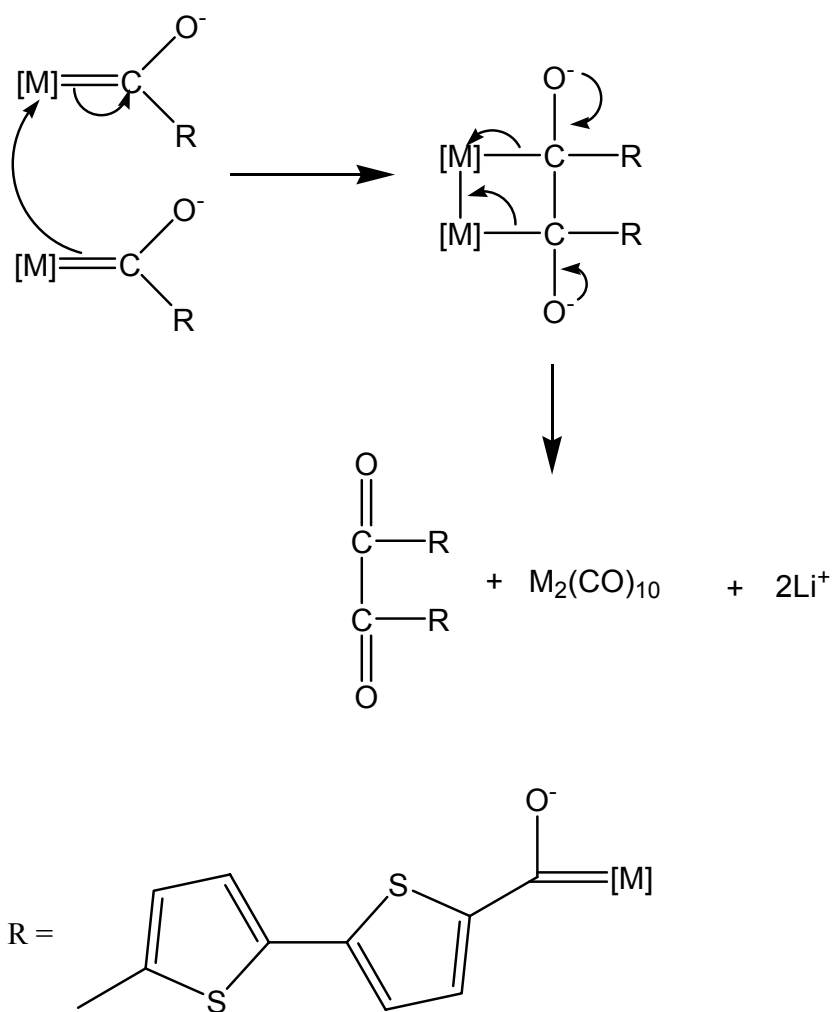**Table 3.5 ^{1}H NMR data of complexes 5-7**

| Assignment	Complexes					
	Chemical shifts, (δ, ppm) and coupling Constants, (J, Hz)					
	5 [M] = Mo		**6** [M] = W		**7** [M] = Cr	
Proton	δ	J_{H-H}	δ	J_{H-H}	δ	J_{H-H}
H_3	8.13 (d)	4.4	8.09 (d)	4.4	8.17 (d)	3.1
H_4	7.34 (d)	4.1	7.36 (d)	3.9	7.36 (d)	3.9
H_7	7.30 (d)	4.4	7.29 (d)	4.4	7.30 (d)	4.4
H_8	7.18 (d)	3.9	7.19 (d)	3.9	7.28 (d)	5.7
H_{13}	7.18 (d)	3.9	7.19 (d)	3.9	7.28 (d)	5.7
H_{14}	7.30 (d)	4.4	7.29 (d)	4.4	7.30 (d)	4.4
H_{17}	7.34 (d)	4.1	7.36 (d)	3.9	7.36 (d)	3.9
H_{18}	8.13 (d)	4.4	8.09 (d)	4.4	8.16 (d)	3.1
O**CH₂**CH₃M	5.04 (q)	7.0	4.96 (q)	7.0	5.14 (q)	7.0
					5.15 (q)	7.0
OCH₂**CH₃**M	1.65 (t)	7.1	1.65 (t)	7.1	1.67 (t)	7.0
O**CH₂**CH₃	-		-		2.82 (q)	7.8
OCH₂**CH₃**	-		-		1.32 (t)	7.5
OH	-		-		1.52 (s)	-

The data support the structures of the complexes. As observed earlier in this chapter that when the highly electrophilic carbene moieties are attached to the bithienylene rings, all signals are shifted further downfield. This was accounted for by the fact that electron density is drawn away from the rings either by the carbene ethoxy groups or by the metals themselves. In all the complexes **5-7**, H_3 and H_{18} signals are observed further downfield as doublets appearing from 8.09 – 8.17 ppm. The spectra of complexes **5** and **6** show very similar splitting pattern for all the proton signals. Due to their symmetry, protons, H_4 and H_{17}, H_7 and H_{14}, H_8 and H_{13}, all appear as doublets ranging from 7.18-7.36 ppm and almost similar coupling constants for complexes **5** and **6** are observed. Only four signals

were observed at the bithiophene region and this strongly suggest the coupling of the two bithiophene moieties. Complexes **5** and **6** are assumed to have been formed at the acylate stage by the coupling of the two biscarbene complexes, and the mechanism is proposed in figure 3.13. However, the proton spectrum of complex **7** shows that H_3 and H_{18} signals are in different environments for they both appear as doublets at 8.17 and 8.16 ppm, suggesting different connectivity between the two bithiophene moieties. The methylene protons for the latter complex also appear as two quartets at 5.14 and 5.15 ppm, as opposed to complexes **5** and **6** where the methylene protons appear at 5.04 and 4.96 ppm, respectively. Methyl protons appear as triplets for all the complexes **5**, **6**, and **7** at 1.65 ppm for **5** and **6** and 1.67 ppm for **7**. There appears to be another ethoxy group on complex **7** where the methyl protons are observed at 1.32ppm as triplets and methylenes as quartets at 2.82ppm. Complex **7** is assumed to have been formed from the reaction with water after alkylation step as suggested by the mechanism in figure 3.14.The OH group resulting from the reaction with water is assigned as singlet at 1.52 ppm.

Fig 3.13 The mechanism suggesting the formation of complexes **5** and **6**.
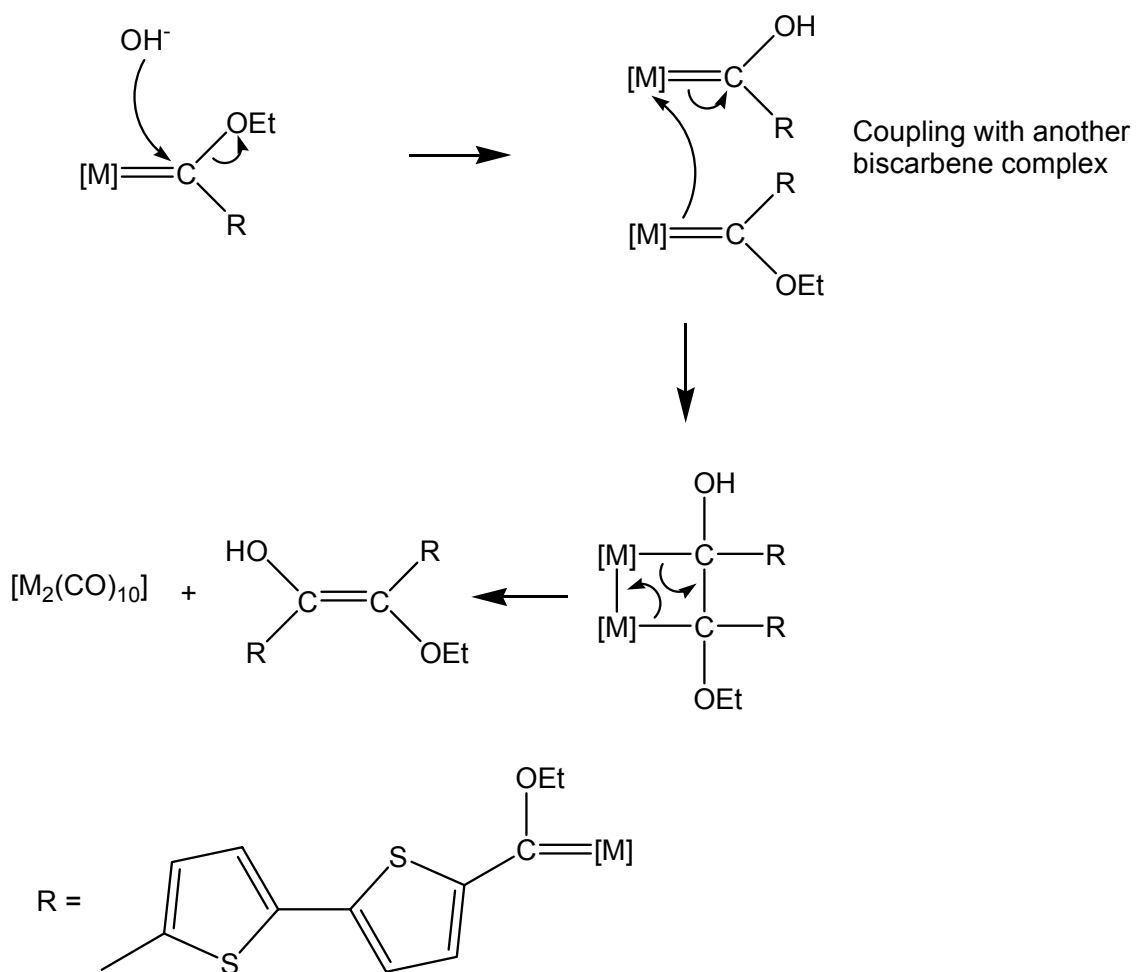
Fig 3.14 The mechanism suggesting the formation of complex **7**.

3.3.2.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data for the complexes **5-7** is shown in table 3.6.

Table 3.6 ^{13}C NMR data of complexes 5-7

Carbon	Chemical shifts (δ, ppm)		
	Complexes		
	5 [M] = Mo	**6** [M] = W	**7** [M] = Cr
Carbenes	C_1 & C_{20} = 327.4	C_1 & C_{20} = 287.1	C_1 & C_{20} = 312.0
C_2; C_{19}	n.o	n.o	n.o
C_3; C_{18}	143.4	143.5	143.0
C_4; C_{17}	127.4	127.4	128.9
C_5; C_{16}	n.o	n.o	146.2
C_6; C_{15}	n.o	n.o	142.6
C_7; C_{14}	125.7	125.7	128.9
C_8; C_{13}	n.o	n.o	134.6
C_9; C_{12}	n.o	n.o	n.o
C_{10}; C_{11}	n.o	n.o	n.o
O**CH$_2$**CH$_3$M	n.o	n.o	77.2
OCH$_2$**CH$_3$**M	15.1	18.1	15.2
M(**CO**)$_5$	trans = 212.3 cis = 206.2	trans = 197.5 cis = 206.2	trans = 223.3 cis = 217.2
O**CH$_2$**CH$_3$	29.7	28.7	22.9
OCH$_2$**CH$_3$**	-	-	14.7
2x CO	n.o	n.o	-

† n.o = not observed.

Due to poor yield of the complexes **5**, **6**, and **7**, not much could be picked up from the ^{13}C NMR spectra. All the carbene carbons could be observed at 327.4ppm for complexes **5** and **6** and 312ppm for complex **7** as they appear further downfield due to deshielding by highly electrophilic metal carbonyls and ethoxy groups. C_3; C_{18} and C_4; C_{17} are all secondary carbons and could be observed. All the quaternary carbons could not be observed. Methyl groups of the ethoxy moieties are well characterized for all these complexes, they are observed at around 15 ppm for **5** and **7** and 18.1 ppm for **6**, as in literature[28].

3.3.2.3 Infrared spectroscopy

The infrared data for the complexes **5-7** is shown in table 3.7.

Table 3.7 Infrared data of the bimetallic bithienylene complexes 5-7.

Band	Stretching vibrational frequency (v_{co}, cm^{-1})		
	5	**6**	**7**
M(**CO**)$_5$	Mo	W	Cr
A$_1^{(1)}$	2064	2063	2055
B	1980	1981	1981
E	-	-	-
A$_1^{(2)}$	1941	1936	1939
C=O	1605	1605	-

A$_1^{(2)}$ and E bands overlap in dichloromethane as solvent resulting in low values for A$_1^{(2)}$.

The wavenumbers of the carbonyl bands for **5-7** lie between 1870 and 2080 cm^{-1}, which clearly shows the presence of terminal carbonyl groups, only. The observed values matched the ones from the literature[30]. Only E bands could not be observed for they overlap with A$_1^{(2)}$ bands. The bands observed at 1605cm^{-1} confirms the presence of acyl groups as the connecting carbons between the two bithienylene moieties in **5** and **6**.

3.3.2.4 Mass spectroscopy data of the bimetallic bithienylene complexes **5** and **6**.

5: M$^+$ = 798.0 *m/z*; I/% = 15.0, M$^+$-2OEt = 702.2 *m/z*; I/% = 28.0, M$^+$-5CO = 558.8 *m/z*; I/% = 44.2, M$^+$-6CO = 527.1 *m/z*; I/% = 24.1.

6: M$^+$ = n.o, M$^+$-5CO = 659.3 *m/z*; I/% = 6.5, M$^+$-7CO = 595.1 *m/z*; I/% = 11.0, M$^+$-8CO = 577.1 *m/z*; I/% = 13.1.

The spectra of **1** and **4** show a molecular ion peak, M^+, and a general fragmentation pattern in which the carbonyls are lost first, followed by the loss of the C(OEt) fragment. For **A**, a molecular ion peak could not be observed, but the fragmentation pattern is similar to the one in **1** and **4**. Similar fragmentation pattern is also observed in van Staden *et al*[22e].

Fragments that are not listed could not be observed.

Chapter 4

Reactions of selected biscarbene complexes with alkynes

4.1 Introduction

Transition metal carbene complexes are recognized as valuable reagents in organic synthesis. Among them, heteroatom stabilized derivatives (Fischer carbene complexes) of group 6 have received increasing interest, particularly in the last two decades[1]. Although many studies highlight the formation of rings of various sizes, e.g. cyclopropane[2], cyclobutane[3], cyclopentane[4] and cycloheptane[5] rings, the most famous reaction of Fischer carbene complexes is by far the coupling of alkenyl (aryl) carbene complexes with alkynes leading to highly substituted phenols (naphthols), a process commonly known as the Dötz reaction or the benzannulation reaction (figure 4.1)[6].

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1. (a) W.D. Wulff, *In Comprehensive Organometallic Chemistry II*, E.W. Abel, F.G. A. Stone, G. Wilkinson, Eds,Pergamon: New York, **1995**, Vol 12, p 465.

   (b) M.P. Doyle, *In Comprehensive Organometallic Chemistry II*, E. W. Abel, F.G. A. Stone, G. Wilkinson, Eds,Pergamon: New York, **1995**, Vol 12, p 387.

   (c) K.H. Dötz, P. Tomuschat, *Chem. Soc. Rev.*, **1996**, 28, 187.

   (d) W.D. Wulff, *Organometallics.*, **1998**, 17, 3116.

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

2. M.S. Brookhart, W.D. Studebaker, *Chem Rev.*, **1987**, 87, 411.

3. L..S. Hegedus, *Tetrahedron.*, **1997,** 53, 4105.

4. J.W. Herndon, *Tetrahedron.*, **2000**, 56, 1257.

5. W.D. Wulff, D. C. Yang, C. K. Murray, *J. Am. Chem. Soc.*, **1988**, 110, 2653.

6. (a) K.H. Dötz, *Angew. Chem., Int. Ed. Engl*, **1975**, 14, 644.

   (b) K.H. Dötz, *Angew. Chem., Int. Ed. Engl*, **1984**, 23, 587.
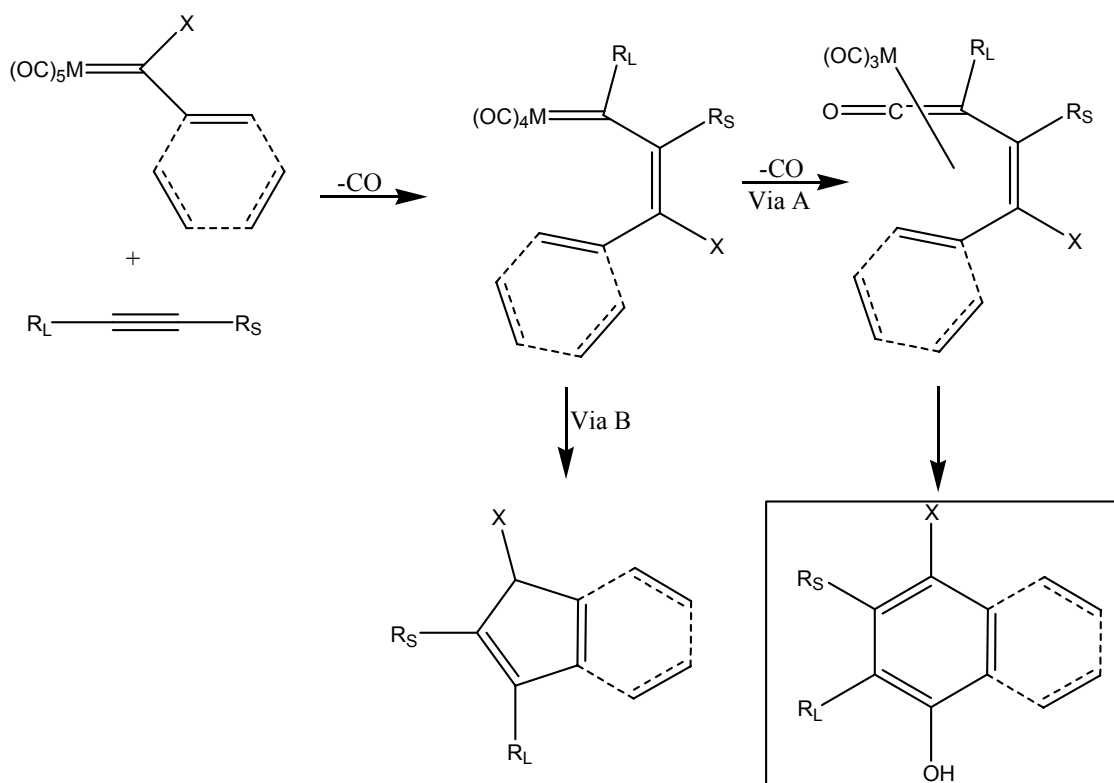
Fig 4.1 An example of a Dötz or the benzannulation reaction.

In the benzannulation reaction two ligands, carbene and CO, of the metal complex and the alkyne are assembled in a regioselective way forming the benzene ring (Fig. 4.1, *via* A). Thus the process represents a general access to benzenoids that has been amply used in synthesis of molecules of interest[7,8,9]. Furthermore, the participation of heteroatom–containing alkynes e.g. tert-butylphosphaacetylene alkynyl complexes[10, 11] are recent examples wherein

7. (a) K.H. Dötz, O. Neuss, M. Nieger, *Synlett.*, **1996**, 995.

   (b) S.R. Pulley, J.P. Carey, *J. Org. Chem.*, **1998**, 63, 5275.

8. K.H. Dötz, R. Ehlenz, *J. Eur. Chem.*, **1997**, 3, 1751.

9. H. Wang, W.D. Wulff, *J. Am. Chem. Soc.*, **1998**, 120, 10573.
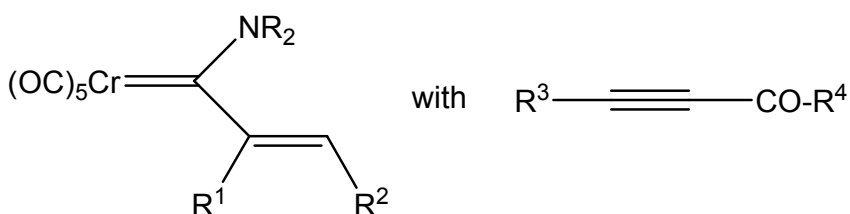
10. K.H. Dötz, A. Tiriliomis, K. Harms, *Tetrahedron.*, **1993**, 49, 5577.

11. (a) A. Rahm, W.D. Wulff, *J. Am. Chem. Soc.*, **1996**, 118, 1807.

   (b) J. W. Herndon, H. Wang, *J. Org. Chem.*, **1998**, 63, 4562.

notable variation have been brought about. The unsaturated bonds in conjunction with the carbene moiety can also act as Michael acceptors[12].

Dötz reactions are mostly thermally conducted, but photoirradiated[13] and drystate[14] methods have been used in order to improve efficiency. Although a large number of benzannulation reactions are known for unactivated alkynes, few reports deal with the use of electron-poor alkynes. Wulff and co-workers[15] have investigated the reaction of alkoxy carbene complexes of chromium with alkynyl ketones and alkynyl esters and found that variable mixtures of lactones (major products of alkynyl ketones) and phenols (major products of alkynyl esters) are formed from the chromium compound in figure 4.2.

$$(OC)_5Cr = \overset{\overset{\displaystyle NR_2}{|}}{\underset{\underset{\displaystyle R^1 \qquad R^2}{||}}{C}} \qquad with \qquad R^3 \text{———} CO\text{-}R^4$$

Fig 4.2 Components for annulation reactions.

The annulations of alkenyl complexes of this kind are more chemoselective, giving high selectivities for 4-methoxyphenol products, which have also been employed as key steps in natural products synthesis[16, 17].

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12. R. Aumann, H. Nienaber, *Adv. Organomet. Chem*., **1997**, 41, 163.

13. (a) B. Weyershausen, K.H. Dötz, *Eur. J. Org. Chem*., **1998**, 1739.

(b) Y.H. Choi, K.S. Rhee, K.S. Kim, G.C Shin, S.C. Shin., *Tetrahedron Lett*., **1995**, 36, 1871.

14. J.P.A. Harrity, W.J. Kerr, D. Middlemiss, *Tetrahedron*., **1993**, 49, 5565.

15. W.D. Wulff, A.M. Gilbert, R.P. Hsung, A. Rahm, *Am. J. Org. Chem*., **1995**, 60, 4566.

16. (a) I. Merino, L..S. Hegedus, *Organometallics*., **1995,** 14, 2522.

(b) D.B. Grotjahn, F.E.K. Kroll, T. Shäfer, K. Harms, K.H. Dötz, *Organometallics*., **1992,** 11, 298.

17. (a) K.H. Dötz, M. Popall, G. Müller, K. Ackerman, *J. Organomet. Chem*., **1990**, 383, 93.

(b) J. King, P. Quayle, J.F. Malone, *Tetrahedron Lett*., **1990**, 31, 5221.

4.2 Formation of π-Aromatic Systems.

4.2.1 Synthesis of naphthols by [3+2+1] cycloaddition.

Recently, benzannulation reactions were reported for coupling of conjugated 1,3-hexadien-5-ynes with Fischer carbene complexes[18]. If the central alkene of this system is replaced by a benzene ring, the benzannulation process fails[19]. The coupling of Fischer carbene complexes with conjugated dienyne systems where the central alkene is contained within a five-membered ring aromatic (i.e. Furan, thiophene and imidazole). And it was discovered that benzofuran rings are easily annulated onto furan, thiophene, and imidazole ring systems[20] in a reaction process involving the coupling of Fischer carbene complexes with either 2-alkenyl-3-alkynylheteroaromatic systems. Other reactions involve pentacarbonylchromium with substituted phenyl, furyl, thienyl, naphthyl and cyclopentylcarbene ligands reacting with various alkynes giving substituted phenanthrene, benzofuran, benzothiophene, naphthol and indene ligands π-coordinated to the tricarbonylchromium fragment[6a,21-23].

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18. J.W. Herndon, Y. Zhang, H. Wang, K. Wang, *Tetrahedron Lett*., **2000**, 41, 8687-8690.

19. (a) T.J. Jackson, J.W. Herndon, *Tetrahedron.*, **2001,** 57, 3859-3868.

    (b) L. Zhang, J.W. Herndon, O*rganometallics*., **2004,** 23, 1231-1235.

20. J.W. Herndon, Y. Zhang, D. Candelaria, *Tetrahedron Lett*., **2005**, 46, 2211-1235.

21. K.H. Dötz, R. Dietz, *Chem. Ber*., **1977**, 110, 1555.

22. K.H. Dötz, M. Mühlmeier, U. Schubert, O. Orama., *J. Organomet. Chem*., **1983**, 247, 187.

23. R. Dietz, K.H. Dötz, D. Neugebauer, *Nouveau. J. Chim*., **1978**, 2, 59.

Benzofurans are structural elements in antimicrobial[24], anti-inflamatory[25], and photobiologically active compounds[26]. Benzofurans can also serve as precursors to biologically important coumarin ring systems[27]. Traditionally these functional groups are most commonly prepared by annulation of a heterocyclic ring onto a pre-existing heterocyclic benzene ring[28]. A less common approach to these ring systems is the annulation of benzene rings onto a pre-existing heterocyclic rings. Annulation provides an established access to bi- and oligocyclic ring systems. Whereas this approach generally keeps the balance of functionalization present in the starting material, a metal-contemplated assembly of building blocks may introduce additional functional groups along the cyclization sequence. Thus, the benzannulation of arylcarbene ligands by an alkyne and carbon monoxide occurring at a $Cr(CO)_3$ template has received a considerable attention as a straightforward route to densely substituted oxygenated arenes[29]. The reaction is compatible with a series of functional groups both in the alkyne and in the carbene ligand; when extended from phenyl to bi- and tricyclic arylcarbene ligands an angular annulation pattern has been generally observed[30], even in cases where an *ortho*-substitution has been applied to force the annulation to linear.

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24. (a) L. Garuti, A. Ferranti, S. Burnelli, L. Varoli, G. Giovanninetti, P. Brigidi, A. Casolari, *Boll. Chim*., **1989**, 128, 136-140.

   (b) R. Royer, J.P. Buisson, L. Rene, R. Cavier, J. Lemoine, *Eur. J. Med. Chem*., **1978**, 13, 407- 409.

25. S. Boddupalli, G. Walkinshaw, B. Wang, U.S. Pat. Appl. Publ. US 2004063975, 2004, *Chem. Abstr*., **2004**, 140, 303515.

26. A. Chillin, P. Manzini, S. Caffieri, P. Rodighiero, A. Guiotto, *J. Heterocycl. Chem*., **2001**, 38, 431-434.

27. T.I. Harayama, K. Katsuno, Y. Nishita, M. Fujii, H. Abe, Y. Takeuchi, *Heterocycles*., **2001**, 54, 319-328.

28. W. Friedrichsen, In *Comprehensive Heterocyclic Chemistry II*; C.W. Bird, A.R. Katritzky, C.W. Rees, E.V.F. Scriven,; Eds; Elsevier: Amsterdam, **1996**, Vol 2, pp 351-393.

29. K.H. Dötz, P. Tomuschat, *Chem. Soc. Rev*., **1999**, 28, 187.

30. K.H. Dötz, R. Dietz, *Chem. Ber*., **1978**, 111, 2517.

So far, there is only a single early report of a linear benzannulation[31]; a more recent study confirmed the preference of angular over linear benzannulation[32] which, however, also may depend on the *ortho*-substitution pattern[33]. The formation of naphthols requires the presence of acceptor ligands in the carbene complex. [3+2+1]-Benzannulation of pentacarbonyl[2-dibenzofuryl(methoxycarbene)]chromium with various alkynes in *tert*-butyl methyl ether at 50 ^{0}C and subsequent silylation with *tert*-butyldimethylsilylchloride or tert-trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester led to benzo[*b*]naphtha[1,2-*d*]furan complexes (figure 4.3)
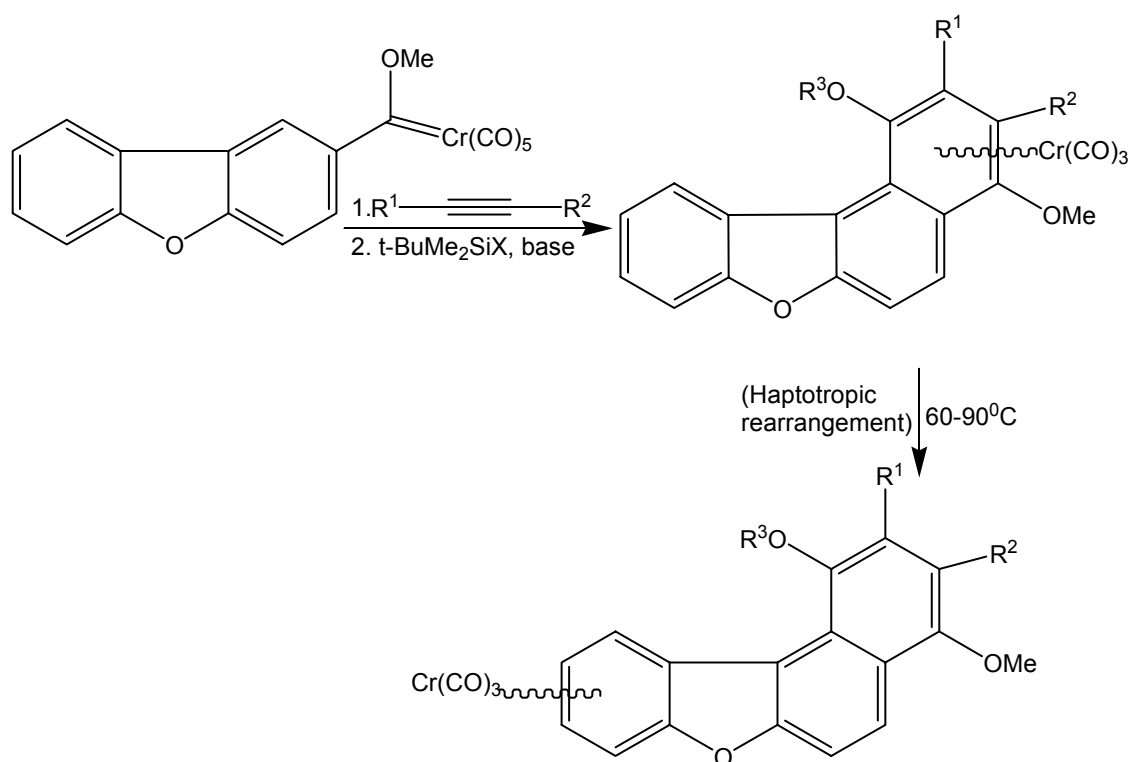
Fig 4.3 Synthesis of benzonaphthofurans via [3+2+1]-benzannulation and haptotropic rearrangement thereof.

31. K.H. Dötz, M. Popall, *Tetrahedron.*, **1985,** 41, 5797.
32. M.F. Semmelhack, S. Ho, D. Cohen, M. Steigerwald, M.C. Lee, G. Lee, A.M. Gilbert, W.D. Wulff, R.G. Ball, *J. Am. Chem. Soc.*, **1994**, 116, 7108.
33. K.H. Dötz, C. Stinner, *Tetrahedron*: Asymmetry 8., **1997**, 1751.

The formation of benzonaphthofurans provides the first example in which an arylcarbene ligand bearing two hydrogen atoms *ortho* to the ring carbon atom connected with the carbene carbon atom undergoes a linear benzannulation. The observation that in contrast to the angular annulation product, the linear annulation is accompanied by decomplexation, is remarkable and deserves further comment. The reason for this behaviour remains unknown currently. Organometallic fragments coordinated to fused arenes are capable of haptotropic migrations along the π-system. The previous kinetic studies on naphthohydroquinoid complexes have demonstrated that under thermodynamic control the metal fragment migrates to the less oxygenated ring along the same arene face[30, 34a-d]. The behaviour of benzonaphthofuran complexes was investigated. It was found that upon warming in di-n-butyl ether to 90[0]C they also underwent a haptotropic rearrangement leading to isomeric complexes[35] (figure 4.3).

4.2.2 Synthesis of heterocycles by [4+2] and [4+1] cycloadditions.

(1-Alkynyl)carbene complexes e.g. $(CO)_5M=C(OEt)C\equiv CPh$ (M = Cr, W) find more and more application in the synthesis of organic compounds[36]. It was shown only

34. (a) T.A. Albright, P. Hofmann, R. Hofmann, C.P. Lillya, P.A. Dobosh, *J. Am. Chem. Soc.*, **1983**, 105, 3396.

(b) Y.F. Opruneko, S.G. Malugina, Y.A. Ustynyuk, N.A. Ustynyuk, D.N. Kravtsov, *J. Organomet. Chem.*, **1988**, 338, 357.

(c) K.H. Dötz, C. Stinner, M. Nieger, *J. Chem. Soc. Chem. Commun.*, **1995**, 2535.

(d) Y. Oprunenko, A. Malyugina, P. Nesterengo, D. Mityuk, O. Malyshev., *J. Organomet. Chem.*, **2000**, 597, 42.

35. H.C. Jahr, M. Nieger, K.H. Dötz, *J. Organomet. Chem.*, **2002**, 641, 185-194.

recently that secondary enaminones[36,37], as well as tertiary cyclic amines undergo addition to C≡C bond of alkynyl carbene complexes, under exceedingly mild conditions to afford conjugated 6-amino-1-metalla-1,3,5-hexatrienes, which can be transformed into cyclopentadienes[37], 2,3-homopyrroles or pyran-2-ylidene complexes. The following shows [4+2] adducts from (1-alkynyl)carbene complex, where M = W or Cr.
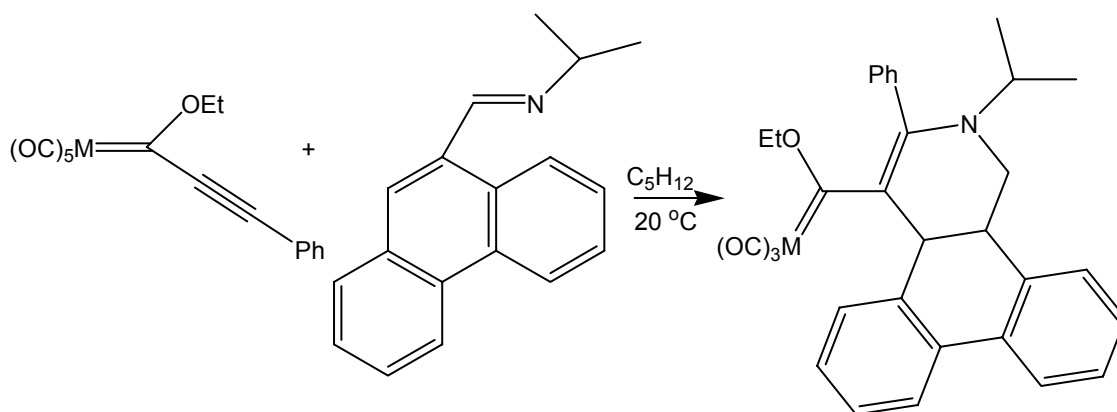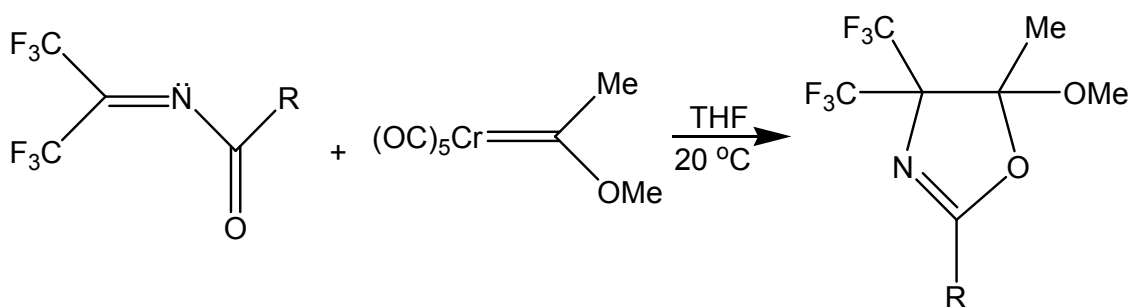
Fig 4.4 [4+2] adduct from (1-alkynyl)carbene complex

[4+1] cylcoaddition is mostly observed when alkylideneamides react with alkoxy- and aminocarbene ligands. The same is true for carbenes of isocyanides which yield dihydro-oxazoles as shown in figure 4.5.

36. R. Aumann, K. Roths, M. Grehl, *Synlett.*, **1993,** 669.

37. R. Aumann, M. Köβmeier, K. Roths, R. Fröhlich, *Synlett.*, **1994,** 1041.

Fig 4.5 [4+1] adduct from aminocarbenes.

4.2.3 Synthesis of indenes by [2+3] cycloaddition.

Cyclopentannulation appears to be the competing reaction that is most frequently encountered. The cyclopentadiene ring is formed *via* the coupling of the carbene ligand and the alkyne without transferring of the CO ligand[38]. Although several parameters (metal, solvent, concentration, carbene heteroatom, etc.) are known to play a role in the outcome of the reaction, the general trend for chromium complexes can be summarized as follows: (i) alkoxy-stabilized aryl carbene complxes lead to mixtures of benzannulation and cyclopentannulation products; (ii) alkoxy-stabilized alkenyl carbene complexes undergo with great preference the benzannulation reaction; (iii) amino-stabilized aryl carbene complexes yield substituted indenes via the cyclopentannulation reaction; (iv) the reaction between amino-stabilized alkenyl Fischer carbene complexes and 1-pentyne can be directed to the formation of phenols, whereas the reaction with internal alkynes fails[15,16]. Phenylcarbene ligands can be annulated by alkynes to give indenes. An example is of this kind of reaction was the reaction of the carbene complex, $(CO)_5CrC(OMe)Ph$, with tolane in a poorly coordinating solvent[39].

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

   (b) H. Schirmer, M. Deusch, F. Stein, T. Labahn, B. Knieriem, A. de Meire, *Angew. Chem., Int. Ed. Engl*, **1999**, 38, 1285.

39. H.C. Foley, L.M. Strubinger, T.S. Targos, G.L. Geoffroy, *J. Am. Chem. Soc.*, **1983**, 105, 3064.

The indene which is the formal [2+3] cycloadduct of the alkyne and the carbene ligand, is formed together with other products such as naphthohydroquinone derivatives and furan derivatives. This reaction is carried out selectively if the chromium compound is replaced by the analogous tungsten complex[40]. The formation of the indene skeleton could take place *via* insertion of the alkyne into the metal-carbene bond.

4.2.4 Synthesis of natural products.

In the past two decades metal carbenes have been developed as valuable reagents for stereoselective organic synthesis[41]. They have been applied in the synthesis of various natural products such as vitamins[41], antibiotics[43], amino acids and peptides[44]. Their impact on the elaboration of carbohydrates, however is still limited but increasing[45]. The first incorporation of a sugar moiety onto a carbene complex was based on the addition carbohydrates to isonitrile complexes of gold and platinum to form (glycosyl)aminocarbene and neomycine B complexes[46,47].

40. J.A. Connor, *Top. Curr. Chem.*, **1977**, 71, 71.

41. (a) J.W. Herndon, *Tetrahedron.*, **2000**, 56, 4893.

    (b) K.H. Dötz, *Angew. Chem.,* **1984**, 96, 573.

42. K.H. Dötz, I. Pruskil, *Chem. Ber.*, **1982**, 115, 1278.

43. M.F. Semmelhack, J.J. Bozell, T. Sato, W.D. Wulff, E. Spiess, A. Zask, *J. Am. Chem. Soc.*, **1982**, 104, 5850.

44. L.S. Hegedus, R. Imwinkelried, M. Alad-Sargent, D. Dvorak, Y. Satoh, *J. Am. Chem. Soc.*, **1990**, 112, 1109.

45. K.H. Dötz, C. Jäkel, W.C. Haase, *J. Organomet. Chem.*, **2001**, 119, 617-618.

46. T. Pill, K. Polborn, W. Beck, *Chem. Ber.*, **1990**, 123, 11.

47. S. Krawielitzki, W. Beck, *Chem. Ber.*, **1997**, 130, 1659.

A transition metal organometallic functionalization of the anomeric center has been known for glycosyl complexes of cobalt[48], iron[49] and manganese[50] which represent nucleophilic sugar synthons. It was only recently that electrophilic counterparts such as Fischer-type sugar metal carbenes have been synthesized[51]. They have been applied to diastereoselective ligand- and metal-centered cycloaddition such as Diels-Alder[52] and [3+2+1] benzannulation reactions[53] as well as to O- and *C*-glycosidation[54,55,56]. O-glycosides play a pivotal role in the chemistry and biology of carbohydrates. Their C-analogues[57] are inherently stable towards hydrolysis and gain increasing importance as carbohydrate mimics in antitumor, antibiotic, antiviral or antibacterial therapy[58]. Other naturally occurring products are arylnaphthalene ligands. Shikonin and alkanin, (figure 4.6) are naphthoquinone natural products. They differ with respect to stereochemistry of the OH⁻ group on the alkene chain. These possess extraordinary biological properties as well. It was shown by several research groups that they inhibit tumor cell growth[59].

48. A. Rosental, H.J. Koch, *Tetrahedron Lett.*, **1967**, 871.

49. G.L.. Trainor, B.E. Smart, *J. Org. Chem.*, **1983**, 48, 2447.

50. P. DeShong, G.A. Slough, V. Elango, G.L.. Trainor, *J. Am. Chem. Soc.*,
    1985, 107, 7788.

51. K.H. Dötz, W. Straub, R. Ehlenz, R. Meisel, K. Peseke, *Angew. Chem.*, **1995**, 107, 2023.
    Angew. Chem., Int. Ed. Engl, **1995**, 34, 1856.

52. B. Weyerhausen, M. Nieger, K.H. Dötz, *J. Org. Chem.*, **1999**, 64, 4206.

53. F. Otto, M. Nieger, K.H. Dötz, *J. Organomet. Chem.*, **2001**, 621, 77.

54. W.-C. Haase, M. Nieger, K.H. Dötz, *Chem. Eur. J.*, **1999**, 5, 2014.

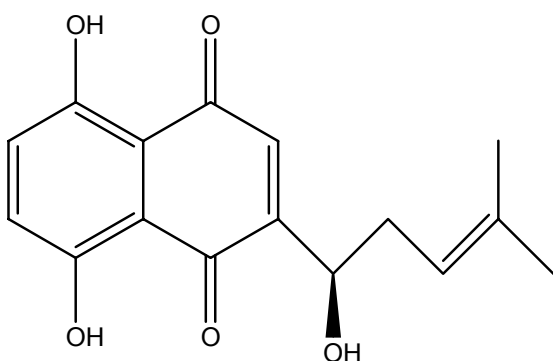55. K.H. Dötz, M. Klumpe, M. Nieger, *Chem. Eur. J.*, **1999**, 5, 691.

56. C. Jäkel, K.H. Dötz, *Tetrahedron.*, **2000**, 56, 2167.

57. F. Nicotra, *Top. Curr. Chem.*, **1997**, 187,1.

58. (a) U. Hacksell, G.D. Daves, *Prog. Med. Chem.*, **1985**, 22, 1.
    (b) K. Suzuki, *Pure. Appl. Chem.*, **1994**, 66, 2175.

59. B.Z. Ahn, K.U. Baik, G.R. Kweon, K. Lim, B.D. Hwang, *J. Med. Chem.*, **1995**, 38, 1044.

Fig 4.6 Shikonin

4.3 The aim of the study

The potential of bimetallic bithienylene biscarbene complexes to yield novel complexes in their reaction with alkynes was investigated. The reaction of monocarbene complexes with Ph-C≡C-Ph has already been extensively studied, so it was then decided that the reactions should be extended by using mixed biscarbene complexes. The objectives were to see whether different products would be formed based on the influence of two different carbene functionalities, and to establish which side of the complexes might be more reactive and whether both sides could be reactive to annulation reactions, respectively. The reactions of thiophene monocarbene complexes of chromium with diphenyl ethyne and pentyne have been briefly reported[21]. The products were obtained *via* a [3+2+1] cycloaddition process according to the Dötz reaction. On heating no migration of the $Cr(CO)_3$- fragment to the thienyl ring was observed. The possibility of preparing σ,π-bimetallic complexes was investigated as well as the preparation of π,π-bimetallic complexes. In chapter 3, we have discussed the synthesis of bimetallic mixed biscarbene complexes. Assuming that the Dötz reaction only occur on one carbene unit and that the expected π-coordination of $Cr(CO)_3$ is found, it will be a synthetic route to σ,π-bimetallic mixed biscarbene complexes, **x** (where the annulation occurs either at M or M' carbene unit), figure 4.7. While, if both carbene units are active and afford [3+2+1] cycloaddition

reaction products, and the Cr(CO)$_3$ fragment stays π-coordinated, bimetallic complexes, **y**, figure 4.7, with a novel π,π-bridging ligand could be isolated.

x

y
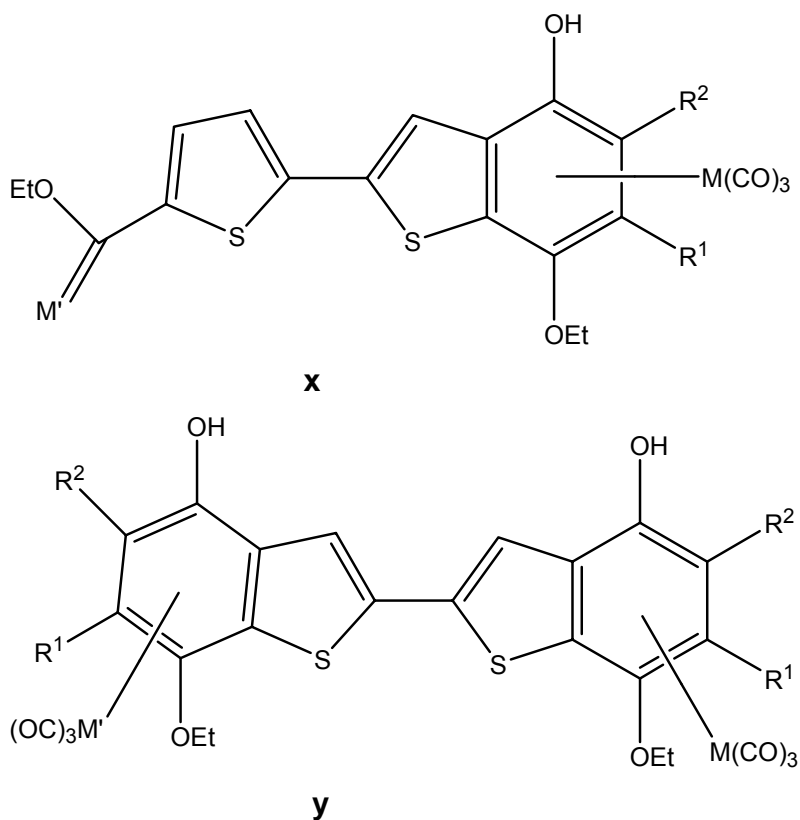
Fig 4.7 Possible σ,π- and π,π-monocarbene complexes.

With this background, a study of the reaction of the bimetallic mixed biscarbene complexes **A**, **1**, and **4** with hex-3-yne was worthwhile.
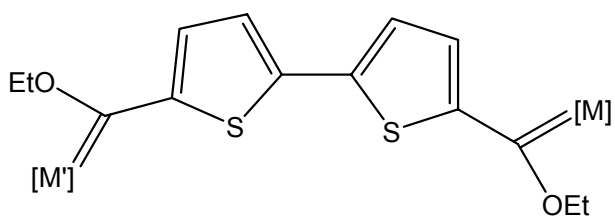
4.4 Reactions with Hex-3-yne

The chromium/manganese bithienylene mixed biscarbene complex **1** was dissolved in THF and two equivalents of hex-3-yne was added. The reaction mixture was refluxed for three hours and three compounds were separated through column chromatography. The first separated band was found to be the starting material (complex **1**). The second band was found to be a known

chromium decomposition product as in van Staden *et al*[60] the third product was found to be the Dötz product **9**. The complex **4** was treated the same way as complex **A** and similar behaviour was observed, three products were separated, the first one being the starting material, the second being the Dötz product **9** and the third being the known molybdenum decomposition product prepared by van Staden *et al*[60].

The formation of complexes **8**, **9** and **10** are accomplished by the same reaction route, see figure 4.8. The mechanism, based on the mechanism proposed for the Dötz reaction, involves (a) a primary CO elimination process to afford a vacant coordination site on the metal to which the alkyne is bonded in a π-fashion, thereby leading to the formation of a *cis*-alkynecarbene complex. In step (b) interligand C-C bond formation between the alkyne and the metal-carbene bond yields a metallacyclobutene, which is expected to be in equilibrium with its ring-opened product. The opening of the ring (c) affords a new biscarbene complex of higher reactivity. Carbonylation (d) of the alkenylcarbene carbon atom by an inserted CO ligand leads to a vinyl ketene system which is kept in s-cis conformation by a diene-like coordination to the metal, this should be regarded as the key intermediate in the reaction of carbonylcarbene complexes with alkynes. (e) cyclization of the vinyl ketene species, involving one of the bithiophene double bonds, affords a metal-coordinated bicyclic cyclohexadienone which after keto-enol tautomerization affords the benzothienyl products **8**, **9** and **10**.

60. M. van Staden, MSc dissertation, Binuclear Bithiophene Biscarbene Complexes (unpublished results), University of Pretoria, 2001.

1: [M] and [M'] = Mn(MeCp)(CO)$_2$, Cr(CO)$_5$; **4**: [M] and [M'] = Cr(CO)$_5$, W(CO)$_5$; **5**: [M] and [M'] = Cr(CO)$_5$, Mo(CO)$_5$ +

9: [M'] = Mn(MeCp)(CO)$_2$, **10**: [M'] = W(CO)$_5$, **11**: [M'] = Mo(CO)$_5$

+

[M'] = Cr(CO)$_5$

M and M' = W(CO)$_5$, Mo(CO)$_5$ or MnMeCp(CO)$_2$

Fig 4.8 The reaction scheme for the production of complexes **8**, **9** and **10**.

4.5 Spectroscopic characterization of the products afforded by the reactions with hex-3-yne.

The complexes **8-10** were characterized using NMR-, infrared- and mass spectrometry. All molecular formulations were based on this data, as the crystal structures could not be obtained. All NMR spectra were recorded in deuterated chloroform,$CDCl_3$. The system of numbering used for the protons and carbon atoms of bithienylene fragment is shown in figure 4.9 and will be used consistently in the discussions, unless otherwise stated.
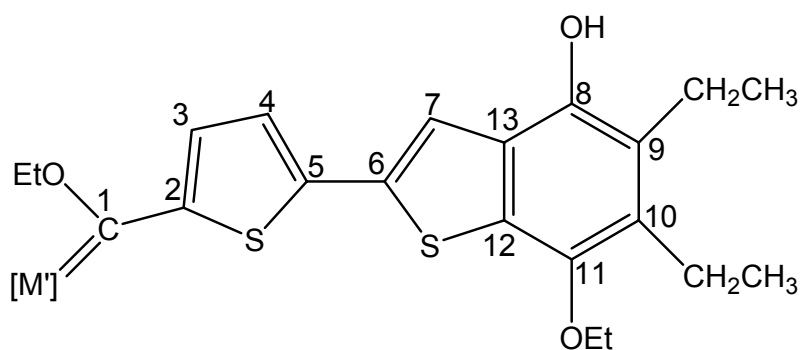
Fig 4.9 Numbering of Ring Carbon Atoms in **8-10**

4.5.1 ^{1}H NMR spectroscopy

All NMR samples were prepared under the inert atmosphere of nitrogen and recorded in deuterated chloroform. The ^{1}H NMR data for the Dötz products **8-10** are summarized in table 4.1.

Table 4.1 ^{1}H NMR data of complexes 8-10

Assignment	Complexes					
	Chemical shifts, (δ, ppm) and coupling Constants, (J, Hz)					
	8 [M] = Mn		**9** [M] = W		**10** [M] = Mo	
Proton	δ	J_{H-H}	δ	J_{H-H}	δ	J_{H-H}
H$_3$	7.78 (d)	3.6	8.15 (d)	4.4	8.14 (d)	4.1
H$_4$	7.69 (d)	3.4	7.68 (d)	5.2	7.69 (d)	5.2
H$_7$	7.59 (s)	-	7.34 (d)	4.1	7.34 (d)	4.4
OH	4.81 (s)	-	5.12 (s)	-	4.85 (s)	-
O**CH$_2$**CH$_3$ (Carbene)	5.03 (q)	6.5	5.05 (q)	7.0	5.05 (q)	7.0
OCH$_2$**CH$_3$** (Carbene)	1.59 (t)	7.0	1.66 (t)	7.2	1.65 (t)	7.0
O**CH$_2$**CH$_3$	4.10 (s;br)	-	4.12 (q)	7.2	4.11 (q)	7.0
OCH$_2$**CH$_3$**	1.46 (s;br)	-	1.48 (t)	7.0	1.49 (t)	7.0
2 x **CH$_2$**CH$_3$	2.61 (s;br) 2.74 (s;br)	-	2.77 (q) 2.73 (q)	7.5 7.8	2.76 (q) 2.73 (q)	7.5 7.8
2 x CH$_2$**CH$_3$**	1.23 (t) 1.18 (t)	7.0 7.0	1.21 (t) 1.19 (t)	7.5 7.5	1.22 (t) 1.20 (t)	7.5 7.5
MeCp	1.80 (s)	-				
Me**Cp**	4.49 (s) 4.36 (s)	-				

As observed earlier in chapter 3 that when the highly electrophilic carbene moieties are attached to the bithienylene rings, all signals are shifted further downfield. Looking at complex **8**, the H$_3$ is a doublet appearing at 7.78ppm and it is strongly deshielded, thus it appears further downfield. H$_3$ for the complexes **9** and **10** is almost the same, appearing at 8.14 and 8.15ppm, respectively,

suggesting that this proton is even more deshielded compared to that in complex **8**. The OH group for all the complexes is distinct, appearing as a singlet ranging from 4.81 – 5.12ppm. Manganese complexes always exhibit lower signals. All the signals are closer to the signals observed in complexes **9** and **10**, but are lower. The methylene protons of the carbene moiety appear at 5.03ppm for **9** as compared to 5.05 ppm for **9** and **10**. This is where all these signals were expected as in literature. The methylene protons are seen at 1.59 ppm for complex **8** and at 1.66 ppm and 1.65 ppm for complexes **9** and **10**. The methylenes of the ethoxy functionality at the benezene ring is consistent in all the complexes ranging from 4.10 – 4.12, ppm while their methyl groups are ranging from 1.46 -1.49 ppm. The CH_2- s of the ethyl groups are observed as broad singlets at 2.61 and 2.74 ppm for complex **8** and are observed as quartets at 2.77 and 2.73 ppm for both complexes **9** and **10**.The methyl groups are observed as triplets ranging from 1.21 – 1.22 ppm and 1.18 – 1.20 ppm in the complexes. The methyl group of the cyclopentadienyl ring in complex **8** was observed at 1.80 ppm, whereas the signals for the Cp ring hydrogens were observed as singlets at the expected of values of 4.49 and 4.36 ppm.

4.5.2 ^{13}C NMR spectroscopy

 The ^{13}C NMR data for the complexes **8-10** are shown in table 4.2.

Table 4.2 ^{13}C NMR data of complexes 8-10

Carbon	Chemical shifts (δ, ppm)		
	Complexes		
	8 [M] = Mn	**9** [M] = W	**10** [M] = Mo
Carbenes	287.9	312.3	304.7
C_2, C_3	n.o	155.9, 124.7	154.5, 124.8
C_4, C_5	n.o	126.0, 142.5	126.2, 142.4
C_6, C_7	n.o	147.0, 126.2	147.1, 126.3
C_8, C_9	n.o	129.3, 134.6	129.4, 134.3
C_{10}, C_{11}	n.o	133.9, n.o	133.8, 161.8
C_{12}, C_{13}	n.o	145, 148.1	145.2, 148.1
O**CH$_2$**CH$_3$M	82.3	77.4	77.6
OCH$_2$**CH$_3$**M	13.5	16.0	16.0
O**CH$_2$**CH$_3$	61.6	61.6	61.6
OCH$_2$**CH$_3$**	14.3	15.6	15.1
M(**CO**)$_5$	M(**CO**)$_2$ = 230.6	202.5 (trans) 197.5 (cis)	212.8 (trans) 206.1 (cis)
2 x **CH$_2$**CH$_3$	134.3	134.3	134.3
2 x CH$_2$**CH$_3$**	15.3	15.2	15.2
MeCp	13.5		
Me**Cp**	83.9 82.7	-	-

† n.o = not observed.

Some signals could be observed in an hour scan, but after a scan of about two hours, they disappear. This is ascribed to the paramagnetic nature of Mn complexes and poor stability at those conditions. Due to unavailability of lower temperature apparatus and poor yield of the complexes, the ^{13}C data is limited. The methylene carbon of the carbene ethoxy group of **8** could be observed at 82.3 ppm and the methyl at 13.5ppm. The CH$_2$- of the ethoxy group was not

observed, but the methyl was observed at 14.3 ppm. The methyl group of the cyclopentadienyl ring in complex **8** was observed at 13.5 ppm and the Cps at 83.9 and 82.3 ppm. All the signals could be observed for complexes **9** and **10**. The carbenes are observed at 312.3 and 3.4.7 ppm respectively. The carbons C_2 – C_{13} could be identified and assigned as in table 4.2. These complexes exhibits similar spectra thus made it easier to assign all the carbons. The metal carbonyls were clearly seen at 202.5 (*trans*) and 197.5 (*cis*), and 212.8 (*trans*) and 206.1 (*cis*), respectively. Methyls of the ethoxy groups were observed at 15.2 ppm for both complexes **9** and **10**. The CH_2- appears at 134.3 ppm. The methyls of the carbene ethoxy groups appear at 16.0 ppm, whereas the CH_2- appears at 61.6 ppm. The CH_2- of the carbene ethoxy groups appear at 77.4 and 77.6 ppm respectively.

4.5.3 Infrared spectroscopy

The infrared data for the complexes **8-10** is shown in table 4.3.

Table 4.3 Infrared data of the complexes 8-10.

Band	Stretching vibrational frequency (v_{co}, cm^{-1})		
	8	**9**	**10**
M(**C**O)$_5$	MnMeCp(CO)$_2$	W	Mo
$A_1^{(1)}$	1933	2064	2064
	-	2056	2056
B		1981	1980
E	-	-	1980
$A_1^{(2)}$	1869	1942	1943

$A_1^{(2)}$ and E bands overlap in dichloromethane as solvent resulting in low values for E.

The frequencies of the carbonyl bands for **8-10** lie between 1870 and 2080 cm^{-1}, which clearly shows the presence of terminal carbonyl groups, only. The

observed values matched the ones from the literature. All the values for the metal carbonyls are comparable to the literature ones.

4.5.4 Mass spectroscopy data of the complexes 8 and 10.

Table 4.4 Mass spectroscopy data of complexes 8 and 10.

Fragment	8		10	
	m/z	*I/%*	*m/z*	*I/%*
M^+	n.o	n.o	n.o	n.o
M^+-CO	521.9	22.9	n.o	n.o
M^+-2CO	491.9	26.5	542.0	25.0
M^+-3CO	-	-	514.0	52.2
M^+-4CO	-	-	486.0	51.9
M^+-5CO	-	-	468.0	79.0
M^+-OEt	599.9	25.0	n.o	n.o
M^+-2OEt	656.8	13.0	598.1	20.0
M^+-OH	483.9	44.0	440.0	89.1

† n.o = not observed

M^+ could not be observed for these two complexes, **8** and **10**. But, the fragmentation pattern also starts with the loss of COEt fragment followed by the loss of carbonyls. This kind of behavior was also observed for thiophene and its derivatives[61].

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61. S. Lotz*, Personal Communication*, 2000.

Chapter 5

Conclusion

In previous studies, the synthesis of mono and biscarbene complexes using spacer units such as thiophene, thienothiophene, terthienyl with metal carbonyls such as $MnMeCp(CO)_3$. $Mo(CO)_6$, $W(CO)_6$ and $Cr(CO)_6$ have been reported. Their reactivity and stability have been studied and reported.

In this study, several mixed biscarbene complexes of bithiophene have been successfully synthesized using metal carbonyls $MnMeCp(CO)_3$, $Mo(CO)_6$, $W(CO)_6$ and $Cr(CO)_6$ and the novel complexes characterized using NMR, IR and some with MS. Three other new compounds were produced with C-C coupling between the two bithiophene molecules. These were also characterized. Kinetic studies could not be performed for these complexes because at elevated temperatures they decompose rapidly. Thus the comment about their stability is based on the amount of the decomposition products formed, which is very little in this regard. In future we intend to study the reactivity of these complexes and the possibility that they can be applied in organic syntheses. We predict it will be very interesting to study bithiophene mixed biscarbene complexes with respect to the conduction of charge in molecular wires, since the studies in this regard have not been performed.

Furthermore we have investigated the reactivity of bithiophene mixed biscarbene complexes with hexyne. The results were the formation of benzannulation or Dötz products. These were fully characterized. From this, we have been able to conclude that the most preferred site for the benzannulation reaction is where a chromium moiety. No reaction could be observed from the reaction involving complexes not having chromium moieties under the reaction conditions we have reported in chapter four.

Chapter 6

Experimental

6.1 Standard operating procedures

All the solvents (hexane, dichloromethane, benzene and tetrahydrofuran) were dried under the inert atmosphere of nitrogen gas following the conventional laboratory methods[1], prior to use . Hexane and benzene were dried and refluxed from sodium metal. Dichloromethane was dried and refluxed from diphosphorus pentoxide. Tetrahydrofuran was dried and refluxed from sodium benzophenone ketyl. Chromatographic separations and purification were performed using nitrogen gas saturated kieselgel (0.063-0.200mm). Polarity of eluting agent was increased gradually, with increasing polarity of compounds which were being separated (starting with 100% hexane and ending with1:1, hexane: dichloromethane). The columns (where necessary) were cooled by circulating cold isopropanol (-30 ^{0}C) through the column jacket. All compounds were synthesised and characterized under an inert atmosphere of argon or nitrogen gas, using standard Schlenk tube methods[2].

6.2 Characterization of compounds

6.2.1 Infrared spectroscopy

Infrared spectra were recorded on a BOMEM Michelson – 100 FT spectrometer. All spectra were recorded in solution with either hexane or dichloromethane.

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1. D.D. Perrin, W.L.F. Armarego, D.R. Perin in *Purification of Laboratory Chemicals*, 2nd edition, Pergamon, New York, **1980**.
2. D.F. Shriver, M.A. Drezdon in *The manipulation of air sensitive compounds*, 2nd edition, John Wiley and Sons, New York, **1986**.

6.2.2 Nuclear magnetic resonance spectrometry

Nuclear magnetic resonance spectra were recorded on a Brüker AC-300 spectrometer. ^{13}C NMR and ^{1}H NMR spectra were recorded at 75.469 MHz and 300.135 MHz, respectively. The signal of the deuterated solvent was used as a reference, for example, for ^{13}C NMR the signal for $CDCl_3$ is observed at 77.00 ppm and for ^{1}H NMR the signal for $CDCl_3$ is observed at 7.24 ppm.

6.2.3 Mass spectrometry

Mass spectra were measured by Mr. T vd Merwe at WITS University on a VG 70 SEQ instrument, using a FAB ionization technique.

6.3 Synthesis of organometallic compounds

6.3.1 Preparation of starting compounds

The following compounds were prepared according to known literature methods: Triethyloxonium tetrafluoroborate[3] and Lithium diisopropylamine[4].

6.3.2 Lithiation of Bithiophene

Dilithiation of bithiophene was involved as the first step in each synthesis. 1.66g (10mmol) of bithiophene was weighed and dissolved in 50ml of tetrahydrofuran (THF) at -50 ^{0}C under argon gas. The colourless solution was continuously stirred, followed by the dropwise addition of n-BuLi (6.25ml, 10mmol, 1.6M in hexane). The solution was stirred at this temperature for 30 minutes, during

which time it changed colour from colourless to milky brown. This was quickly followed by the addition of the chosen transition metal carbonyl.

6.3.3 The synthesis of bithiophene manganese-chromium mixed biscarbene complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}MnMeCp(CO)$_2$] (**1**)

A lithiated bithiophene solution was cooled further to -78 ^{o}C while stirring, followed by the addition of 1.6ml (10mmol) of methylcyclopentadienylmanganesetricarbonyl [MnCpMe(CO)$_3$]. The reaction mixture was stirred for 1 hour at this temperature and then allowed to rise to 20 ^{0}C (room temperature), where the stirring was continued for further 15 minutes.

The reaction mixture was then cooled to -20 ^{o}C, followed by the dropwise addition of 1.07g (10mmol) lithium diisopropylamine (LDA). This solution was further cooled to -78 ^{o}C and then 2.20g (10mmol) of Cr(CO)$_6$ was gradually added, while stirring was continued for 30 minutes at this temperature.

The temperature of the reaction mixture was then allowed to warm to 20 ^{o}C (room temperature) and stirring was continued for 1 hour at this temperature during which time the reaction mixture turned dark brown in colour. The solvent (THF) was then removed *in vacuo* and replaced with 50ml of dichloromethane. This was then cooled to -30 ^{o}C and 3.80g (20mmol) of triethyloxonium tetrafluoroborate (Et$_3$OBF$_4$) dissolved in 20ml of dichloromethane, was carefully added to the stirred mixture.

3. H. Meerwein, *Org. Synth*., 46, **1966**, 113.

4. L. Brandsma, H. Verkruijsse, "Preparative Organometallic Chemistry I", Springer- Verlag, Berlin Heidelberg, **1987**.

Stirring was maintained for an hour and then the solution was allowed to warm up to room temperature, during which it turned very dark purple in colour. The mixture was washed through a filter containing silica gel and sodium sulphate with dichloromethane and the solvent was removed under reduced pressure.

The reaction mixture was purified with column chromatography. The mixture was dissolved in dichloromethane and adsorbed onto silica gel. Six bands were separated starting with pure hexane as eluent. The polarity was increased by adding some dichloromethane. The first orange product was identified as a monocarbene complex, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_3S\}]$, 0.4980g (15%). The second deep purple product was found to be the biscarbene complex, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_2SC(OEt\})Cr(CO)_5]$,1.060g (20%). The third purple product was found to be the biscarbene complex, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_2SC(OH)C(OEt)C_4H_2S-C_4H_2SC(OEt\}]Cr(CO)_5]$ (**7**), 0.3710g (5%). The forth brown product was found to be the monocarbene complex, $[MeCpMn(CO)_2\{C(OEt)C_4H_3S\}]$, 0.3200g (10%). The fifth purple blue product was identified as a mixed biscarbene complex, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_2SC(OEt)\}MeCpMn(CO)_2]$ (**1**), 2.370g (45%). The sixth reddish blue compound was found to be a decomposition product, $[Cr(CO)_5\{C(OEt)C_4H_2S-C_4H_2SC(O)OEt\}]$, 0.3110g (8%).

6.3.4 The synthesis of the bithiophene manganese-molybdenum mixed biscarbene complex, $[MeCpMn(CO)_2\{C(OEt)C_4H_2S$ $C_4H_2SC(OEt)\}Mo(CO)_5]$ (**2**)
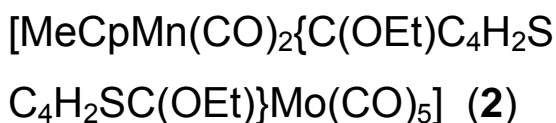
The procedure for the synthesis of this mixed biscarbene complex was followed exactly as in **1**, above. After the addition of 10mmol MnCpMe(CO)$_3$, the second lithiation was carried out using 10mmol LDA, followed by the addition of 2.640g (10mmol) molybdenum hexacarbonyl, Mo(CO)$_6$. The alkylation was also done with the same amount of Et$_3$OBF$_4$ (10mmol) and six bands were separated with

column chromatography. The first orange band was identified as a monocarbene complex of molybdenum, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}], 0.5510g (15%). The second purple band was found to be a biscarbene complex of molybdenum, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})Mo(CO)$_5$], 1.200g (20%). The third purple band was identified as a molybdenum biscarbene complex, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)C(O)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})Mo(CO)$_5$] (**5**), 0.3160g (5%). The fourth orange-red band was identified as a monocarbene complex of manganese, [MeCpMn(CO)$_2${C(OEt)C$_4$H$_3$S}], 0.3200g (10%). The fifth purple-blue band was identified as a mixed biscarbene of molybdenum and manganese, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}MeCpMn(CO)$_2$] (**2**), 2.420g (43%). The sixth reddish blue band was found to be a decomposition product, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}], 0.3000g (7%).

6.3.5 The synthesis of the bithiophene manganese-tungsten mixed biscarbene complex, [MeCpMn(CO)$_2${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}W(CO)$_5$] (**3**)

As in **1** and **2**, the procedure was the same for the synthesis of this compound. 3.520g (10mmol) tungsten hexacarbonyl was used in this reaction. Six bands were separated from the reaction using hexane and dichloromethane for increasing the polarity on the column. The first orange product was identified as a monocarbene complex of tungsten, [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}], 0.6570g (15%).The second deep purple product was found to be a biscarbene complex of tungsten [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})W(CO)$_5$], 0.3700g (5%). The third purple product was identified as a tungsten biscarbene complex, [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)C(O)C$_4$H$_2$S-C$_4$H$_2$SC(OEt}]W(CO)$_5$] (**6**), 0.3500g (5%).The fourth orange-red product was identified as a monocarbene complex of manganese, [MeCpMn(CO)$_2${C(OEt)C$_4$H$_3$S}], 0.3200g (10%).

The fifth purple-blue product was identified as a mixed biscarbene complex of tungsten and manganese, [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}MeCpMn(CO)$_2$] (**3**), 2.710g (43%). The sixth reddish blue product was found to be a decomposition product, [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}], 0.3460g (7%).

6.3.6 The synthesis of the bithiophene chromium-tungsten mixed biscarbene complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}W(CO)$_5$] (**A**)

Similar path and scaling was followed as in **1**, **2** and **3** for the synthesis of this compound. Subsequently, three bands were now separated. The first orange band was found to compose of two monocarbene complexes, [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}] and [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}], both constituting 20%. The second deep purple product was found to be a mixed biscarbene complex of tungsten and chromium, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}W(CO)$_5$] (**A**), 4.570g (72%).The third reddish blue product was found to be a decomposition product, [W(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}], 0.3960g (8%).

6.3.7 The synthesis of the bithiophene chromium-molybdenum mixed biscarbene complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}Mo(CO)$_5$] (**4**)

This compound was also synthesized the exactly same way as the other ones (**A**,**1**, **2**, **3**). As in **A**, three bands were separated. The first orange band was found to compose of two monocarbene complexes, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}] and [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_3$S}], both constituting 20%.
The second deep purple product was found to be a mixed biscarbene complex of molybdenum and chromium, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt)}Mo(CO)$_5$] (**4**),

4.070g (72%).The third reddish blue product was found to be a decomposition product, [Mo(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}], 0.3390g (8%).

6.4 Selected reactions of bithiophene mixed biscarbene complexes with an alkyne.

6.4.1 The reaction of chromium-manganese bithiophene mixed biscarbene complex (**1**) with hex-3-yne.

0.2700g (0.41mmol) of the complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})MnMeCp(CO)$_2$] was dissolved in THF and stirred. Four equivalents of 3-hexyne, 0.4ml (8.0 mmol) was added to the stirred solution. This was refluxed at 50^{0}C for three hours under the inert conditions of nitrogen. The reaction was then stopped and the solvent was removed under reduced pressure.
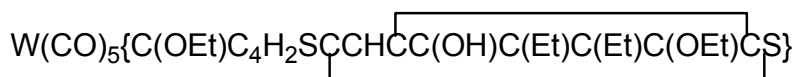
Three products were separated with column chromatography using hexane and dichloromethane as eluting agents. The first purple band was found to be the starting compound, 0.0335g (15.5%). The second reddish-blue band was identified as the decomposition product, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}] 0.02314g (14,5%). The third reddish band was characterized as

MnMeCp(CO)$_2${C(OEt)C$_4$H$_2$SCCHCC(OH)C(Et)C(Et)C(OEt)CS} (**8**) 0.1452g (69%).

6.4.2 The reaction of chromium-tungsten bithiophene mixed biscarbene complex with hex-3-yne.

1.589g (2.0mmol) of the complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})W(CO)$_5$] was dissolved in THF and stirred. Two equivalents of 3-hexyne, 0.46ml (4.0

mmol) was added to the stirred solution. This was refluxed at 50^0C for three hours under inert conditions of nitrogen. The reaction was then stopped and the solvent was removed under reduced pressure.

Three products were separated with column chromatography using hexane and dichloromethane as eluting agents. The first purple band was found to be the starting compound, 0.1907g (15%). The second reddish-blue band was identified as the decomposition product, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}] 0.1050g (13,5%). The third reddish band was

 characterized as the complex,

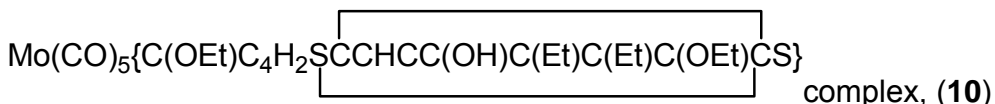W(CO)$_5${C(OEt)C$_4$H$_2$SCCHCC(OH)C(Et)C(Et)C(OEt)CS}

(**9**) 0.8690g (70%).

6.4.3 The reaction of chromium-molybdenum bithiophene mixed biscarbene complex with hex-3-yne.

1.4128g (2.0mmol) of the complex, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(OEt})Mo(CO)$_5$] was dissolved in THF and stirred. Two equivalents of 3-hexyne, 0.46ml (4.0 mmol) was added to the stirred solution. This was refluxed at 50^0C for three hours under the nitrogen. The reaction was then stopped and the solvent was removed under reduced pressure.

Three products were separated with column chromatography using hexane and dichloromethane as eluting agents. The first purple band was found to be the starting compound, 0.1752g (15.5%). The second reddish blue band was identified as the decomposition product, [Cr(CO)$_5${C(OEt)C$_4$H$_2$S-C$_4$H$_2$SC(O)OEt}] 0.1284g (16,5%). The third reddish band was characterized as the

Mo(CO)$_5${C(OEt)C$_4$H$_2$SCCHCC(OH)C(Et)C(Et)C(OEt)CS} complex, (**10**)

0.7636g (69,3%).