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Synthesis of metal complexes with thiophene ligands

by

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Submitted in partial fulfilment of the degree

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Supervisor: Professor Simon Lotz

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Thank you!
Marilé

Summary

The syntheses of carbene complexes with thiophene ligands were performed. Conjugated ligands comprising one (thiophene), two (thienothiophene) and three (dithienothiophene) condensed thiophene units were utilized in the syntheses. The reactivity, stability and structural features of the novel complexes were prepared. Metal carbonyls used to prepare the novel carbene complexes, were $Cr(CO)_6$, $W(CO)_6$, $Mo(CO)_6$, $MnCp(CO)_3$ en $Mn(MeCp)(CO)_3$. The carbene complexes were prepared *via* the classical Fischer method, which constitutes the reaction of the dilithiated thiophene derivative with the respective metal carbonyl complex, followed by the subsequent quenching with triethyl oxonium tetrafluoroborate to afford the alkoxy carbene complexes. In most cases the reactions afforded monocarbene complexes, biscarbene complexes and decomposition products. These decomposition products were formed on reaction of the biscarbene complexes with oxygen, affording an ester functionality on one side of the thiophene ligand and a monocarbene moiety on the other side. In the case of molybdenum, unexpected C-C coupling reactions yielded complexes containing extended thiophene spacers. Spectroscopical data and crystal structure determinations were employed in characterizing the novel complexes. It was concluded that, by increasing the number of thiophene units in the condensed ligand, the stability of the carbene complexes is enhanced.

Iron complexes of thiophene and thienothiophene were synthesized, employing several synthetic routes, in order to try and obtain optimum yields. The stabilities of these complexes were mutually compared. Several compounds were isolated which represented products formed by intermolecular C-C coupling reactions. In this case, however, it was concluded that by increasing the number of thiophene units in the ligand, the stability of the complexes decreased. These studies are to be extended towards a material science program and the results of this project will aid in the design of complexes specifically tailored for electronic transfer within the molecule.

Opsomming

Die sintese van karbeenkomplekse met tiofeen ligande is uitgevoer. Gekonjugeerde ligande wat uit een (tiofeen), twee (tiënotiofeen) en drie (ditiënotiofeen) gekondenseerde tiofeen eenhede bestaan, is in hierdie sinteses gebruik. Die reaktiwiteit, stabiliteit en struktuur eienskappe van die nuwe komplekse is vergelyk. Metaalkarboniele wat gebruik is in die bereiding van die nuwe karbeenkomplekse, is $Cr(CO)_6$, $W(CO)_6$, $Mo(CO)_6$, $MnCp(CO)_3$ en $Mn(MeCp)(CO)_3$. Die karbeenkomplekse is berei volgens die klassieke Fischer metode, wat die reaksie van die gedilitieërde tiofeen derivaat met die onderskeie metaalkarboniel komplekse behels, gevolg deur alkilering met behulp van triëtiel oksonium tetrafluoroboraat om alkoksi-karbeen komplekse te lewer. In die meeste gevalle is die monokarbeenkompleks, die biskarbeenkompleks asook 'n ontbindingsproduk verkry. Hierdie ontbindingsproduk is gevorm in die reaksie van die biskarbeenkomplekse met suurstof, wat 'n ester funksionaliteit aan die een kant van die tiofeen eenheid en 'n monokarbeen fragment aan die ander kant van die ligand tot gevolg het. Onverwagte C-C koppelingsreaksies het in die geval van molibdeen plaasgevind en komplekse met uitgebreide eenhede is gevorm. Spektroskopiese data en kristalstruktuurbepalings is gebruik om die nuwe komplekse te karakteriseer. Daar is tot die gevolgtrekking gekom dat, deur die aantal tiofeen eenhede in die gekondenseerde ringsisteem te vermeerder, die stabiliteit van die komplekse toeneem.

Yster komplekse van tiofeen en tiënotiofeen is gesintetiseer deur van verskeie sintese roetes gebruik te maak om die optimum opbrengs te probeer verkry. Die stabiliteite van die komplekse is onderling met mekaar vergelyk. Verskeie verbindings is geïsoleer wat produkte verteenwoordig wat gevorm is deur intermolekulêre C-C koppelingsreaksies. In hierdie geval is daar tot die slotsom gekom dat deur die aantal tiofeen eenhede in die ringsisteem te vermeerder, die stabiliteite van die komplekse afneem. Hierdie studie sal uitgebrei word tot 'n program in materiale en die resultate van hierdie projek sal aangewend word in die ontwerp van komplekse, spesiaal geformuleer vir elektroniese oordrag in die molekule.

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List of abbreviations

br	:	broad
Bu	:	butyl
Cp*	:	η^5-C_5Me_5
Cp	:	η^5-C_5H_5
d	:	doublet
dec	:	decomposition
DMF	:	dimethyl formamide
DMTT	:	3,6-dimethylthieno[3,2-*b*]thiophene
DTT	:	dithieno[3,2-*b*:2',3'-*d*]thiophene
Et	:	ethyl
HMPT	:	hexamethylphosphoric triamide
IR	:	infrared
m	:	multiplet
Me	:	methyl
MeCp	:	η^5-$C_5H_4CH_3$
NLO	:	non-linear optical
NMR	:	Nuclear magnetic resonance spectroscopy
n.o.	:	not observed
Ph	:	phenyl
q	:	quartet
s	:	singlet
t	:	triplet
T	:	thiophene/ thienyl/ thienylene
TT	:	thieno[3,2-*b*]thiophene
THF	:	tetrahydrofuran
TMS-Cl	:	trimethylchlorosilane
TMEDA	:	tetramethyl ethylene diamine
Tol	:	toluene

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List of compounds

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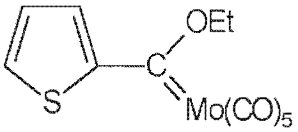

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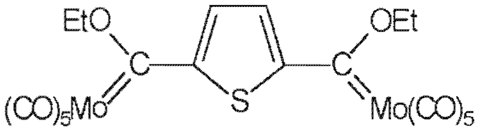

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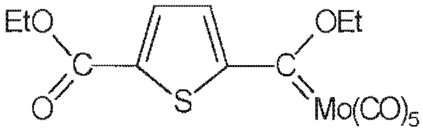

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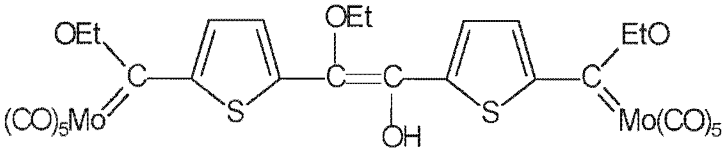

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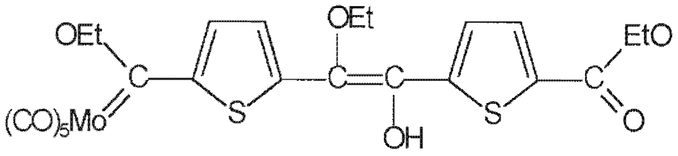

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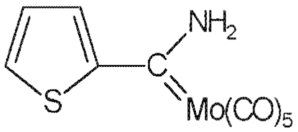
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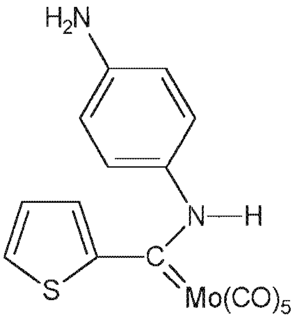
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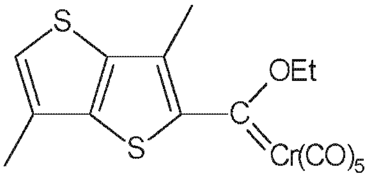
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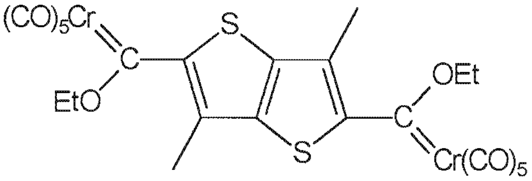
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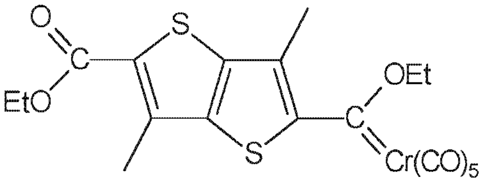
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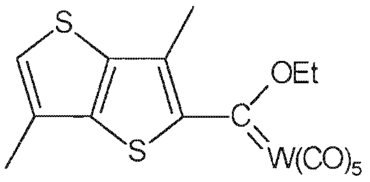
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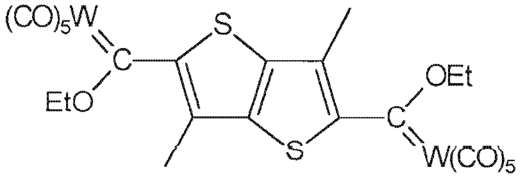
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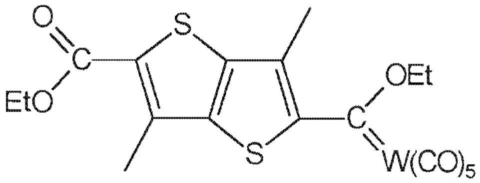
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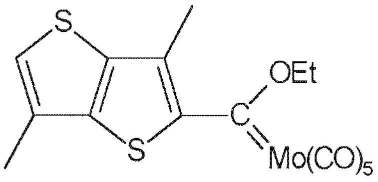
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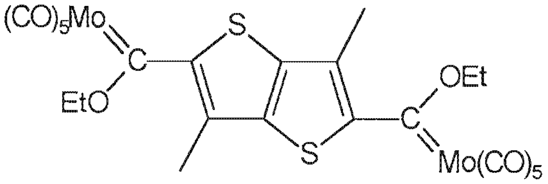
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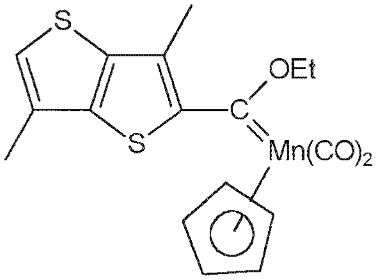
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C
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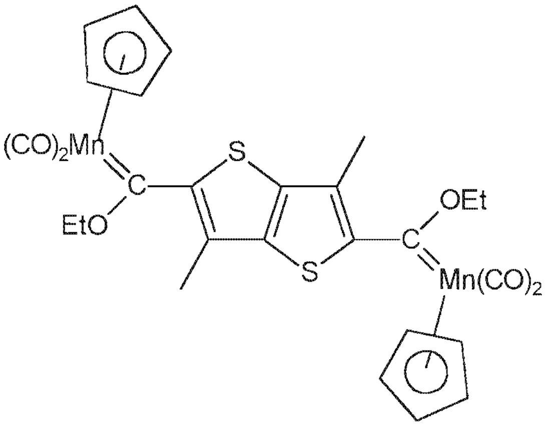
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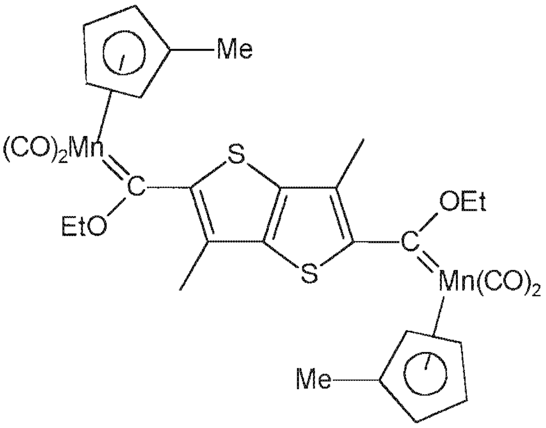
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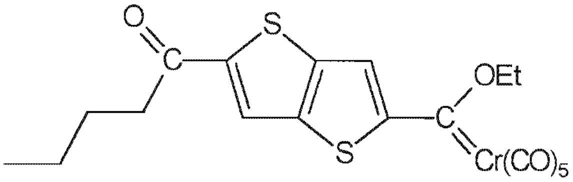
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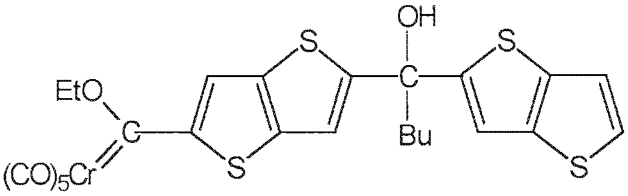
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S
C
Bu
S

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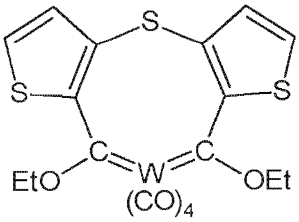
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S
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W
C
OEt
(CO)4

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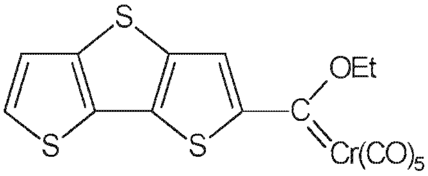
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C
S
S
Cr(CO)5

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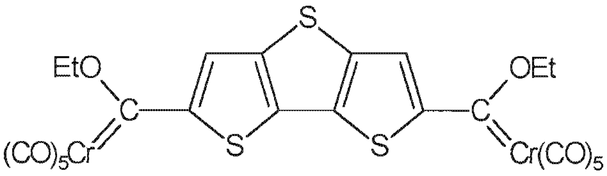
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OEt
C
C
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S
S
Cr(CO)5

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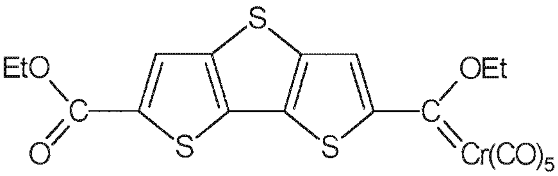
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OEt
C
C
O
S
S
Cr(CO)5

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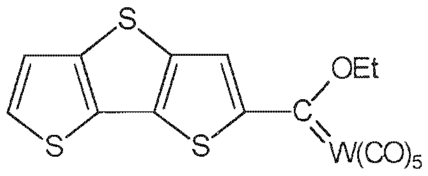
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S
S
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C
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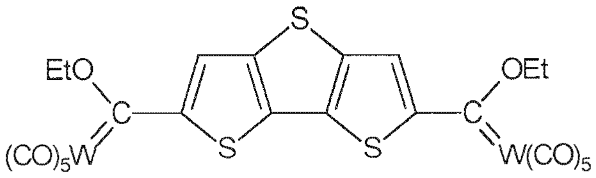
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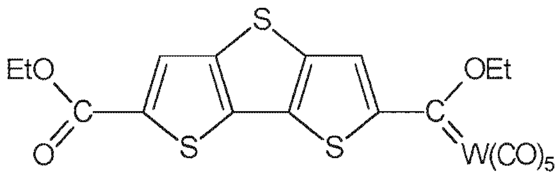
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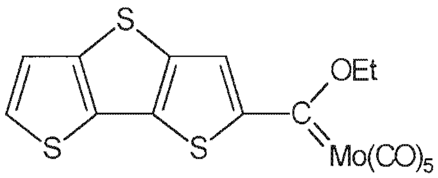
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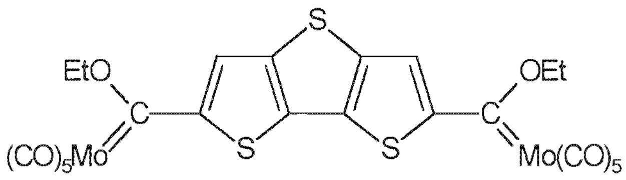
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Mo(CO)5

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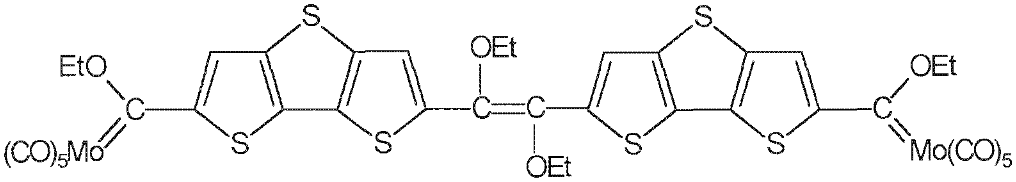
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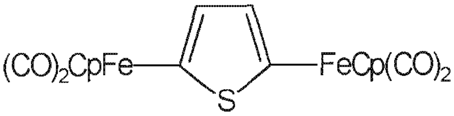
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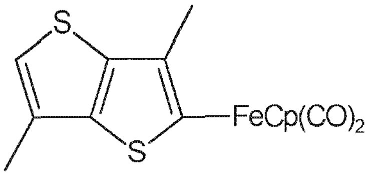
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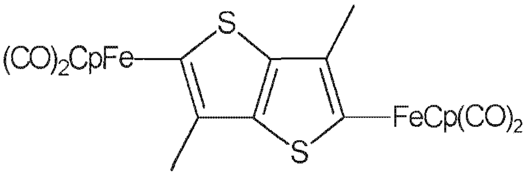
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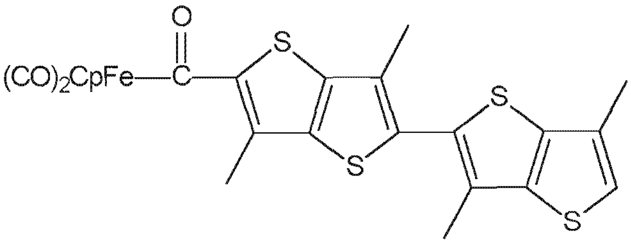
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C
S
S
S
S

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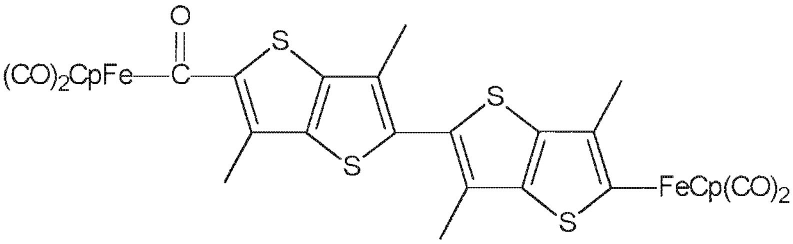
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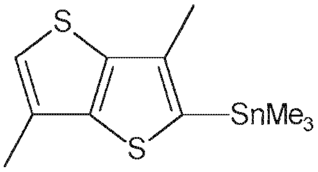
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S
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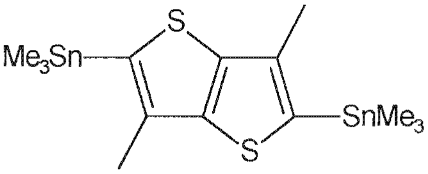
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S
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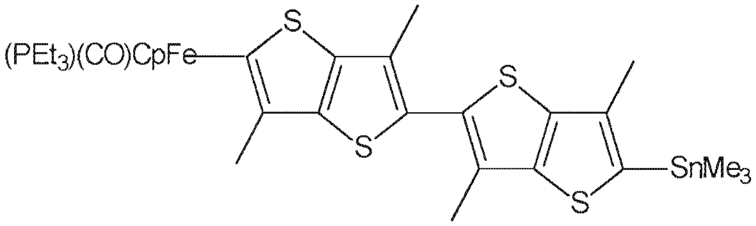
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1 Introduction

The past few decades have witnessed intense research work worldwide in the field of conductive polymers, a class of conjugated organic materials which combines the mechanical qualities of polymers with the electrical conductivity of metals[1]. In this context, polythiophenes and their derivatives have occupied an important position, firstly because of their environmental stability and secondly because of the versatility of the thiophene moiety in lending itself to synthetic modification. Polythiophenes have been identified as molecules with potential electro-optical properties and the most stable molecular switching devices discovered to date are thiophene derivatives[2]. Coordination of transition metals to thiophene or its derivatives leads to the formation of complexes, in this case carbene complexes, with unique properties and diverse application possibilities.

1. Complexes with unsaturated metal-to-carbon double bonds

1.1 Carbene complexes

Complexes containing metal-carbon double bonds are generally referred to as metal-carbene complexes. Without a heteroatom directly bonded to the carbene carbon atom, the compounds are called metal-alkylidene complexes. The first stable transition metal carbene complex was synthesized and characterized by Fischer and Maasböl in 1964[3]. Since then different synthetic routes have been developed for the synthesis of these and similar complexes.

---

[1] N.J. Long, *Angew. Chem. Int. Ed. Engl.*, 34, **1995**, 21.

[2] G.M. Tsivgoulis, J.-M. Lehn, *Angew. Chem. Int., Ed. Engl.*, 34, **1995**, 1119.

[3] E.O. Fischer and A. Maasböl, *Angew. Chem.*, 76, **1964**, 645.

Two different types of carbene complexes can be distinguished. The first Fischer-type carbene complexes are characterized by an electrophilic carbene carbon atom, the metal-coordinated sp^2-carbon atom (figure 1.1). These complexes are readily synthesized by the reaction of metal carbonyls of transition metals like chromium, tungsten, molybdenum, iron, rhenium, ruthenium and manganese with various organolithium reagents.

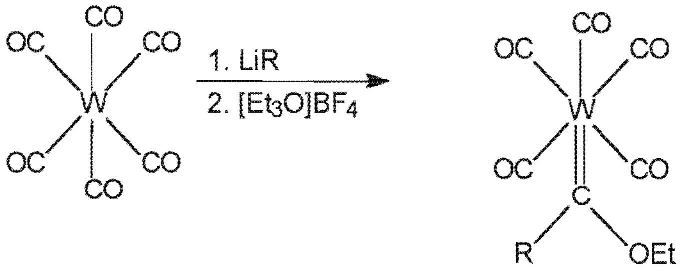

Figure 1.1 An example of a Fischer carbene complex

The second type is the Shrock carbene complexes in which the carbene carbon atom is nucleophilic and displays an ylide-like reactivity (figure 1.2). These complexes are afforded using metals in high oxidation states with strong donor ligands, for instance alkyl or cyclopentadienyl, and weak acceptor ligands. Often the carbene ligand is simply a methylene group.

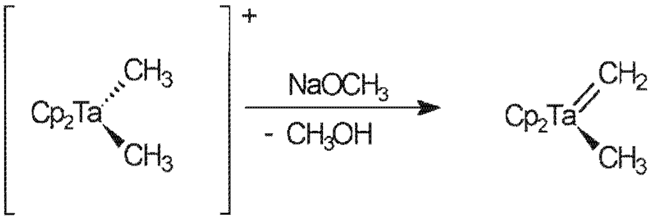

Figure 1.2 An example of a Schrock-carbene complex

In recent years there has been much interest in the activity of Fischer carbenes with respect to their ability to act as reagents for the synthesis of organic compounds. Several review articles and books have addressed this topic[4], which has been explored extensively and applied in various organic syntheses. Fischer carbene complexes can undergo reactions at several sites and the chemical properties of these complexes are outlined in figure 1.3.

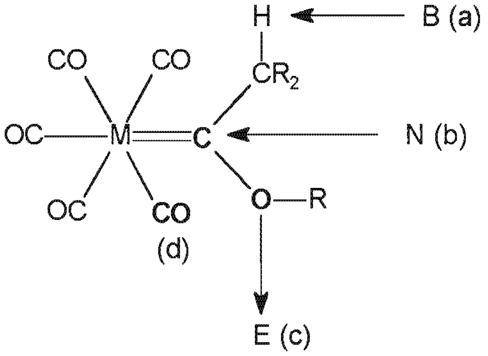

Figure 1.3 Reactivity of Fischer carbene complexes

Owing to the acidity of the α-CH groups, alkylcarbene complexes are deprotonated by bases (B) to form metal carbene anions (route a), while nucleophilic attack (N) occurs at the electrophilic carbene carbon atom (route b) e.g. aminolysis. Electrophiles (E), for instance Lewis acids, are coordinated to the alkoxy substituent (route c), leading to the formation of metal-coordinated carbyne complexes; while carbonyl substitution by other ligands can occur *via* route d.

Applications of carbene complexes in organic syntheses have been widely employed and recognized for their usefulness. The strategy is to use metal complexes to establish a metal-to-carbon bond, modify it by further reactions and subsequently cleave the new ligand from the metal moiety. Applying this concept to various carbene complexes, a large range of compounds were formed including β-lactams from imines (figure 1.4), cyclobutanones from alkenes and esters from

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[4] (a) L.S. Hegedus, *Transition Metals in the Synthesis of Complex Organic Molecules*, University Science Books, Mill Valley, California, **1994**. (b) K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH Verlag Chemie, Weinheim, **1983**. (c) M. Schuster, S. Blechert, *Angew. Chem. Int. Ed. Engl.*, 36, **1997**, 2036. (d) W.D. Wulff, *Organometallics*, 17, **1998**, 3116. (d) R. Aumann, R. Fröhlich, J. Prigge, O. Meyer, *Organometallics*, 18, **1999**, 1369. (e) M.M. Abd-Elzaher, H. Fischer, *J. Organomet. Chem.*, 588, **1999**, 235.

alcohols[5, 6, 7].

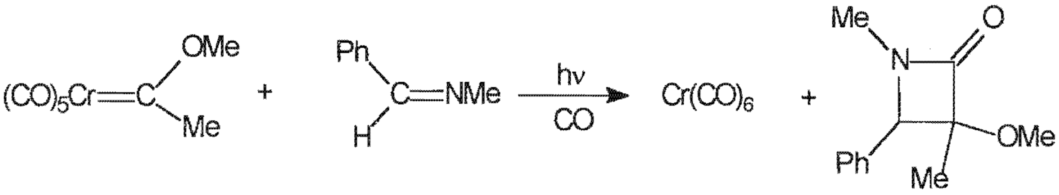

Figure 1.4 Employing a carbene complex to synthesize a β-lactam

Carbene complexes have been employed in carbon-carbon bond formation in organic synthesis[8]. Carbenes react under mild conditions with a number of non-heteroatom substituted alkynes to yield annelated reaction products. These reactions are referred to in literature as Dötz reactions. Complexes containing pentacarbonylchromium moieties with phenyl-[9], naphtyl-[10], furyl- and thienyl[11] substituted carbene ligands have been reacted with various alkynes to give substituted naphthol, phenanthrene, benzofuran and benzothiophene ligands π-coordinated to a tricarbonylchromium fragment.

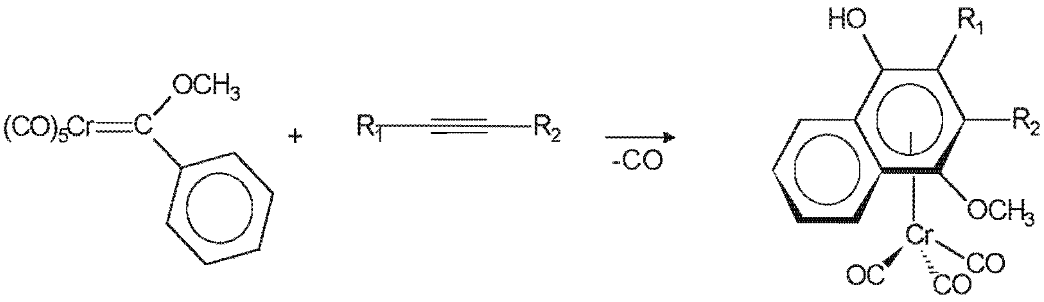

Figure 1.5 Reaction of carbene with alkyne

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On considering the reaction between pentacarbonyl[methoxy(phenyl)carbene]chromium and an alkyne (figure 1.5), we find the reaction product to be 4-methoxy-1-naphthol, which is π-bonded to a $Cr(CO)_3$ moiety. The unsubstituted ring of the naphthol ligand and the $C(OCH_3)$ unit of the second ring originate from the carbene ligand, while the C(OH) group is derived from a carbonyl ligand. Alkoxy carbene carbonyl complexes are employed in the synthesis of natural products such as peptides, vitamins K and E and antibiotics, by forming the hydroquinone skeleton *via* cycloaddition of alkyne, carbene and carbonyl ligands[12].

Carbene complexes also play important roles as intermediates in olefin metathesis[13]. Grubbs *et al*[14] synthesized ruthenium(II) carbene complexes of the type *trans*-$[Ru{=}CHCH{=}CPh_2(PPh_3)_2Cl_2]$, to catalyze the polymerization of highly strained cyclic olefins.

1.2 Cumulene and related complexes

Carbene complexes with cumulated double bonds of the form $M{=}(C)_nR_2$ (figure 1.6) encompass a class of organometallic compound containing a metal moiety coordinated to a carbon-rich unsaturated chain. Linear, unsaturated carbon chain complexes have recently attracted considerable interest due to their physical and chemical properties[15]. Transition metal complexes of this structural type have been proposed as one-dimensional molecular wires[16] and exhibit both liquid crystalline[17] and nonlinear optical properties (NLO)[18]. The maximum chain length achieved

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[12] K. H. Dötz in K.H. Dötz, H. Fischer, P.Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH Verlag, Weinheim, **1983**, p. 218-226.

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[18] (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.

so far is n=5, synthesized and characterized in 1994 only[19]. Since then, a few reports describing the syntheses of similar compounds, including group 6 metal complexes, have appeared[20]. However, complexes containing even-numbered carbon chains seem to be restricted to the ruthenium-butatrienylidene complex prepared by Lomprey and Selegue[21]. Theoretical calculations[22] suggest that the carbon atoms are alternatively electron-poor and electron-rich, on moving along the chain from the metal centre. This reactivity is confirmed by the tendency of allenylidene complexes to add nucleophiles at C_γ[23], while the protonation of vinilydenes to carbynes reflects the ease of addition of electrophiles to C_β[24].

$M=C=C=C_nR_2$	$M=C=C=CR_2$	$M=C=CR_2$
Metallacumulene complex	Allenylidene complex	Vinylidene complex

Figure 1.6 Cumulene complexes

Allenylidene complexes have been known since 1976[25], but thorough investigation of these compounds has been hampered by the lack of a feasible preparation method. They are generally synthesized *via* (i) transformation of alkenyl- and alkynyl carbene complexes[25b], (ii) coordination of a C_3 skeleton dianion, either $[C{\equiv}CC(OR)R]^{2-}$ or $Li_2C_3Ph_2$[26] or (iii) the most recent and

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[19] D. Péron, A. Romero, P.H. Dixneuf, *Gazz. Chim. Ital.*, 124, **1994**, 497.

[20] (a) D. Touchard, P. Haquette, A. Daridor, L. Toupet, P.H. Dixneuf, *J. Am. Chem. Soc.*, 116, **1994**, 11157. (b) G. Roth, H. Fischer, *Organometallics*, 15, **1996**, 1139. (c) G. Roth, H. Fischer, *Organometallics*, 15, **1996**, 5766. (d) R.W. Lass, P. Steinert, J. Wolf, H. Werner, *Chem. Eur. J.*, 2, **1996**, 19. (e) G. Roth, D. Reindl, M. Gockel, C. Troll, H. Fischer, *Organometallics*, 17, **1998**, 1393.

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straightforward method employed by Selegue and co-workers[27]. This synthesis comprises the reactions of alkyn-3-ols with metal complexes eg. $[RuCpCl(PR_3)_2]$ in polar media to yield hydroxyvinylidene intermediates, which spontaneously dehydrate *in situ* to form allenylidene complexes. Since this discovery, several allenylidene derivatives have been produced using this method, eg. iron[28], rhodium[29] and ruthenium[30] derivatives. The same method is now directed towards the building of bimetallic systems with allenylidene ligands[31] or bridges[32].

Vinylidene complexes, the most simple form of cumulene ligands, can be prepared in several ways, for instance by using metal acetylide, acyl complexes, vinyl complexes, olefins, carbene complexes or 1-alkynes. An overview of all the synthetic preparations and applications of vinylidene complexes is available in review articles by Stang[33] and Bruce[34]. Complexes containing these species are likely intermediates in coupling of alkynes to give enynes[35] or butatrienes[36], and in the synthesis of unsaturated ketones from alkynes and allylic alcohols[37].

1.3 Binuclear metal complexes bridged by linear unsaturated carbon chains

Complexes in which two transition metals are bridged by linear unsaturated carbon chains have

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

[28] S. Nakanishi, K.I. Goda, S.I. Uchiyoma, Y. Otsuji, *Bull. Chem. Soc. Jpn.*, 65, **1992**, 2560.

[29] (a) R. Wiedemann, P. Steinert, O. Gevert, H. Werner, *J. Am. Chem. Soc.*, 118, **1996**, 2495. (b) I. Kovacik, M. Laubender, H. Werner, *Organometallics*, 16, **1997**, 5607. (c) D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, *Organometallics*, 17, **1998**, 3844.

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

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[37] B.M. Trost, R.J. Kulawiec, *J. Am. Chem. Soc.*, 114, **1992**, 5579.

recently attracted much interest in view of their new material properties[38] and as model systems for surface carbides in heterogeneous catalysis[39]. These species, MC_nM', can bridge either two similar or two different transition metal fragments.

In complexes where two similar metal fragments are bridged, complexes where n=2 are the most common. Even though all three valence bond descriptions (figure 1.7) have experimental support[39], most of the complexes synthesized contain an acetylenic μ-C≡C bridge. The cumulenic structure M=C=C=M was only observed in a few titanium and tantalum complexes.

$$\text{M-C}\equiv\text{C-M} \quad \leftrightarrow \quad \text{M=C=C=M} \quad \leftrightarrow \quad \text{M}\equiv\text{C-C}\equiv\text{M}$$

Figure 1.7 Resonance structures for the MC_2M species

It has been experimentally observed that compounds with an even C_n chain are much more common than complexes containing an uneven number of carbons in the chain. Several four-[40], six- and eight-carbon bridged complexes[41] are known and, depending on the d^n configuration, display either a polyynic (reduced) or a cumulenic (oxidized) structure (figure 1.8). These bimetallic iron chain bridged compounds where n=2-8 were developed by Lapinte and co-worker[42].

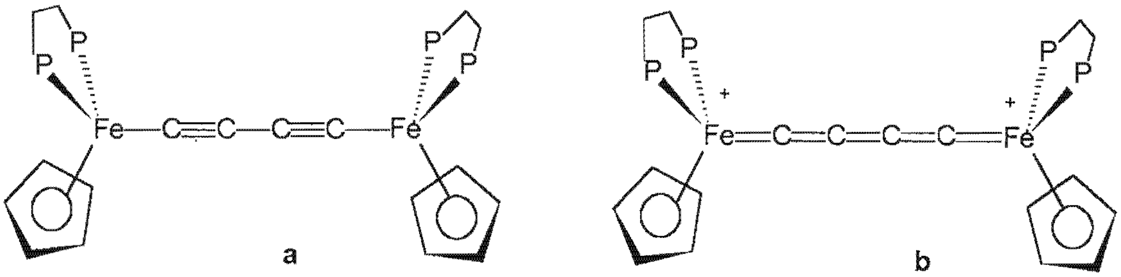

Figure 1.8 (**a**) Polyynic structure and (**b**) oxidized structure

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[38] M.H. Chisholm, *Angew. Chem. Int. Ed. Engl.*, 30, **1991**, 673.

[39] W. Beck, B. Niemer, M. Wieser, *Angew. Chem. Int. Ed. Engl.*, 32, **1993**, 923.

[40] Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.*, 115, **1993**, 8509.

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[42] F. Coat, C. Lapinte, *Organometallics*, 15, **1996**, 477.

The complex with the highest number of carbon atoms in the chain, $[\{ReCp^*(PPh_3)(NO)\}_2(\mu\text{-}C_{20})]$ was recently synthesized by Gladysz and co-workers[43]. The longest polyyne structurally characterized to date is a C_{12} complex. Two groups simultaneously published crystal structures of this type of complex, a diplatinum complex synthesized by Gladysz *et al*[44] *via* Hay coupling of two C_6 mono-platinum complexes and a diiron complex prepared by Akita and co-workers[45].

Complexes containing two different transition metal building blocks, linked by C_n bridges (n=1-5), have only recently become accessible[15]. Synthesis of these compounds, particularly for those containing organometallic substituents, turned out to be remarkably easy[46]. These complexes were proposed as a new class of one-dimensional molecular wires[16]. Very few compounds have been synthesized with an odd number of carbons in the C_n chain[47]. Only one C_3 bridged complex has been structurally characterized, namely $[\{ReCp^*(PPh_3)(NO)\}(\mu\text{-}C_3)\{MnCp(CO)_2\}]$. For each of the C_3 and C_5 chains two possible valence structures exist (figure 1.9). However, structural and spectroscopic information indicate that the cumulenic forms dominate over the alkyne-carbyne forms[48].

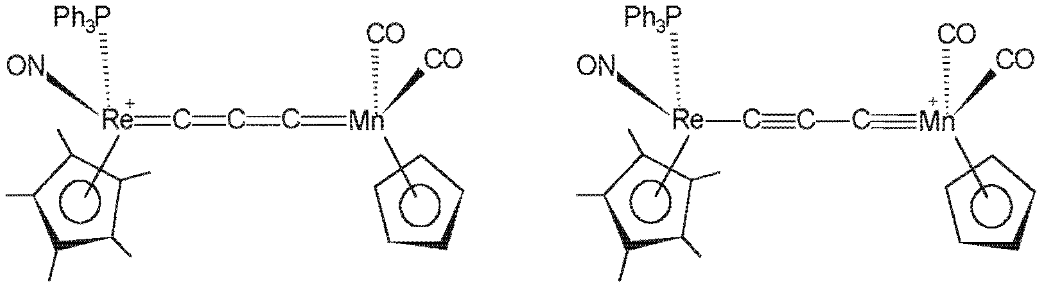

Figure 1.9 Valence structures of C_3 bridged chain with different metal fragments

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[48] W. Weng, T. Bartik, J.A. Gladysz, *Angew. Chem. Int. Ed. Engl.*, 33, **1994**, 2199.

Until recently, examples of π-conjugated metal-bridged trinuclear biscarbene complexes were limited to the C_4HgC_4-bridged complex $[(CO)_5W{=}C(NMe_2)C{\equiv}CC{\equiv}CHgC{\equiv}CC{\equiv}CC(NMe_2){=}W(CO)_5]$, prepared by Fischer *et al*[49]. Since then, the synthesis of bis-, tris- and tetrakis(ethynylcarbene) complexes was reported[50]. These complexes are readily prepared by nucleophilic substitution of the lithiated ethynylcarbene complex $[M(CO)_5\{{=}C(NMe_2)C{\equiv}CLi\}]$ (M = W, Cr) for the chlorides in $[Cl_mM'(L_n)]$ (m = 2-4). The central linking atom M' can be a transition metal, a main group metal or any other main group element.

1.4 Binuclear metal complexes bridged by conjugated ligands

A large number of binuclear complexes with conjugated bridges have been reported. 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, including pyrazine, such as the Creutz-Taube ion[51] (figure 1.10), 4,4'-bipyridine[52] and related heteroaromatic groups[53].

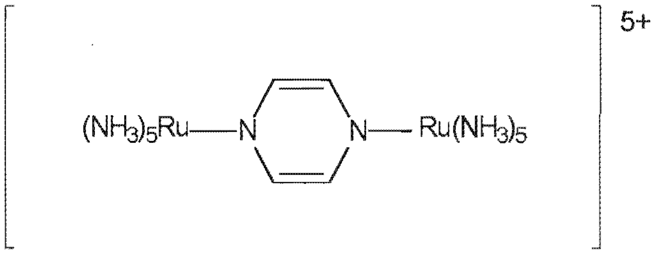

Figure 1.10 The Creutz-Taube ion

Sponsler and co-workers[54] have recently reported the first examples of delocalized mixed-valence

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[49] C. Hartbaum, H. Fischer, *Chem. Ber./Recl.*, 130, **1997**, 1063.

[50] C. Hartbaum, G. Roth, H. Fischer, *Eur. J. Inorg. Chem.*, **1998**, 191.

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Fe^{II}/Fe^{III} complexes containing butadienediyl bridges (figure 1.11), prepared by one-electron oxidation of the corresponding Fe^{II}/Fe^{II} complexes. Since then several mixed valence complexes of this type have been synthesized, eg. a Ru^{II}/Ru^{III} complex prepared by Moreira and co-workers[55].

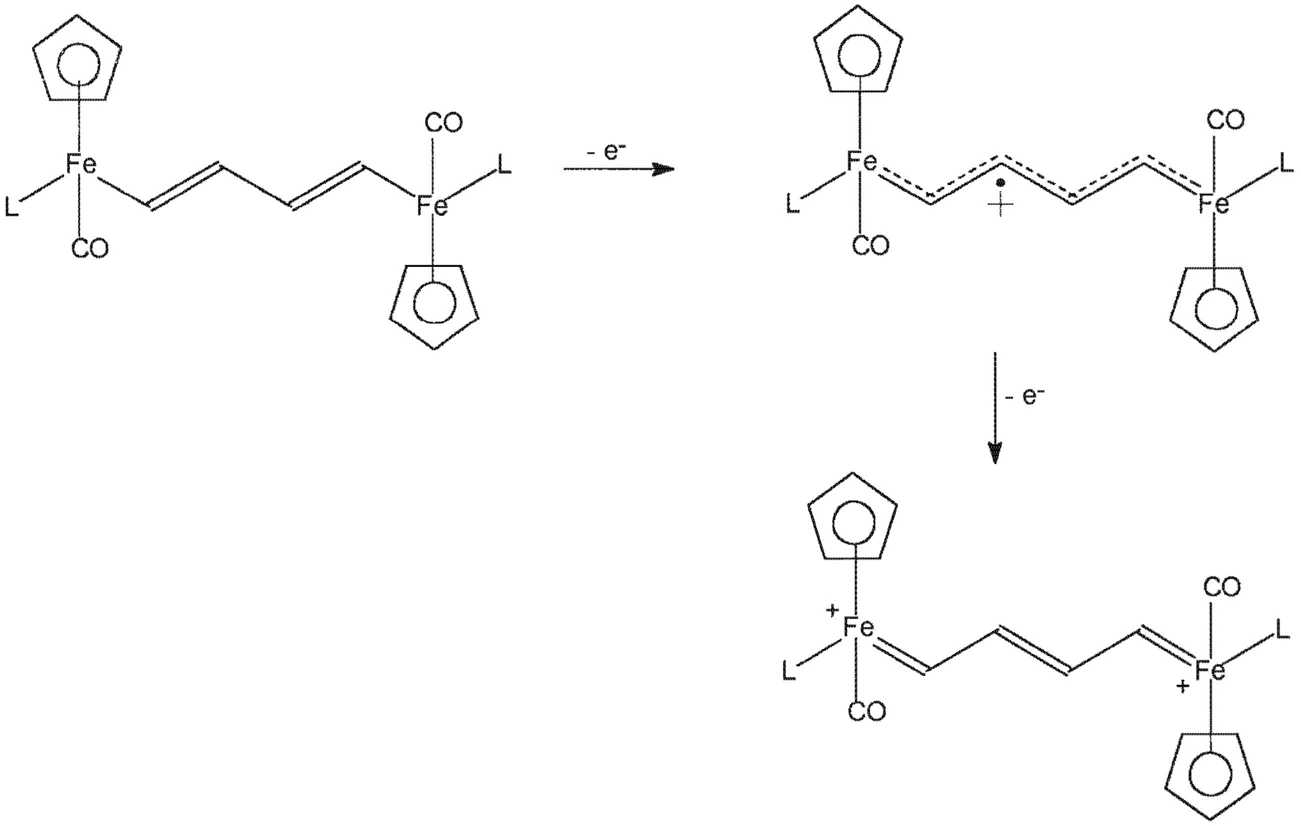

Figure 1.11 Fe^{II}/Fe^{III} complexes containing butadienediyl bridges

Organometallic complexes in which two metal-containing fragments are bridged by arene[56] or heteroarene ligands[57] have enjoyed considerable attention recently since they serve as models for the repeating units in related organometallic polymers[58]. It was found that increasing the number of fused aromatic rings in the bridging groups of such materials, i.e. in going from 1,4-C_6H_4

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[55] I.S. Moreira, D.W. Franco, *Inorg. Chem.*, 33, **1994**, 1607.

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

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to 9,10-$C_{14}H_8$[59], increased the degree of intermetallic conjugation in complexes having two metal centers directly joined to the aromatic core by metal-carbon σ bonds, as has been demonstrated for conjugated organic polymers[60]. The two metal centers do indeed interact and they transfer significant electron density to the arene ring. Hunter and co-workers[61] prepared the phenylene-bridged complexes of iron and manganese as well as iron complexes of quinoline and related bridges. The structures of many of the quinoline derivatives were similar to those of related biologically active materials, including herbicides, fungicides and insecticides.

2. Thiophene and related compounds

Thiophenes are well known for their occurrence in fossil fuels[62] and the coordination chemistry of these compounds has received recent attention because of its relevance to the metal-catalyzed hydrodesulfurization of the fossil fuels[63]. A mechanism for the hydrodesulfurization was proposed by Angelici and co-workers[64] on the basis of organometallic model compound and catalytic reactor studies. Thiophenes are aromatic compounds and display coordination properties closer to those of arenes than thioethers. On comparing the ionization potential of thiophene (8.9 eV) and benzene (9.3 e V), it is found that thiophene is slightly more nucleophilic than benzene. *Ab initio* calculations[65] seem to indicate accumulation of negative charge on the 2- and 5-carbon atoms and a positive charge on the sulfur atom. Coordination can occur through the sulfur atom (S), through the 2- or 5-carbon or both (η^1) or through the π-clouds of the C(2)=C(3) or C(4)=C(5) bonds (η^2) or both (η^4). Whereas η^4-coordination implies a sp^3-hybridized sulfur atom which is bent out of the plane, the η^5-mode involves all the atoms of the ring, including the sulfur atom, and a planar ligand is encountered for complexes of this type. Examples of coordination to all of these sites can be

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[60] P.N. Prasad, D.R. Ulrich, *Non-linear Electroactive Polymers*, Plenum, New York, **1988**.

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[65] T.B. Rauchfuss, *Prog. Inorg. Chem.*, 39, **1991**, 259.

found in literature[66].

Oligomers of thiophene are also compounds of current interest because many of them show photo-enhanced biological activities[67], while α-polymerization of thiophene produces crystalline, electroconductive polythiophenes[68]. A wide variety of thiophene oligomers and derivatives have been synthesized mainly with the prospect of obtaining precursor compounds for molecular devices and electroconductive polymers. Condensed thiophene derivatives and polythiophenes have found wide application as potential conducting polymers[69], electron acceptors[70], hydrogen-poor heterocycles[71], organic conductors or superconductors[72] and materials with non-linear optical properties[73]. Oligothiophenes seem to be particularly appealing components to use as bridging ligands for they are likely to permit strong metal-metal interactions over long distances. This aspect of their chemistry has unfortunately received very little attention. One recent example was the use of 2,5-di(4-pyridyl)thiophene as a bridge between two $\{Ru(NH_3)_5\}^{2+/3+}$ fragments. It was observed that the electrochemical interaction between the metal centers was moderately stronger than that across a 1,4-di(4-pyridyl)butadiene bridge[74].

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[74] A.C. Ribou, J.P. Launay, K. Takahashi, T. Nihira, S. Tarutani, C.W. Spangler, *Inorg. Chem.*, 33, **1994**, 1325.

3. Aim of this study

The coordination chemistry of thiophene to transition metals has been extensively studied and several review articles have appeared in this regard [65, 66a]. Thiophene derivatives have been investigated for materials exhibiting NLO properties. It was suggested that incorporation of metal centres and thiophene moieties is expected to enhance the conducting properties of the molecule[1]. The coordination of transition metals to thiophene moieties has been extended to include bithiophene[75], the most elementary polythiophene. On the contrary, the coordination chemistry of condensed thiophenes to transition metal moieties has not been studied at all, although they are considered to be very promising molecules in the field of electro active materials. A convenient, high-yield synthetic method for the preparation of these ring systems remains a challenging objective, since such a method may encourage more in-depth research studies of these systems.

As first objective, the synthesis of Fischer carbene complexes containing condensed thiophene molecules as ligands was contemplated. Although several Fischer carbene complexes with thiophene as ligand have already been synthesized[76], the molybdenum analogue was prepared in this study for comparison with the novel condensed thiophene complexes. It is well known that the carbonyl groups of molybdenum hexacarbonyl are more labile than those of chromium hexacarbonyl or tungsten hexacarbonyl[77] and therefore lends itself to unique reactivity and coordination possibilities. Aminolysis of this complex to enhance the stability, was proposed. The result of this study is discussed in chapter **2**. The synthesis of Fischer carbene complexes of thieno[3,2-*b*]thiophene, 3,6-dimethylthieno[3,2-*b*]thiophene and dithieno[3,2-b:2',3'-*d*]thiophene with group 6 transition metals was devised (figure 1.12). These condensed thiophene units can act as a conjugated π-system to afford communication between the metal functionalities. The results of this investigation are addressed in chapters **3** and **4**.

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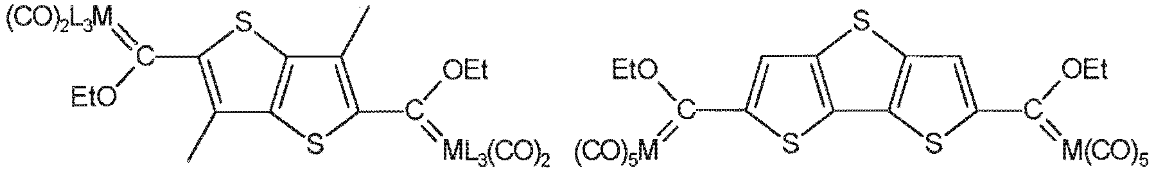
[75] S. Maiorana, A. Papagni, E. Ligandro, A. Persoons, K. Clay, S. Houbrechts, W. Porzio, *Gazz. Chim. Ital.*, 125, **1995**, 377.

[76] (a) J.A. Connor, E.M. Jones, E.W. Randall, E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, **1972**, 2419. (b) Y.M. Terblans, H.M. Roos, S. Lotz, *J. Organomet. Chem.*, 566, **1998**, 133.

[77] Ch. Elschenbroich, A. Salzer, *Organometallics, A Concise Introduction*, VCH Verlag, Weinheim, **1992**, 232.



M = Cr, W, Mo, Mn
L = CO
L_3 = Cp, CpMe

M = Cr, W, Mo

Figure 1.12 Biscarbene complexes of condensed thiophene complexes

The structure of a diiron thiophene complex has been reported[65] and is shown in figure 1.13. This compound was prepared, reacting the 2,5-dilithiated thienylene species with two equivalents of [FeCp$(CO)_2$I], for purposes of comparison and the syntheses of similar iron complexes with thiophene and thienothiophene were thus attempted. The synthesis, stability and reactivity of these complexes are discussed in chapter **5**.

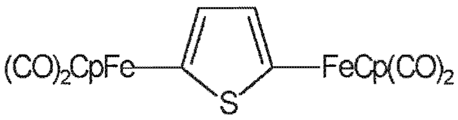


Figure 1.13 Diiron thiophene complex

The second aspect of this study deals with the stability of the dinuclear complexes and the involvement of the thiophene rings in stabilizing the metal-carbon bonds. It was anticipated that condensed thiophene rings should afford a more rigid spacer ligand, whereas linear oligothiophene spacers would be more flexible and probably less stable. In this project, a formal stability study was not conducted but was simply taken to be represented by the amount of change in the composition of the complexes over a certain period of time, in solid state as well as in solution. The stability of the individual complexes was compared relatively to one another. Explanations were based on electronic and geometrical factors which were deduced from spectral data recorded in solution and structural data measured in the solid state. Instability resulting from a favourable entropy factor was not considered and we assumed it to be the same for comparable complexes and was hence ignored.

This study represents the initial stage in our laboratories for the design, synthesis and testing of compounds which display properties of charge transfer *via* a common spacer ligand for possible application in material science. Future investigations will focus on:

(i) the synthesis of mixed metal carbene complexes with the objective of creating a naturally polarized spacer ligand. The creation of a "push-pull" effect by incorporating electron-poor and electron-rich transition metal fragments in the same molecule is envisaged by varying the metal atom, different oxidation states of the metal and the ligand environment. The isolation of the decomposition products in this study, with a monocarbene moiety and an ester functional group on opposite sides of the conjugated spacer ligand, indicated the possibilities of utilizing such systems;

(ii) the synthesis of bis-alkyl and biscarbyne complexes and their modification in enhancing the delocalization of electron density in the ligand system;

(iii) the development of a convenient method for the measuring of the magnitude of charge transfer in π-conjugated systems;

(iv) the correlation of spectral data and structural features with charge transfer properties.

2

Carbene complexes of Thiophene

1. General

Recent studies of the interaction between thiophene and transition metals have revealed an intricate and diverse coordination chemistry. Motivation for these studies originated to a large extent from the understanding of the mechanism of catalytic hydrodesulfurization (HDS), the industrial process by which sulfur is removed from fossil fuels[1]. Thiophenes are amongst the most difficult sulfur-containing compounds targeted in the HDS process to desulfurize and thus of particular interest.

Several types of thiophene (T) coordination modes to transition metals are known. Prior to 1985 only complexes of the η^5-coordination mode were known, but since then complexes exhibiting η^1-, η^2- and η^4-coordination modes have been synthesized[2]. Few S-bound complexes have been isolated, for example $[Ru(NH_3)_5T]^{2+}$, $[FeCp(CO)_2T]^+$, $[FeCp(NCMe)_2(2,5\text{-}Me_2T)]^+$ and $[W(CO)_3(PCy_3)_2T]$[3]. In all cases the thiophene is easily replaced by weak ligands since the coordinating nature of the sulfur atom in thiophene is not strong. This weak coordinating ability of the sulfur atom results from delocalization of the sulfur nonbonding electrons into the π system of the ring. Arce *et al*[4] reported the synthesis of $[Os_3(C_4H_4S)H_2(CO)_9]$, a complex exhibiting the η^2-

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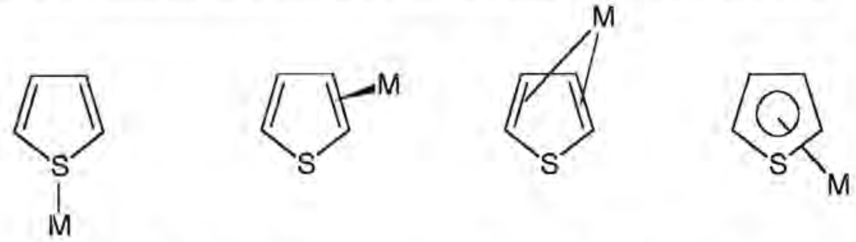
[1] B.C. Gates, J.R. Katzer, G.C.A. Schuit, *Chemistry of Catalytic Processes*; McGraw-Hill; New York, **1979**.

[2] (a) A.E. Ogilvy, A.E. Skaugest, T.B. Rauchfuss, *Organometallics*, 8, **1989**, 2739. (b) R. Cordone, W.D. Harman, H. Taube, *J. Am. Chem. Soc.*, 111, **1989**, 5969. (c) R.J. Angelici, *Acc. Chem. Res.*, 21, **1988**, 387.

[3] (a) C.G. Kühn, H. Taube, *J. Am. Chem. Soc.*, 98, **1976**, 689. (b) J.D. Goodrich, P.N. Nickias, J.P. Selegue, *Inorg. Chem.*, 26, **1987**, 3424. (c) D. Catheline, D. Astruc, *J. Organomet. Chem.*, 272, **1984**, 417. (d) H.J. Wasserman, G.J. Kubas, R.R. Ryan, *J. Am. Chem. Soc.*, 108, **1986**, 2294.

[4] A.J. Arce, Y. De Sanctis, A.J. Deeming, *J. Organomet. Chem.*, 311, **1986**, 371.

coordination mode, while the first evidence for η^4-thiophene complexes were observed by Huckett and Angelici[5], who prepared the complex $[IrCp^{*}T]$. Several η^5-coordinated complexes can be found in literature, e.g. $[Cr(\eta^5\text{-}T)(CO)_3]$[6]. The general stability of these η^5-thiophene complexes suggests that this may be the preferred bonding mode to transition metals on catalytic surfaces. All of these modes have been implicated as important intermediates in the HDS process.



S-coordination η^2-coordination η^4-coordination η^5-coordination

Figure 2.1 Coordination modes of thiophene to one transition metal

Coordination of thiophene to more than one transition metal can also occur at different sites on the thiophene ring. An example where the thiophene is coordinated through the diene to one metal, while the sulfur atom is bonded to another metal, is the complex $[Fe(CO)_3\{\mu\text{-}\eta^2,S\text{-}T\}Re(CO)_2Cp^{*}]$[7]. Angelici *et al* recently synthesized the first thiophene complexes coordinated to three metal centres namely the complexes $\{\mu_3\text{-}\eta^4,S,S\}[IrCp(2,5\text{-}Me_2T)][Mo_2(CO)_4Cp_2]$[8] and $\{\mu_3\text{-}\eta^4,S,S\}[IrCp(2,5\text{-}Me_2T)][Fe_2(CO)_7]$[9], both exhibiting the $\{\mu_3\text{-}\eta^4,S,S\}$-bonding mode. In these coordination modes, the planarity of the thiophene ring is destroyed and the sulfur atom is bent out of the plane of the four carbon atoms. This is the reason for the stability of these complexes since, compared to the weak S donor ability of free thiophene, the sulfur atom in η^4-thiophene complexes is an excellent donor.

The η^1:η^5-coordination mode of thiophene has received considerable attention in our laboratories

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[5] S.C. Huckett, R.J. Angelici, *Organometallics*, 7, **1988**, 1491.

[6] E.O. Fischer, K. Öfele, *Chem. Ber.*, 91, **1958**, 2395.

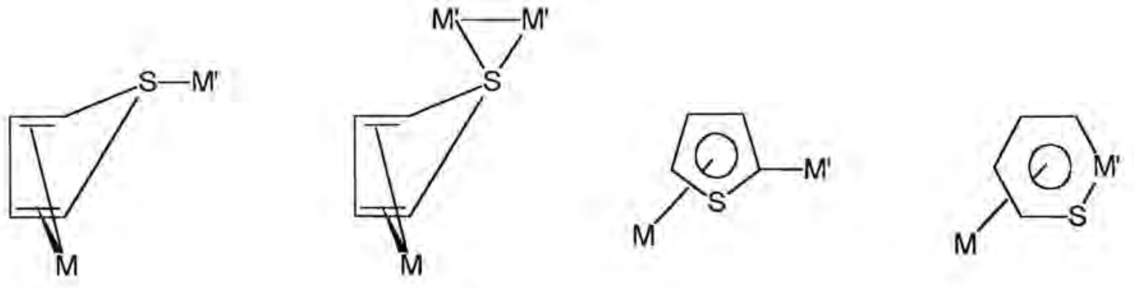
[7] M.G. Choi, R.J. Angelici, *J. Am. Chem. Soc.*, 111, **1989**, 8753.

[8] J. Chen, R.J. Angelici, *Organometallics*, 9, **1990**, 879.

[9] J. Chen, L.M. Daniels, R.J. Angelici, *Polyhedron*, 9, **1990**,1883.

and various bimetallic complexes were synthesized including $[Pt(\eta^1\text{-}C_4H_3S)L_2\{(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_4H_3S)Cr(CO)_3\}]$[10] and $[Mn(CO)_5\{\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_4H_3S\}Cr(CO)_3]$[11]. The latter complex was found to undergo a metal exchange reaction in solution[12].

The C-S bond cleavage is observed in a base-catalyzed reaction where the iridium in $[IrCp^*(\eta^4\text{-}2,5\text{-}Me_2T)]$ inserts into a C-S bond of the η^4-thiophene to give the ring-opened iridathiabenzene $[IrCp^*(C,S\text{-}2,5\text{-}Me_2T)]$, a six-membered ring. This iridathiabenzene ring reacts with various metal carbonyls to yield η^6-coordinated complexes of the type $[IrCp^*\{\eta^6\text{-}(C,S\text{-}2,5\text{-}Me_2T)\}\,ML_3]$, (M = W, Cr, Mo; L = CO, Fc^+, Cp)[13]. Metal insertion into the C-S bond of thiophene has also been recorded for Pt(0) and Re(0) metal moieties[14]. Russian workers have described the preparation of the compound $[FeCp(CO)_2(C_4H_3S)]$[15], which was reacted with $Fe_3(CO)_{12}$ to yield a trimetallic thiaferrole complex[16].



η^4,S-coordination η^4,S,S-μ_3-coordination η^1:η^5-coordination C,S:η^6-coordination

Figure 2.2 Coordination modes of thiophene to more than one transition metal

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[10] A. du Toit, M. Landman, S. Lotz, *J. Chem. Soc., Dalton Trans.*, **1997**, 2955.

[11] T.A. Waldbach, P.H. van Rooyen, S. Lotz, Organometallics, 12, **1993**, 4250.

[12] (a) T.A. Waldbach, P.H. van Rooyen, S. Lotz, *Angew. Chem. Int. Ed. Engl.*, 32, **1993**, 711. (b) T.A. Waldbach, R. van Eldik, P.H. van Rooyen, S. Lotz, *Organometallics*, 16, **1997**, 4056.

[13] J. Chen, V.G. Young, R.J. Angelici, *J. Am. Chem. Soc.*, 117, **1995**, 6362.

[14] J.J. Garcia, A. Arevalo, V. Montiel, F. del Rio, B. Quiros, H. Adams, P.M. Maitlis, *Organometallics*, 16, **1997**, 3216.

[15] A.N. Nesmeyanov, N.E. Kolobova, L.V. Goncharenko, K.N. Anisimov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, **1976**, 142.

[16] A.E. Ogilvy, M. Draganjac, T.B. Rauchfuss, S.R. Wilson, *Organometallics*, 7, **1988**, 1171.

2. Carbene complexes of arenes and heterocycles

Ab initio calculations indicate that the 2- and 5-positions of thiophene are the most active sites on the ring for nucleophilic attack while the sulfur atom carries a positive charge. It is therefore clear that deprotonation with lithium reagents can be readily accomplished, first abstracting the 2-proton and then the 5-proton in forming the dilithiated species. Since the synthesis of Fischer carbene complexes involves the nucleophilic attack of RLi reagents on carbonyl ligands, the synthesis of thiophene substituted alkoxy carbene complexes seems to be accessible by a combination of these two procedures.

2.1 Monocarbene complexes

The original carbene complex synthesized by Fischer and Maasböl[17], [W(CO)$_5$C(OMe)Ph], is also the first example of a carbene complex containing an aromatic substituent. Shortly after this discovery, the structural data of the complexes [W(CO)$_5$C(OMe)Ph] and [Cr(CO)$_5$C(OMe)Ph][18] were published which clearly showed the sp^2-character of the carbene carbon. In addition to the transition metals' synergic d(t_{2g})-p π-interaction with the carbene carbon, the important role of the heteroatom (X) lone-pair in p_C-p_X π-bonding to stabilize the "singlet" carbene carbon was soon recognized[19] (figure 2.3). A phenyl or heteroarene substituent is incorporated into the π-delocalized network surrounding the carbene carbon and may act as an electron withdrawing or electron donating substituent. Of interest for the latter is the stable [W(CO)$_5$C(Ph)Ph] carbene complex, which could be synthesized from the complex [W(CO)$_5$C(OEt)Ph][20]. The complexes [W(CO)$_5$C(OMe)Ph] and [Cr(CO)$_5$C(OMe)Ph] together with the [MnCp(CO)$_2$C(OMe)Ph] carbene complex were synthesized to investigate the electrophilic activity of the carbonyl ligands. To determine whether carbene complexes can accommodate dinuclear metal carbonyl complexes,

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[17] E.O. Fischer, A. Maasböl, *Angew. Chem.*, 76, **1964**, 645.

[18] O.S. Mills, A.D. Redhouse, J. Chem. Soc. A, **1968**, 642.

[19] (a) E.O. Fischer, *Angew. Chem. Int. Ed. Engl.*, 86, **1974**, 651. (b) F.A. Cotton, C.M. Lukehart, *Prog. Inorg. Chem.*, 16, **1972**, 487.

[20] C.P. Casey, *J. Am. Chem. Soc.*, 95, **1973**, 5833.

Fischer *et al*[21] synthesized the dinuclear $Mn_2(CO)_9$ carbene complex $[Mn_2(CO)_9C(OEt)Ph]$. The iron carbene complex with phenyl as substituent, $[Fe(CO)_4C(OEt)Ph]$ is also known[22], but Fischer-type carbene complexes of iron containing carbonyl ligands have been relatively inaccessible, mostly due to the preferred alkylation of the metal centre instead of the oxygen[23].

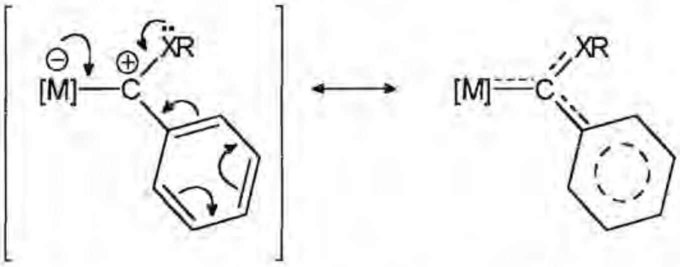

Figure 2.3 π-delocalized network around carbene carbon in arene carbene complex

Connor and Jones[24] synthesized the monocarbene complexes of chromium of the type $[Cr(CO)_5C(OR)R']$ where R' = 2-thienyl and 2-furyl in order to investigate the influence of different R-groups on the stability of the empty p_z orbital on the carbene carbon. The thienyl carbene complex of tungsten was prepared by Aoki *et al*[25]. Angelici and co-workers[26] recently reported the synthesis of a cationic 2-thienylidene carbene complex of rhenium, formed by C-H bond activation in a S-thiophene complex (figure 2.4).

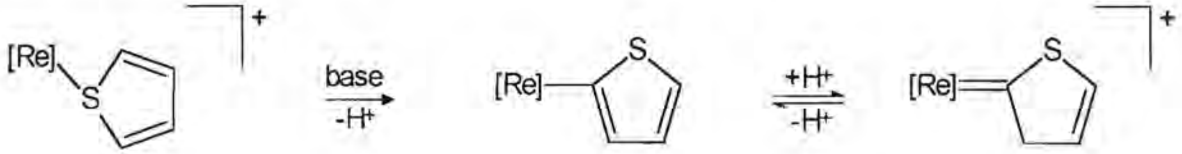

Figure 2.4 Formation of 2-thienylidene carbene complex

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[21] E.O. Fischer, E. Offhaus, *Chem. Ber.*, 102, **1969**, 2549.

[22] D.J. Cardin, B. Cetinkaya, M.F. Lappert, *Chem. Rev.*, 72, **1972**, 545.

[23] (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.

[24] J.A. Connor, E.M. Jones, *J. Chem. Soc. A*, **1971**, 1974.

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

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

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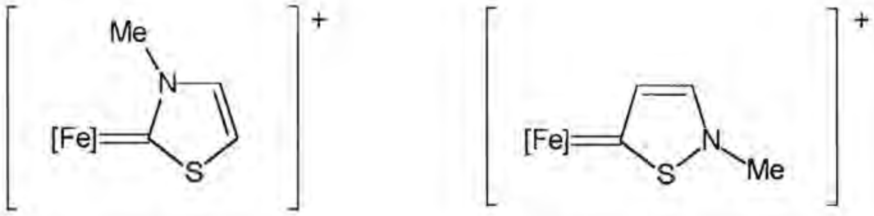
b14339043

The precursor [ReCp(NO)(PPh$_3$)thiophene)]$^+$ undergoes deprotonation by a strong base to give the 2-thienyl complex [ReCp(NO)(PPh$_3$)(2-thienyl)]. Re-protonation of the latter with triflic acid does not regenerate the S-thiophene complex but instead protonation occurs at the 3-position to form a thienylidene carbene product.

Monocarbene complexes of 2,2'-bithiophene have been synthesized recently[27]. These complexes were specifically tailored to contain pentacarbonyl transition metal units, which are known to be strong electron-withdrawing groups, on the one side of a conjugated system. The second thiophene moiety would represent the electron-donor counterpart, to obtain a "push-pull" situation in the molecule. The chromium and tungsten complexes were isolated and subjected to HRS (Hyper-Rayleigh Scattering) measurements to evaluate the NLO responses of these systems. It was concluded that the preliminary evaluation looked promising, although no later paper on this subject has appeared since.

Raubenheimer *et al*[28] described the synthesis of carbene complexes of iron by the addition of thiazolyl- or isothiazolyl-lithium to [FeCp(CO)$_2$Cl] and the subsequent alkylation or protonation of the products. In the thiazolylidene complexes the N-atom is in an α-position with respect to the coordinated carbene carbon, as is typical for known aminocarbene complexes, while the isothiazolinylidene complexes are unique since the nucleophilic heteroatom is situated γ to the coordinated carbon atom.



Thiazolyl complex

Isothiazolyl complex

Figure 2.5 Thiazolyl and isothiazolyl carbene complexes

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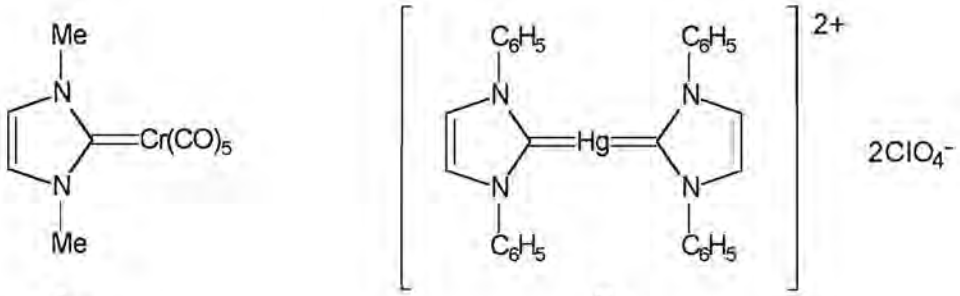
[27] S. Maiorana, A. Papagni, E. Licandro, A. Persoons, K. Clay, S. Houbrechts, W. Porzio, *Gazz. Chim. Ital.*, 125, **1995**, 377.

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

In 1968 Wanzlick and Öfele discovered that heterocyclic carbenes derived from imidazolium and pyrazolium salts form extraordinarily stable complexes with certain transition metals. The syntheses of the complexes pentacarbonyl(1,3-dimethylimidazoline-2-ylidene)chromium(0) **A** and bis(1,3-diphenylimidazoline-2-ylidene)mercury(II) diperchlorate **B** were described[29,30] (figure 2.6). They could however not isolate free carbenes. Arduengo opened the access to free, isolable N-heterocyclic carbenes in 1991[31]. In these complexes the metal-carbon bond is much less reactive than in Fischer- and Schrock-type carbene complexes. Renewed interest in these complexes have recently been sparked by Hermann *et al* because of the advantages of N-heterocyclic carbenes as ligands in organometallic catalysts, where they extend the scope of application reached by phosphines.[32]



A **B**

Figure 2.6 First N-heterocyclic carbene complexes

2.2 Biscarbene complexes

Fischer[33] employed his classical method of synthesizing carbene complexes to prepare the 1,4-phenylene biscarbene complexes of chromium and tungsten. These complexes were prepared by reacting *p*-phenylene dilithium with the relevant metal carbonyl complex. The synthesis of

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

[30] K. Öfele, *J. Organomet. Chem.*, 12, **1968**, 42.

[31] (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.

[32] W.A. Hermann, C. Köcher, *Angew. Chem. Int. Ed. Engl.*, 36, **1997**, 2162.

[33] E.O. Fischer, W. Röll, N. Hoa Tran Huy, K. Ackermann, *Chem. Ber.*, 115, **1982**, 2951.

biscarbene complexes where *o*-phenylene dilithium is utilized to afford 1,4-chelating tetracarbonyl biscarbene complexes of chromium, tungsten and molybdenum (figure 2.7) was described in the same article. This carbene study was extended to include the biphenylene ligand[34]. Biscarbene complexes of chromium and tungsten were prepared in a similar fashion and an X-ray diffraction study of the chromium complex showed that the molecule was centrosymmetric and the rings strictly coplanar. In a structural study of free biphenylene the rings were found to be twisted[35].

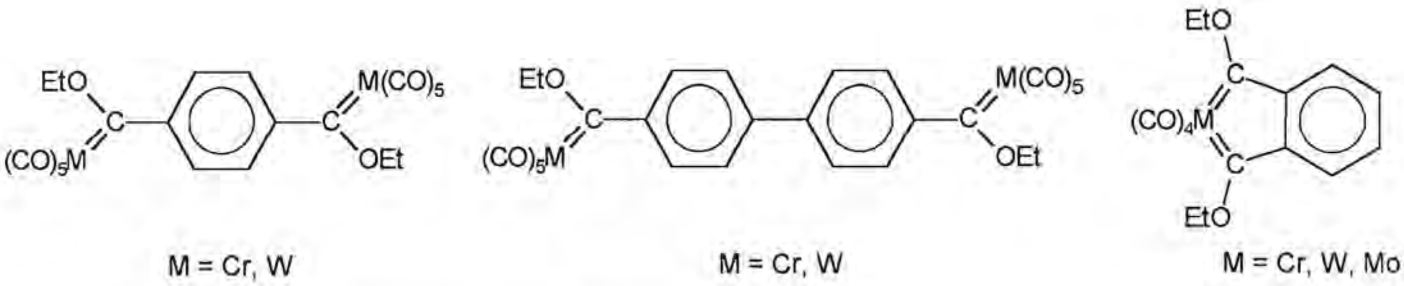

Figure 2.7 Phenylene biscarbene complexes

Synthesis of the biscarbene complex of tungsten with anthracene as bridging unit[36] was attempted to try and establish whether the functional group $W(CO)_5C(OMe)$ could withdraw electron density from dienes and thus assist in inverse Diels-Alder reactions. The complex was prepared starting from 9,10-dibromoanthracene, reacted with tungsten carbonyl and alkylated using trifluoromethane sulfonic acid ester.

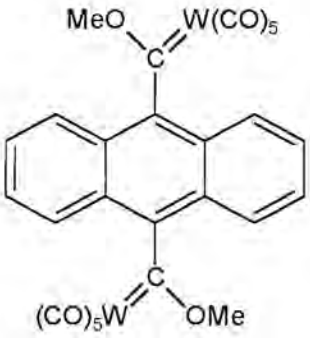

Figure 2.8 Bimetallic biscarbene complex with anthracene as bridging unit

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[34] N. Hoa Tran Huy, P. Lefloch, F. Robert, Y. Jeannin, *J. Organomet. Chem.*, 327, **1987**, 211.

[35] G. Charbonneau, Y. Delugeard, *Acta Cryst. B*, 33, **1977**, 1586.

[36] T. Albrecht, J. Sauer, *Tetrahedron Lett.*, 35, **1994**, 561.

Dinuclear biscarbene complexes incorporating thienylene moieties have been synthesized in our laboratories recently. The biscarbene complexes of chromium, tungsten and manganese with thiophene as bridging unit were prepared[37] and the crystal structure of the chromium biscarbene complex was determined. The reactions of the complexes in refluxing carbon disulphide, hexane and acetone were investigated. The intention was to investigate the possibility of forming dinuclear biscarbene complexes with coupled olefinic units, resulting in an extended spacer between the metal moieties. No evidence of such reaction products was observed. Instead, the corresponding o-ethylthienyl carboxylate monocarbene complexes and o-ethylthienyl thiocarboxylate monocarbene complexes were isolated, as shown in figure 2.9

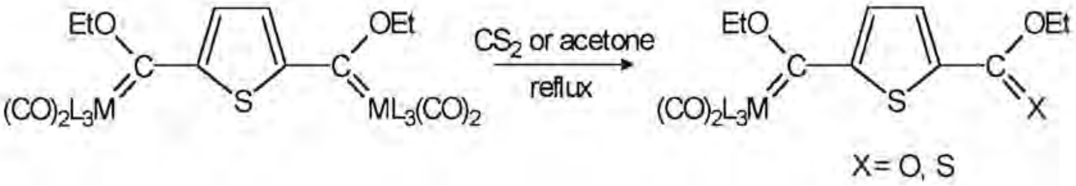

Figure 2.9 Decomposition of biscarbene complexes

Since thiophene derivatives have been largely used in studies for materials exhibiting non-linear optical properties both as spacer and as conjugating linking groups, this prompted the study related to the synthesis of carbene complexes of 2,2'-bithiophene. With this objective in mind, the first biscarbene complex containing two different metal moieties was synthesized (figure 2.10)[27]. However, mixtures of reaction products resulted, due to an inefficient method of synthesis, which complicated purification of the products.

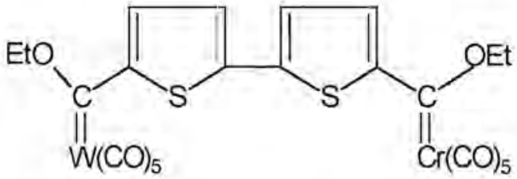

Figure 2.10 Biscarbene complex containing two different metal moieties

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[37] Y.M. Terblans, H.M. Roos, S. Lotz, *J. Organomet. Chem.*, 566, **1998**, 133.

3. Synthesis of carbene complexes of Thiophene

Once the interesting decomposition patterns of biscarbene complexes of the type $[M(CO)_5\{\mu\text{-}T\}M(CO)_5]$ (M = Cr, W) were recognized[37], this prompted a further study of the synthesis of analogous complexes of molybdenum. It is well known that the carbonyl ligands of molybdenum pentacarbonyl are much more labile than those of the corresponding tungsten or chromium complexes[38] and vacant coordination sites are generated more readily. These coordination sites are thus available for coordination of heteroatoms and the availability of carbonyls could facilitate carbonyl insertion processes. It was therefore anticipated that, in the light of the decomposition reactions of the biscarbene complexes of thiophene, different reaction patterns were possible for similar molybdenum complexes.

Seeing that the biscarbene complexes of chromium and tungsten have already been synthesized[37], it was envisaged to prepare the molybdenum analogues of these complexes to compare stabilities of the different products. According to Fischer[39] the stability of carbene complexes increases in the order $LMo(CO)_5 < LCr(CO)_5 < LW(CO)_5$. The trend was confirmed in this series of carbene complexes, since the biscarbene complex of molybdenum turned out to be highly unstable while the chromium and tungsten analogues are known to be fairly stable.

The novel molybdenum carbene complexes of thiophene were synthesized using the classical Fischer method. Thiophene is readily monolithiated as well as dilithiated with n-butyllithium[40]. The dimetallation of thiophene is done in hexane rather than in THF or ether solvents, since it was found that the ether solvent is attacked under forcing conditions. Addition of a strongly polar co-solvent, such as HMPT, does not lead to the introduction of a second metal atom, but instead causes ring-opening of the THF. Using hexane as solvent, the n-butyllithium TMEDA complex is capable of abstracting both the 2- and 5-protons of the thiophene upon adding two equivalents

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[38] Ch. Elschenbroich, A. Salzer, *Organometallics, A Concise Introduction*, VCH Verlag, Weinheim, **1992**, 232.

[39] K.H. Dötz, H. Fischer, P. Hofmann, I.R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes;* VCH Verlag Chemie: Weinheim, **1983**.

[40] L. Brandsma, H. Verkruijsse, *Preparative Organometallic Chemistry I*, Springer-Verlag, Berlin/Heidelberg, **1987**.

of the base to one equivalent of thiophene. The first deprotonation occurs at a low temperature (-10° C or lower) while the removal of the second proton is afforded at elevated temperatures. Upon addition of the metal carbonyl, nucleophilic attack of the dianion of thienylene occurred at carbonyl carbon atoms of two $Mo(CO)_6$ complexes to form a dilithium diacylmetallated product. The subsequent quenching of the dilithium salt with triethyloxonium tetrafluoroborate yielded the desired biscarbene complex. In most cases the reactions afforded both the mono- and biscarbene complexes together with a decomposition product and not only the expected biscarbene product. The general reaction scheme is outlined in figure 2.11.

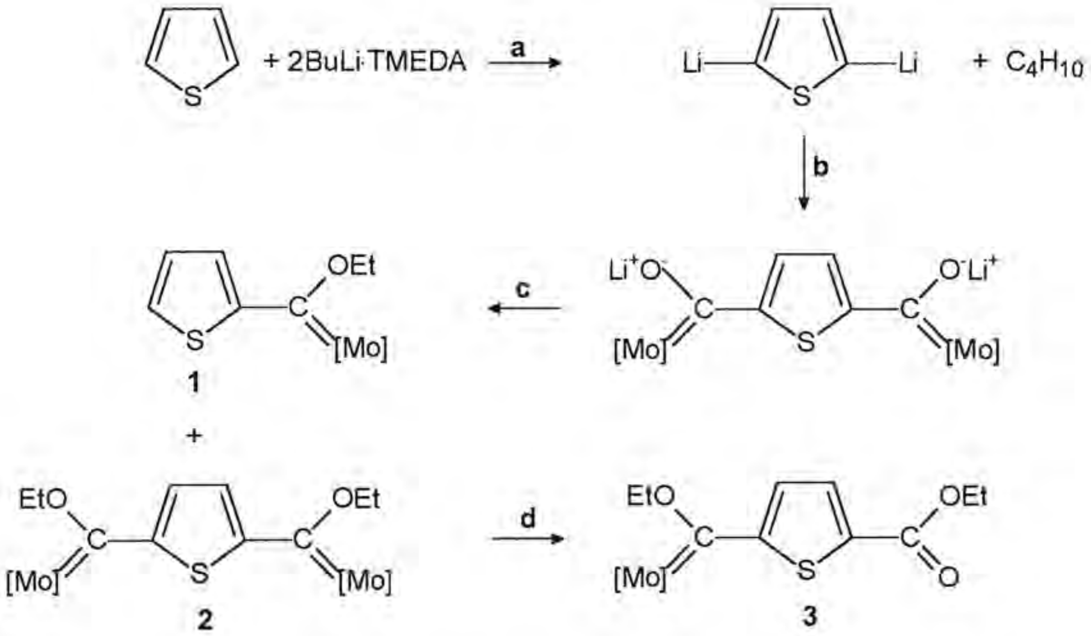

Figure 2.11 Procedure for preparation of carbene complexes
Reagents: (**a**) Hexane, reflux; (**b**) 2 eq. $Mo(CO)_6$, THF, -20°C; (**c**) 2 eq. $[Et_3O][BF_4]$, CH_2Cl_2 (**d**) O_2, acetone

The monocarbene complex, **1**, was crystallized from a hexane:dichloromethane (1:1) solution and afforded orange-red crystals. The purple biscarbene complex, **2**, was isolated and characterized spectroscopically, but was unstable and decomposed in inert atmosphere after a few hours. In solution decomposition occurred even more rapidly. Complex **3**, the decomposition product, was found to be relatively stable and could be fully characterized. Other byproducts from the reaction, isolated in lower yields, are the purple complex **4**, the orange-red complex **5**, both of which are even less stable than complex **2**, and a yellow organic product, which was found to be the bis(ester) complex with two ethoxy substituents on the two internal carbon atoms. These complexes were characterized spectroscopically and the structures assigned were based primarily on the proton NMR data, infrared and mass spectra. The formation of complexes **4** and **5** is suggested to have ensued *via* the route illustrated in figure 2.12. The biscarbene complex **2** was found to be highly unstable and thus activated for further modifications. It is proposed that one of the metal fragments of this complex was displaced by a carbonyl group (**a**). Analogous reactions involving such a process have been reported[41]. Deprotonation of a monocarbene complex is accomplished by the presence of the TMEDA base and nucleophilic attack on this carbonyl centre by the deprotonated monocarbene complex (**b**) affords complex **4**, after protonation. Complex **5**, which is analogous to **3**, is yielded from the reaction of O_2 (**c**) with complex **4**. (compare step **d** figure 2.11)

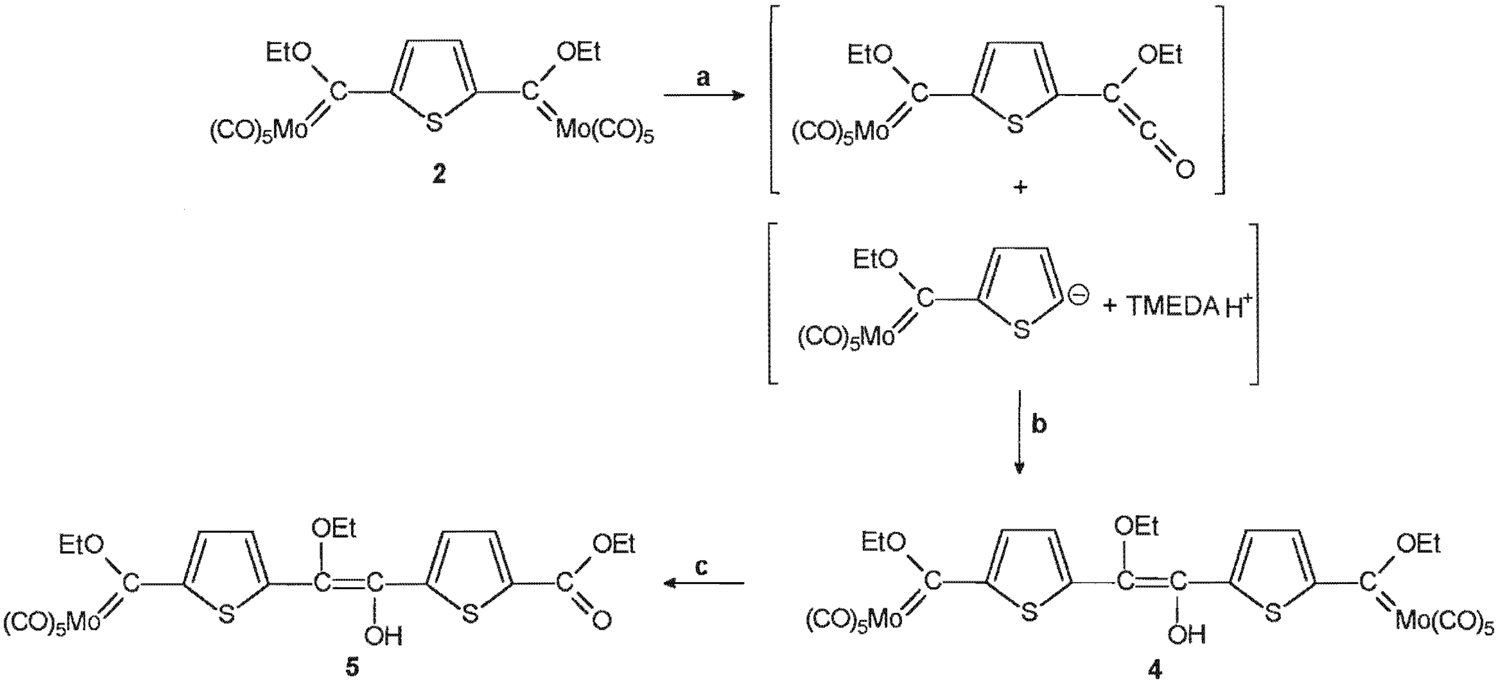

Figure 2.12 Proposed mechanism for the formation of complexes **4** and **5**

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[41] (a) K.H. Dötz, B. Fügen-Köster, *Chem. Ber.*, 113, **1980**, 1449. (b) W.D. Wulff, P.-C. Tang, *J. Am. Chem. Soc.*, 106, **1984**, 434.

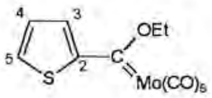
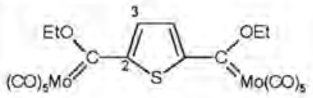
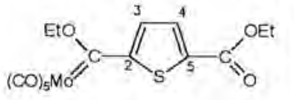
3.1 Spectroscopic characterization of novel carbene complexes

The carbene complexes were characterized using NMR and infrared spectroscopy and mass spectrometry. Due to the instability of complexes **4** and **5**, it was impossible to record satisfactory ^{13}C NMR spectra of the complexes, since decomposition occurred in solution. Confirmation of the molecular structure of **1** was obtained from a single crystal X-ray diffraction study.

3.1.1 ^{1}H NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform as solvent unless otherwise specified. The ^{1}H NMR data for complexes **1-3** are summarized in table 2.1, while the data for complexes **4** and **5** are tabulated in table 2.2.

Table 2.1 ^{1}H NMR data of complexes 1, 2 and 3

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **1**		 **2**		 **3**	
	δ	J	δ	J	δ	J
H3	8.18 (dd)	4.0 1.1	7.98 (s)	-	8.03 (d)	4.1
H4	7.20 (dd)	5.0 4.1	-	-	7.76 (d)	4.4
H5	7.75 (dd)	5.0 1.0	-	-	-	-
OCH$_2$CH$_3$-M	5.07 (q)	7.1	5.10 (q)	7.0	5.09 (q)	7.1
OCH$_2$CH$_3$-O	-	-	-	-	4.37 (q)	7.2
OCH$_2$**CH$_3$**-M	1.64 (t)	7.1	1.67 (t)	7.0	1.67 (t)	7.0
OCH$_2$**CH$_3$**-O	-	-	-	-	1.38 (t)	7.1

The data support the proposed molecular structures of the complexes. The chemical shifts for the protons of thiophene are at 7.20 ppm for H2 and H5 and at 6.96 ppm for H3 and H4[42]. On comparing these literature values with the corresponding values of the complexes, it is evident that the coordination to a metal fragment has a marked influence on the chemical shifts of the protons. The protons of the complexes are shifted more downfield than for the uncoordinated thiophene. Upon coordination to the metal, the carbene moiety causes draining of electron density from the double bonds of the thiophene ring to the electrophilic carbene moiety. Assignments of the thienyl protons are based on assignments made by Gronowitz[43]. From the NMR data of complex **1** it is observed that the chemical shift of H3 is downfield compared to its position on the spectrum of **2**, while the chemical shift of H4 is upfield. This can be explained when considering the resonance structures of the complex as shown in figure 2.13. The π-resonance effect affords positive charges on H3 and H5 respectively and thus deshielding of these two protons emanates, causing the downfield shift. It is concluded that H3 will shift more downfield than H5 since it is closer to the carbene moiety. The proton H4, however, is not affected by the resonance effect and its chemical shift is therefore comparable with the chemical shift of free thiophene.

Figure 2.13 Draining of electrons in monocarbene complex

In the case of the biscarbene complex, **2**, the ring protons are affected by two metal nuclei and the combined withdrawing effect of the two carbene substituents results in an unfavourable electronic effect. Two positive charges are generated on two adjacent carbon atoms, as shown in figure 2.14. On considering complex **3**, it is clear that both substituents cause draining of electrons away from the ring but that the influence of the ester group is less profound than the influence of the carbene moiety since the deshielding of H4 is less than for H3.

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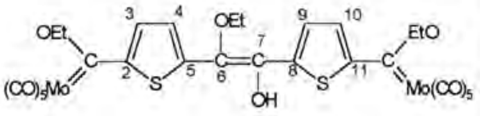
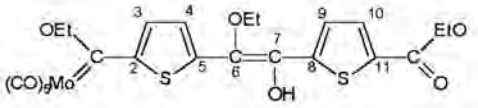
[42] R.J. Abrahams, J. Fischer, P. Loftus, *Introduction to NMR Spectroscopy*, John Wiley and Sons, **1988**.

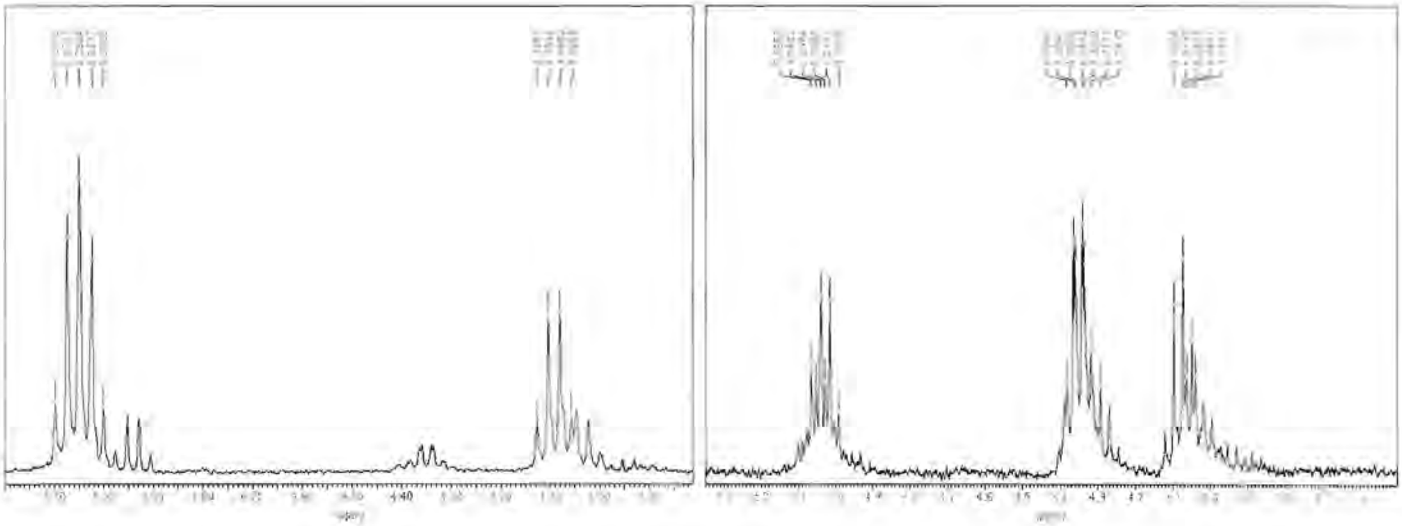
[43] S. Gronowitz, *Adv. Heterocycl. Chem.*, 1, **1963**, 1.

Figure 2.14 Draining of electrons in biscarbene complexes

Table 2.2 **^{1}H NMR data of complexes 4 and 5**

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)			
	 **4**		 **5**	
	δ	J	δ	J
H3	8.03 (d)	4.4	8.03 (d)	4.4
H4	7.20 (d)	4.4	7.21 (d)	4.4
H9	7.33 (d)	4.4	7.16 (d)	4.4
H10	8.10 (d)	4.4	7.71 (d)	4.4
OCH$_2$CH$_3$-M	5.04 (q) 5.06 (q)	7.2 7.2	5.03 (q)	7.1
OCH$_2$CH$_3$-O	-	-	4.35 (q)	7.0
OCH$_2$CH$_3$-C	4.09 (q)	7.0	4.08 (q)	7.0
OCH$_2$**CH$_3$**-M	1.64 (t) 1.65 (t)	7.2 7.2	1.64 (t)	7.1
OCH$_2$**CH$_3$**-O	-	-	1.37 (t)	7.0
OCH$_2$**CH$_3$**-C	1.51 (t)	7.0	1.49 (t)	7.0
-OH	6.73 (s)	-	6.57 (s)	-

The methylene regions on the spectra of complexes **4** and **5** are depicted in figure 2.15. The purple colour of **4** is indicative of biscarbene complexes with thiophene spacers and the spectrum of **4** in the methylene region displays two resonances. The intensity of the downfield signal is double that of the upfield signal, indicating two carbene ethoxy units to one additional ethoxy substituent. Notably, the spectrum of complex **4** reveals two overlapping quartet signals for the methylene groups of the alkoxy groups on the two carbene carbons. This can be explained by the different chemical environments of the two methylene groups due to the alcohol functional group on the one and the ethoxy group on the other of the two central carbons, thereby destroying the centre of symmetry present in biscarbene complexes such as complex **2**. On the spectrum of complex **5** three signals are present in the methylene region. An additional signal appears at 4.35 ppm and now three signals of equal intensity are found.



(a) (b)

Figure 2.15 Methylene proton region on the ^{1}H NMR spectra of complexes (a) **4** and (b) **5**

It is thus clear that one carbene moiety of **4** has been replaced by an ester functional group to yield **5**. Characteristic in this study is the chemical shifts of the methylene protons of the ethoxy groups which were found above 5.0 ppm for carbene moieties, around 4.3 ppm for ester ethoxy functionalities and at 4.0 ppm for ethoxy substituents. Although we favour the structural representation shown for complex **5**, we cannot exclude the possibility that the ethoxy and hydroxy substituents may change places to give an alternative structure. However, the large difference in chemical shifts of the OH resonances on the spectra of **4** and **5** was taken to indicate that the OH substituent is positioned on the carbon atom nearest to the thiophene ring where the carbene moiety is substituted by a ester functional group for complex **5**. A "push-pull" effect is introduced in **5**, where two different end-groups are present in the molecule.

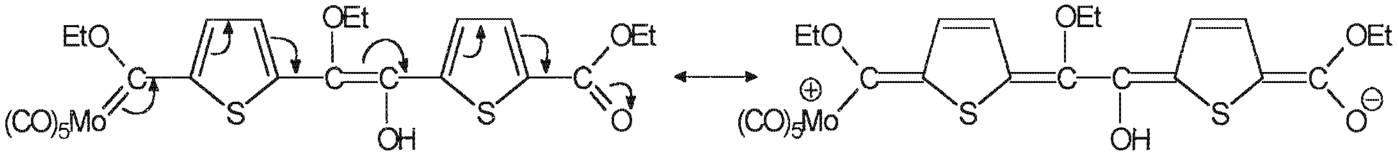


Figure 2.16 π-delocalization in complex **5**

On the spectrum of the organic bis(ester) product, only two quartet signals of equal intensity are observed in the methylene region, one at 4.05 ppm (J = 7.1 Hz) and one at 4.35 ppm (J = 7.1 Hz). These two resonances correspond to the methylene protons of the ethoxy functionality on a centre carbon atom and to a methylene group of an ester end group. The quartet signal associated with the methylene protons of the ethoxy group of the carbene moiety of complexes **4** and **5,** is absent on this spectrum. The corresponding methyl signals of these two ethoxy groups are observed at 1.49 and 1.37 ppm, respectively.

On comparing the chemical shift values of complexes **4** and **5** with those of complexes **1**, **2** and **3**, it is interesting to note that the chemical shift values of the different ethoxy groups are observed at characteristic positions on the spectra of all the compounds. In general the values correspond well, especially on relating the resonances of the monocarbene complex **1** and the decomposition product **3** to the corresponding protons on the spectra of complexes **4** and **5**. Complex **5** can be seen as a combination of these two complexes and it is thus not surprising that the values are very comparable.

3.1.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data of complexes **1-3** are given in table 2.3 while the spectrum for complex **3** is depicted in figure 2.17. Complexes **4** and **5** decomposed during the recording of the spectra. On the ^{13}C NMR spectrum of complex **4** the following peaks (ppm) were observed and assigned:

212.8, 212.6 (CO *trans*); 206.2, 206.0 (CO *cis*); 141.9 (C3); 140.8 (C10); 129.6 (C4); 128.6 (C9); 111.5 (C6); 99.7 (C7); 77.7, 77.2, 68.4 (OCH_2CH_3); 15.5, 15.1, 14.9 ($OCH_2\mathbf{CH_3}$).

Table 2.3 **^{13}C NMR data of complexes 1, 2, and 3**

Carbon	Chemical shifts (δ, ppm)		
	1	**2**	**3**
	δ	δ	δ
Carbene	307.2	312.4	310.8
C2	150.1	154.5	162.3
C3	136.2	136.9	139.4
C4	128.9	136.9	133.0
C5	141.4	154.5	159.4
$O\mathbf{CH_2}CH_3$-M	77.8	78.3	78.2
$O\mathbf{CH_2}CH_3$-O	-	-	61.9
$OCH_2\mathbf{CH_3}$-M	15.1	15.0	15.0
$OCH_2\mathbf{CH_3}$-O	-	-	14.2
$M(CO)_5$	206.1 (*cis*) 212.8 (*trans*)	205.6 (*cis*) 212.9 (*trans*)	205.7 (*cis*) 212.7 (*trans*)
C=O	-	-	206.1

Chemical shift values of carbene carbon atoms fluctuate in a very broad range starting at 200 ppm, for aminocarbene complexes[44], to 400 ppm, for some silicon complexes[45]. They depend mainly on the R and R' groups of the carbene C(R)R' but also on the metal, although to a smaller degree, considering the interaction of the d orbitals on the metal and the p_z orbital of the carbene carbon. Deshielding of the carbenium ion is encountered and it can therefore be concluded that carbene carbon atoms in their metal complexes bear a partial positive charge. The chemical shift of carbene ligands as a function of R decreases for complexes of chromium and tungsten as follows: Me> Ph> 1-ferrocenyl> 2-thienyl> 2-furyl[24]. This decrease is in accordance with the

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

[45] E.O. Fischer, T. Selmayr, F.R. Kreissl, U. Schubert, *Chem. Ber.*, 110, **1977**, 574.

lowering of donor properties of these substituents. The carbene carbons are shifted more downfield for biscarbene complexes than for monocarbene or decomposition complexes. This trend was observed on comparing the spectra of complexes **1**, **2** and **3**, with respective values of 307.2 ppm, 312.4 ppm and 310.8 ppm. This tendency is not observed for the C2 carbon, since the value observed for complex **3** is further downfield than for complexes **1** and **2**. The electron withdrawing effect of the ester functionality is suggested to contribute to the deshielding of this carbon. In fact, both carbons C2 and C5 of complexes **5** are observed at higher chemical shifts than the C2 value on the spectra of complexes 1 and **2**. This can be attributed to the polarization effect of the two different end-capped moieties. The chemical shift value obtained for the carbonyl group of the ester moiety is more downfield than the value associated with organic ester carbonyl groups. This is ascribed to the electron-withdrawing influence of the metal fragment on the opposite side of the thiophene ring. The metal carbonyls seem to be little affected by the change in substituents on the carbene carbon.

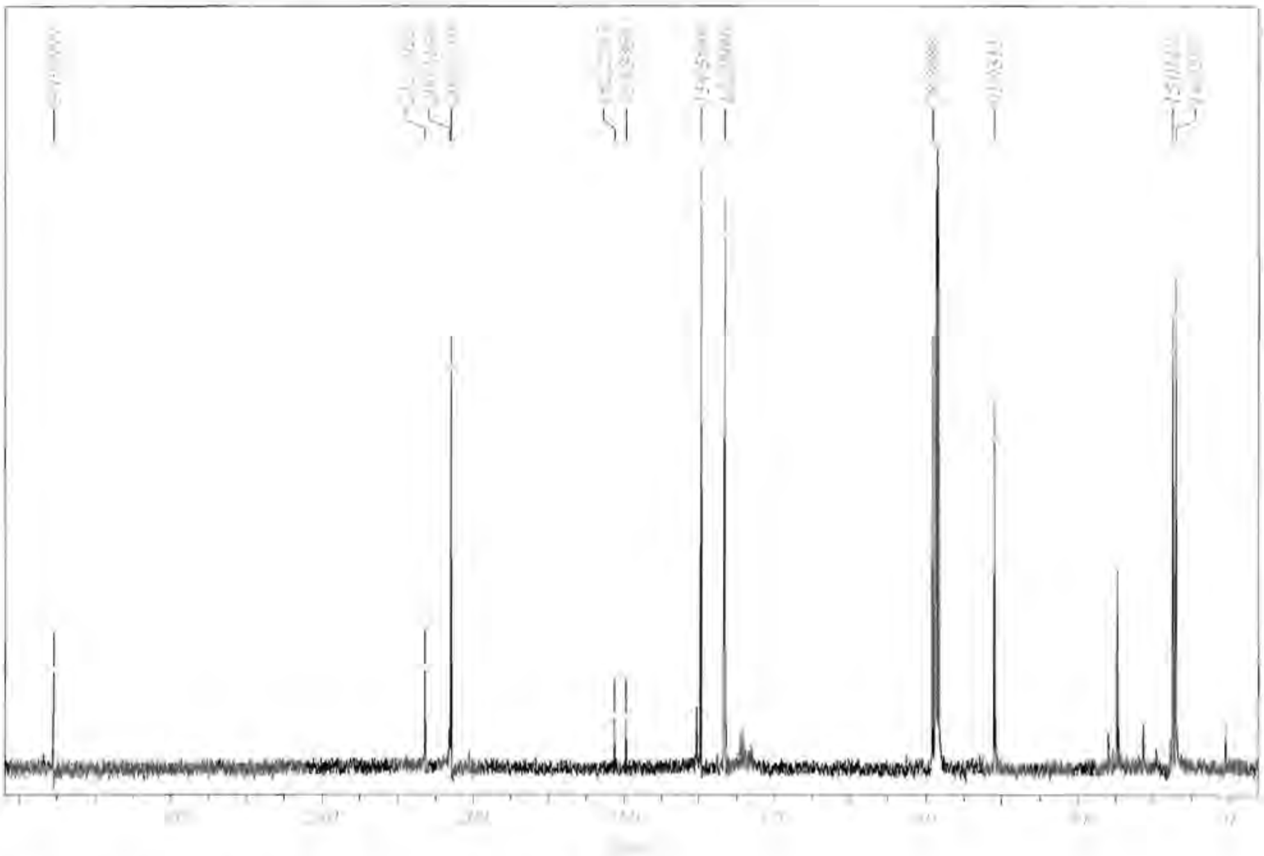

Figure 2.17 ^{13}C NMR spectrum of complex **3**

Chemical shift values for terminal metal carbonyls lie in the range 150 to 240 ppm. Within a group of metals, shielding of the carbonyl nucleus increases with increasing atomic number, for example the carbonyl chemical shifts of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ are found at 212, 202 and 192 respectively. In the spectra of the carbene complexes two signals are observed for the metal pentacarbonyl moiety. This is attributed to *cis* and *trans* carbonyl ligands.

3.1.3 Infrared Spectroscopy

The C-O stretching vibrational frequencies, in contrast to M-C stretching frequencies can be viewed as being independent from other vibrations in the molecule. In carbene carbonyl complexes, bands caused by ν_{CO} vibrations occur at lower energies than in the corresponding metal carbonyl complexes. This shows that carbene ligands possess weaker π-acceptor properties compared to the carbonyl group.

The infrared data of complexes **1**-**5** are outlined in table 2.4.

Table 2.4 Infrared data of complexes 1-5

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})				
	1	**2**	**3**	**4**	**5**
$A_1^{(1)}$	2066 2067	2064	2065	2064	2065
B	1983 1986	1985	1982	1983	1982
$A_1^{(2)}$	1942 1957	1943	1942	1942	1943
E	1942 1948	1943	1942	1942	1943

First set of values recorded in dichloromethane, second set in hexane

On the infrared spectra of pentacarbonyl metal carbene complexes, three absorption bands can be distinguished in the terminal carbonyl region, *i.e* two A_1 and one E band, as is expected for C_{4v} symmetry. When the carbene carbon has a bulky substituent, the E band is sometimes split and the formally IR-forbidden B band is observed, due to distortion of the equatorial plane of carbonyls. Most of the spectra were recorded in dichloromethane as solvent due to solubility problems in hexane as solvent and hence the $A_1^{(2)}$ and E bands overlap in the spectra. For the spectra recorded in hexane as solvent both bands are visible and the $A_1^{(2)}$ is characteristically observed as a shoulder on the higher wavenumber side of the E band.

3.1.4 Mass spectrometry

The fragmentation patterns of complexes **1**-**3** are summarized in table 2.5. A molecular ion peak, M^+, was observed on the spectra for each of the complexes. A general fragmentation pattern was identified. The fragmentation patterns of both complexes **1** and **3** are based on the ^{98}Mo isotope, while the pattern for complex **2** is based on one ^{98}Mo isotope and one ^{96}Mo isotope.

The fragmentation pattern of complex **2** seems to follow two different routes after the initial stepwise loss of six carbonyls. For the first route, the loss of the rest of the carbonyls ensues, followed by the normal degradation pattern with the loss of the ethyl group and then the CO fragment. The second route have more possibilities, of which one is shown, and involves the loss of the ethyl and CO groups before disintegration of the rest of the carbonyls. The two different fragmentation routes are illustrated in figure 2.18.

Table 2.5 Fragmentation patterns of complexes 1, 2 and 3

Complex	Fragment ions (I, %)
1	377.8 (17) M^+; 349.8 (25) M^+ - CO; 321.9 (32) M^+ - 2CO; 293.8 (33) M^+ - 3CO; 265.8 (69) M^+ - 4CO; 237.9 (100) M^+ - 5CO; 208.9 (76) M^+ -5CO -CH_2CH_3
2	669.3 (24) M^+; 613.2 (10) M^+ - 2CO; 585.0 (15) M^+ - 3CO; 557.2 (15) M^+ - 4CO; 501.2 (79) M^+ - 6CO; 473.1 (49) M^+ - 7CO; 445.2 (73) M^+ - 8CO; 417.2 (54) M^+ - 9CO; 389.0 (73) M^+ - 10CO; 360.0 (49) M^+ - 10CO - CH_2CH_3, 331.1 (54) M^+ - 10CO - 2CH_2CH_3; 303.0 (42) M^+ - 11CO - 2CH_2CH_3; 275.0 (100) M^+ - 12CO - 2CH_2CH_3
3	450.4 (4) M^+; 422.4 (5) M^+ - CO; 394.3 (6) M^+ - 2CO; 366.3 (5) M^+ - 3CO; 338.4 (12) M^+ - 4CO; 310.3 (43) M^+ - 5CO; 281.1 (27) M^+ - 5CO - CH_2CH_3; 253.1 (11) M^+ - 6CO - CH_2CH_3; 155.1 (54) $C_7H_7O_2S^+$; 139.1 (22) $C_7H_7OS^+$

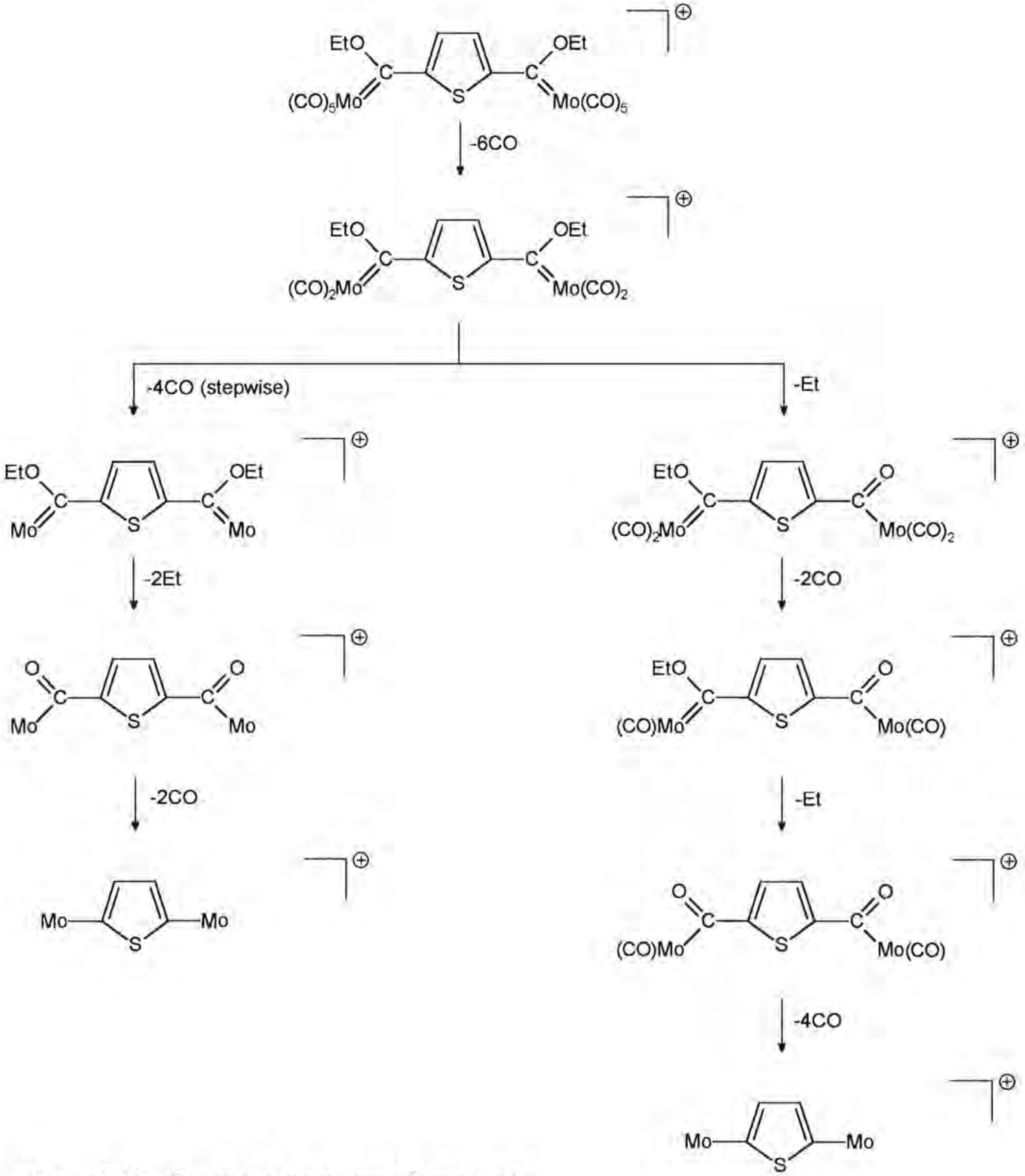

Figure 2.18 Fragmentation pattern of complex **2**

3.1.5 X-ray Crystallography

A single crystal X-ray diffraction study confirmed the molecular structure of complex **1**. Single crystals of the monocarbene complex **1** were afforded from a dichloromethane:hexane (1:1) solution. The complex crystallized as orange-red cubic crystals.

Figure 2.19 represent a ball-and-stick plot of the structure. Selected bond lengths and angles are tabulated in table 2.6.

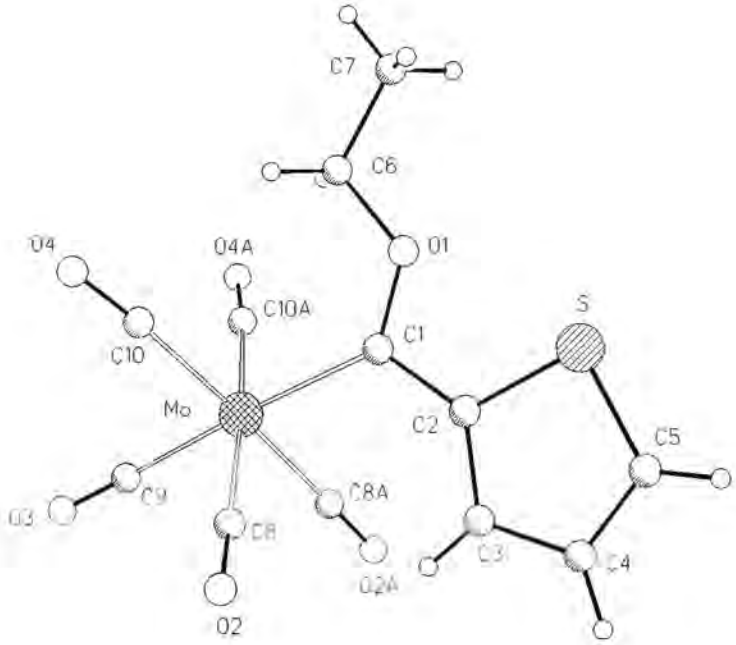

Figure 2.19 Ball-and-stick plot of complex **1**

The crystal structure of free thiophene was determined by Harshbarger *et al*[46]. The bond lengths were found to be 1.718(4) Å for S-C(2), 1.370(4) Å for C(2)-C(3) and 1.442(2) Å for C(3)-C(4). The bond angles were determined as 92.0(3)° for C(2)-S-C(5) and 112.0(3)° for S-C(2)-C(3).

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[46] W.R. Harshbarger, S.H. Bauer, *Acta. Cryst.*, B26, **1970**, 1010.

Table 2.6 Selected bond lengths and angles of 1

1	Bond Lengths (Å)	1	Bond angles (°)
Mo-C(1)	2.226(5)	C(5)-S-C(2)	91.9(3)
S-C(5)	1.705(6)	C(1)-O(1)-C(6)	122.5(4)
S-C(2)	1.756(5)	O(1)-C(1)-C(2)	106.3(4)
O(1)-C(1)	1.333(6)	O(1)-C(1)-Mo	129.4(4)
O(1)-C(6)	1.450(7)	C(2)-C(1)-Mo	124.3(4)
C(1)-C(2)	1.457(8)	C(3)-C(2)-S	109.4(4)
C(2)-C(3)	1.390(8)	C(2)-C(3)-C(4)	114.1(5)
C(3)-C(4)	1.409(8)	C(5)-C(4)-C(3)	111.8(5)
C(4)-C(5)	1.378(9)	C(4)-C(5)-S	112.8(5)

The six ligands, five carbonyl groups and one carbene, are arranged octahedrally around the molybdenum centre. The carbonyl ligands in the equatorial plane are staggered relative to the carbene ligand as is manifested by the C1-Mo-C8, C1-Mo-C8A, C1-Mo-C10 and C1-Mo-C10A angles of 88.3(2)°, 88.3(2)°, 95.5(2)° and 95.5(2)° respectively. Two carbonyls are bent towards the carbene carbon and two are bent away from it.

The torsion angle S-C(2)-C(3)-C(4) is 0.169(1)° while the torsion angle C(4)-C(5)-S-C(2) has a value of -1.695(1)° which indicates that the thienyl ring is planar. The thienyl ring, carbene carbon and metal atom are also in the same plane, with the sulfur and oxygen atoms on the same side of the C(1)-C(2) bond. The carbene carbon has sp^2-character which is indicated by the Mo-C1-O1, Mo-C1-C2 and O1-C1-C2 angles of 127.6(5)°, 125.6(5)° and 106.8(6)° respectively. These bond angles differ from the expected value of 120 ° for a sp^2-hybridized carbon atom but are typical for alkoxy carbene complexes. This deformation of the complex may be attributed to steric as well as electronic factors[47].

On comparing the bond lengths of the thienyl ring in complex **1** with the bond lengths of uncoordinated thiophene, it was found that all of the bonds are longer in the complex except for the C(3)-C(4) bond which is shorter in the complex. The C(carbene)-C(thienyl) bond is also shorter

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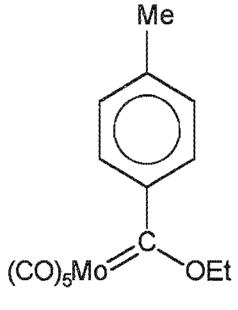
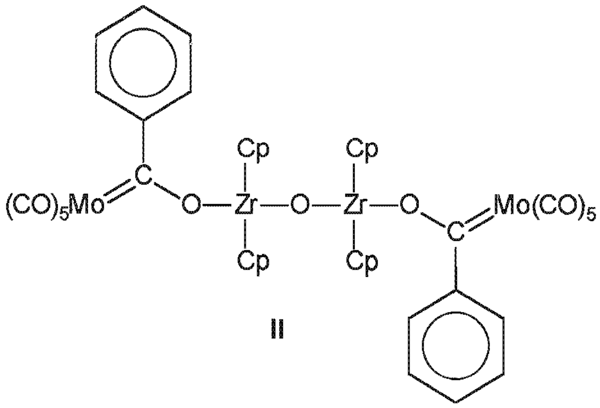
[47] R.J. Goddard, R. Hoffmann, E.D. Jemmis, *J. Am. Chem. Soc.*, 102, **1980**, 7667.

(1.457(8) Å) than normal C-C single bonds (1.51(3) Å)[19b]. The Mo-C(carbene) bond length is comparable with values determined for complexes in literature (figure 2.20) e.g. for [Mo(CO)$_5$C(OEt)p-Tol] **I** the M-C(carbene) bond length was calculated as 2.189 Å[48] and for [(μ-O){Mo(CO)$_5$C(Ph)OZrCp$_2$)}$_2$] **II** the M-C(carbene) bond length was calculated as 2.195 Å[49].



I



II

Figure 2.20 Structures of reference complexes **I** and **II**

The Mo-C(O) bond length in Mo(CO)$_6$ is 2.06 Å. The average Mo-C(O) bond length in complex **1** was determined as 2.01 Å, with the *trans* Mo-C(O) bond being the shortest due to poorer π-acceptor properties of the carbene ligand. For the two reference complexes **I** and **II** the corresponding bond lengths are cited as 2.01 Å and 2.02 Å, respectively. These values are as expected significantly smaller than the value estimated for a Mo-C single bond (2.33 Å)[50] and indicate double-bond character for the molybdenum-carbon carbonyl bonds. The bond angles of the thienyl ring in complex **1** differ from the angles in uncoordinated thiophene which shows that the thienyl ring is somewhat more distorted in the complex than in free thiophene, indicating ring involvement in stabilizing the carbene carbon.

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[48] D. Xiaoping, L. Genpei, C. Zhongguo, T. Youqi, C. Jiabi, L. Guixin, X. Weihua, *J. Struct. Chem.*, 7, **1988**, 22.

[49] G. Erker, U. Dorf, C. Kruger, Y. Tsay, *Organometallics*, 6, **1987**, 680.

[50] Ch. Elschenbroich, A. Salzer, *Organometallics, A Concise Introduction*, VCH Verlag, Weinheim, **1992**, 229.

4. Aminocarbene complexes

Fischer carbene complexes are often referred to as electrophilic carbene complexes since the carbene carbon is susceptible to nucleophilic attack. Nucleophilic substitution reactions of Fischer carbene complexes with amines were investigated by Connor and Fischer[51]. The reaction is similar to the aminolysis of esters to form amides since the $M(CO)_5$-moiety is electronically similar to a carbonyl oxygen atom. Nucleophilic attack by the nitrogen lone pair on the carbene carbon atom leads to the elimination of alcohol and the formation of the aminocarbene product.

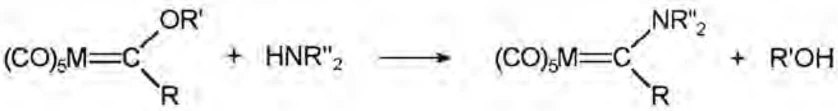

Figure 2.21 Aminolysis reaction of carbene complex

From the early days of carbene chemistry, it was recognized that aminocarbene complexes are more stable than their alkoxy analogues. This was ascribed to greater participation of the nitrogen lone pair compared to oxygen in stabilizing the electrophilic carbene carbon. Indications that amino substituents could stabilize carbene ligands bound to mid-valent group 6 metal centres were later provided by the observations of Kreissl that, while $[W(\equiv CC_6H_4Me\text{-}4)Cp(CO)_2]$ reacts with hydrogen chloride to form the acyl complex $[W(\eta^2\text{-}C(O)CH_2C_6H_4Me\text{-}4)Cp(CO)Cl_2]$[52], the same reagent with $[W(\equiv CNEt_2)Cp(CO)_2]$ affords the aminomethylene complex $[W(=CHNEt_2)CpCl(CO)_2]$[53]. Fillipou[54] recently obtained similar results for chromium.

Unfortunately the aminolysis of alkoxycarbene complexes is limited to unhindered primary and, in some cases, secondary amines, and is restricted to those alkoxy carbene complexes accessible from organolithium reagents. An alternative and very efficient method for the preparation of

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[51] J.A. Connor, E.O. Fischer, *J. Chem. Soc. (A)*, **1969**, 578.

[52] F.R. Kreissl, W.J. Sieber, M. Wolfgruber, J. Riede, *Angew. Chem. Int. Ed. Engl.*, 23, **1984**, 640.

[53] F.R. Kreissl, W.J. Sieber, M. Wolfgruber, *J. Organomet. Chem.*, 270, **1984**, C45.

[54] A.C. Fillipou, D. Wossner, B. Lungwitz, G. Kociokkohn, *Angew. Chem. Int. Ed. Engl.*, 35, **1996**, 876.

chromium aminocarbene complexes was introduced by Hegedus *et al*[55]. It involves the reaction of $Cr(CO)_5^{2-}$ with tertiary amides in the presence of chlorotrimethylsilane. The reaction is believed to proceed via nucleophilic addition of $Cr(CO)_5^{2-}$ to the carbonyl group of an amide followed by the O-silylation of the adduct. Subsequent reaction with an excess of chlorotrimethylsilane affords the product and elimination of hexamethyldisiloxane ensues, as shown in figure 2.22.

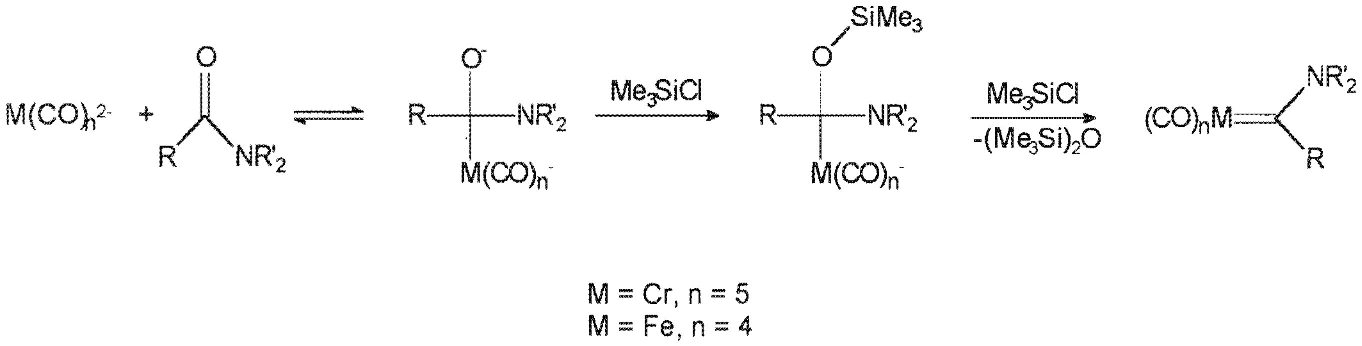

Figure 2.22 Synthesis of aminocarbene complexes

This method has recently been utilized to prepare iron aminocarbene complexes lacking α-hydrogens[56]. This study has been extended to include the preparation of (μ-bis(aminocarbene)dimetal complexes of chromium and iron[57] and has led to the preparation of a mixed chromium-iron bisaminocarbene complex. The general method of preparing chromium aminocarbene complexes, which involves the aminolysis of alkoxy carbene complexes, can in principle also be employed to prepare iron aminocarbene complexes, but iron alkoxy carbene complexes are not as easy to synthesize as the chromium analogues[58].

Recently the application of aminocarbene complexes in organic synthesis was undertaken and substantial differences in the reactivity patterns of these complexes compared to alkoxy carbene complexes have been observed. For example, aryl(alkylamino)carbene complexes undergo

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[55] R. Imwinkelried, L.S. Hegedus, *Organometallics*, 7, **1988**, 702.

[56] D. Dvořák, *Organometallics*, 14, **1995**, 570.

[57] M. Havránek, M. Hušák, D. Dvořák, *Organometallics*, 14, **1995**, 5024.

[58] M.F. Semmelhack, R. Tamura, *J. Am. Chem. Soc.*, 105, **1983**, 4099.

thermal reactions with alkynes to give indanones or aminoindenes[59], while N-acylation[60] of these complexes produce intermediate products which can be converted to a number of unusual organic compounds. Hegedus *et al* investigated the photolytic reactions of aminocarbene complexes to produce amino-β-lactams[61] and α-amino acid esters[62].

4.1 Aminolysis reactions of monocarbene complex 1

In order to test the viability of using diamines in linking two carbene fragments in binuclear biscarbene complexes, the reactions of **1** with various amines were investigated. Also, exchanging an alkoxy carbene for an aminocarbene implies changing the bonding properties of the substituents around the carbene carbon and should influence the role of the thienyl substituent.

The molybdenum monocarbene complex **1** was utilized in reactions with amines to yield aminocarbene complexes **6** and **7**. The reactions were effected in diethyl ether and the products purified by chromatography on silica gel. Similar behaviour has been described previously for mono- and chelating biscarbene complexes[63].

The two amines used in the reactions were ammonia (NH_3) and 1,4-phenylene diamine. The 1,4-phenylene diamine was chosen to try and substitute the diamine ligand at both active positions to obtain a diaminodicarbene complex in spite of the concern that it may be too bulky for the system. Werner[64] showed that the mechanism for aminolysis involves more than one amine to activate the carbene carbon. This implies that only small amines will affect this type of reaction. Nevertheless two equivalents of monocarbene were reacted with one equivalent of 1,4-phenylene diamine, but unfortunately the target product was not formed. Instead only one position was substituted as figure 2.23 illustrates.

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[59] A. Yamashita, *Tetrahedron Lett.*, 27, **1986**, 5915.

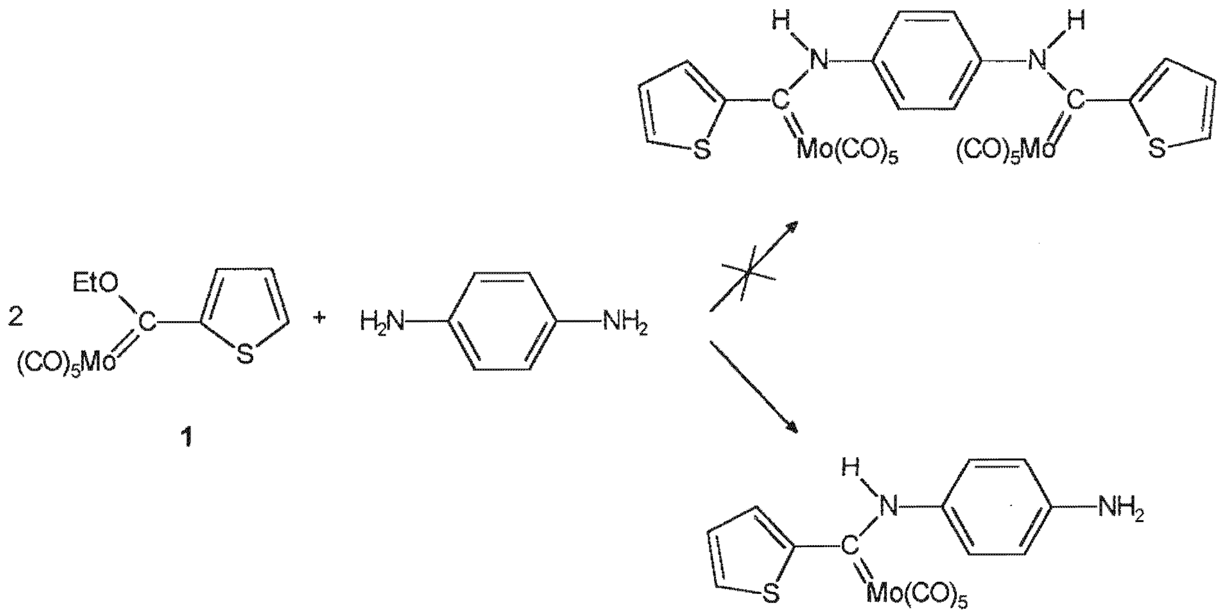
[60] R. Aumann, H. Heinan, *Chem. Ber.*, 122, **1989**, 1139.

[61] L.S. Hegedus, S. D'Andrea, *J. Org. Chem.*, 53, **1988**, 3113.

[62] L.S. Hegedus, G. deWeck, S. D'Andrea, *J. Am. Chem. Soc.*, 110, **1988**, 2122.

[63] E.O. Fischer, M. Leupold, *Chem. Ber.*, 105, **1972**, 599.

[64] H. Werner, E.O. Fischer, B. Heckl, C.G. Kreiter, *J. Organomet. Chem.*, 28, **1971**, 367.



1

7

Figure 2.23 Reaction of **1** with 1,4-phenylene diamine

Similar results were obtained by Fischer *et al*[65]. They reacted the carbene complex [$Cr(CO)_5C(OCH_3)CH_3$] with several diamines in order to synthesize diaminodicarbene complexes. The diamines used were benzidine, *o*-tolidine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane and 1,10-diaminodecane. While diaminodicarbene complexes were afforded for all the aliphatic diamines, only diamino-monocarbene complexes were obtained for the aromatic diamine compounds. This was in part attributed to the reduced basicity of the free amino moiety caused by the action of the strongly electron-withdrawing aminocarbene group on the free amino group through the aromatic system. In aliphatic systems this effect is much weaker since there is no π-system present and therefore both amino groups are accessible for bonding. A better approach would be to employ small amines in the aminolysis of the biscarbene molybdenum complex **2**. Reaction of **2** with ammonia in ether resulted in a rapid colour change from purple to red, but the isolation of new products proved troublesome. Many products were formed in low yields, some of which were not stable. Chromatography on silica gel

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[65] E.O. Fischer, S. Fontana, *J. Organomet. Chem.*, 40, **1972**, 367.

failed and products were poorly soluble. This approach was abandoned as it had inherent failures, bearing in mind that the precursor **2** is unstable in etheral solutions.

4.2 Spectroscopic characterization of novel aminocarbene complexes

The aminocarbene complexes **6** and **7** were characterized with ^{1}H NMR-, ^{13}C NMR-, infrared spectroscopy and mass spectrometry. All NMR spectra were recorded in deuterated chloroform as solvent.

4.2.1 ^{1}H NMR spectroscopy

The proton NMR data of the two complexes are summarized in table 2.7. In the spectrum of **6** two different broad peaks are observed for the two NH_2 protons. The Z-proton is more downfield than the E-proton[34]. The two NH_2 proton peaks appear downfield, which is consistent with the double bond character of the C(carbene)-N bond.

Mills *et al*[66] embarked on a structural study to determine the influence of replacement of the oxygen substituent (alkoxy carbene complexes) by a nitrogen substituent (aminocarbene complexes). Structural data indicate double bond character of both the metal-carbon and carbon-oxygen bonds[67]. However, the metal-carbon bond has less double bond character in complexes **6** and **7** because of competitive back-donation. Since -NH_2 is a much better π-donor than -OEt, it is expected that the introduction of the nitrogen atom will result in greater double bond character of the C(carbene)-N bond and less double bond character of the C(carbene)-M bond. This double bond character of the C(carbene)-NH_2 is manifested in the deshielding of these two protons (8.2-8.4 ppm), which usually appear at 2.8-4.0 ppm on a ^{1}H NMR spectrum, resulting in a downfield shift. The same phenomenon is observed in the spectrum of complex **7**. In fact, the NH peak is shifted even more downfield (9.93 ppm) due to the electron-withdrawing nature of the phenyl diamine substituent, causing deshielding of the N-proton. Coupling constants were employed to assist in the assignment of the aromatic protons.

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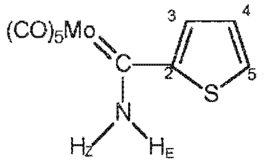
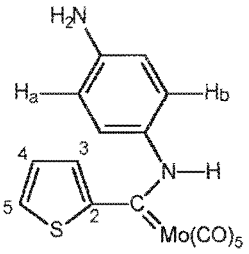
[66] P.E. Baikie, E.O. Fischer, O.S. Mills, *J. Chem. Soc., Chem. Commun.*, **1967**, 1966.

[67] O.S. Mills, A.D. Redhouse, *J. Chem. Soc., Chem. Commun.*, **1966**, 814.

Table 2.7 **^{1}H NMR data of complexes 6 and 7**

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)			
	 **6**		 **7**	
	δ	J	δ	J
H3	7.72 (d)	4.5	7.56 (dd)	4.0 1.0
H4	7.24 (dd)	4.5 4.5	7.16 (dd)	4.0 4.0
H5	7.71 (d)	4.5	7.54 (dd)	4.0 1.0
NH$_E$	8.21 (broad s)	-	-	-
NH$_Z$	8.36 (broad s)	-	-	-
NH	-	-	9.93 (broad s)	-
NH$_2$	-	-	3.89 (s)	-
Ph(H$_a$)	-	-	6.74 (d)	9.0
Ph(H$_b$)	-	-	7.14 (d)	9.0

The thienyl protons of the complexes are observed in the range 7.1-8.2 ppm with H3 the most downfield, followed by H5 and H4. On comparing the chemical shift values for H3 in complexes **1**, **6** and **7**, the chemical shift values decrease in the order **1**>**6**>**7**. A difference of 0.6 ppm in chemical shift values of H3 is observed for the different complexes. A possible explanation for this specific order is that, in complex **1** the thienyl ring donates electron density to the positively charged carbene carbon to stabilize it, to compensate for the poorer π-donor property of the ethoxy group. Therefore H3 is deshielded because of the draining of electrons from the ring and shifts more downfield. In complex **6** the amine group is a relatively better π-donor and lessens the contribution from the thienyl ring to stabilize the carbene carbon. Hence the more upfield shift of H3 in complex **6**. In complex **7** the phenylene diamine substituent is even more electron donating than NH_2 because of the presence of the electron donating NH_2 substituent on the 4-position of the phenyl ring. This results in the upfield shift of H3 in complex **7** compared to its position on the spectra of complexes **1** and **6**, due to a smaller demand on electron stabilization of the thienyl ring. This pattern is also observed for protons H4 and H5 for all three complexes although the chemical shift differences between these protons on the different spectra are less profound.

4.2.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data of complexes **6** and **7** are listed in table 2.8.

Table 2.8 ^{13}C **NMR data of complex 6 and 7**

Carbon	Chemical shifts (δ, ppm)	
	6	**7**
	δ	δ
Carbene	257.5	258.0
C2	152.2	155.9
C3	133.1	128.8
C4	129.1	128.6
C5	133.1	130.1
C_a (phenyl)	-	115.2
C_b (phenyl)	-	128.1
$C(NH_2)$	-	133.9
C(NH)	-	147.6
$M(CO)_5$	206.7 (*cis*) 213.0 (*trans*)	206.6 (*cis*) 214.0 (*trans*)

On comparing the ^{13}C NMR data of complexes **6** and **7** with those of complexes **1-3**, it is clear that the signals from the carbene carbons in the ethoxy compounds are at lower field than those from amino complexes. The chemical shift difference is *ca* 50 ppm. This can be accounted for by the greater degree of C(carbene)-X π-bonding where X = N rather than X = O and results in greater shielding of the carbene carbon in aminocarbene complexes.

The carbon atoms of the thienyl ring are little affected by the change in substituents. The chemical shift values for complexes **6** and **7** are slightly more upfield than for the analogous ethoxy carbene complex **1**.

4.2.3 Infrared Spectroscopy

The infrared data of complexes **6** and **7** are summarized in table 2.9.

Table 2.9 Infrared data for complexes 6 and 7

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})	
	6	**7**
$A_1^{(1)}$	2066	2062
B	1981	1980
$A_1^{(2)}$	1931[a]	1931[a]
E	1931	1931

[a] The $A_1^{(1)}$ and E bands overlap

The structure of carbene complexes may be understood in terms of three limiting forms (**A**, **B** and **C**) which contribute to the stabilization of the formally electron-deficient carbene carbon (figure 2.24). In limiting structure **A** the substituent R serves as a π-donor, while in limiting structure **B** substituent Y serves as a π-donor. Limiting structure **C** is stabilized by π-donation from the metal. Structural evidence[68,69] led to the assumption that amine substituents are better π-donors than ethoxy substituents. Therefore the contribution of limiting structure **A** becomes more important where amine substituents are concerned, while metal π-donation is a larger contributing factor in

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[68] M.Y. Darensbourg, D.J. Darensbourg, *Inorg. Chem.*, 9, **1970**, 32.

[69] J.A. Connor, J.P. Lloyd, *Chem. Rev.*, **1970**, 3237.

the case of ethoxy substituents. Aryl substituents are generally poor π-donors to the carbene carbon and as a result carbene complexes with aryl substituents must either have substantial π-donation from the other substituent or a substantial contribution from limiting form **C**. Carbene complexes with π-donor substituents (structures **A** and **B**) will have low M-C(carbene) bond orders. The opposite is true for complexes with poor π-donor substituents (structure **C**).

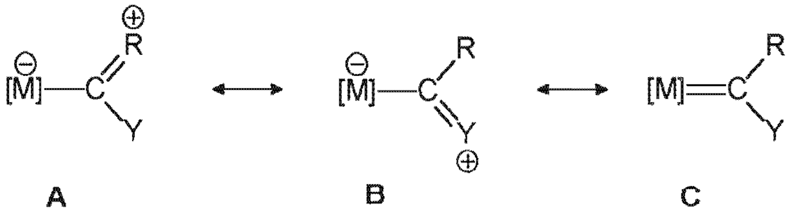

Figure 2.24 Limiting structures for carbene complexes

Transition metal carbonyl bonds can be described as two resonance structures (figure 2.25). In the case of the ethoxy carbene complex, metal π-donation is necessary to stabilize the electrophilic carbene carbon. Backbonding from the metal to the carbonyl carbon decreases hence decreasing the M-C(carbonyl) bond order and simultaneously increasing the C(carbonyl)-O bond order. For aminocarbene complexes, less metal π-donation to the carbene carbon is necessary since the amine substituent stabilizes the carbene carbon. Backbonding from the metal to the carbonyl carbon increases resulting in a higher M-C(carbonyl) bond order and a decrease in the C(carbonyl)-O bond order. This explains the lower stretching frequencies observed on the spectra of complexes **6** and **7** compared to those of the ethoxy carbene complexes **1**-**3**, which is especially pronounced in the vibration wavenumber for the $A_1^{(2)}$ band.

Figure 2.25 Resonance structures for M-C-O bonds

4.2.4 Mass spectrometry

In the mass spectra of complexes **6** and **7** a molecular ion peak, M^+, was obtained for each complex. The fragmentation patterns for both molecules are similar, starting with the initial loss of the carbonyl ligands. Stepwise fragmentation of the carbonyls is observed, followed by the loss of the metal. Fragmentation patterns were based on the ^{98}Mo isotope. The amine substituent and carbene carbon remain bonded to the thiophene ligand. This is contradictory to the fragmentation patterns observed for the ethoxy carbene complexes **1-3** where loss of the ethoxy group precedes the loss of the metal moiety.

Table 2.10 gives the most important peaks and fragment ions associated with these in the spectra of the aminocarbene complexes **6** and **7**.

Table 2.10 Fragmentation patterns of complexes 6 and 7

Complex	Fragment ions (I, %)
6	349.0 (15) M^+; 321.0 (10) M^+ - CO; 292.9 (15) M^+ - 2CO; 264.9 (18) M^+ - 3CO; 237.0 (29) M^+ - 4CO; 209.0 (55) M^+ - 5CO; 111.0 (39) $C_5H_5SN^+$; 83.0 (6) $C_4H_3S^+$
7	440.0 (0.04) M^+; 412.2 (0.3) M^+ - CO; 356.1 (0.4) M^+ - 3CO; 328.1 (0.2) M^+ -4CO; 300.0 (0.7) M^+ - 5CO; 202.1 (100) $C_{11}H_{10}SN_2^+$; 201.1 (61) $C_{11}H_9SN_2^+$; 108.1 (19) $C_5H_2SN^+$

3

Carbene complexes of Thienothiophene

1. General

The interest in thiophenes as molecules with potential electro-optical properties for use as molecular devices[1] was recently extended to thieno[3,2-*b*]thiophenes[2]. Research in this area has unfortunately been impeded by the lack of convenient synthetic methods.

All isomeric thienothiophenes are known (figure 3.1). Thieno[3,2-*b*]thiophene (**I**) was first synthesized by Friedmann[3] during his studies on the action of sulfur on octane and octene under pressure. Under these conditions dimethylthienothiophene, thiophene and other byproducts were yielded. Friedman assumed the formation of 3,4-dimethylthieno[2,3-*b*]thiophene as the result of octane isomerization, but Horton[4] correctly identified the product obtained by Friedmann as thieno[3,2-*b*]thiophene (**I**). Thieno[2,3-*b*]thiophene (II) was the first of the thienothiophene isomers to be synthesized. Biedermann and Jacobson[5] prepared **II** in 1% yield by heating a mixture of citric acid and P_2S_3. Thieno[3,4-*b*]thiophene (**III**), an unstable compound at room temperature[6], was prepared by Cava and Pollack[7] which involved the thermal decomposition of 1H,3H-benzo[*c*]thiophene sulfoxide. The fourth isomer, thieno[3,4-*c*]thiophene (**IV**), is a condensed heterocycle with formally tetracovalent sulfur. Derivatives of this isomer were synthesized by Cava

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[1] J.M. Tour, *Chem. Rev.*, 96, **1996**, 37.

[2] J. Nakayama, H. Dong, K. Sawada, A. Ishii, S. Kumakura, *Tetrahedron*, 52, **1996**, 471.

[3] W. Friedmann, *Ber.*, 49, **1916**, 1344.

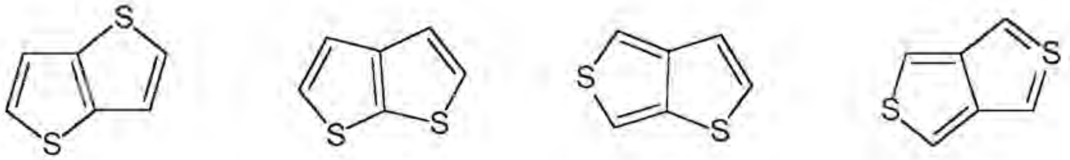
[4] A.W. Horton, *J. Org. Chem.*, 14, **1949**, 760.

[5] A. Biedermann, P. Jacobson, *Ber.*, 19, **1886**, 2444.

[6] H. Wynberg, D.J. Zwanenburg, *Tetrahedron Lett.*, **1967**, 761.

[7] M.P. Cava, N.M. Pollack, *J. Am. Chem. Soc.*, 88, **1966**, 4112.

and Pollack[8] while the unsubstituted compound could not yet be isolated.



I II III IV

Figure 3.1 Isomers of thienothiophene

Stabilities of the isomers differ considerably. Thieno[3,2-*b*]thiophene (**I**) and thieno[2,3-*b*]thiophene (**II**) are both stable compounds at room temperature while thieno[3,4-*b*]thiophene (**III**) can only be stored at temperatures below -40°C. Thieno[3,4-*c*]thienothiophene (**IV**) was found to be 192 kJ less stable than thieno[3,2-*b*]thiophene (**I**)[9]. Von Rague Schleyer *et al*[10] calculated the relative energies of the four positional isomers to determine their stability order which was found to be **I** > **II** > **III** > **IV**. This study was conducted to determine the relationship between the thermodynamic stability of the heterocycles and their aromaticity. It was concluded that no direct correlation exists between the two properties, since the most aromatic isomer was found to be isomer **IV**[11]. The aromaticity was then found to decrease in the following order: **I** > **II** > **III**. Substituted thienothiophenes were prepared with the aim to increase the stability of the compounds. Electron-withdrawing substituents greatly increased the stability. Thieno[3,4-*b*]thiophene-2-carboxylic acid and its methyl ester are stable at 20°C[12]. Electron donor substituents do not have the same effect, since 4,6-dimethylthieno[3,4-*b*]thiophene is an unstable compound[13]. From reactivity studies done on heterocycles it is clear that it is difficult to define quantitatively the reactivity of a given

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[8] M.P. Cava, N.M. Pollack, *J. Am. Chem. Soc.*, 89, **1967**, 3639.

[9] D.T. Clark, *Tetrahedron Lett.*, **1967**, 5257.

[10] G. Subramanian, P. von Rague Schleyer, H. Jiao, *Angew. Chem. Int. Ed. Engl.*, 35, **1996**, 2638.

[11] C.W. Bird, *Tetrahedron*, 43, **1987**, 4725.

[12] V.P. Litvinov, G. Fraenkel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1968**, 1828.

[13] O. Dann, W. Dimmling, *Ber.*, 87, **1954**, 373.

position[14]. This is due to the high polarisability of the molecule. Reactivity of the thienothiophenes was investigated by Archer and Taylor[15]. Detritiation in trifluoroacetic acid at 70°C has provided the only fully quantitative data for these compounds. This data was compared with data obtained for thiophene under the same conditions. From this data it was found that the α-positions are in each case more reactive than the β-positions, as is the case for thiophene. It was also observed that both positions are more reactive at the [2,3-*b*] isomer (**II**) than at the [3,2-*b*] isomer (**I**). The relative reactivities at the α-position of thieno[2,3-*b*]thiophene (**II**), thieno[3,2-*b*]thiophene (**I**) and thiophene are 7.4:7.0:1.0.

Examples of compounds containing thienothiophenes as bridging ligands are limited in literature. In an attempt to enhance the electron density and transmission properties for potential non-linear optical applications of thieno[3,2-*b*]thiophene, the synthesis of 2-arylthieno[3,2-*b*]thiophene was planned[16]. Various synthetic routes were proposed for this synthesis and intermediate complexes included the metal complexes 2-tributylstannylthieno[3,2-*b*]thiophene, thieno[3,2-*b*]thiophen-2-ylboronic acid and 2-thieno[3,2-*b*]thienylzinc chloride. These compounds were prepared from lithio precursors. Various other α-substituted complexes have been synthesized in a similar manner *via* this monometallated derivative e.g. selenium and tellurium[17] compounds. 2,5-Disubstituted thieno[3,2-*b*]thiophenes were prepared by dilithiation of thieno[3,2-*b*]thiophene followed by the subsequent reaction with electrophiles. Several silyl complexes were synthesized in this fashion[18]. In the same paper the syntheses of 3,6-disubstituted derivatives were reported, prepared *via* Br-Li exchange reactions involving 3,6-dibromothieno[3,2-*b*]thiophene. Isomeric bis(9-hydroxyfluoren-9-yl)thienothiophenes (figure 3.2) were discussed as hosts in host-guest clathrate crystals in reactions that are designated as solid-state photosolvolysis[19]. Guest ethanol molecules in the clathrate crystals reacted photochemically with the diol host compounds to cause photosubstitution

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[14] H.B. Amin, R. Taylor, *J. Chem. Soc., Perkin Trans 2*, **1978**, 1053.

[15] W.J. Archer, R. Taylor, *J. Chem. Soc., Perkin Trans 2*, **1982**, 295.

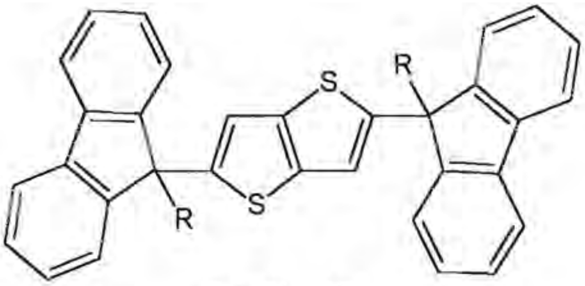
[16] D. Prim, G. Kirsch, *J. Chem. Soc., Perkin Trans 1*, **1994**, 2603.

[17] M. Blenkle, P. Boldt, C. Bräuchle, W. Grahn, I. Ledoux, H. Nerenz, S. Stadler, J. Wichern, J. Zyss, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1377.

[18] L.S. Fuller, B. Iddon, K.A. Smith, *J. Chem. Soc., Perkin Trans 1*, **1997**, 3465.

[19] N. Hayashi, Y. Mazaki, K. Kobayashi, *Tetrahedron Lett.*, 35, **1994**, 5883.

in the solid-state.



R = OH, OEt

Figure 3.2 Bis(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene

Unlike thiophene, the coordination chemistry of thieno[3,2-*b*]thiophene and its derivatives in transition metal complexes has not yet been exploited. In our laboratories we are interested in comparing stabilities, properties and structural features of linear chained thiophene (bithiophene and terthiophene) with condensed thiophene (thieno[3,2-*b*]thiophene and dithieno[3,2-*b*]thiophene) as they present themselves in ligands in coordination chemistry. Previously we have found that 3,6-dimethylthieno[3,2-*b*]thiophene form binuclear σ,π-complexes where the ligand uses the π-system of one ring to coordinate to a $Cr(CO)_3$-moiety and the lone-pair of electrons on the S-atom to bond to a $Cr(CO)_5$-fragment[20]. This utilizes the aromatic electrons of one ring while the other ring is left with a S-coordinated sulfur atom and an olefin.

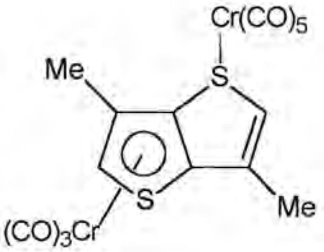


Figure 3.3 Binuclear σ,π-complex of 3,6-dimethylthieno[3,2-*b*]thiophene

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[20] M. Landman, M.Sc. thesis, *Novel π-Heteroarene Complexes of Chromium(0)*, University of Pretoria, **1997**.

2. Synthesis of Thienothiophenes

The synthesis of thieno[3,2-*b*]thiophene was based on the method of Goldfarb and co-workers[21] and was prepared in 50% overall yield. The synthetic route is depicted in figure 3.4.

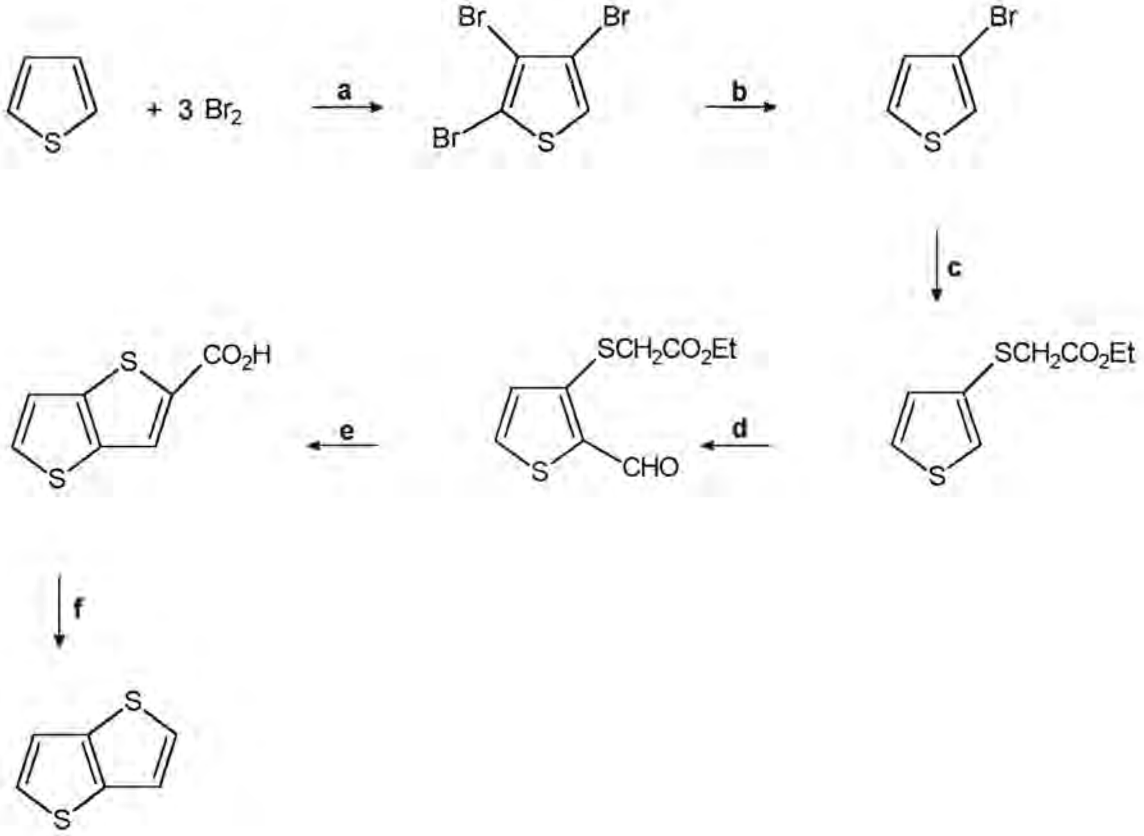

Figure 3.4 Reagents: (**a**) Et_2O, 48% HBr, 75°C; (**b**) Zn, CH_3COOH, reflux; (**c**) n-BuLi, -70°C, S_8, $BrCH_2CO_2Et$; (**d**) $POCl_3$, DMF; (**e**) NaOMe, MeOH, heat; (**f**) Quinoline, Cu powder, heat

Synthesis of 2,3,5-tribromothiophene was effected according to the method described by Brandsma and Verkruijsse[22] and involves the reaction of bromine and thiophene in diethyl ether at elevated temperatures. The target product (90%) and HBr were yielded. Reduction of 2,3,5-

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[21] Y.A.L. Goldfarb, V.P. Litvinov, S. Ozolin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **1965**, 510.

[22] L. Brandsma, H.D. Verkruijsse, *Synth. Commun.*, 18, **1988**, 1763.

tribromothiophene to 3-bromothiophene (55%)[23] was performed using two equivalents of zinc powder in acetic acid. Reaction of 3-bromothiophene with elemental sulfur followed by the addition of ethylbromoacetate yielded ethyl(3-thienothio)acetate (73%). Upon reacting this acetate-substituted thiophene with phosphorus oxychloride in N,N-dimethylformamide, an aldehyde group was added at the 2-position to afford ethyl(2-formyl-3-thienothio)acetate in this Vilsmeier formylation reaction. Cyclisation occurred under basic conditions and the subsequent decarboxylation using copper powder and quinoline yielded thieno[3,2-*b*]thiophene[21].

Since no practical short-step synthesis for thieno[3,2-*b*]thiophene or substituted derivatives thereof were available in literature, the utilization of thienothiophenes in organic synthesis has been limited. Then, in 1994, Choi *et al*[24] reported a one-pot synthesis of 3,6-dimethylthieno[3,2-*b*]thiophene. The synthesis is based on the discovery made by Teste and Lozac'h[25] that the reaction of 2,5-dimethyl-3-hexyne-2,5-diol with elemental sulfur affords 3,6-dimethylthieno[3,2-*b*]thiophene, although the yield was low. Choi *et al* re-examined this reaction and varied the reaction conditions until they obtained 3,6-dimethylthieno[3,2-*b*]thiophene in a reasonable yield. They found that by heating a mixture of 2,5-dimethyl-3-hexyne-2,5-diol and sulfur in benzene in an autoclave provided the optimum yield for the target product (figure 3.5).

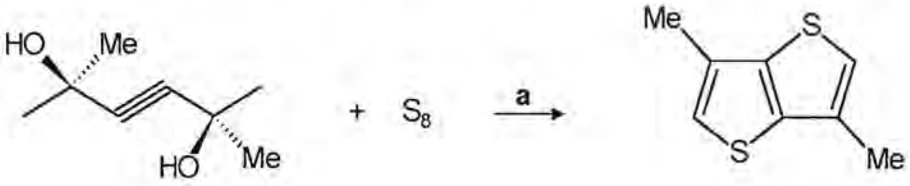

Figure 3.5 Reagents: (a) Benzene, 200°C, 12h

The use of this ligand was preferred over unsubstituted thieno[3,2-*b*]thiophene in the syntheses of the novel carbene complexes due to the easy preparation method described for this compound.

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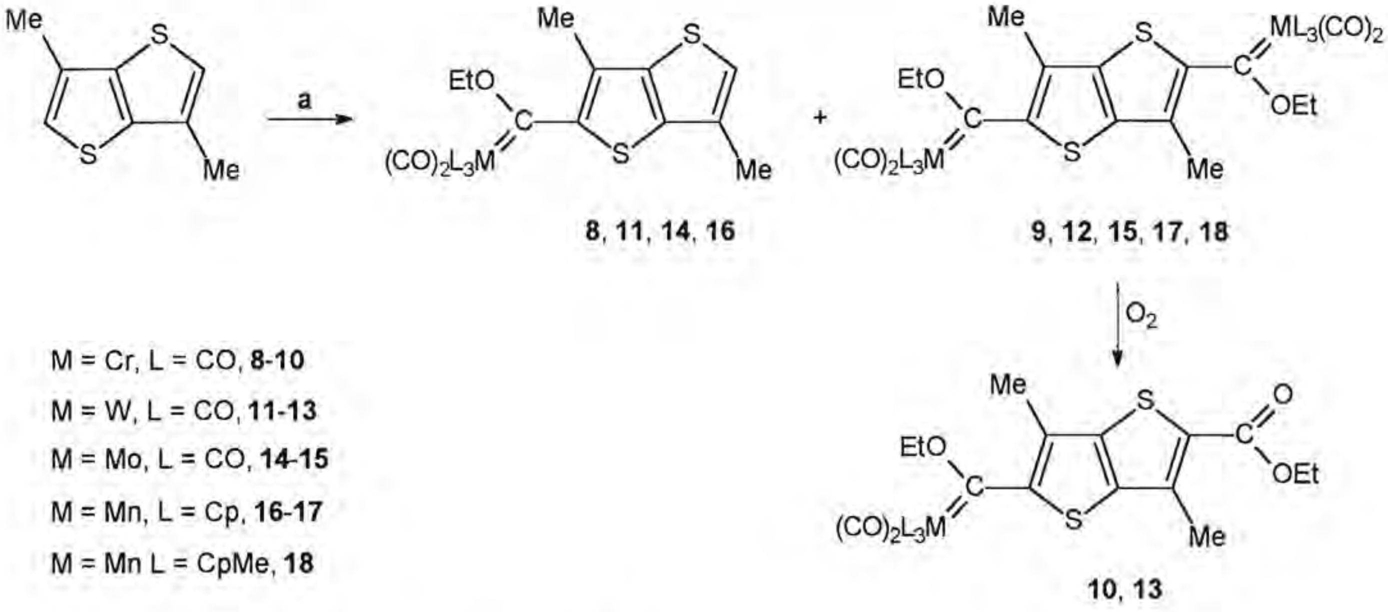
[23] S. Gronowitz, T. Raznikiewicz, *Org. Synth. Coll.*, 5, **1973**, 149.

[24] K.S. Choi, K. Sawada, H. Dong, M. Hoshino, J. Nakayama, *Heterocycles*, 38, **1994**, 143.

[25] J. Teste, N. Lozac'h, *Bull. Soc. Chim. Fr.*, **1955**, 422.

3. Synthesis of carbene complexes of Thienothiophene and derivatives

The dimetallation of thieno[3,2-*b*]thiophene and 3,6-dimethylthieno[3,2-*b*]thiophene was based on the method described by Bugge[26]. The reactions were carried out in hexane and TMEDA was introduced together with butyllithium to form 2,7-dilithio species at elevated temperatures. Formation of biscarbene complexes ensued after addition of hexacarbonyl metal complexes and the subsequent quenching with the alkylating agent $Et_3O{\cdot}BF_4$. Following this procedure, 3,6-dimethylthieno[3,2-*b*]thiophene was reacted with the metal complexes $Cr(CO)_6$, $W(CO)_6$, $Mo(CO)_6$, $MnCp(CO)_3$ and $Mn(MeCp)(CO)_3$ to yield the different biscarbene complexes. Again, as for the thiophene analogues, in most cases the monocarbene complexes as well as decomposition products were also isolated and not only the expected biscarbene complexes. Complexes **8-18** were prepared in this manner. The synthetic procedure for the preparation of these complexes is outlined in figure 3.6.



M = Cr, L = CO, **8-10**
M = W, L = CO, **11-13**
M = Mo, L = CO, **14-15**
M = Mn, L = Cp, **16-17**
M = Mn L = CpMe, **18**

Figure 3.6 Synthesis of complexes **8-18**
Reagents: **a** (i) 2 eq. n-BuLi (ii) $ML_3(CO)_3$ (iii) $Et_3O{\cdot}BF_4$

Interesting to note was that the reaction of 3,6-dimethylthieno[3,2-*b*]thiophene with the

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[26] A. Bugge, *Acta Chem. Scand.*, 22, **1968**, 63.

manganese metal complexes almost exclusively yielded the biscarbene complexes. In both cases no decomposition product was formed and only for the reaction with [MnCp(CO)$_3$] could the monocarbene complex be isolated in a low yield. This is in contrast with the rest of the reactions where the monocarbene was usually the main product of the reaction and the biscarbene was formed in lower yields. In all of the reactions the well known butyl carbene complex [Cr(CO)$_5$C(OEt)Bu] was formed as a result of the excess butyl lithium in the reaction mixture due to insufficient dilithiation of the thienothiophene substrate.

Monocarbene complexes of chromium and tungsten, **8** and **11**, were crystallized from hexane:dichloromethane (1:1) solutions to afford red-orange needles. The biscarbene analogues of these complexes, **9** and **12**, yielded purple-black crystals when crystallized from the same solvent mixture. X-ray diffraction studies confirmed the structures of these compounds. The decomposition products, **10** and **13**, isolated together with the respective mono- and biscarbene complexes, although in low yield, were characterized spectroscopically and were orange coloured. For the reaction of molybdenum hexacarbonyl with the dilithiated 3,6-dimethylthieno[3,2-*b*]thiophene species, the products were similar to the products obtained from the chromium and tungsten reactions. The red-orange monocarbene complex **14** was isolated together with the purple biscarbene complex **15**. Both the yellow monocarbene complex **16** and the purple-brown biscarbene complex **17** were obtained from the reaction of [MnCp(CO)$_3$] and 3,6-dimethylthieno[3,2-*b*]thiophene while the purple-brown biscarbene complex **18** formed exclusively in the reaction of the lithiated agent with [Mn(MeCp)(CO)$_3$]. Single crystals of this complex were obtained from a 1:1 hexane:dichloromethane solution and subjected to X-ray diffraction studies.

The products isolated from the reaction of [Cr(CO)$_6$] and lithiated thieno[3,2-*b*]thiophene, instead of the dimethyl analogue, did not resemble those obtained from the similar reaction using 3,6-dimethylthieno[3,2-*b*]thiophene. Although the synthetic procedure followed was identical, complexes **19** and **20** were isolated, instead of the expected monocarbene and biscarbene complexes. The structure determinations of complexes **19** and **20** were based on the data collected by the use of NMR spectroscopy, infrared data and mass spectrometry. The structure of complex **19** was confirmed by single crystal X-ray determination. The formation of product **19** can be explained by the reaction of a deprotonated thienothiophene monocarbene complex with a butyl carbene to give an ylide intermediate. Elimination of an ethoxy group ensues. The base

TMEDA deprotonates the ring at the 7-position of this carbene complex, while the conjugated acid assists in the removal of the ethoxy group from the ylide. Oxidation of the more reactive butyl carbene end of the biscarbene affords the final product **19**. All the steps in this proposed reaction route have precedents in literature.

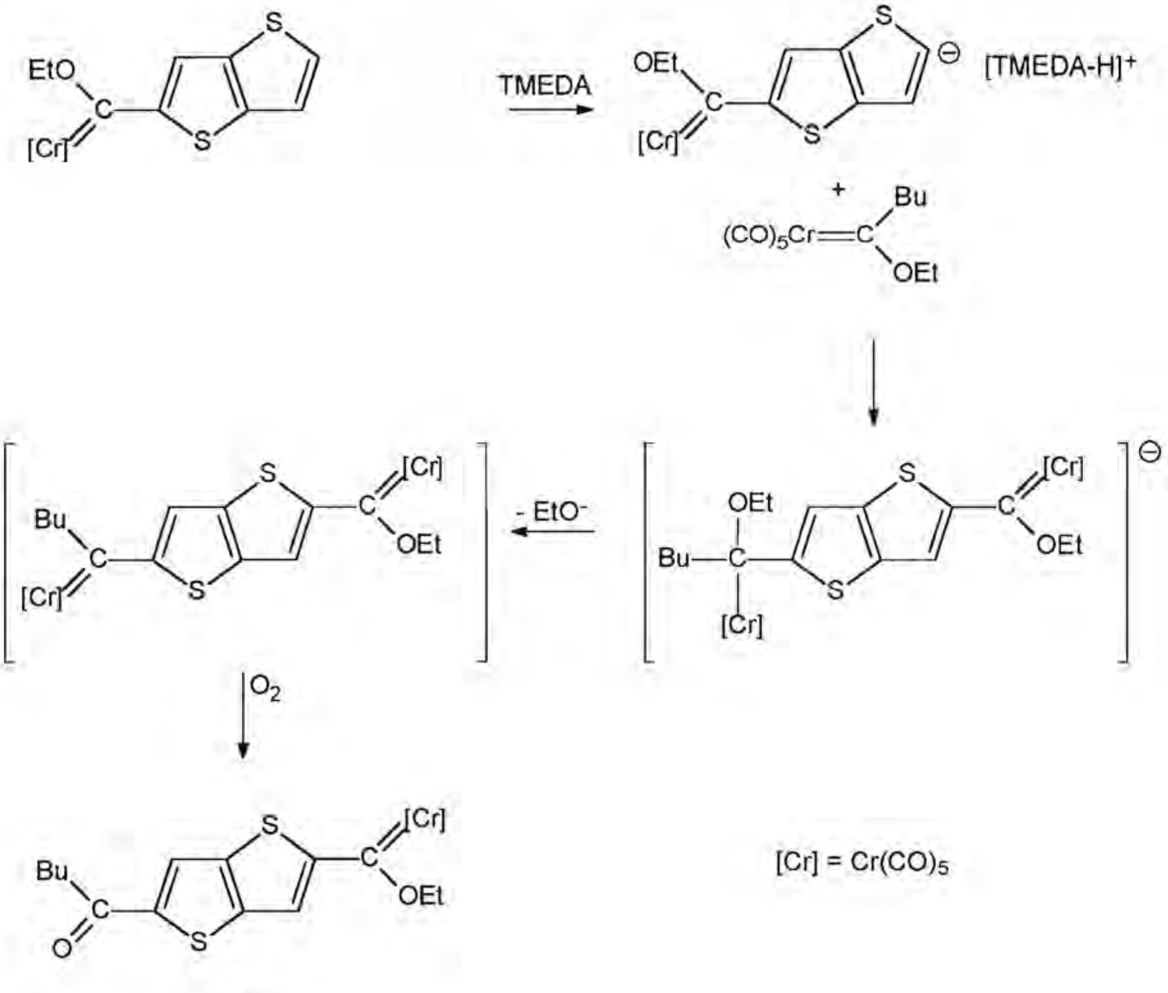


Figure 3.7 Proposed mechanism for the formation of **19**

Other less likely reaction routes which could also lead to the formation of complex **19**, include the synthesis *via* the formation of a bis-acyllated intermediate. It is assumed that the intermediate, before alkylation, reacts with (i) a third butyl group in a nucleophilic addition reaction, or is (ii) selectively oxidized in the reaction mixture before being attacked by a butyl group. In both cases the products are suggested to have formed by reaction on the bis-acyllated product before alkylation of the reaction mixture was effected. In the first case (figure 3.8) the route prescribes that the thieno[3,2-*b*]thiophene and the $M(CO)_5$ metal moiety have the ability to withdraw electron density to such an extent that one of the electrophilic carbene carbons is still accessible for nucleophilic attack by an excess of n-BuLi. Such a process comprises the reduction of one of the metal carbonyl units and has not yet been recognized in monocarbene complexes. This type of product was however not isolated for the dimethylthienothiophene ligand and discredits thus this mechanism.

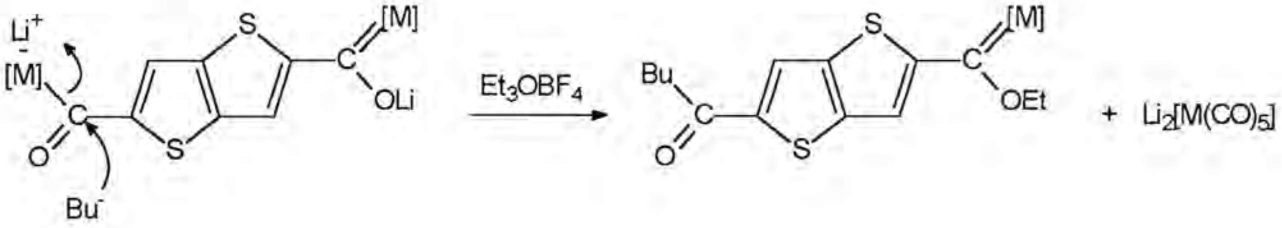
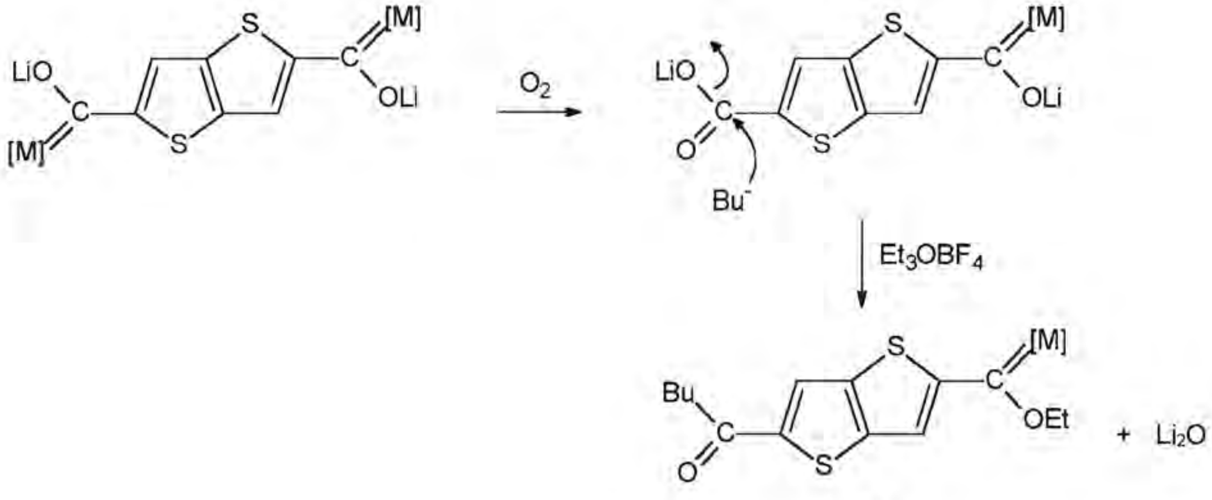


Figure 3.8 Formation of complex **19** *via* a bis-acyllated intermediate



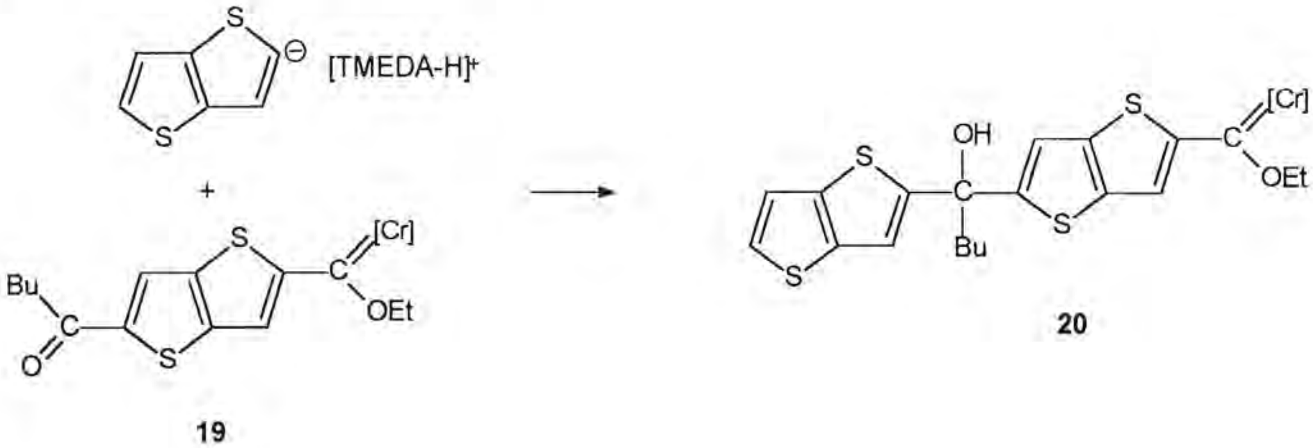
19

Figure 3.9 Formation of complex **19** *via* selective oxidation

Alternatively, complex **19** could have been formed by diffusion of O_2 through the silicon tubing, whereby one of the metal moieties is replaced by an oxygen atom. Upon attack of the butyl carbanion on this carbon, Li_2O is released and product **19** is formed (figure 3.9). Again such a mechanism is unlikely as a similar product was not isolated for the reaction of $Cr(CO)_6$ and the dimethyl analogue of this ligand.

The proposed formation of complex **20** emanated from the deprotonation of thienothiophene by the base TMEDA and the subsequent nucleophilic attack of this anion at the carbonyl group of complex **19**, followed by the protonation of the oxyanion by the $[TMEDA\text{-}H]^+$ species (figure 3.10).

Figure 3.10 Formation of complex **20**



3.1 Spectroscopic characterization of novel carbene complexes

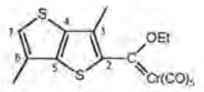
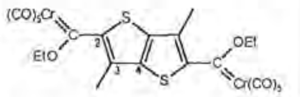
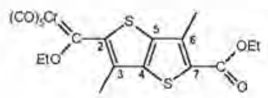
Complexes **8-20** were characterized spectroscopically using NMR and IR spectroscopy and mass spectrometry. The structures of compounds **8**, **9**, **11**, **12**, **16**, **18** and **19** were confirmed with X-ray crystallography.

3.1.1 ^{1}H NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform as solvent unless otherwise specified. The ^{1}H NMR data for chromium complexes **8-10** are summarized in table 3.1, the tungsten complexes **11-13** in table 3.2 and the molybdenum complexes **14** and **15** in table 3.3. The data for compounds **16-18**, the manganese complexes, are given in table 3.4, while the data of the two thieno[3,2-*b*]thiophene chromium complexes **19** and **20** are reported in table 3.5.

The chemical shifts for the protons of free 3,6-dimethylthieno[3,2-*b*]thiophene are at 6.92 ppm for H2 and H7 and at 2.33 ppm for the methyl substituents on C3 and C6[2]. The ^{1}H NMR spectrum of thieno[3,2-*b*]thiophene was recorded in CDCl$_3$ and two doublets at 7.55 ppm (H2 and H7) and 7.24 ppm (H3 and H6) were observed.

Table 3.1 ^{1}H NMR data of complexes 8, 9 and 10

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **8**		 **9**		 **10**	
	δ	J	δ	J	δ	J
H7	7.18 (q)	1.2	-	-	-	-
OCH$_2$CH$_3$-M	5.19 (q)	7.0	5.19 (q)	7.1	5.20 (q)	6.9
OCH$_2$CH$_3$-O	-	-	-	-	4.35 (q)	7.2
OCH$_2$**CH$_3$**-M	1.71 (t)	7.1	1.74 (t)	7.1	1.72 (t)	6.9
OCH$_2$**CH$_3$**-O	-	-	-	-	1.38 (t)	7.2
Me3	2.47 (s)	-	2.47 (s)	-	2.70 (s)	-
Me6	2.41 (d)	1.0	2.47 (s)	-	2.43 (s)	-

A quartet peak is observed for the H7 proton on the spectrum of the monocarbene complex **8**, while a singlet was expected. The methyl protons of the methyl group C6 resonate as a doublet, indicating J^4_{H-H} coupling of these protons with H7.

The electron withdrawing effect of the carbene moiety is prominent on comparing the chemical shift values of the two methyl groups on C3 and C6 respectively for the three complexes. On the spectrum of the monocarbene complex **8** the methyl group on position 3 is more affected by the influence of the carbene moiety than the methyl substituent on position 6, causing a downfield shift of these protons. On the spectrum of complex **9**, the biscarbene complex, both methyl groups are affected by the electrophilic carbene fragment and both methyl groups are observed downfield compared to the values for the unsubstituted ligand. By replacing one carbene moiety with an ester functional group, the competitive electron withdrawing effects cause a significant downfield shift in the value of the methyl proton on C3, while the methyl group on the carbon adjacent to the ester substituent is also shifted downfield but only marginally so, as is observed on the spectrum of complex **10**. From this it is concluded that the carbene fragment is more electron withdrawing than an ester group.

On the NMR spectrum of complex **10**, the decomposition product, evidence for the further decomposition of this product to the bis(ethylester) (figure 3.11) is observed. Signals were observed at 4.34 (4H, q, J = 7.0), 2.34 (6H, s) and 1.37 ppm (6H, t, J = 7.0).

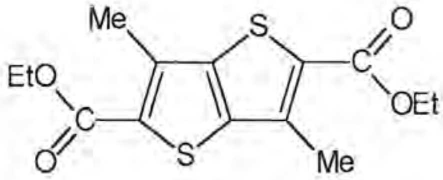
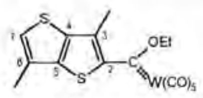
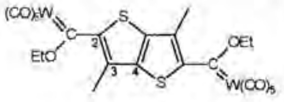
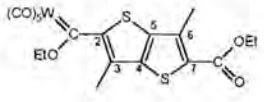


Figure 3.11 The bis(ethylester) of 3,6-dimethylthieno[3,2-*b*]thiophene

For the data in table 3.2, the monocarbene complex, **11**, again displays a quartet signal for the H7 proton due to coupling with the methyl group on C6, which is observed as a doublet, and correlates with the analogous peaks observed on the spectrum of complex **8**. It is interesting to note the significant difference in chemical shift values of the OCH_2CH_3 peak on the spectra of these three tungsten complexes compared to the same peak on the spectra of the three chromium complexes. The peak is observed significantly more upfield for the tungsten complexes than for the chromium complexes, denoting that these chemical shifts are fairly characteristic for a specific metal and unaffected by the other carbene substituent.

Table 3.2 **^{1}H NMR data of complexes 11, 12 and 13**

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **11**		 **12**		 **13**	
	δ	J	δ	J	δ	J
H7	7.22 (q)	1.1	-	-	-	-
$\mathbf{OCH_2}CH_3$-M	5.02 (q)	7.1	5.04 (q)	7.1	5.03 (q)	7.2
$\mathbf{OCH_2}CH_3$-O	-	-	-	-	4.36 (q)	7.2
$OCH_2\mathbf{CH_3}$-M	1.69 (t)	7.1	1.72 (t)	7.1	1.70 (t)	7.2
$OCH_2\mathbf{CH_3}$-O	-	-	-	-	1.39 (t)	7.2
Me3	2.48 (s)	-	2.48 (s)	-	2.70 (s)	-
Me6	2.41 (d)	1.1	2.48 (s)	-	2.44 (s)	-

Also characteristic, is the position of the methylene resonances of the ester groups at *ca.* 4.35 ppm for both complexes **10** and **13**, showing that the influence of the different metals is not carried through the rings to the other side of the thienothiophene rings. In figure 3.12 the characteristic positions of the methylene groups as observed for different functional groups in the novel carbene complexes (**1**-**30**) are illustrated.

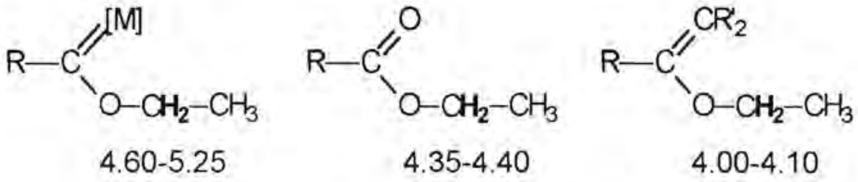


Figure 3.12 Characteristic positions of the methylene protons (ppm) on ^{1}H NMR spectra

The chemical shift values for the methyl protons of the ethoxy substituent are seemingly more insensitive to the different metal substituents and the difference in the values for the tungsten and chromium complexes is less profound.

Table 3.3 ^{1}H NMR data of complexes 14 and 15

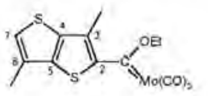
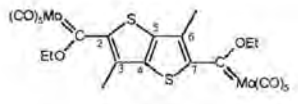
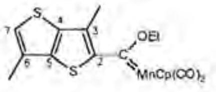
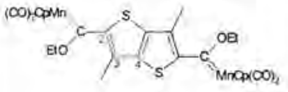
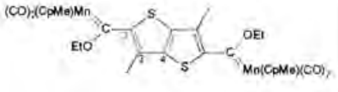
Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)			
	 **14**		 **15**	
	δ	J	δ	J
H7	7.21 (s)	-	-	-
$\mathbf{OCH_2}CH_3$-M	5.08 (q)	7.0	5.13 (q)	7.1
$OCH_2\mathbf{CH_3}$-M	1.69 (t)	7.1	1.73 (t)	7.1
Me3	2.50 (s)	-	2.52 (s)	-
Me6	2.41 (s)	-	2.52 (s)	-

Table 3.4 ^{1}H NMR data of complexes 16, 17 and 18

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **16**		 **17**		 **18**	
	δ	J	δ	J	δ	J
H7	6.94 (s)	-	-	-	-	-
$\mathbf{OCH_2}CH_3$-M	4.67 (q)	6.9	4.67 (q)	7.0	4.74 (q)	6.7
$OCH_2\mathbf{CH_3}$-M	1.52 (t)	6.9	1.52 (t)	7.0	1.53 (t)	6.8
Me3	2.34 (s)	-	2.26 (s)	-	2.26 (s)	-
Me6	2.27 (s)	-	2.26 (s)	-	2.26 (s)	-
Cp	4.67 (s)	-	4.67 (s)	-	4.55 (s) 4.43 (s)	-
CpMe	-	-	-	-	1.85 (s)	-

On the spectra of complexes **14** and **15** (table 3.3), the methylene protons of these two molybdenum complexes are observed at chemical shift values intermediate of those of the chromium and tungsten complexes, *i.e.* Cr > Mo > W, following the trend of their relative positions on the periodic table. The values for the methyl protons of the ethoxy substituent of the different complexes are again very comparable.

On comparing the chemical shift values of H7 on the different monocarbene spectra of the data in table 3.4, the value obtained for complex **16** is conspicuously lower than for complexes **8**, **11** and **14** and is comparable with the value of 3,6-dimethylthieno[3,2-*b*]thiophene. This same trend was also observed for a series of carbene metal complexes prepared with thiophene as bridging ligand[27]. The protons of the ethoxy group of all three manganese products are likewise shifted more upfield compared to the chemical shift values of the analogous chromium, tungsten and molybdenum complexes. It can thus be concluded that the coordination of the manganese metal moiety causes less electron draining from the ring system than coordinating a Cr, W or Mo metal pentacarbonyl fragment. The presence of an electron donating group such as cyclopentadienyl on the manganese metal fragment can account for the shielding effect observed on the spectra of **16**, **17** and **18**. The replacement of three carbonyl groups, which are electron-withdrawing, with a cyclopentadienyl ligand on the metal fragment, increases the contribution of the metal moiety in stabilizing the electrophilic carbene carbon and lessens the role of either the ring system or the ethoxy group.

On the spectrum of **18**, two singlet resonances are observed for the Cp protons while only one singlet is found on the spectra of **16** and **17**, since the Cp group of **18** is substituted with a methyl group on one position and thus gives rise to two non-equivalent groups of two protons. The electron donating effect of this methyl group is evident from the upfield shift of the Cp protons on the spectrum of **18** compared to those of unsubstituted Cp.

On comparing the data for complexes **19** and **20** in table 3.5, the methylene protons are observed as quartets at 5.21 ppm and 5.14 ppm, respectively. The OH-signal is not observed on the spectrum of complex **20**. The protons on the ring system of the two complexes correspond well with one another and the values for the second thienothiophene unit in complex **20** are comparable to the data for DMTT. The positions of the butyl groups on the respective spectra are

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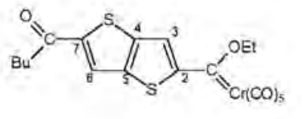
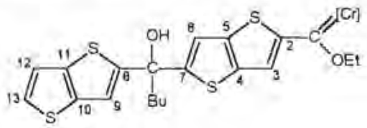
[27] Y.M. Terblans, H.M. Roos, S. Lotz, *J. Organomet. Chem.*, 566, **1998**, 133.

almost identical.

Table 3.5 **^{1}H NMR data of complexes 19 and 20**

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)			
	 **19**		 **20**	
	δ	J	δ	J
H3	8.33 (s)	-	8.36 (s)	-
H6	7.82 (s)	-	7.88 (s)	-
H9	-	-	6.99 (s)	-
H12	-	-	7.59 (d)	5.1
H13	-	-	7.27 (d)	5.1
O**CH$_2$**CH$_3$-M	5.21 (q)	7.0	5.14 (q)	7.1
OCH$_2$**CH$_3$**-M	1.69 (t)	7.0	1.65 (t)	7.1
C(O)**CH$_2$**CH$_2$CH$_2$CH$_3$	2.93 (t)	7.3	2.91 (t)	7.3
C(O)CH$_2$**CH$_2$**CH$_2$CH$_3$	1.74 (t)	7.5	1.75 (t)	7.3
C(O)CH$_2$CH$_2$**CH$_2$**CH$_3$	1.42 (t)	7.5	1.43 (t)	7.3
C(O)CH$_2$CH$_2$CH$_2$**CH$_3$**	0.95 (t)	7.3	0.94 (t)	7.3

3.1.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data of chromium complexes **8-10** are summarized in table 3.6, the tungsten and molybdenum complexes **11-15** in table 3.7. The data for compounds **16-18**, the manganese complexes, are given in table 3.8, while the data of the two thieno[3,2-*b*]thiophene chromium complexes **19** and **20** are reported in table 3.9. Assignment of the spectra of the complexes as well as the uncoordinated DMTT was based on ^{13}C NMR studies of selenolo[3,2-*b*]selenophene[28].

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[28] S. Gronowitz, T. Frejd, A.-B. Hörnfeldt, *Chemica Scripta*, 5, **1974**, 236.

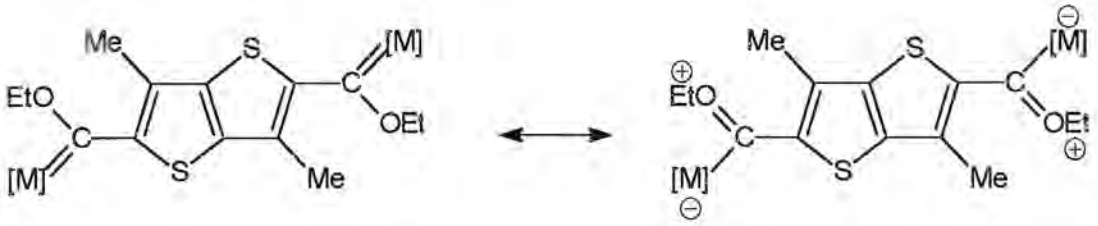
Table 3.6 **^{13}C NMR data of complexes 8, 9 and 10**

Carbon	Chemical shifts (δ, ppm)		
	8	**9**	**10**
	δ	δ	δ
Carbene	318.7	n.o.	317.9
C2	150.1	167.7	163.6
C3	130.8	131.9	130.6
C4	144.7	149.8	142.7
C5	142.6	149.8	142.0
C6	129.5	131.9	129.7
C7	128.2	167.7	163.1
O**CH$_2$**CH$_3$-M	76.4	76.6	76.4
O**CH$_2$**CH$_3$-O	-	-	61.4
OCH$_2$**CH$_3$**-M	15.6	15.5	15.6
OCH$_2$**CH$_3$**-O	-	-	14.4
Me3	18.6	17.6	17.7
Me6	14.7	17.6	15.0
M(CO)$_5$	216.8 (*cis*) 222.8 (*trans*)	216.3 (*cis*) 223.6 (*trans*)	216.7 (*cis*) 223.3 (*trans*)

Due to the poor solubility of the biscarbene complex in deuterated chloroform, the spectrum of complex **9** is of an unsatisfactory quality and the carbene peak was not observed. Use of different solvents did not, however, improve the situation, since the complex was even less soluble in acetone, dichloromethane and benzene. This same problem was also encountered for the biscarbene complex of tungsten, complex **12**, and again the carbene peak was absent on the spectrum.

The chemical shift values (ppm) for the carbon atoms of uncoordinated 3,6-dimethylthieno[3,2-*b*]thiophene are at 121.8 (C2 and C7), 130.1 (C4 and C5), 140.0 (C3 and C6) and 14.6 (Me)[2]. The ^{13}C NMR spectrum of thieno[3,2-*b*]thiophene was recorded in CDCl$_3$ and the chemical shift values (ppm) observed for the different resonance peaks were assigned as follows: 131.7 (C2 and C7), 119.7 (C3 and C6) and 139.7 (C4 and C5). On the spectrum of complex **10**, the decomposition product, evidence for the existence of the bis(ethylester) complex was observed, as was the case for the ^{1}H NMR spectrum. It is therefore suggested that the decomposition product undergoes further decomposition in solution to form this compound by substitution of the second metal fragment by an oxygen atom. Resonance peaks were found at the following chemical shift values (ppm): 162.8 (**C**(O)OEt), 138.5 (C2 and C7), 128.4 (C3, C6) and 130.5 (C4 and C5). This product is also present on the spectrum of the decomposition product of tungsten, complex **13**.

Carbene carbon resonance peaks are found at characteristic values for the different metals. The values fall within the range of 317 to 319 ppm for the chromium complexes, while the molybdenum complexes display values slightly lower at 306 to 309 ppm and the carbene carbon resonances are observed at 292 to 297 ppm on the tungsten spectra. This same sequence is noted for the position of the $M(CO)_5$ peaks on the different spectra, *i.e.* the $Cr(CO)_5$ chemical shift values are at the highest chemical shift values and the $W(CO)_5$ resonance peaks at the lowest chemical shift values, correlating with their positions on the periodic table. An increase in the atomic number of metals in the same period leads to an increase in the shielding of the carbonyl groups. In each case the difference in chemical shift value ($\Delta\delta$), on changing the metal from chromium to molybdenum to tungsten, is approximately 10 ppm. The methylene carbons of the different metal spectra reveal the opposite trend. The methylene carbons of the ethoxy group of the carbene on the spectra of the chromium complexes are observed upfield from those of molybdenum while those of the tungsten complexes are found downfield. The methylene carbons of the chromium complexes are thus the most shielded. The sequence for the methylene protons is therefore W > Mo > Cr. This phenomenon can be best described by considering two resonance structures **I** and **II** (figure 3.13). Resonance structure **I** is more important for biscarbene complexes than structure **II**. Important, however, is the contribution of structure **II** to the final molecule, causing small differences in the chemical shifts of the methylene protons. The contribution of structure **II** is more significant for the tungsten complexes compared to those of chromium. Structure **II** shows the deshielding of the ethoxy groups and consequently shielding of the carbene-metal moiety, evident in the upfield shift in $M(CO)_5$ values. The methyl carbons of the ethoxy groups, however, seem to be less affected by the different resonance structures and fall within the range of 15.2 to 15.6 ppm for all the complexes.



I II

Figure 3.13 Resonance structures **I** and **II**

Table 3.7 **^{13}C NMR data of complexes 11-15**

Carbon	Chemical shifts (δ, ppm)				
	11	**12**	**13**	**14**	**15**
	δ	δ	δ	δ	δ
Carbene	292.6	n.o.	296.3	308.4	306.6
C2	150.2	164.9	162.8	149.6	154.2
C3	132.1	123.5	130.0	131.4	136.1
C4	144.1	149.3	144.7	143.7	140.2
C5	144.1	149.3	141.3	143.2	140.2
C6	131.0	123.5	129.7	130.9	136.1
C7	128.8	164.9	159.3	128.8	154.2
OCH$_2$CH$_3$-M	79.0	79.6	79.5	78.2	78.8
OCH$_2$CH$_3$-O	-	-	61.5	-	-
OCH$_2$**CH$_3$**-M	15.4	15.3	15.2	15.5	15.5
OCH$_2$**CH$_3$**-O	-	-	14.2	-	-
Me3	18.9	18.4	18.4	18.8	18.2
Me6	14.6	18.4	14.8	14.7	18.2
M(CO)$_5$	197.8 (*cis*) 201.9 (*trans*)	197.3 (*cis*) 202.2 (*trans*)	197.8 (*cis*) 202.3 (*trans*)	206.1 (*cis*) 212.6 (*trans*)	205.7 (*cis*) 212.7 (*trans*)

It is interesting to note that the chemical shift value of C2, the *ipso* carbon atom coordinated to the carbene moiety, is conspicuously lower for the three monocarbene complexes than for the biscarbene and decomposition products. The value for C2 varies from 150.1 to 155.3 ppm for the monocarbene complexes while the corresponding value for the biscarbene and decomposition complexes ranges between 154.2 and 167.5 ppm. The reason for this occurrence is attributed to the electron withdrawing effect of the carbene-metal fragment (figure 3.14). In the case of the monocarbene complexes, only one carbene moiety is coordinated to the ring system, whereas the coordination of two electron withdrawing substituents, as is the case for the biscarbene and decomposition products, enhances the draining of electrons from the ligand. Therefore the deshielding effect on C2 (and C7) is more substantial for the biscarbene complexes and decomposition complexes than for the monocarbene compounds.

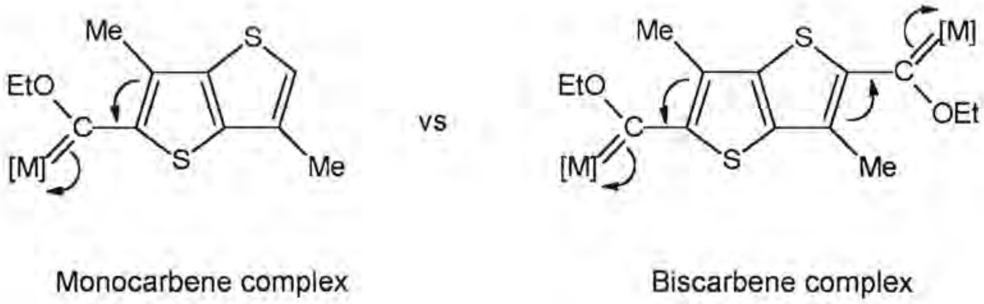


Figure 3.14 Electron draining in monocarbene and biscarbene complexes

For the data of complexes **14** and **15** in table 3.7, the methyl substituents on the ring system is notably affected by the coordination of the ligand to an electron withdrawing substituent. This is evident from the large chemical shift difference between Me3 and Me6 on the spectrum of complex **14**, the monocarbene product. A difference of 4 ppm is observed in that Me3, the methyl group adjacent to the carbene substituent, is shifted downfield compared to Me3 of the uncoordinated ligand. The chemical shift value for Me6, 14.7 ppm, is comparable with the value obtained for Me6 of the uncoordinated ligand, which was found to be 14.6 ppm. This methyl substituent (Me6) can thus serve as a probe to determine the influence of the carbene substituent on the second ring of the condensed ring system. It is therefore concluded that the impact of an electron withdrawing substituent only affects the ring directly coordinated to it.

Table 3.8 **^{13}C NMR data of complexes 16, 17 and 18**

Carbon	Chemical shifts (δ, ppm)		
	16	**17**	**18**
	δ	δ	δ
Carbene	321.2	320.1	319.2
C2	155.3	165.1	167.5
C3	130.3	123.0	122.0
C4	141.0	143.3	142.9
C5	141.5	143.3	142.9
C6	122.0	123.0	122.0
C7	123.1	165.1	167.5
O**CH$_2$**CH$_3$-M	72.3	72.7	72.9
OCH$_2$**CH$_3$**-M	15.4	15.4	15.6
Me3	15.2	15.1	15.4
Me6	14.7	15.1	15.4
Cp	86.3	86.5	85.0 86.5
CpMe	-	-	13.7
M(CO)$_2$	231.3	231.2	231.7

Two single peaks were observed for the Cp carbons on the spectrum of complex **16**, indicating two groups of non-equivalent carbon atoms. The quaternary carbon, bonded to the methyl substituent, was not observed. The M(CO)$_2$ peak is observed downfield from the values obtained for M(CO)$_5$ (M = Cr, W, Mo) peaks observed on the spectra of similar complexes .

The resonances on the ^{13}C NMR spectrum of complex **20** confirm the presence of two thienothiophene rings in this complex, while the data obtained correlates well with the data of complex **19**. These complexes are thus closely related and the environments of the carbon atoms are similar. The values obtained for the chemical shifts of the second thienothiophene unit are comparable to those of the free ligand.

Table 3.9 ^{13}**C NMR data of complexes 19 and 20**

Carbon	Chemical shifts (δ, ppm)	
	19	**20**
	δ	δ
Carbene	317.0	317.9
C2	164.0	164.1
C3, C4, C5, C6, C10, C11	146.8, 139.4, 134.4	146.8, 139.4, 139.2, 134.3, 132.5
C7	155.1	155.1
C8	-	146.1
C9	-	139.2
C12	-	120.1
C13	-	124.3
$O\mathbf{CH_2}CH_3$-M	75.7	75.7
$\mathbf{CH_2}CH_2CH_2CH_3$	43.0	38.7
$CH_2\mathbf{CH_2}CH_2CH_3$	25.5	27.0
$CH_2CH_2\mathbf{CH_2}CH_3$	22.8	22.4
$CH_2CH_2CH_2\mathbf{CH_3}$	13.9	13.8
$OCH_2\mathbf{CH_3}$-M	15.1	15.1
$M(CO)_5$	217.5 (*cis*) 223.5 (*trans*)	217.5 (*cis*) 223.7 (*trans*)
C=O	194.5	-

3.1.3 Infrared Spectroscopy

The infrared data of complexes **8-15** are outlined in table 3.10, while table 3.12 contains the infrared data of complexes **16**, **17** and **18**. The data of complexes **19** and **20** are given in table 3.13.

The spectrum of complex **17** is depicted in figure 3.15.

Table 3.10 Infrared data[a] of complexes 8-15 in carbonyl region

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})							
	8	**9**	**10**	**11**	**12**	**13**	**14**	**15**
$A_1^{(1)}$	2055 2056	2053 2054	2057	2063 2065	2062	2065	2064	2063
B	1979 1986	1986 1984	1984	1989 1982	1983	1985	1983	1988
$A_1^{(2)}$	1938 1952	1941 1956	1940	1933 1949	1938	1936	1941	1946
E	1938 1942	1941 1948	1940	1933 1939	1938	1936	1941	1946

[a]First set of values recorded in dichloromethane, second set in hexane

Table 3.11 Literature carbonyl stretching frequency values

Complex	Band				Reference
	$A_1^{(1)}$	B	$A_1^{(2)}$	E	
$Cr(CO)_5C(OEt)T$	2063	1987	1961	1950	29
$Cr(CO)_5C(OEt)Ph$	2062[a]	1963	1954	1942	31
$W(CO)_5C(OEt)T$	2070	1977	1952	1944	30
$W(CO)_5C(OMe)Ph$	2079[b]	1992	1953	1953	32

[a] Spectrum recorded in pentane; [b] Spectrum recorded in nujol

The experimental values obtained for the various complexes correlate well with values reported in literature (table 3.11). On comparing the stretching frequencies of the monocarbene complex [$Cr(CO)_5C(OEt)T$][29] with those obtained for the monocarbene complex **8**, it was concluded that the higher electron density is found on the metal nuclei with thienothiophene bridging ligands. This is confirmed by comparing the values obtained for complex [$W(CO)_5C(OEt)T$][30] with the stretching frequencies of complex **11**. The lower wavenumbers observed for complexes **8** and **11**, indicate stronger metal-carbonyl back bonding and thus a decrease in C-O bond order. This implies weaker

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[29] J.A. Connor, E.M. Jones, *J. Chem. Soc. A*, **1971**, 1974.

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

metal to carbene carbon π-bonding. Alternatively, the substituents on the carbene carbon may play a greater role in stabilizing the electrophilic carbene carbon. The values reported for the monocarbene complexes of chromium and tungsten containing a phenyl substituent, $[Cr(CO)_5C(OEt)Ph]$[31] and $[W(CO)_5C(OMe)Ph]$[32], are even higher than for the thienyl carbene complexes, implying that the phenyl unit is a poorer donor of electron density compared to the thienyl or, consequently, the thienothienyl substituent.

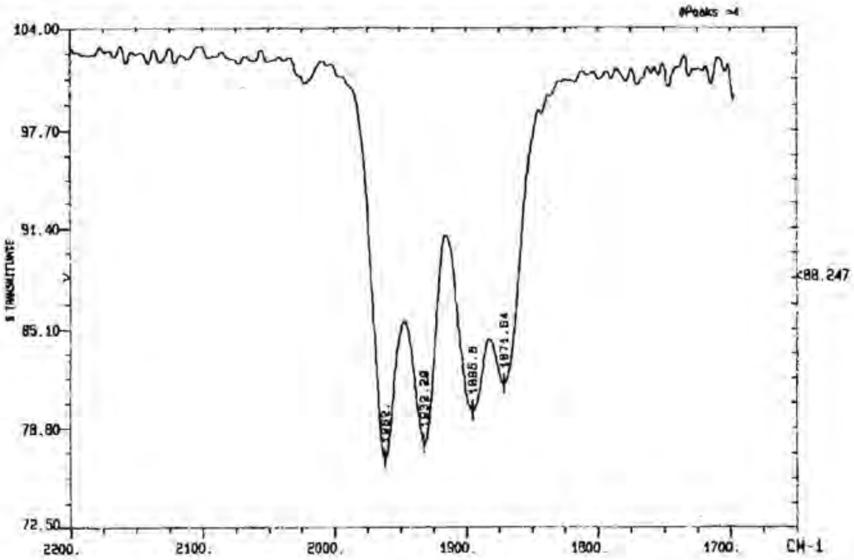

Figure 3.15 Carbonyl region on the infrared spectrum of complex **17**

Table 3.12 Infrared data[a] of complexes 16-18 in carbonyl region

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})		
	16	**17**	**18**
A'	1961, 1933	1962, 1932	1958, 1929
A"	1893, 1871	1896, 1872	1892, 1868

[a]Values recorded in dichloromethane

On the infrared spectra of all three compounds the carbonyl stretching frequencies are observed as four strong bands, instead of the usual two bands expected for these complexes. It is thus

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[31] M.Y. Darensbourg, D.J. Darensbourg, *Inorg. Chem.*, 9, **1970**, 32.

[32] E.O. Fischer, A. Maasböl, *Chem. Ber.*, 100, **1967**, 2445.

concluded that more than one isomer exist in solution. The plane of the substituents of the carbon has two possible orientations relative to the cyclopentadienyl ring: coplanar or perpendicular. Restricted rotation around the carbene-metal bond leads to the existence of two separate conformational isomers and two different positions for the Cp ring relative to the ethoxy group and the thiophene ring system (figure 3.16). Literature reports disclose the same occurrence on the IR spectra of $[\mathrm{MnCp(CO)_2\{C(OMe)Ph\}}]$[33], $[\mathrm{MnCp(CO)_2\{C(OEt)Ph\}}]$[34], $[\mathrm{Cr(\eta^6\text{-}Ar)(CO)_2\{C(OMe)Ph\}}]$[35] and $[\mathrm{MnCp(CO)_2\{\eta^2\text{-}C_2H_4\}}]$[36].

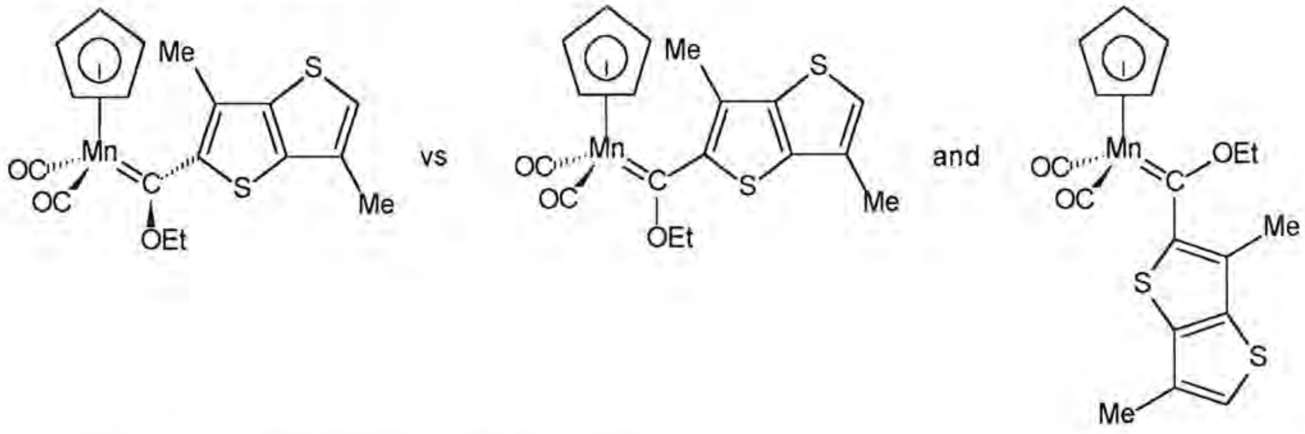

Figure 3.16 Conformational isomers of complex **16**

Table 3.13 Infrared data[a] of complexes 19 and 20 in carbonyl region

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})	
	19	**20**
$A_1^{(2)}$	2058	2056
B	1978	1981
$A_1^{(1)}$	1943	1938
E	1943	1938

[a]Values recorded in dichloromethane

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[33] E.O. Fischer, R.L. Clough and P. Stückler, *J. Organomet. Chem.*, 120, **1976**, C6.

[34] E.O. Fischer, E.W. Meineke, F.R. Kreissl, *Chem. Ber.*, 110, **1977**, 1140.

[35] H.-J. Beck, E.O. Fischer, C.G. Kreiter, *J. Organomet. Chem.*, 26, **1971**, C41.

[36] H. Alt, M. Herberhold, C.G. Kreiter, H. Strack, *J. Organomet. Chem.*, 77, **1974**, 353.

3.1.4 Mass spectrometry

The fragmentation patterns of complexes **8-19** are reported in table 3.14. The molecular ion peak, M^+, was observed for all the complexes except on the mass spectrum of complex **9**. On the spectrum of complex **15** only the molecular ion peak could be assigned because of the lack of a distinguishable fragmentation pattern.

Table 3.14 Fragmentation patterns of complexes 8-19

Complex	Fragment ions (I, %)
8	415.9 (4) M^+; 387.9 (18) M^+ - CO; 359.9 (17) M^+ - 2CO; 331.9 (8) M^+ - 3CO; 303.9 (35) M^+ - 4CO; 275.9 (100) M^+ - 5CO; 246.9 (78) M^+ - 5CO -CH_2CH_3; 218.9 (79) M^+ - 6CO - CH_2CH_3; 167.1 (35) $C_8H_7S_2^+$
9	635.8 (24) M^+ - CO; 551.8 (15) M^+ - 4CO; 523.7 (79) M^+ - 5CO; 495.8 (49) M^+ - 6CO; 467.9 (73) M^+ - 7CO; 411.9 (54) M^+ - 9CO; 383.9 (73) M^+ - 10CO; 355.0 (49) M^+ - 10CO - CH_2CH_3
10	488.2 (2) M^+; 460.2 (10) M^+ - CO; 432.1 (6) M^+ - 2CO; 404.0 (2) M^+ - 3CO; 376.1 (21) M^+ - 4CO; 348.1 (93) M^+ - 5CO; 319.1 (30) M^+ - 5CO - CH_2CH_3; 291.0 (10) M^+ - 6CO - CH_2CH_3
11	547.8 (19) M^+, 519.7 (36) M^+ - CO; 491.8 (17) M^+ - 2CO; 463.8 (18) M^+ - 3CO; 435.8 (30) M^+ - 4CO; 407.8 (100) M^+ - 5CO; 378.8 (37) M^+ - 5CO - CH_2CH_3; 350.9 (71) M^+ - 6CO - CH_2CH_3; 167.1 (33) $C_8H_7S_2^+$
12	931.9 (22) M^+; 902.9 (26) M^+ - CO; 873.8 (15) M^+ - 2CO; 818.4 (14) M^+ - 4CO; 787.8 (14) M^+ - 5CO; 760.2 (72) M^+ - 6CO; 732.9 (43) M^+ - 7CO; 703.8 (48) M^+ - 8CO; 675.9 (36) M^+ - 9CO; 647.9 (45) M^+ - 10CO; 618.9 (35) M^+ - 10CO - CH_2CH_3; 590.9 (44) M^+ - 11CO - CH_2CH_3; 562.9 (40) M^+ - 11CO - $2CH_2CH_3$; 534.9 (50) M^+ - 12CO - $2CH_2CH_3$
13	620.2 (1) M^+; 592.1 (2) M^+ - CO; 564.3 (1) M^+ - 2CO; 536.1 (1) M^+ - 3CO; 508.3 (2) M^+ - 4CO; 480.2 (9) M^+ - 5CO; 451.2 (2) M^+ - 5CO - CH_2CH_3; 423.0 (4) M^+ - 6CO - CH_2CH_3; 407.1 (2) M^+ - 6CO - CH_2CH_3 - O
14	462.2 (4) M^+; 434.2 (9) M^+ - CO; 406.2 (6) M^+ - 2CO; 378.1 (8) M^+ - 3CO; 350.1 (8) M^+ - 4CO; 322.1 (41) M^+ - 5CO; 293.1 (6) M^+ - 5CO - CH_2CH_3; 265.1 (15) M^+ - 6CO - CH_2CH_3; 167.1 (32) $C_8H_7S_2^+$
15	752.2 (3) M^+

Complex	Fragment ions (I, %)
16	400.0 (5) M^+; 371.0 (1) M^+ - CO; 344.0 (57) M^+ - 2CO; 315.0 (13) M^+ - 2CO - CH_2CH_3; 286.9 (100) M^+ - 3CO - CH_2CH_3; 221.9 (37) M^+ - 3CO - CH_2CH_3 - Cp; 167.0 (34) $C_8H_7S_2^+$
17	632.7 (12) M^+; 604.7 (1) M^+ - CO; 576.7 (81) M^+ - 2CO; 548.7 (1) M^+ - 3CO; 520.6 (100) M^+ - 4CO; 491.5 (15) M^+ - 4CO - CH_2CH_3; 463.5 (66) M^+ - 5CO - CH_2CH_3; 434.4 (15) M^+ - 5CO - 2CH_2CH_3; 406.3 (44) M^+ - 6CO - 2CH_2CH_3; 341.2 (13) M^+ - 6CO - 2CH_2CH_3 - Cp; 287.2 (15) M^+ - 6CO - 2CH_2CH_3 - Cp - Mn; 222.1 (5) M^+ - 6CO - 2CH_2CH_3 - 2Cp - Mn; 167.1 (9) $C_8H_7S_2^+$
18	660.5 (7) M^+; 604.4 (73) M^+ - 2CO; 548.3 (100) M^+ - 4CO; 519.2 (11) M^+ - 4CO - CH_2CH_3; 491.2 (36) M^+ - 5CO - CH_2CH_3; 462.2 (6) M^+ - 5CO - 2CH_2CH_3; 434.5 (25) M^+ - 6CO - 2CH_2CH_3
19	472.4 (1) M^+; 444.3 (1) M^+ - CO; 416.3 (1) M^+ - 2CO; 388.3 (1) M^+ - 3CO; 360.2 (4) M^+ - 4CO; 332.3 (27) M^+ - 5CO; 303.2 (7) M^+ - 5CO - CH_2CH_3; 275.1 (7) M^+ - 6CO - CH_2CH_3

All the complexes follow the same basic fragmentation pattern, which starts with the stepwise loss of the carbonyl groups. This is followed by the elimination of the ethyl fragment of the ethoxy group after which the remaining CO moiety is lost. In the case of the biscarbene complexes the loss of one ethyl group and one CO group precedes the loss of the second ethyl group and the second CO fragment. This is obvious on considering the pattern of the two manganese biscarbene complexes **17** and **18**.

The existence of the bis(ethylester) thienothiophene complex, observed on the NMR spectra of complexes **10** and **13**, is confirmed by the presence of its molecular ion peak, $M^+ = 312$, on the mass spectra of both compounds.

3.1.5 X-ray Crystallography

Single crystal X-ray diffraction studies were employed to confirm the molecular structures of complexes **8**, **9**, **11**, **12**, **16**, **18** and **19**. Single crystals of these carbene complexes were obtained from dichloromethane:hexane (1:1) solutions. Complex **8** crystallized as orange needles while complex **9** gave deep-purple needle-like crystals. The orange-red needle-like crystals were characterized as complex **11** and the deep-purple tungsten biscarbene complex **12** gave small, needle-like crystals. Complex **16** gave yellow-brown cubic crystals. Complex **18** crystallized as black crystals. The crystals of complex **19** were cubic and had a purple-red colour. Figures 3.17 to 3.22 and figure 3.24 represent ball-and-stick plots of these respective structures. Selected bond lengths and angles are tabulated in tables 3.15, 3.17, 3.19, 3.20, 3.22, 3.23 and 3.25.

3.1.5.1 Crystal structure of complex 8

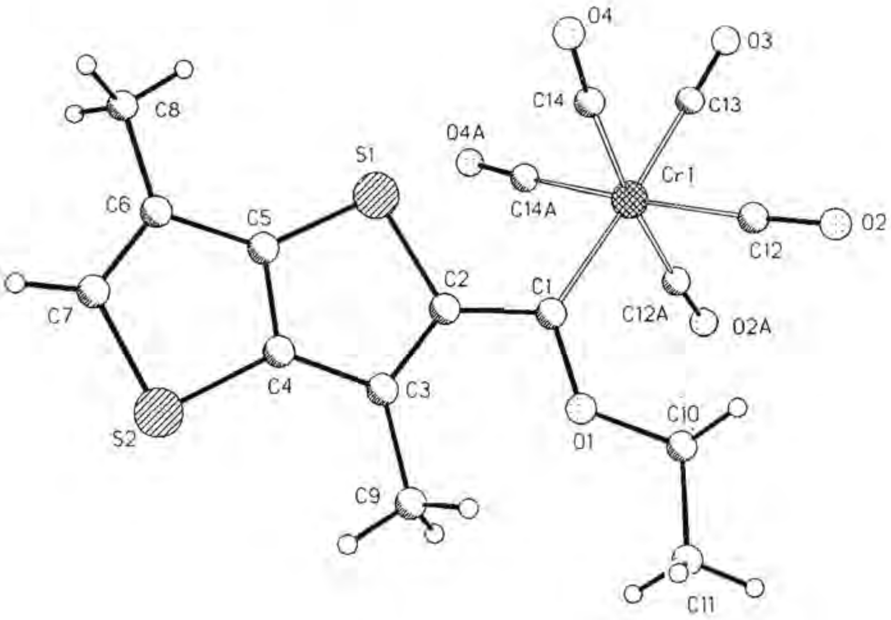

Figure 3.17 Ball-and-stick plot of complex **8**

The crystal structure of uncoordinated thieno[3,2-*b*]thiophene was determined by Cox *et al*[37] and the bond lengths were found to be as follows: S(1)-C(2) 1.72 Å, C(2)-C(3) 1.36 Å, C(3)-C(4) 1.41 Å, C(4)-C(5) 1.36 Å and C(5)-S(1) 1.74 Å. The bond angles were determined as C(2)-S(1)-C(5) 91.2°, S(1)-C(2)-C(3) 116.5°, C(2)-C(3)-C(4) 111.7°, C(3)-C(4)-C(5) 114.3° and C(4)-C(5)-S(1) 110.2°.

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[37] E.G. Cox, R.J.J.H. Gillot, G.A. Jeffrey, *Acta Crystallogr.*, 2, **1949**, 356.

Table 3.15 Selected bond lengths and angles of complex 8

8	**Bond lengths (Å)**	**8**	**Bond angles (°)**
Cr(1)-C(1)	2.081(4)	C(7)-S(2)-C(4)	89.5(2)
S(1)-C(5)	1.722(4)	C(5)-S(1)-C(2)	92.1(2)
S(1)-C(2)	1.751(4)	C(1)-O(1)-C(10)	123.6(3)
S(2)-C(7)	1.721(5)	O(1)-C(1)-C(2)	104.9(3)
S(2)-C(4)	1.729(4)	O(1)-C(1)-Cr(1)	128.6(3)
O(1)-C(1)	1.317(5)	C(2)-C(1)-Cr(1)	126.5(3)
O(1)-C(10)	1.457(5)	C(3)-C(2)-S(1)	111.5(3)
C(1)-C(2)	1.469(6)	C(2) C(3)-C(4)	109.8(4)
C(2)-C(3)	1.413(6)	C(5)-C(4)-C(3)	116.3(4)
C(3)-C(4)	1.411(6)	C(5)-C(4)-S(2)	111.0(3)
C(4)-C(5)	1.377(6)	C(3)-C(4)-S(2)	132.7(3)
C(5)-C(6)	1.341(7)	C(6)-C(7)-S(2)	116.4(4)
C(6)-C(7)	1.431(6)	C(7)-C(6)-C(5)	108.5(4)
		C(4)-C(5)-C(6)	114.6(4)
		C(4)-C(5)-S(1)	110.3(3)

From the structure of complex **8** it is noted that the heteroaromatic ring, the carbene carbon and the metal are coplanar. The metal fragment is orientated towards the sulfur atom and away from the methyl substituent on the ring. The Cr metal is approximately octahedrally arranged with two of the cis-carbonyl ligands bending away from the carbene carbon. This is indicated by the bond angles of 94.5(1)° for C(12)A-Cr(1)-C(1). On considering the positions of the ethyl group of the ethoxy substituent relative to the metal fragment in the solid state, the Z-isomer of this complex along the carbene-O bond is observed. This is in accordance with the observation in literature that the Z-isomer is by far the most popular arrangement in crystal structures of ethoxy- or methoxy-substituted carbene complexes of octahedrally coordinated metals[38].

On comparing the bond lengths of the ring system in the structure of complex **8** with those of free

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[38] (a) O.S. Mills, A.D. Redhouse, *J. Chem. Soc. A*, **1968**, 642. (b) G. Huttner, B. Krieg, *Chem. Ber.*, 105, **1972**, 67. (c) U. Schubert, *Organometallics*, 1, **1982**, 1085.

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thieno[3,2-*b*]thiophene, all of the bonds are longer (or equal) in the complex except for the C(5)-C(6) bond which is shorter. These bond lengths are all in the range between the characteristic bond distances of a C(sp^2)-C(sp^2) single bond (1.46 Å) and a C(sp^2)-C(sp^2) double bond (1.32 Å)[39]. The bonds are therefore more delocalized in the complex than for the free ligand. This effect is more apparent in the thiophene ring fragment directly coordinated to the carbene moiety and diminishes on going to the second conjugated ring fragment.

The metal-carbene carbon bond length is 2.08(1) Å, while the arene-carbene carbon bond is 1.47(1) Å. The bond between oxygen and the carbene carbon is 1.32(1) Å and the distance between the oxygen and the ethyl group is 1.46(1) Å. These values are very similar to literature values obtained for other monocarbene complexes of chromium pentacarbonyl (table 3.16) of the type [$Cr(CO)_5C(OR)R'$].

Table 3.16 Literature values

Complex	Bond length (Å)				Reference
	M-$C_{carbene}$	$C_{carbene}$-O	O-R	$C_{carbene}$-R'	
$Cr(CO)_5C(OMe)Ph$	2.04(3)	1.33(2)	1.46	1.47(4)	38(a)
$Cr(CO)_5C(OEt)Me$	2.05(1)	1.31(1)	-	1.51(1)	40
$Cr(CO)_5C(OH)Ph$	2.05(1)	1.32(1)	-	-	41
$Cr(CO)_5C[OSi(SiMe_3)_3]$1-furyl	2.03(1)	1.32(1)	-	1.45(1)	42

The Cr-carbene bond of 2.08(1) Å, compared to a Cr(0)-C single bond of 2.21 Å and a Cr-C double bond of 1.91 Å in $Cr(CO)_6$, together with the $C_{carbene}$-O bond distance of 1.32(1) Å, compared to the values found in diethyl ether (1.43 Å) and acetone (1.23 Å)[43], indicate partial double bond

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[39] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans 2*, **1987**, S1.

[40] K.H. Dötz, H. Fischer, P.Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH Verlag, Weinheim, **1983**, p.94.

[41] R.J. Klinger, J.C. Huffman, J.K. Kochi, *Inorg. Chem.*, 20, **1981**, 34.

[42] U. Schubert, M. Wiener, F.H. Köhler, *Chem. Ber.*, 112, **1979**, 708.

[43] A.W. Parkins, R.C. Poller, *An Introduction to Organometallic Chemistry*, Macmillan Publishers, London, **1986**, p.53.

character for both bonds. The carbene plane is staggered with the *cis*-carbonyl ligands and the *trans*-carbonyl C-Cr bond length is 0.04 Å shorter than the average *cis*-carbonyl C-Cr bond length.

3.1.5.2 Crystal structure of complex 9

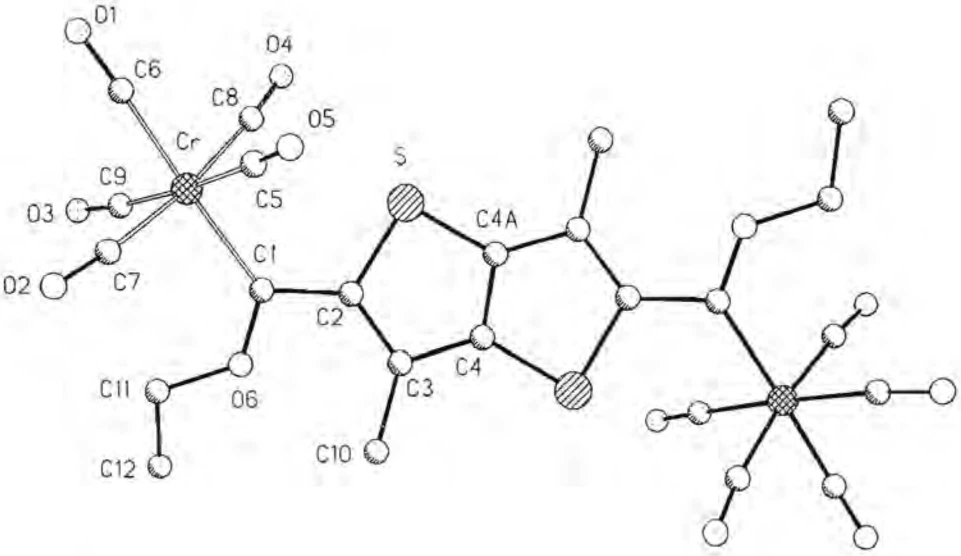

Figure 3.18 Ball-and-stick plot of complex **9**

The arene ring system, carbene carbons and metals in the structure of complex **9** are coplanar and the molecule is centrosymmetric. The planar nature of this arene spacer is ideal for π-conjugation and metal-metal communication through this bridging ligand. The two $Cr(CO)_5$ metal fragments are found on opposite sides of the spacer ligand, positioned towards the sulfur atom and away from the methyl substituent on the ring, similar to the structure of complex **8**. This is in contrast with the structure of the biscarbene complex of chromium pentacarbonyl, constituting a thienylene spacer[27]. In this complex, the metal fragments are found on the same side of the thiophene ring and on the side opposite to the sulfur atom in the ring. However, for the biscarbene complex of chromium pentacarbonyl with biphenylene as bridging ligand, the metal moieties are again on opposite sides of the axis connecting the two carbene carbon atoms[44]. The *cis*-carbonyl

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[44] N. Hoa Tran Huy, P. Lefloch, F. Robert, J. Jeannin, *J. Organomet. Chem.*, 327, **1987**, 211.

groups in **9** are staggered relative to the carbene carbon. The *trans*-carbonyl C-Cr bond distance is 0.02 Å shorter than the average *cis*-carbonyl C-Cr bond length.

The bond lengths of the ring system are all longer or similar to those of free thieno[3,2-*b*]thiophene except for C(4A)-S, which is shorter. The suggested delocalization in the ring system is promoted by the observed bond distances, which are all very similar, and correspond to distances between characteristic C(sp^2) single bonds and C(sp^2) double bonds. In contrast to the observation made for complex **8**, the delocalization in this complex occurs throughout the whole arene system, aided by the influence of the second metal fragment, which is absent in complex **8**.

The bond angles of the thieno[3,2-*b*]thiophene substituent for complex **9** differ marginally from those of the free DMTT, indicating a slight distortion of the arene ring due to metal coordination.

Table 3.17 Selected bond lengths and angles of complex 9

9	**Bond lengths** (Å)	**9**	**Bond angles** (°)
Cr-C(1)	2.068(3)	C(3)-C(2)-S	113.1(2)
S-C(4A)	1.721(2)	C(2)-C(3)-C(4)	109.3(2)
S-C(2)	1.745(3)	C(4)-C(4A)-S	110.8(2)
C(1)-C(2)	1.473(4)	C(4A)-S-C(2)	91.1(1)
C(2)-C(3)	1.393(4)	O(6)-C(1)-C(2)	105.0(2)
C(3)-C(4)	1.415(4)	O(6)-C(1)-Cr	129.2(2)
C(4A)-C(4)	1.378(5)	C(2)-C(1)-Cr	125.7(2)
O(6)-C(1)	1.325(3)		
O(6)-C(11)	1.449(3)		

The Cr-$C_{carbene}$ distance of 2.07(1) Å falls within the range of Cr-$C_{carbene}$ distances (2.00-2.10 Å) reported for alkoxy carbene complexes of chromium and can be compared with literature values of similar biscarbene complexes given in table 3.18.

Table 3.18 Literature values

Complex	Bond length (Å)				Reference
	M-$C_{carbene}$	$C_{carbene}$-O	O-R	$C_{carbene}$-R'	
[{Cr(CO)$_5$C(OEt)}$_2$T]	2.04(1)	1.32(1)	1.45(1)	1.47(1)	27
[{Cr(CO)$_5$C(OEt}$_2$biphenylene]	2.05(1)	1.32(1)	-	1.49(1)	44

3.1.5.3 Crystal structure of complex 11

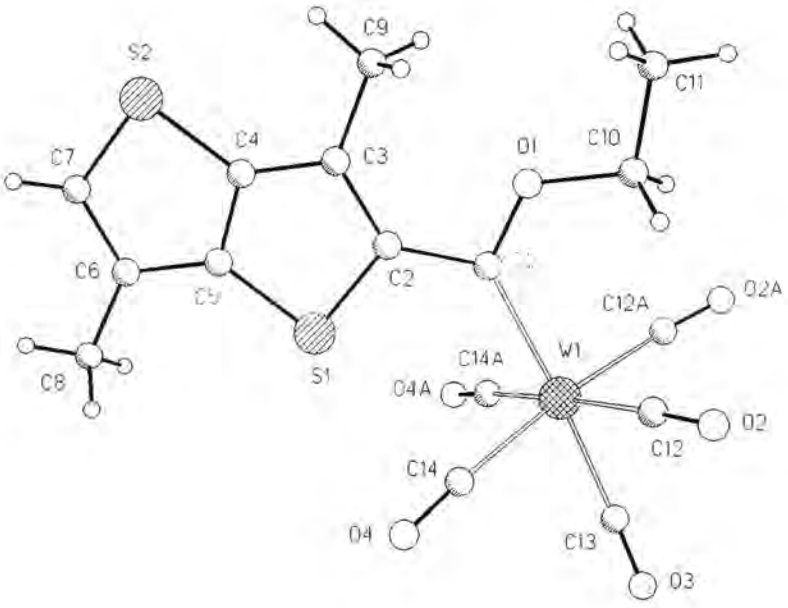

Figure 3.19 Ball-and-stick plot of complex **11**

It is interesting to note that the C(2)-S bond length is conspicuously longer for all of the complexes than the rest of the C-S bonds. The lengthening of all the C-S bonds compared to those in the free ligand implies that the sulfur atoms are less involved in the delocalization through the ring system in the complexes. The involvement of the sulfur atom in the aromaticity of the free ligand is much more significant. The C(2)-S bond in the complexes is the most affected by this result because of the coordination of the carbene moiety at C2.

Table 3.19 Selected bond lengths and angles of complex 11

11	**Bond lengths** (Å)	**11**	**Bond angles** (°)
W-C(1)	2.219(6)	C(7)-S(2)-C(4)	92.0(3)
S(1)-C(5)	1.727(6)	C(5)-S(1)-C(2)	91.3(3)
S(1)-C(2)	1.771(7)	O(1)-C(1)-C(2)	104.5(5)
S(2)-C(7)	1.733(8)	O(1)-C(1)-W	128.1(5)
S(2)-C(4)	1.746(7)	C(2)-C(1)-W	127.3(5)
O(1)-C(1)	1.345(8)	C(3)-C(2)-S(1)	111.1(5)
O(1)-C(10)	1.456(9)	C(2)-C(3)-C(4)	110.9(6)
C(1)-C(2)	1.460(9)	C(5)-C(4)-C(3)	116.3(6)
C(2)-C(3)	1.402(8)	C(5)-C(4)-S(2)	110.0(6)
C(3)-C(4)	1.395(10)	C(3)-C(4)-S(2)	133.7(5)
C(4)-C(7)	1.399(10)	C(4)-C(5)-C(6)	115.6(6)
C(5)-C(6)	1.428(11)	C(4)-C(5)-S(1)	109.6(6)
C(6)-C(7)	1.398(10)	C(7)-C(6)-C(5)	109.0(8)
		C(6)-C(7)-S(2)	114.2(6)

3.1.5.4 Crystal structure of complex 12

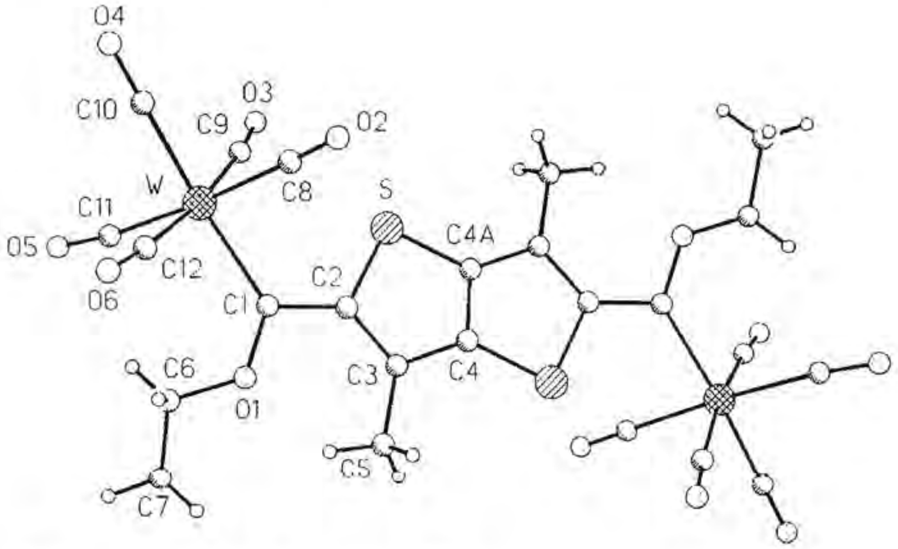

Figure 3.20 Ball-and-stick plot of complex **12**

Table 3.20 Selected bond lengths and angles of complex 12

12	**Bond lengths (Å)**	**12**	**Bond angles (°)**
W-C(1)	2.221(8)	C(3)-C(2)-S	113.2(5)
S-C(4A)	1.728(7)	C(2)-C(3)-C(4)	118.0(5)
S-C(2)	1.761(7)	C(4)-C(4A)-S	109.4(6)
C(1)-C(2)	1.460(10)	C(4A)-S-C(2)	90.9(3)
C(2)-C(3)	1.399(10)	O(1)-C(1)-C(2)	105.9(6)
C(3)-C(4)	1.427(9)	O(1)-C(1)-W	128.2(5)
C(4A)-C(4)	1.390(15)	C(2)-C(1)-W	125.7(5)
O(1)-C(1)	1.342(9)		
O(1)-C(6)	1.452(9)		

The structure of complex **12** is very similar to the structure of complex **9**. Delocalization through the ring is again implied by the lengthening of the arene ring carbon-carbon bond distances. The metal-carbene bond length is now, however, 2.22(1) Å for the larger tungsten metal atom, compared to the value of 2.07(1) Å for the smaller chromium atom. The average carbonyl-metal bond length is also 0.15 Å longer in this structure compared to the structures containing chromium metal atoms (complexes **8** and **9**).

The methyl substituents on the condensed ligand is coplanar to the carbene plane for all four structures (complexes **8**, **9**, **11** and **12**).

In table 3.21 literature values are reported for mono- and biscarbene complexes of tungsten. The bond distances for complexes **11** and **12** are very comparable with these values, although the metal-carbene value for complex **12** is significantly longer (2.22(1) Å) than the average bond distance (2.13 Å) reported for the analogous complexes in this table. This trend was also observed for the chromium complexes **8** and **9**, signifying that back bonding from the metal to the carbene carbon is reduced and that the thienothiophene fragment is a better π-donor than phenyl, thiophene or anthracene in comparable complexes.

Table 3.21 **Literature values**

Complex	Bond length (Å)				Reference
	M-$C_{carbene}$	$C_{carbene}$-O	O-R	$C_{carbene}$-R'	
$W(CO)_5C(OMe)Ph$	2.05	1.31	1.43	1.49	[45]
$W(CO)_5C(Ph)Ph$	2.15(1)	-	-	1.45(2), 1.51(2)	[46]
$[\{W(CO)_5C(OEt)\}_2T]$	2.15(1)	1.33(1)	1.47(1)	1.46(1)	[47]
$[\{W(CO)_5C(OMe)\}_2(\text{anthracendiyl})]$	2.16(1)	1.31(1)	-	1.50(1)	[48]

3.1.5.5 Crystal structure of complex 16

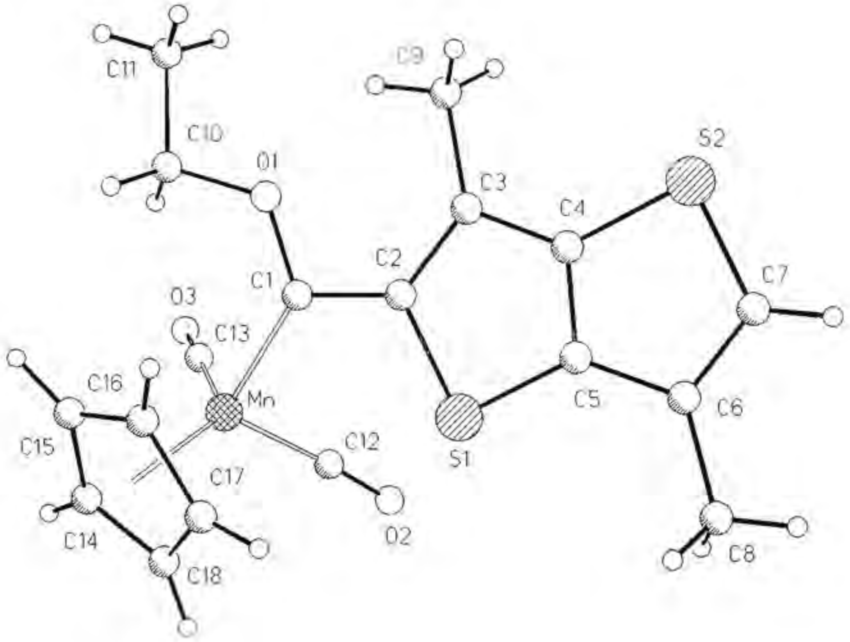

Figure 3.21 Ball-and-stick plot of complex **16**

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[45] O.S. Mills, A.D. Redhouse, *Angew. Chem. Int. Ed. Engl.*, 4, **1965**, 1142.

[46] C.P. Casey, T.J. Burkhardt, C.A. Bunnel, J.C. Calabrese, *J. Am. Chem. Soc.*, 99, **1977**, 2127.

[47] Y.M. Terblans, PhD thesis, *Thiophene Bimetallic Carbene Complexes*, University of Pretoria, **1996**.

[48] T. Albrecht, J. Sauer, *Tetrahedron Lett.*, 35, **1994**, 561.

Table 3.22 Selected bond lengths and angles of complex 16

16	Bond lengths (Å)	16	Bond angles (°)
Mn-C(1)	1.944(6)	C(5)-S(1)-C(2)	91.3(3)
S(1)-C(5)	1.721(6)	C(7)-S(2)-C(4)	90.1(3)
S(1)-C(2)	1.765(6)	C(1)-O(1)-C(10)	122.8(5)
S(2)-C(7)	1.734(6)	O(1)-C(1)-C(2)	106.2(5)
S(2)-C(4)	1.737(8)	O(1)-C(1)-Mn	127.8(4)
O(1)-C(1)	1.344(7)	C(2)-C(1)-Mn	126.0(4)
O(1)-C(10)	1.454(8)	C(3)-C(2)-S(1)	112.3(4)
C(1)-C(2)	1.460(8)	C(2)-C(3)-C(4)	109.4(5)
C(2)-C(3)	1.410(8)	C(5)-C(4)-C(3)	115.4(5)
C(3)-C(4)	1.430(9)	C(5)-C(4)-S(2)	111.6(5)
C(4)-C(7)	1.382(9)	C(3)-C(4)-S(2)	132.9(5)
C(5)-C(6)	1.447(9)	C(4)-C(5)-C(6)	114.5(5)
C(6)-C(7)	1.373(10)	C(4)-C(5)-S(1)	111.5(5)
		C(7)-C(6)-C(5)	108.5(6)
		C(6)-C(7)-S(2)	115.3(5)

The steric effect of the methyl substituent on the ring system is evident in considering the angles C(1)-C(2)-C(3) and C(1)-C(2)-S(1) around the sp^2-hybridized ring carbon C(2). These angles are 129.6(5)° and 112.3(4)°, respectively, and are an indication of the degree of distortion. Seeing that in the ring system the carbene carbon and the metal atom are all in the same plane, it is clear that the ethoxy substituent on the carbene carbon and the methyl group on the heteroaromatic ring are competing for the same space, which is sterically unfavourable. The molecule is therefore distorted to accommodate both of these groups, which causes the deviation in bond angles. The heteroaromatic ring is bent towards the metal moiety. It has previously been suggested that the methyl substituent on the ring is the reason for the metal orientation towards the sulfur atom and not the opposite conformation as is observed in complexes with thiophene[27] and unsubstituted thienothiophene spacer units (see complex **19**). Bond lengths in this complex are comparable to literature values reported for similar complexes (table 3.24), although the carbene-metal bond is slightly longer than the average value determined in literature.

3.1.5.6 Crystal structure of complex 18

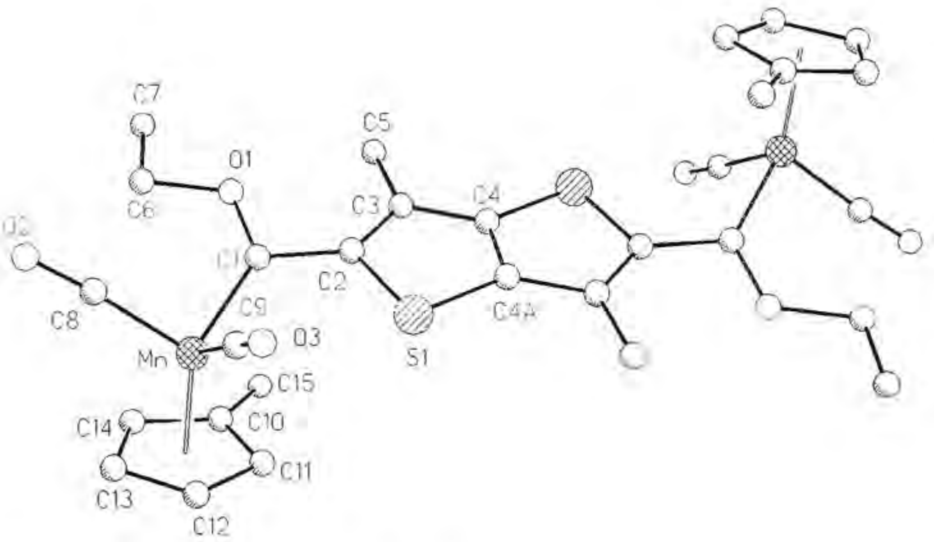

Figure 3.22 Ball-and-stick plot of complex **18**

From figure 3.22 it is clear that the conformation of the complex is such that the carbene plane (formed by the metal, the carbene carbon and the two substituents R and R') is perpendicular to the mirror plane of the $MnCp(CO)_2$ fragment. Although this conformation is electronically the more unfavourable[38c], it is sterically preferred. The two conformations differ by the relative orientation of the carbene plane and the mirror plane of the metal fragment: co-planar or perpendicular (figure 3.23).

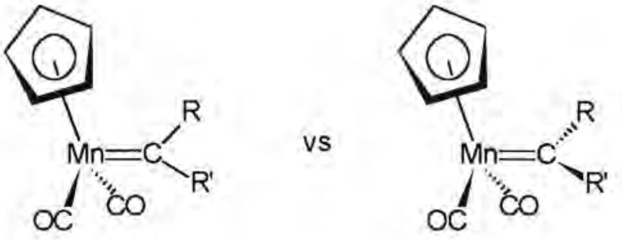

Figure 3.23 Conformations of $MnCp(CO)_2$ carbene complexes

The geometry around the manganese centre is pseudotetrahedral and the cyclopentadienyl ring is parallel to the carbene plane with the orientation of the methyl substituent coinciding with the Mn-carbene bond.

Table 3.23 Selected bond lengths and angles of complex 18

18	**Bond lengths** (Å)	**18**	**Bond angles** (°)
Mn-C(1)	1.922(5)	C(3)-C(2)-S	112.9(3)
S-C(4A)	1.733(5)	C(2)-C(3)-C(4)	109.7(4)
S-C(2)	1.761(5)	C(4)-C(4A)-S	110.8(5)
C(1)-C(2)	1.485(7)	C(4A)-S-C(2)	91.2(2)
C(2)-C(3)	1.394(7)	O(1)-C(1)-C(2)	105.1(4)
C(3)-C(4)	1.428(7)	O(1)-C(1)-Mn	129.9(3)
C(4A)-C(4)	1.388(10)	C(2)-C(1)-Mn	124.8(4)
O(1)-C(1)	1.338(6)		
O(1)-C(6)	1.465(6)		

The Mn-carbene bond of 1.922(5) Å is somewhat longer than the average value obtained for literature examples of mono- and biscarbene complexes containing a manganese metal fragment (see table 3.24). This value is, however, considerably shorter than the metal-carbene bond distances observed in the analogous chromium and tungsten complexes. The bond angles around the carbene carbon seem to be insensitive to change in the metal.

Table 3.24 Literature values

Complex	**Bond length** (Å)			**Reference**
	M-$C_{carbene}$	$C_{carbene}$-O	$C_{carbene}$-R'	
$MnCp(CO)_2C(OMe)menthyl$	1.89(2)	1.33(2)	1.53(2)	49
$MnCp(CO)_2C(OEt)Ph$	1.87(1)	1.36(2)	1.54(2)	38c
$MnCp(CO)_2C(Ph)Ph$	1.89(2)	-	-	38c
$[\mu\text{-}O\{MnCp(CO)_2CPh\}_2]$	1.85(2), 1.88(5)	-	-	50

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[49] S. Fontana, U. Schubert, E.O. Fischer, *J. Organomet. Chem.*, 146, **1978**, 39.

[50] E.O. Fischer, J. Chen, U. Schubert, *Z. Naturforsch., Teil B*, 37, **1982**, 1284.

3.1.5.7 Crystal structure of complex 19

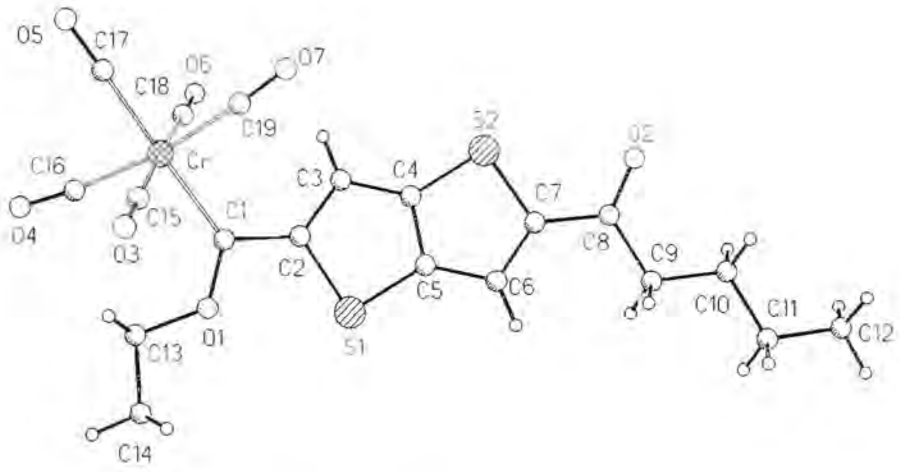

Figure 3.24 Ball-and-stick plot of complex **19**

Table 3.25 Selected bond lengths and angles of complex 19

19	**Bond lengths** (Å)	**19**	**Bond angles** (°)
Cr-C(1)	2.059(3)	C(7)-S(2)-C(4)	90.68(13)
S(1)-C(5)	1.729(3)	C(5)-S(1)-C(2)	90.96(13)
S(1)-C(2)	1.765(3)	C(1)-O(1)-C(13)	122.8(2)
S(2)-C(4)	1.733(3)	O(1)-C(1)-C(2)	105.4(2)
S(2)-C(7)	1.752(3)	O(1)-C(1)-Cr	130.0(2)
O(1)-C(1)	1.335(3)	C(2)-C(1)-Cr	124.20(19)
O(1)-C(13)	1.465(3)	C(3)-C(2)-S(1)	111.7(2)
C(1)-C(2)	1.464(4)	C(2)-C(3)-C(4)	112.1(2)
C(2)-C(3)	1.384(4)	C(5)-C(4)-C(3)	113.6(2)
C(3)-C(4)	1.408(4)	C(5)-C(4)-S(2)	111.4(2)
C(4)-C(5)	1.399(4)	C(3)-C(4)-S(2)	134.8(2)
C(5)-C(6)	1.417(4)	C(6)-C(7)-S(2)	113.1(2)
C(6)-C(7)	1.381(4)	C(7)-C(6)-C(5)	111.1(3)
C(7)-C(8)	1.477(4)	C(4)-C(5)-C(6)	113.8(2)
		C(4)-C(5)-S(1)	111.4(2)

The ring system in this structure is again planar and lies within the plane of the carbene carbon and the metal atom and now includes the carbonyl group at C7. The metal-carbene distance is very similar to those encountered for complexes **8** and **9**. Interesting to note is that the orientation of the metal fragment is opposite to all the structures containing the 3,6-dimethylthieno[3,2-*b*]thiophene unit and is directed away from the sulfur atom in the ring system, on the opposite side of the ring. This phenomenon may be attributed to the absence of the methyl substituent on the ring, eliminating any steric reason for positioning itself away from the sulfur atom. This is also the preferred orientation for the metal moiety in thienyl ethoxy carbene complexes[27].

4

Carbene complexes of Dithienothiophene

1. General

Dithienothiophenes (DTT) are polycondensed heteroaromatic molecules consisting of three condensed thiophene rings. New interest in compounds of this type arose since dithienothiophenes possess three different types of π-conjugation which play an important role as a spacer and donor[1] and these compounds give rise to conjugated polymers with unique properties[2]. The first compound of this series, dithieno[2,3-*b*:3',2'-*d*]thiophene (**II**), was prepared by Pandya and Tilak[3] who cyclized 2,5-bis(dimethoxyethylthio)thiophene with polyphosphoric acid. Altogether six isomers of dithienothiophene are known and have been synthesized (figure 4.1). Although dithieno[3,2-*b*:2',3'-*d*]thiophene (**I**) has been prepared and employed in various syntheses[4], the synthetic inconvenience of dithieno[2,3-*b*:3',2'-*d*]thiophene (**II**) and dithieno[3,4-*b*:3',4'-*d*]thiophene (**III**) had prevented the use of these substrates in organic synthesis in the past. Recently, however, Iyoda *et al*[5] reported a convenient method for the synthesis of **II** and **III** which involves the palladium-catalyzed cyclization of a dibromo-precursor.

Complexes **IV** and **V** were prepared by De Jong *et al*[6] *via* the appropriate dibromo intermediates followed by oxidative ring closure using copper(II) chloride. Compound **VI** was synthesized by converting the suitable dibromodithienyl intermediate into an unstable thiol which, without isolation, was treated with cuprous oxide to yield dithieno[2,3-*b*:2',3'-

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[1] K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, *Chem. Lett.*, **1987**, 2339.

[2] C. Taliani, G. Ruani, R. Zanboni, *Synth. Met.*, 28, **1989**, C507.

[3] L.J. Pandya, B.D. Tilak, *J. Sci. Ind. Res., Sect. B*, 18, **1959**, 371.

[4] F. de Jong, M.J. Janssen, *J. Org. Chem.*, 36, **1971**, 1645.

[5] M. Iyoda, M. Miura, S. Sasaki, S.M.H. Kabir, Y. Kuwatani, M. Yoshida, *Tetrahedron Lett.*, 38, **1997**, 4581.

[6] F. de Jong, M.J. Janssen, *J. Org. Chem.*, 36, **1971**, 1998.

d]thiophene[7]. The relative electrophilic reactivity[8] of compounds **I**, **II** and **VI** were determined by the detritiation of all positions of the isomeric dithienothiophenes in trifluoroacetic acid at 70°C. The results showed that the order of reactivity for the three compounds are **II** > **VI** > **I** for the α-position and **VI** > **II** > **I** for the β-position.

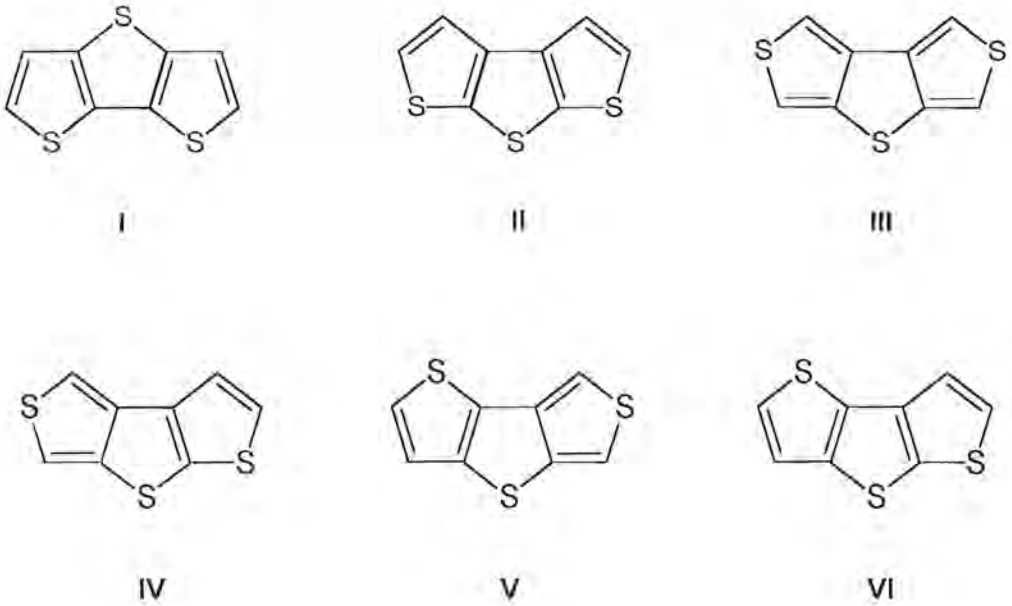

Figure 4.1 Dithienothiophenes

Since a rigid backbone and bulky groups are required in the design of host molecules for crystalline inclusion compounds[9], Mazaki *et al*[10] designed a new host series using linearly condensed thiophenes. They have synthesized a series of compounds (figure 4.2) since the rigid belt-like structure of condensed thiophenes is expected to provide a range of inclusion capacities and cavities in the crystals. The host compounds were prepared by dilithiation of the precursor thiophene derivative followed by treatment with cyclohexylketone, benzophenone and fluorenone. High yields were obtained.

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[7] K.T. Potts, D. McKeough, *J. Am. Chem. Soc.*, 95, **1973**, 2750.

[8] W.J. Archer, R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 301.

[9] J.L. Atwood, J.E.D. Davies, D.D. MacNicol, *Inclusion Compounds*, Academic Press, London, **1984**.

[10] Y. Mazaki, N. Hayashi, K. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1992**, 1381.

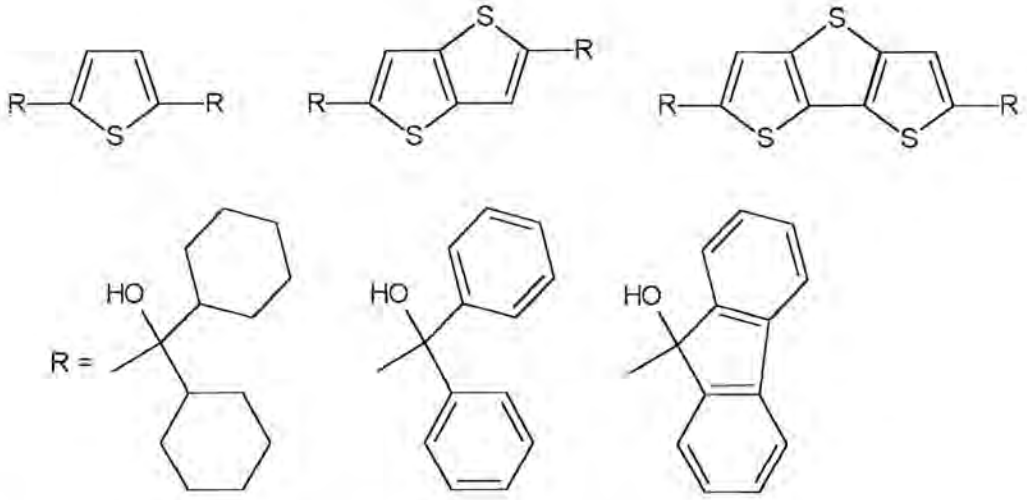

Figure 4.2 Inclusion compounds of thiophene derivatives

Polymerization of compounds **I**, **II** and **III** has received considerable attention lately. Li *et al*[11] reported the design and synthesis of new organic semiconductors for thin film transistors (TFT) application using dithieno[3,2-*b*:2',3'-*d*]thiophene (**I**) as building block. In previous studies it was observed that the dimer of the fused thiophene α,α'-bis(dithieno[3,2-*b*:2',3'-*d*]thiophene) (BDT) was found to have an unusual π-stacked structure and high conducting properties. The synthesis of polymeric dithieno[3,4-*b*:3',4'-*d*]thiophene (**III**) *via* electrochemical polymerization was reported by Catellani *et al*[12].

The coordination properties of dithienothiophene with transition metal complexes have not yet been investigated.

2. Synthesis of Dithieno[3,2-*b*:2',3'-*d*]thiophene

The synthesis of dithieno[3,2-*b*:2',3'-*d*]thiophene (I) was based on the work done by De Jong and Janssen[4], where 3-bromothiophene is used as starting material. The general reaction scheme is set out in figure 4.3. The yields of the products, however, could not be met and the oxidative ring closure step (step **c**, figure 4.3), especially proved to be challenging.

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[11] X. Li, H. Sirringhaus, F. Garnier, A.B. Holmes, S.C. Moratti, N. Feeder, W. Clegg, S.J. Teat, R.H. Friend, *J. Am. Chem. Soc.*, 120, **1998**, 2206.

[12] M. Catellani, T. Caronna, S.V. Meille, *J. Chem. Soc., Chem. Commun.*, **1994**, 1911.

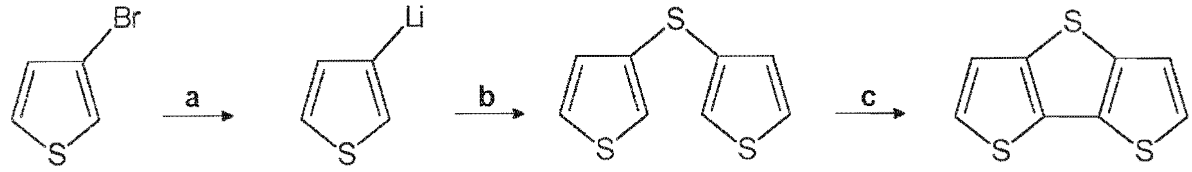

Figure 4.3 Reagents: **(a)** n-BuLi, ether, reflux; **(b)** $(C_6H_5SO_2)_2S$, ether, -70°C; **(c)** 2 n-BuLi, $CuCl_2$

Since this synthesis was time-consuming and the reaction yields were unsatisfactory, a new synthetic route was considered, using 2,2'-bithiophene as starting material. The idea for this synthesis originated from work done by Ohshita *et al*[13]. Dithienosiloles were afforded when 3,3'-dilithio-5,5'-bis(trimethylsilyl)-2,2'-bithiophene, prepared from the reaction of n-butyllithium and 3,3'-dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene, was treated with dichlorodiphenylsilane. Replacement of the silyl groups with bromine atoms yielded dibromodithienosilole. Lithiation and the subsequent hydrolysis of the resulting dilithiodithienosilole afforded 4,4-diphenyldithienosilole. The prospect of utilizing this synthetic method to synthesize dithieno[3,2-*b*:2',3'-*d*]thiophene by substituting dichlorodiphenylsilane for sulfur dichloride was suggested. The proposed reaction scheme is outlined in figure 4.4.

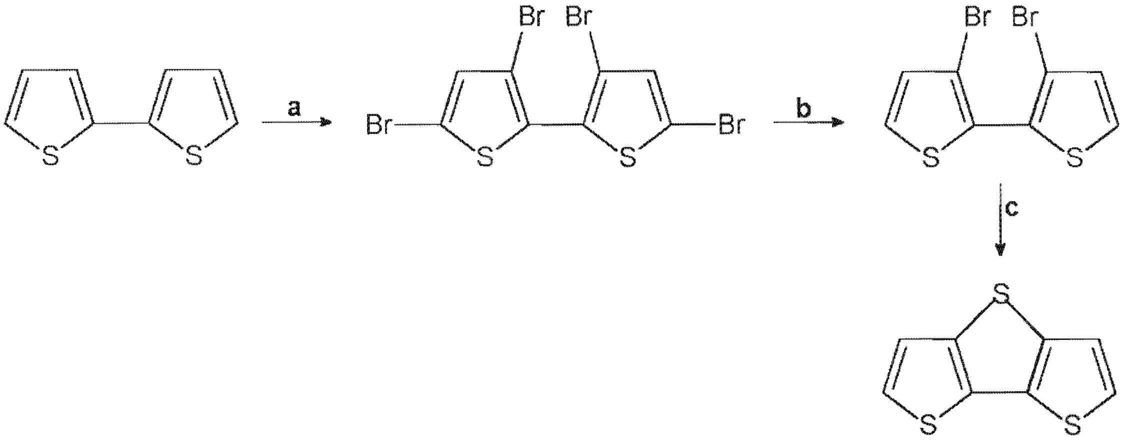

Figure 4.4 Reagents: **(a)** Br_2 (excess), reflux 24h; **(b)** Zn, reflux; **(c)** 2 eq. n-BuLi, SCl_2, THF, 0°C

2,2'-Bithiophene was treated with excess bromine to afford 3,3',5,5'-tetrabromo-2,2'-

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[13] J.Ohshita, M. Nodono, T. Watanabe, Y. Ueno, A. Kunai, Y. Harima, K. Yamashita, M. Ishikawa, *J. Organomet. Chem.*, 553, **1998**, 487.

bithiophene[14]. Reaction of this tetrabromo product with zinc dust at elevated temperatures resulted in selective α-debromination to yield 3,3'-dibromo-2,2'-bithiophene. Lithiation of 3,3'-dibromo-2,2'-bithiophene with n-butyllithium, followed by the reaction with sulfur dichloride[15], afforded the target product, but unfortunately the desired compound was dissolved in a viscous oil which formed as byproduct. All attempts to separate the two products failed and this method was also found to be unsatisfactory.

In an final attempt to synthesize dithieno[3,2-*b*:2',3'-*d*]thiophene a combination of the methods described by De Jong *et al*[4] and Brandsma *et al*[15] was employed. 3-Bromothiophene was lithiated and the 3-lithiothiophene species was reacted with sulfur dichloride to yield di(3-thienyl)sulphide. Ring closure of this compound, using n-butyllithium followed by $CuCl_2$, gave dithieno[3,2-*b*:2',3'-*d*]thiophene (I) in low yields.

Seeing that the ring closure reaction was the most problematic step in the synthesis of the ligand, it was inferred that the lithiation of di(3-thienyl)sulphide was incomplete and that this was the reason for the failure in obtaining the target product. To establish whether this speculation had any credibility, a test reaction was conducted. After the dimetallation of di(3-thienyl)sulphide, one equivalent of tungsten hexacarbonyl was added, followed by the alkylation of the resulting dilithium salt with Et_3OBF_4. A green biscarbene complex **21** (figure 4.5) was yielded, refuting the assumption. The system for numbering of the atoms for characterization purposes is shown. Interestingly, no coordination of the linking sulfur atom was observed whereby two five-membered rings would result in a tricarbonyl complex. The infrared data supported a tetracarbonyl complex and a molecular ion peak at m/z = 660 confirmed a mononuclear complex.

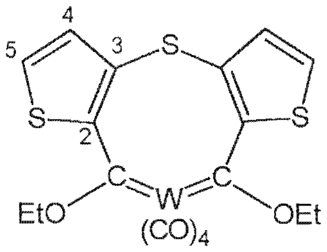

Figure 4.5 Structure of complex 21

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[14] S.C. Ng, H.S.O. Chan, H.H. Huang, R.S.H. Seow, *J. Chem. Res. (M)*, **1996**, 1285.

[15] L. Brandsma, H. Verkruijsse, *Preparative Polar Organometallic Chemistry I*, Springer-Verlag, Berlin Heidelberg, **1987**, p.162.

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3. Synthesis of carbene complexes of Dithieno[3,2-*b*:2',3'-*d*]thiophene

On comparing the σ$^+$-values of the different positions of dithieno[3,2-*b*:2',3'-*d*]thiophene (figure 4.6), it is evident that the 2- and 9-positions are the most reactive. This was confirmed by electrophilic substitution studies done on the different dithienothiophene isomers by Archer and Taylor[8].

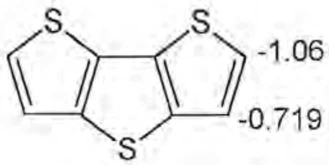

Figure 4.6 σ$^+$-values

Dimetallation of dithieno[3,2-*b*:2',3'-*d*]thiophene was effected according to the method employed by Brandsma *et al* for the dimetallation of thiophene[16]. This metallation involved the use of n-butyllithium and TMEDA in hexane at elevated temperatures. Deprotonation of dithieno[3,2-*b*:2',3'-*d*]thiophene, by using two equivalents of n-butyllithium to one equivalent of substrate, occurred at positions 2 and 9.

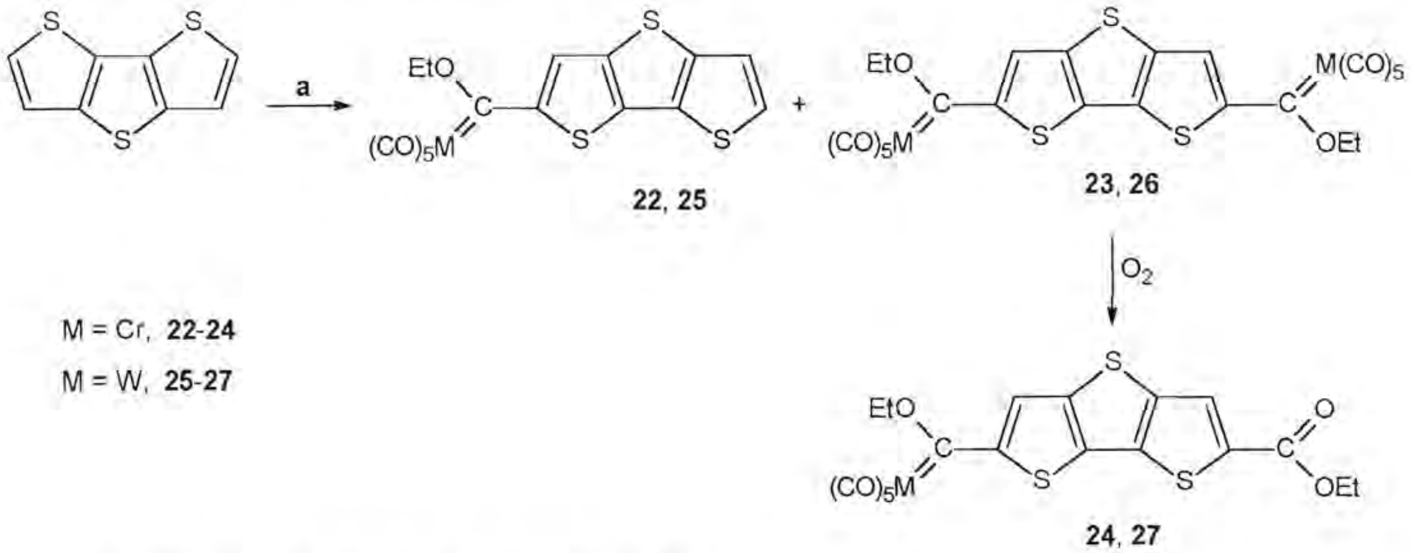

Figure 4.7 Synthesis of complexes **22-27**
Reagents: **a**(i) 2 eq. n-BuLi (ii) $ML_3(CO)_3$ (iii) $Et_3O\,BF_4$

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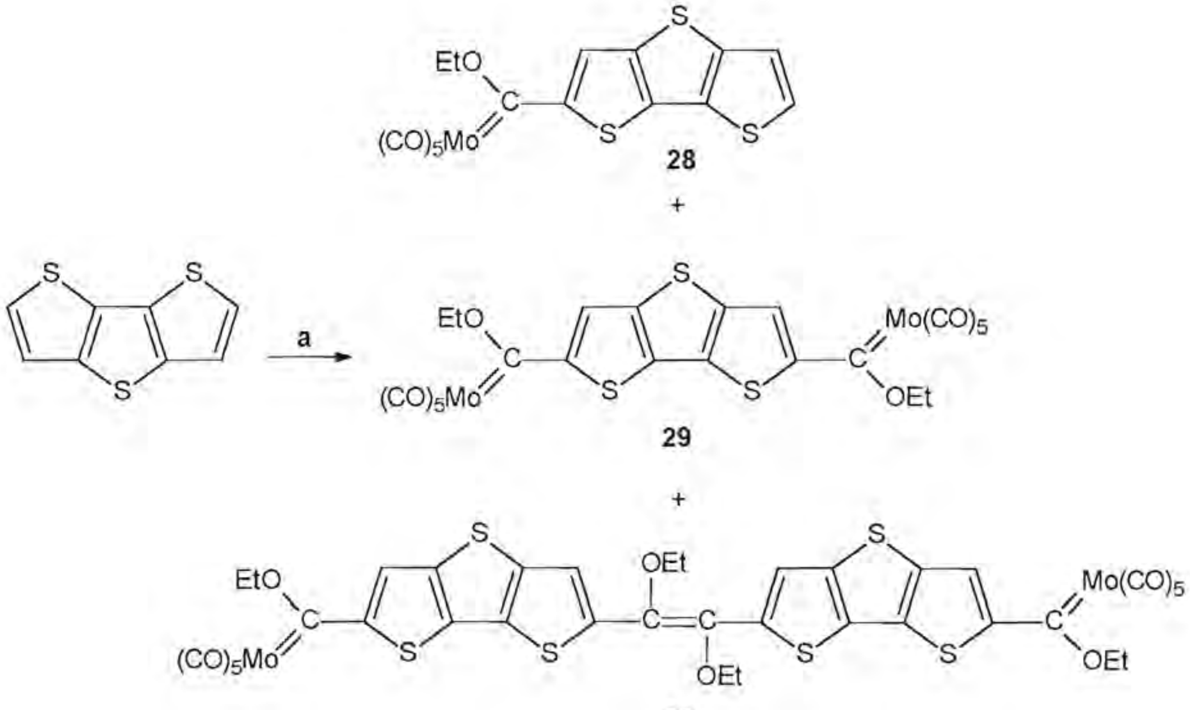
[16] L. Brandsma, H. Verkruijsse, *Preparative Polar Organometallic Chemistry I*, Springer-Verlag, Berlin Heidelberg, **1987**, p.164.

Carbene complexes of chromium, tungsten and molybdenum were afforded employing the general Fischer method described in Chapter **2**. Upon reaction of $Cr(CO)_6$ with the dimetallated species and subsequent quenching with the alkylating agent, three products were afforded *i.e.* the orange monocarbene complex **22**, the purple biscarbene complex **23** as well as the pink-orange decomposition product, complex **24**. Three analogous compounds were yielded upon reaction with tungsten hexacarbonyl. Complexes **25**, **26** and **27** were isolated with column chromatography. The general synthetic procedure for the formation of these complexes is given in figure 4.7. The reaction between molybdenum hexacarbonyl and the dimetallated species afforded, after alkylation, three products. The first was the orange-red monocarbene complex, **28**, while the biscarbene complex **29** had a purple colour. The third purple-pink product that was isolated, complex **30**, was not the expected decomposition product, but was instead characterized as a biscarbene product formed by a carbene-carbene coupling reaction (figure 4.8).

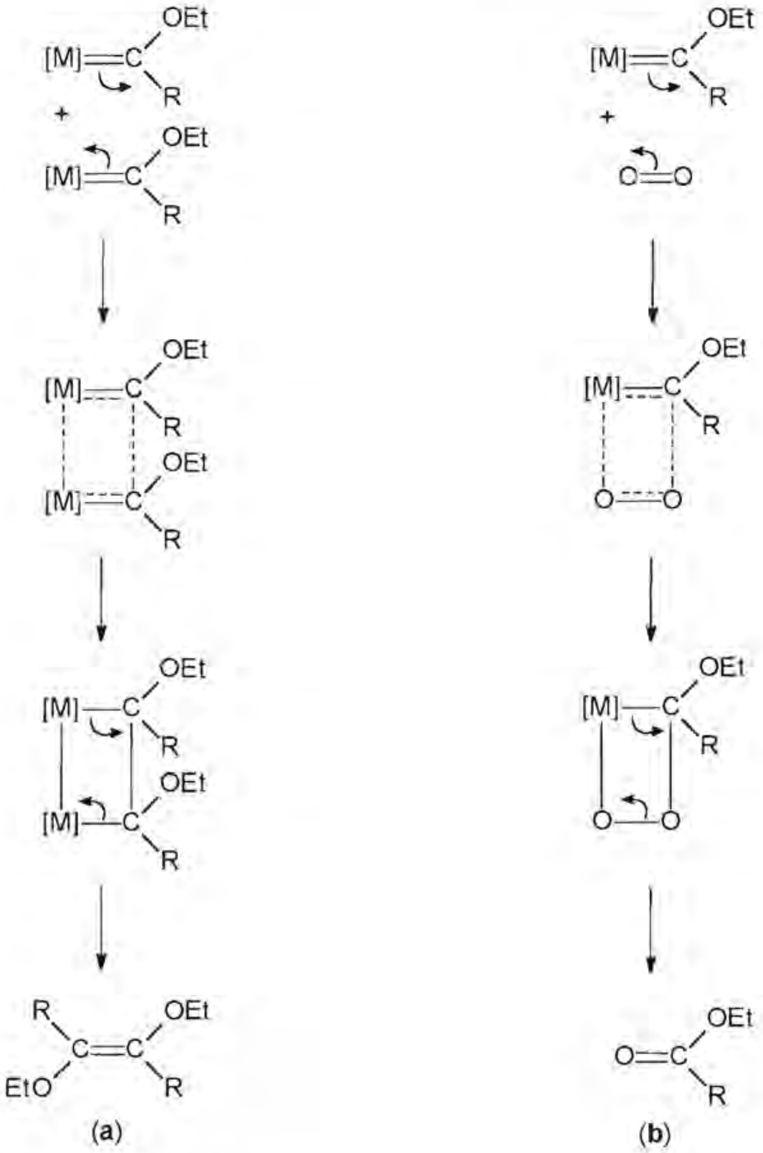


30

Figure 4.8 Synthesis of complexes **28-30**

Reagents: **a**(i) 2 eq. n-BuLi (ii) $M(CO)_6$ (iii) $Et_3O{\cdot}BF_4$

This biscarbene complex contained an extended conjugated bridging ligand. The difference between the formation of this product and the normal decomposition product is illustrated in figure 4.9. The formation of complex **28** constitutes the reaction between two biscarbene complexes, resulting in C-C bond formation and the elimination of a molybdenum species, yielding a growing biscarbene complex. This product has the possibility of, on repeating this process, forming a growing conducting polymer.



R = dithieno[3,2-*b*;2',3'-*d*]thiophene

Figure 4.9 Formation of (**a**) complex **30** and (**b**) decomposition products **24** and **27**

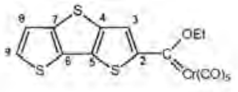
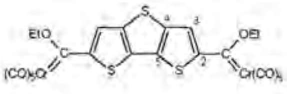
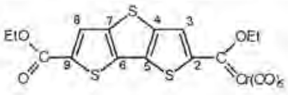
3.1 Spectroscopic characterization of novel carbene complexes

The carbene complexes were characterized using NMR and infrared spectroscopy and mass spectrometry. Confirmation of the molecular structures of compounds **22**, **23** and **27** were obtained from single crystal X-ray diffraction studies.

3.1.1 ^{1}H NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform as solvent unless otherwise specified. The ^{1}H NMR data for complexes **22-30** are summarized in tables 4.1, 4.2 and 4.3.

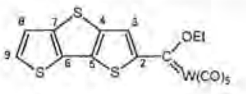
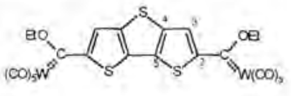
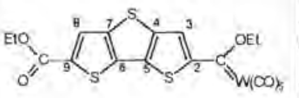
Table 4.1 ^{1}H NMR data of complexes 22-24

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **22**		 **23**		 **24**	
	δ	J	δ	J	δ	J
H3	8.42 (s)	-	8.38 (s)	-	8.41 (s)	-
H8	7.32 (d)	5.2	-	-	8.00 (s)	-
H9	7.57 (d)	5.2	-	-	-	-
O**CH$_2$**CH$_3$-M	5.17 (q)	7.0	5.20 (q)	7.0	5.19 (q)	7.0
O**CH$_2$**CH$_3$-O	-	-	-	-	4.40 (q)	7.0
OCH$_2$**CH$_3$**-M	1.68 (t)	7.0	1.69 (t)	7.0	1.69 (t)	7.0
OCH$_2$**CH$_3$**-O	-	-	-	-	1.40 (t)	7.0

In the ^{1}H NMR spectrum of complex **21** two broad singlet peaks are observed for protons H4 and H5 at δ 7.30 and 7.58 ppm respectively. The O**CH$_2$**CH$_3$ protons are observed at 4.51 ppm as a quartet but again the resolution was not satisfactory. This value is lower than the normal biscarbene values observed in similar complexes, indicating that the protons are more shielded in this case. It is thus suggested that the carbene moieties are less electrophilic due to the influence of both moieties on one metal fragment instead of being bonded to two separate metal fragments. A $J^3_{H\text{-}H}$ coupling constant of 7.5 Hz was calculated for coupling to the methyl protons. Two triplet signals were observed at 1.72 and 1.60 ppm for the two OCH$_2$**CH$_3$** groups since this is a fluxional molecule and the two ethoxy groups are free to rotate. Therefore they are in different chemical environments and two independent peaks are observed.

The chemical shift values, recorded in deuterated chloroform, for uncoordinated dithieno[3,2-*b*:2',3'-*d*]thiophene are 7.34 (H2, H9) and 7.27 (H3, H8). It is evident from the data in tables 4.1-4.3 that the coordination of metal moieties to the ligand has a significant influence on the electronic distribution of the complex. The substantial chemical shift differences for protons H3 and H8 on the spectra of the biscarbene complexes and the decomposition complexes compared to that of DTT indicate that the electrophilic carbene-metal moiety withdraws electron density from the ring, deshielding the protons on the ring and causing a downfield shift. On the spectra of the monocarbene complexes a similar trait is noticed and it is interesting to note that the protons furthest away from the metal fragment, H9 and, to a lesser extent, H8, are likewise affected due to conjugation in the ring system.

Table 4.2 ^{1}H NMR data of complexes 25-27

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **25**		 **26**		 **27**	
	δ	J	δ	J	δ	J
H3	8.35 (s)	-	8.29 (s)	-	8.32 (s)	-
H8	7.31 (d)	5.2	8.29 (s)	-	8.00 (s)	-
H9	7.59 (d)	5.2	-	-	-	-
O**CH$_2$**CH$_3$-M	4.99 (q)	7.0	5.00 (q)	7.2	5.00 (q)	7.0
O**CH$_2$**CH$_3$-O	-	-	-	-	4.40 (q)	7.2
OCH$_2$**CH$_3$**-M	1.66 (t)	7.0	1.68 (t)	7.0	1.67 (t)	7.0
OCH$_2$**CH$_3$**-O	-	-	-	-	1.40 (t)	7.0

On comparing the chemical shift values of the methylene protons of the ethoxy groups of the carbenes for different metal complexes, it seems to make little difference whether the ligand is coordinated to one or two carbene-metal moieties. It appears however that the chemical shift values are affected by the nature of the metal fragment. Characteristic values are observed for chromium, while the values for molybdenum are slightly lower and the chemical shifts for the tungsten complexes are observed upfield compared to the other metal complexes. The chemical shift values obtained for the novel carbene metal complexes correspond well with values obtained in literature. Values for the ethoxy protons of the chromium and tungsten monocarbene carbene complexes with thiophene as bridging unit were reported as 5.16, 1.65 ppm and 4.99, 1.64 ppm respectively[17]. The spectra of the biscarbene analogues of these complexes[18] displayed values of 5.21, 1.69 ppm (Cr) and 4.98, 1.68 ppm (W). The proton spectrum of complex **27** is depicted in figure 4.10. The analogous molybdenum decomposition product of complexes **24** (Cr) and **27** (W) was only observed in a very low yield on TLC. This product could not be isolated.

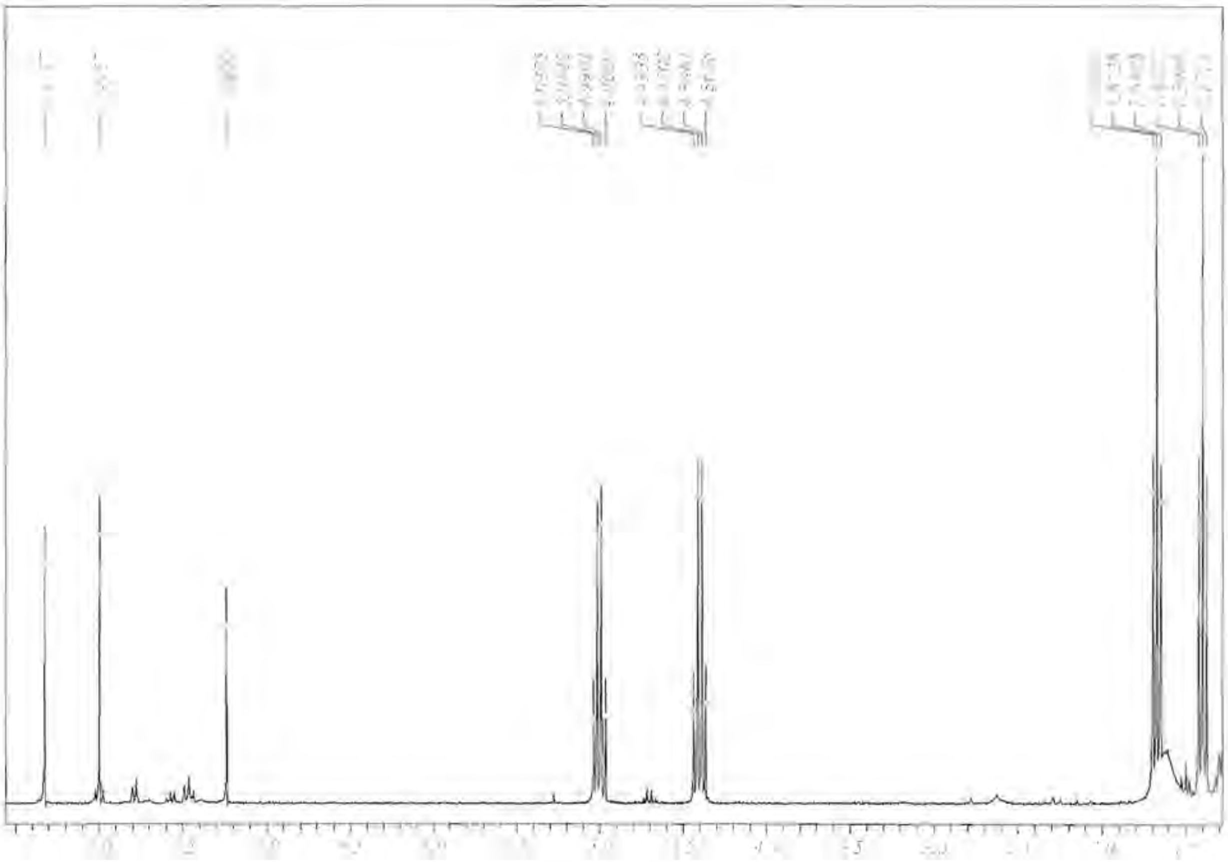


Figure 4.10 Proton spectrum of the tungsten decomposition product, complex **27**

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[17] M.Y. Darensbourg, D.J. Darensbourg, *Inorg. Chem.*, 9, **1970**, 32.

[18] Y.M. Terblans, H.M. Roos, S. Lotz, *J. Organomet. Chem.*, 566, **1998**, 133.

Indication of the existence of this decomposition product can be found on the spectrum of complex **30**, where the small quartet at 4.35 ppm is associated with the methylene protons of the ester functionality of this product. The main pattern of decomposition, instead, leads to a carbene-carbene coupling reaction of the biscarbene complex **29** to yield an extended spacer. Characteristic for **30** is the intensity ratio of the methylene resonances and the chemical shift at 4.00 ppm. This again highlights differences in the chemistry of biscarbene complexes of molybdenum compared to chromium and tungsten.

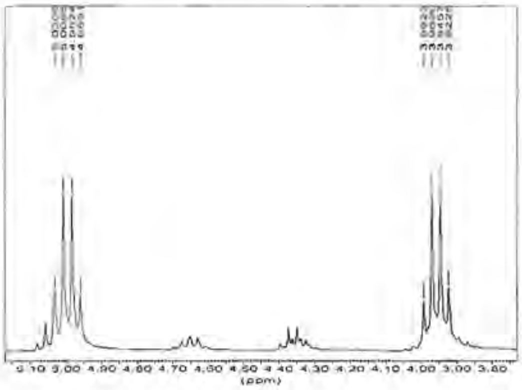
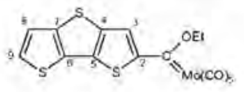
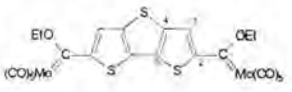
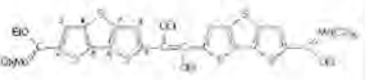


Figure 4.11 Methylene region on the ^{1}H NMR spectrum of complex **30**

Table 4.3 **^{1}H NMR data of complexes 28-30**

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **28**		 **29**		 **30**	
	δ	J	δ	J	δ	J
H3	8.38 (s)	-	8.33 (s)	-	8.34 (s)	-
H8	7.33 (d)	5.2	-	-	7.28 (s)	-
H9	7.59 (d)	5.4	-	-	-	-
O**CH$_2$**CH$_3$-M	5.07 (q)	7.1	5.09 (q)	7.0	5.04 (q)	7.4
O**CH$_2$**CH$_3$-O	-	-	-	-	4.00 (q)	7.0
OCH$_2$**CH$_3$**-M	1.66 (t)	7.0	1.68 (t)	7.1	1.63 (t)	7.0
OCH$_2$**CH$_3$**-O	-	-	-	-	1.40 (t)	7.0

3.1.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data of complexes **22-30** are given in table 4.4.

Table 4.4 ^{13}C NMR data of complexes 22, 23, 24, 25, 27, 28, 29 and 30

Carbon	Chemical shifts (δ, ppm)							
	22	**23**	**24**	**25**	**27**	**28**	**29**	**30**
	δ	δ	δ	δ	δ	δ	δ	δ
Carbene	312.0	314.8	314.4	286.7	288.6	302.6	n.o.	302.3
C2	154.4	157.5	161.9	158.0	161.9	n.o.	156.1	155.7
C3	135.0	133.4	134.1	135.6	134.7	135.6	133.7	135.3
C4, C5, C6, C7	142.8 146.8	137.0 146.1	137.7 140.9 144.6 145.1	142.6 146.0	132.4 137.8 138.3 145.3	142.6 147.0	136.2 146.8	138.5 139.2 142.7 142.8
C8	121.1	-	126.6	121.2	126.7	121.1	-	122.1
C9	130.7	-	156.2	130.9	159.6	130.9	-	146.6
O**CH$_2$**CH$_3$ -M	75.8	76.2	76.1	78.2	78.5	77.2	77.9	77.4
O**CH$_2$**CH$_3$ -O	-	-	61.8	-	61.9	-	-	67.5
OCH$_2$**CH$_3$** -M	15.2	15.1	15.2	15.0	14.9	15.1	15.0	15.1
OCH$_2$**CH$_3$** -O	-	-	14.3	-	14.3	-	-	15.6
M(CO)$_5$	217.1 (*cis*) 223.2 (*trans*)	216.8 (*cis*) 223.2 (*trans*)	216.9 (*cis*) 223.2 (*trans*)	197.6 (*cis*) 202.3 (*trans*)	197.4 (*cis*) 202.3 (*trans*)	206.1 (*cis*) 212.7 (*trans*)	205.9 (*cis*) 212.1 (*trans*)	206.1 (*cis*) 212.7 (*trans*)
C=O	-	-	n.o.	-	198.2	-	-	-
C-OEt	-	-	-	-	-	-	-	108.1

On the ^{13}C NMR spectrum of complex **21** the carbene peak was observed at δ 290.8 ppm. This value correlates well with values determined for the novel tungsten monocarbene complexes as well as literature values[19]. This value supports the deduction made from the ^{1}H NMR data that the carbene carbon is less electrophilic in this complex and the carbene carbon therefore more shielded. Two signals were obtained for the tetracarbonyl-metal moiety at 212.4 ppm and 204.5 ppm, corresponding to the CO_{trans} and CO_{cis} carbonyl ligands respectively. The quaternary carbon signal at 158.0 ppm was assigned to C2 while the peak for C3 was observed at 139.1 ppm. Signals for C4 and C5 were found at 129.8 and 121.3 ppm, the higher value being assigned to C5 due to its position next to the heteroatom. On the spectrum two different signals are observed for the carbons of the two ethoxy groups. Again, confirming the ^{1}H NMR data, it is concluded that the two ethoxy groups are in different chemical environments. The chemical shift values for the two -O**CH**$_2$CH$_3$ are 79.7 and 79.4 ppm and for the methyl groups are 14.8 and 14.1 ppm. From these values as well as the other proton NMR data it is clear that the methyl groups are for some unknown reason more affected than the -OCH$_2$CH$_3$ groups, since the chemical shift difference is more prominent. A crystal structure could throw light on this observation, but all attempts to isolate crystals suitable for X-ray structural studies, unfortunately, failed.

The ^{13}C NMR spectrum of complex **26** was of an unsatisfactory quality since the poor solubility of the product in $CDCl_3$ prevented the acquisition of a decent data set. The following peaks (ppm) were observed on the spectrum and assigned to the different carbon atoms: 202.3 ($M(CO)_5$ *trans*); 197.6 ($M(CO)_5$ *cis*); 133.8 (C3); 78.6 (O**CH**$_2$CH$_3$-M); 14.9 (OCH$_2$**CH**$_3$-M). On many of the spectra a resonance peak at 182.2 ppm was observed. This peak was assigned to free CO which was released during the recording of the spectra and was dissolved by the solvent. The position of the methylene resonances as well as the methyl resonances of the ethoxy group were found to have characteristic values, depending on the functionality of adjacent groups. These values were consistent for all complexes irrespective of the number of conjugated thiophene moieties and, to a large extent, independent of the metal fragment (figure 4.12).

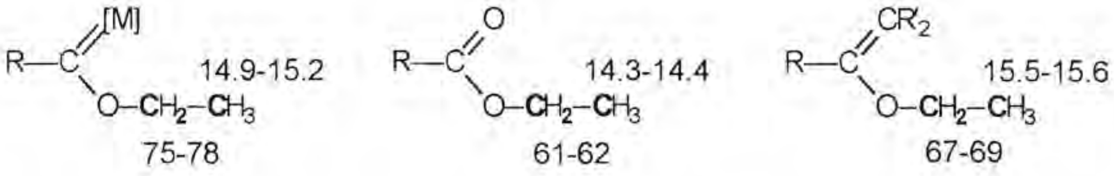


Figure 4.12 Characteristic positions of the ethoxy carbons on ^{13}C NMR spectra (ppm)

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[19] E.O. Fischer, T. Selmayr, F.R. Kreissl, U. Schubert, *Chem. Ber.*, 110, **1977**, 2547.

Although the resonances of the methylene carbons are largely independent, a small difference is still noted for the different metal complexes. The methylene carbon peaks of the carbene ethoxy group on the spectra of the chromium complexes are all observed at 75.5-76.2 ppm, while the corresponding peaks were found at 78.2-78.9 ppm for the tungsten complexes and at 77.2-77.9 ppm for the molybdenum complexes. The trend is thus W > Mo > Cr, corresponding to the size of the metal atom and the relative positions of the metals on the periodic table. This same sequence is observed for the corresponding methyl carbons of the different metal complexes but in the opposite order.

3.1.3 Infrared Spectroscopy

The infrared data of complexes **22-30** are outlined in table 4.5.

Table 4.5 Infrared data[a] of complexes 22-30 in the carbonyl region

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})								
	22	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
$A_1^{(1)}$	2056	2054	2056	2064	2064	2066	2066 2066	2064 2066	2066 2066
B	1982	1979	1978	1976	1979	1979	1981 1989	1981 1989	1983 1989
$A_1^{(2)}$	1941	1944	1942	1937	1937	1939	1944 1950	1946 1954	1944 1952
E	1941	1944	1942	1937	1937	1939	1944 1950	1946 1954	1944 1952

[a] First set of values recorded in dichloromethane, second set in hexane

The IR spectrum of complex **21** was recorded in hexane and in dichloromethane. Since this is a tetracarbonyl-metal complex, four infrared active bands were observed in the carbonyl stretching frequency region. On the hexane spectrum four distinct bands can be distinguished, while degeneracy of the $A_1^{(2)}$ and B_1 bands occurs in dichloromethane and only three peaks are observed. On the spectrum recorded in hexane peaks were observed at the following wavenumbers: 2025 cm^{-1} ($A_1^{(1)}$), 1955 cm^{-1} ($A_1^{(2)}$), 1942 cm^{-1} (B_1) and 1889 cm^{-1} (B_2). The three bands on the spectrum recorded in dichloromethane were observed at 2022 cm^{-1} ($A_1^{(1)}$), 1944 cm^{-1} ($A_1^{(2)}$ and B_1) and 1869 cm^{-1} (B_2). These values correspond well with values obtained for a similar tungsten biscarbene complex prepared by Fischer *et al*[20]. Values for the 1,4-chelated *o*-phenylene tetracarbonyl tungsten ethoxy biscarbene complex are only marginally higher than for complex **21** and are: 2032 cm^{-1} ($A_1^{(1)}$), 1957 cm^{-1} ($A_1^{(2)}$), 1947 cm^{-1} (B_1) and 1896 cm^{-1} (B_2).

The carbonyl vibration frequencies of the ester groups of complexes **24** and **27** were observed as lower intensity bands at 1650 cm^{-1} and 1652 cm^{-1}, respectively. This band was noticeably absent on the spectrum of complex **30**.

3.1.4 Mass spectrometry

The data for the fragmentation of complexes **21-28** are presented in table 4.6.

From the data in table 4.6 it is evident that the monocarbene complexes, biscarbene complexes and decomposition complexes have different fragmentation patterns respectively. The monocarbene complexes show initial fragmentation of five carbonyl groups followed by the loss of the ethyl group and eventually the elimination of the carbene carbonyl group. On the spectra of the biscarbene complexes the M^+ peaks were not observed. Instead, on all three spectra the M^+ - 4CO fragmentation peak was the peak observed at highest m/z-value. A definite fragmentation pattern for the biscarbene complexes could not be distinguished. However, certain discernable fragments could be identified which were present on all three spectra. The first meaningful peak was identified as the M^+ ion of the decomposition product i.e. one metal carbonyl fragment was replaced by an ester group. After this the consecutive loss of five carbonyl groups is observed and the peaks associated with these fragments could be assigned. Interestingly, the principal ion on all three spectra is found at a m/z value of 340, which corresponds to a fragment ion where both carbene fragments are replaced by ester groups. The fragmentation patterns of the decomposition products are very similar to that of the monocarbene complexes. The molecular ion peak was observed in all three cases and the fragmentation started with the stepwise loss of three carbonyl groups. In the spectrum of **24** the consequent loss of carbonyl groups ensued, while the elimination of the ethyl group preceded the further loss of the carbonyl groups in the spectrum of **27**.

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[20] E.O. Fischer, W. Röll, N. Hoa Tran Huy, K. Ackermann, *Chem. Ber.*, 115, **1982**, 2951.

Table 4.6 Fragmentation patterns of complexes 21-28

Complex	Fragment ions (I, %)
21	606.2 (2) M$^+$; 578.1 (4) M$^+$ - CO; 550.1 (1) M$^+$ - 2CO; 522.2 (1) M$^+$ - 3CO; 494.2 (6) M$^+$ - 4CO; 465.1 (3) M$^+$ - 4CO - Et; 436.0 (12) M$^+$ - 4CO - 2Et; 408.9 (5) M$^+$ - 5CO - 2Et; 380.0 (6) M$^+$ - 6CO - 2Et
22	444.1 (8) M$^+$; 416.2 (19) M$^+$ - CO; 388.1 (15) M$^+$ - 2CO; 360.1 (11) M$^+$ - 3CO; 332.2 (43) M$^+$- 4CO; 304.1 (96) M$^+$- 5CO; 275.0 (72) M$^+$- 5CO - Et; 247.0 (81) M$^+$- 6CO - Et
23	580.1 (12) M$^+$ - 4CO; 516.2 (44) **24**$^+$; 488.3 (29), **24**$^+$ - CO; 460.2 (16) **24**$^+$ - 2CO; 432.2 (32) **24**$^+$ - 3CO; 404.2 (76) **24**$^+$ - 4CO; 376.2 (14) **24**$^+$ - 5CO
24	516.2 (1) M$^+$; 488.2 (2) M$^+$ - CO; 460.1 (2) M$^+$ - 2CO; 432.2 (1) M$^+$ - 3CO; 404.2 (8) M$^+$ - 4CO; 376.1 (36) M$^+$ - 5CO; 347.2 (17) M$^+$ - 5CO - Et; 319.1 (11) M$^+$ - 6CO - Et
25	576.2 (49) M$^+$; 548.2 (23) M$^+$- CO; 520.0 (27) M$^+$- 2CO; 491.2 (9) M$^+$- 3CO; 463.1 (71) M$^+$- 4CO; 435.1 (100) M$^+$- 5CO; 407.1 (51) M$^+$- 5CO -Et; 379.1 (87) M$^+$- 6CO -Et
26	844.2 (6) M$^+$ - 4CO; 648.1 (17) **27**$^+$; 620.2 (12) **27**$^+$ - CO; 592.0 (13) **27**$^+$ - 2CO; 564.0 (30) **27**$^+$ - 3CO; 536.1 (41) **27**$^+$ - 4CO; 508.2 (73) **27**$^+$ - 5CO
27	648.5 (32) M$^+$; 620.4 (16) M$^+$ - CO; 592.4 (24) M$^+$ - 2CO; 563.4 (8) M$^+$ - 2CO - Et; 535.4 (57) M$^+$ - 3CO - Et; 507.4 (83) M$^+$ - 4CO - Et; 479.4 (36) M$^+$ - 5CO - Et; 451.3 (67) M$^+$ - 6CO - Et
28	488.7 (5) M$^+$; 461.0 (13) M$^+$ - CO; 432.5 (2) M$^+$ - 2CO; 404.5 (7) M$^+$ - 3CO; 376.5 (8) M$^+$ - 4CO; 348.4 (32) M$^+$ - 5CO; 319.3 (6) M$^+$ - 5CO - Et; 291.3 (20) M$^+$ - 6CO - Et

3.1.5 X-ray Crystallography

Single crystal X-ray structure determinations confirmed the structures of complexes **22**, **23** and **27**. The crystals were afforded from dichloromethane:hexane (1:1) solutions for complexes **22** and **23** and from chloroform:hexane (1:1) solutions for complex **27**. Complex **22** crystallized as orange-red needles, while complex **23** afforded small, dark purple needle-like crystals. The crystals of complex **27** were orange needles. Figures 4.14, 4.15 and 4.17 represent ball-and-stick plots of the respective structures. Selected bond lengths and angles are given in tables 4.7, 4.8 and 4.10. The crystal structure of uncoordinated dithieno[3,2-*b*:2',3'-*d*]thiophene was determined by Bertinelli *et al*[21]. In figure 4.13 the determined bond lengths and angles are indicated for this compound.

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[21] F. Bertinelli, P. Palmieri, C. Stremmenos, G. Pelizzi, C. Taliani, *J. Phys. Chem.*, 87, **1983**, 2317.

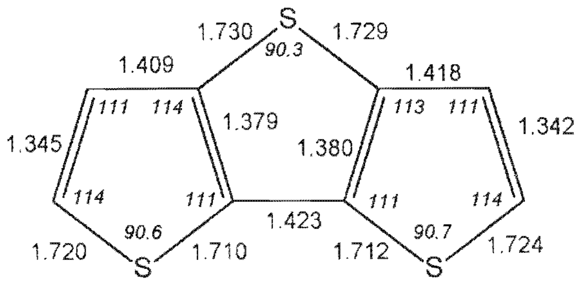

Figure 4.13 Bond lengths (Å) and bond angles (°) of dithieno[3,2-*b*:2',3'-*d*]thiophene

3.1.5.1 Crystal structure of complex 22

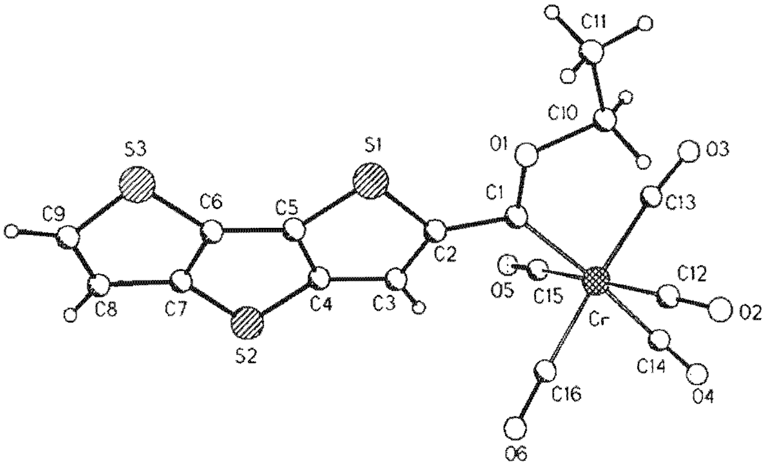

Figure 4.14 Ball-and-stick plot of complex **22**

The Cr metal is in the centre of an octahedral ligand environment in complex **22**. The heteroaromatic ring system in the structure is planar and in the same plane as the carbene carbon and the metal atom. The metal moiety is orientated away from the sulfur atom on the opposite side of the ring, similar to the structures obtained for complexes **1**, **19** and structures of similar thiophene complexes reported in literature[18]. The bond lengths of the ring system in complex **22** are all longer or similar to the bond lengths determined for the same bonds in the structure of the dithienothiophene[21]. It is therefore assumed that the effect of delocalization is present in this structure as was indicated for the structures of the complexes discussed in Chapter 3. Bond angles of the dithienothiophene ring in the complex differ slightly from the literature values for DTT, indicating distortion of the rings on coordination to the carbene moiety.

Table 4.7 **Selected bond lengths and angles of complex 22**

22	Bond lengths (Å)	22	Bond angles (°)
Cr-C(1)	2.091(7)	C(5)-S(1)-C(2)	91.2(3)
S(1)-C(5)	1.722(7)	C(7)-S(2)-C(4)	89.4(3)
S(1)-C(2)	1.765(7)	C(9)-S(3)-C(6)	90.1(4)
S(2)-C(4)	1.765(7)	C(1)-O(1)-C(10)	123.3(5)
S(2)-C(7)	1.742(8)	O(1)-C(1)-C(2)	105.2(6)
S(3)-C(9)	1.727(8)	O(1)-C(1)-Cr	129.3(5)
S(3)-C(6)	1.729(7)	C(2)-C(1)-Cr	125.5(5)
O(1)-C(1)	1.332(8)	C(3)-C(2)-S(1)	111.3(5)
O(1)-C(10)	1.457(8)	C(2)-C(3)-C(4)	111.1(6)
C(1)-C(2)	1.448(9)	C(5)-C(4)-C(3)	114.9(6)
C(2)-C(3)	1.401(9)	C(5)-C(4)-S(2)	112.7(5)
C(3)-C(4)	1.403(10)	C(4)-C(5)-C(6)	112.3(6)
C(4)-C(5)	1.380(10)	C(4)-C(5)-S(1)	111.5(5)
C(5)-C(6)	1.427(10)	C(7)-C(6)-C(5)	112.0(7)
C(6)-C(7)	1.383(10)	C(7)-C(6)-S(3)	111.2(5)
C(7)-C(8)	1.444(10)	C(6)-C(7)-C(8)	114.2(7)
C(8)-C(9)	1.353(12)	C(6)-C(7)-S(2)	113.5(5)
		C(9)-C(8)-C(7)	108.7(7)
		C(8)-C(9)-S(3)	115.8(6)

3.1.5.2 Crystal structure of complex 23

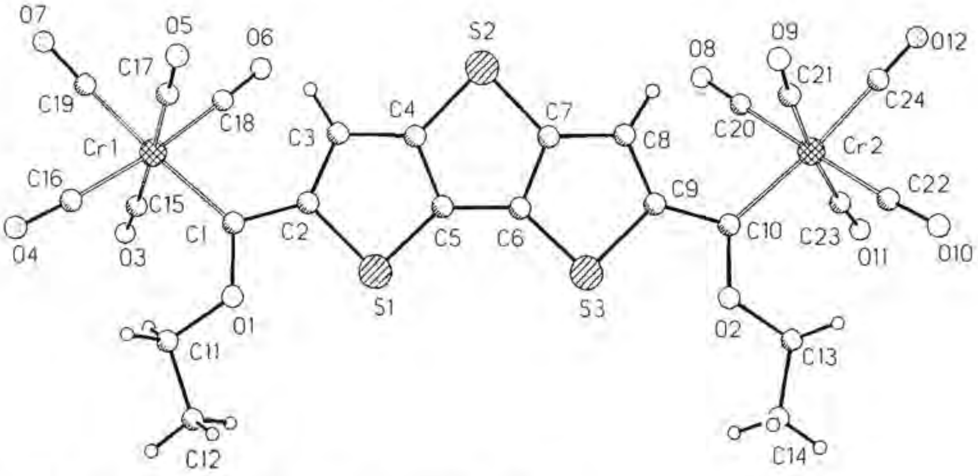

Figure 4.15 Ball-and-stick plot of complex **23**

A plane of symmetry is found in complex **23** which is perpendicular to the bridging ligand, intersecting S(2) and bisecting the C(5)-C(6) bond of the ring. The additional ring places the metal fragments on the same side of the line connecting the two carbene carbons.

Table 4.8 Selected bond lengths and angles of complex 23

23	Bond lengths (Å)	23	Bond angles (°)
Cr(1)-C(1)	2.051(9)	C(5)-S(1)-C(2)	91.2(4)
Cr(2)-C(10)	2.077(9)	C(7)-S(2)-C(4)	89.3(4)
S(1)-C(5)	1.727(8)	C(9)-S(3)-C(6)	91.5(4)
S(1)-C(2)	1.760(8)	C(1)-O(1)-C(11)	123.5(7)
S(2)-C(7)	1.740(8)	C(10)-O(2)-C(13)	123.8(7)
S(2)-C(4)	1.744(8)	O(1)-C(1)-C(2)	104.2(7)
S(3)-C(6)	1.713(9)	O(1)-C(1)-Cr(1)	130.1(6)
S(3)-C(9)	1.776(8)	C(2)-C(1)-Cr(1)	125.7(6)
O(1)-C(1)	1.333(10)	O(2)-C(10)-C(9)	105.9(7)
O(2)-C(10)	1.327(10)	O(2)-C(10)-Cr(2)	130.1(6)
O(1)-C(11)	1.474(10)	C(9)-C(10)-Cr(2)	124.0(6)
O(2)-C(13)	1.457(11)	C(3)-C(2)-S(1)	111.1(6)
C(1)-C(2)	1.454(11)	C(2)-C(3)-C(4)	112.3(8)
C(9)-C(10)	1.460(12)	C(5)-C(4)-C(3)	113.2(7)
C(2)-C(3)	1.396(11)	C(5)-C(4)-S(2)	113.5(6)
C(3)-C(4)	1.415(11)	C(4)-C(5)-C(6)	112.7(7)
C(4)-C(5)	1.384(11)	C(4)-C(5)-S(1)	112.1(6)
C(5)-C(6)	1.426(12)	C(7)-C(6)-C(5)	110.4(8)
C(6)-C(7)	1.405(11)	C(7)-C(6)-S(3)	112.2(6)
C(7)-C(8)	1.407(12)	C(6)-C(7)-C(8)	112.7(8)
C(8)-C(9)	1.393(12)	C(6)-C(7)-S(2)	114.1(6)
		C(9)-C(8)-C(7)	113.3(8)
		C(8)-C(9)-S(3)	110.3(6)

In table 4.9 literature values are reported for bond lengths of similar chromium mono- and biscarbene complexes as well as selected bond lengths of complexes **8**, **9** and **19**.

Table 4.9 **Literature values**

Complex	**Bond length** (Å)				**Reference**
	M-$C_{carbene}$	$C_{carbene}$-O	O-R	$C_{carbene}$-R'	
$Cr(CO)_5C(OMe)Ph$	2.04(3)	1.33(2)	1.46	1.47(4)	22
$Cr(CO)_5C(OEt)Me$	2.05(1)	1.31(1)	-	1.51(1)	23
$Cr(CO)_5C(OH)Ph$	2.05(1)	1.32(1)	-	-	24
$Cr(CO)_5C[OSi(SiMe_3)_3]$1-furyl	2.03(1)	1.32(1)	-	1.45(1)	25
$[\{Cr(CO)_5C(OEt)\}_2T]$	2.04(1)	1.32(1)	1.45(1)	1.47(1)	18
$[\{Cr(CO)_5C(OEt\}_2$biphenylene]	2.05(1)	1.32(1)	-	1.49(1)	26
Complex **8**	2.08(1)	1.32(1)	1.46(1)	1.47(1)	-
Complex **9**	2.07(1)	1.33(1)	1.45(1)	1.47(1)	-
Complex **19**	2.06(1)	1.34(1)	1.47(1)	1.46(1)	-

The bond distances of the C(2)-S(1) and C(9)-S(3) bonds are markedly longer than the rest of the C-S bonds of the ring system. This implies that these two bonds are the most affected by the coordination of DTT to the metal-carbene moieties and that the delocalization of the electron density in the ring excludes the sulfur atoms of the ring (figure 4.16). This effect is supported by the longer metal-carbene carbon bonds (2.08(1) Å av) and shorter C(1)-C(2) bond (1.45(1) Å av), since a normal C-C (single bond) is 1.51(3) Å[27].

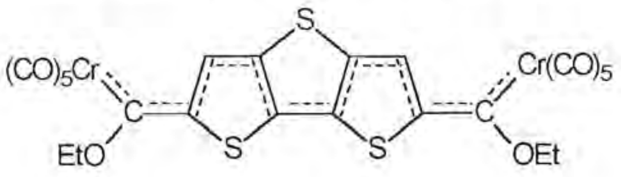

Figure 4.16 Delocalization of electron density in complex **23**

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[22] U. Schubert, *Organometallics*, 1, **1982**, 1085.

[23] K.H. Dötz, H. Fischer, P.Hofmann, F.R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH Verlag, Weinheim, **1983**, p.94.

[24] R.J. Klinger, J.C. Huffman, J.K. Kochi, *Inorg. Chem.*, 20, **1981**, 34.

[25] U. Schubert, M. Wiener, F.H. Köhler, *Chem. Ber.*, 112, **1979**, 708.

[26] N.H. Tran Huy, P. Lefloch, F. Robert, J. Jeannin, *J. Organomet. Chem.*, 327, **1987**, 211.

[27] F.A. Cotton, C.M. Lukehart, *Prog. Inorg. Chem.*, 16, **1972**, 487.

In literature[28], the value obtained for a C(sp^2)-C(aryl) bond for a conjugated arene was 1.470 Å and for an unconjugated arene 1.488 Å.

The angles O(1)-C(1)-C(2), O(1)-C(1)-Cr(1) and C(2)-C(1)-Cr(1) of 104.2(7)°, 130.1(6)° and 125.7(6)° respectively are typical for Fischer carbene complexes[29]. These values are similar to the values obtained for chromium complexes **8**, **9**, **19** and **22**.

3.1.5.3 Crystal structure of complex 27

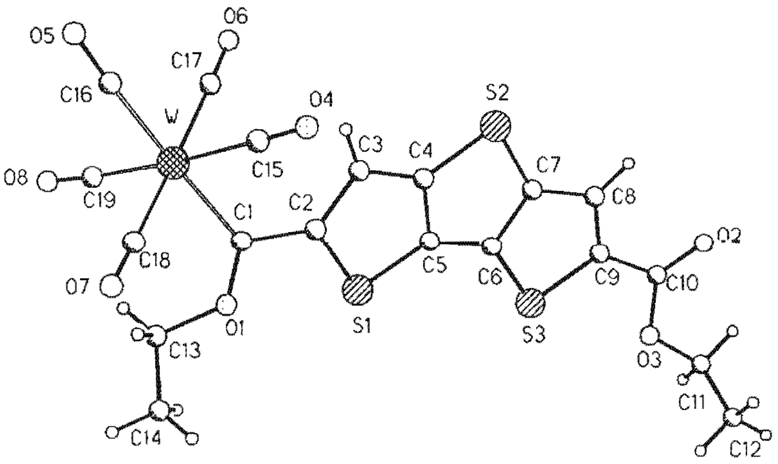

Figure 4.17 Ball-and-stick plot of complex **27**

The ethoxy group of the ester functionality in complex **27** is orientated towards the sulfur atom of the ligand, similar to the position inhabited by the ethoxy group on the carbene carbon. The bond angles surrounding C10, the carbon associated with the ester moiety, were determined as O(2)-C(10)-C(9) 123.5(8)°, O(3)-C(10)-C(9) 111.6(7)° and O(2)-C(10)-O(3) 124.9(8)° while the similar bond angles around the carbene carbon C(1) were found to be O(1)-C(1)-C(2) 105.2(7)°, O(1)-C(1)-W 130.2(5)° and C(2)-C(1)-W 124.6(6)°.

Delocalization of the electron density is evident in the lengthening of the C(2)-C(3) and C(4)-

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[28] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, *J. Chem. Soc., Perkin 2*, **1987**, S1.

[29] U. Schubert, *Coord. Chem. Rev.*, 55, **1984**, 261.

C(5) bonds of 1.400(11) Å and 1.406(11) Å, the latter is now comparable with the bond length of 1.405(10) Å for C(3)-C(4). This delocalization diminishes on proceeding to the next ring fragment, moving further away from the metal-carbene moiety. This implies that the ester functionality does not contribute much to the delocalization of the ring.

Table 4.10 Selected bond lengths and angles of complex 27

27	Bond lengths (Å)	27	Bond angles (°)
W-C(1)	2.194(9)	C(5)-S(1)-C(2)	91.3(4)
S(1)-C(5)	1.729(7)	C(7)-S(2)-C(4)	89.5(4)
S(1)-C(2)	1.765(8)	C(9)-S(3)-C(6)	90.6(4)
S(2)-C(4)	1.739(7)	C(1)-O(1)-C(13)	121.3(6)
S(2)-C(7)	1.747(8)	O(1)-C(1)-C(2)	105.2(7)
S(3)-C(6)	1.718(8)	O(1)-C(1)-W	130.2(5)
S(3)-C(9)	1.746(8)	C(2)-C(1)-W	124.6(6)
O(1)-C(1)	1.332(10)	C(3)-C(2)-S(1)	111.1(6)
O(1)-C(13)	1.445(8)	C(2)-C(3)-C(4)	112.7(7)
O(2)-C(10)	1.206(9)	C(5)-C(4)-C(3)	113.3(7)
C(1)-C(2)	1.488(10)	C(5)-C(4)-S(2)	113.4(6)
C(9)-C(10)	1.477(11)	C(4)-C(5)-C(6)	111.9(7)
C(2)-C(3)	1.400(11)	C(4)-C(5)-S(1)	111.6(6)
C(3)-C(4)	1.405(10)	C(7)-C(6)-C(5)	111.5(7)
C(4)-C(5)	1.406(11)	C(7)-C(6)-S(3)	111.7(6)
C(5)-C(6)	1.416(10)	C(6)-C(7)-C(8)	112.5(8)
C(6)-C(7)	1.401(11)	C(6)-C(7)-S(2)	113.6(6)
C(7)-C(8)	1.426(11)	C(9)-C(8)-C(7)	111.8(7)
C(8)-C(9)	1.349(12)	C(8)-C(9)-S(3)	113.4(6)

5

Iron complexes of Thiophene derivatives

1. General

Organometallic complexes in which two metal-containing fragments are bridged by arene or heteroarene ligands can serve as models for repeating units in related organometallic polymers[1,2]. By increasing the number of fused aromatic rings in the bridging group of such material, the degree of intermetallic conjugation is expected to increase in complexes having two metal centres σ-bonded to the rings[3]. To determine the magnitude of this effect, Hunter *et al*[4] studied fused heteroarene ligands substituted by $FeCp(CO)_2$-moieties and derivatives thereof. Heteroarene ligands used in this study included quinoline, quinazoline and quinoxaline, all compounds containing a nitrogen atom in the aromatic system. The new complexes were prepared by reacting $Na[FeCp(CO)_2]$ with the heterocyclic compounds containing halide substituents at low temperatures. Nucleophilic displacement takes place as the more activated chlorine atoms bonded to the heteroarene ring is displaced by the strong $[FeCp(CO)_2]^-$ nucleophiles (figure 5.1).

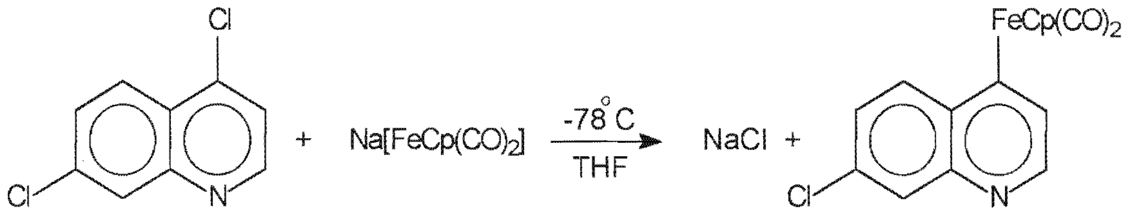

Figure 5.1 Synthesis of a monosubstituted quinoline complex

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[1] R. McDonald, K.C. Sturge, A.D. Hunter, L. Shilliday, *Organometallics*, 11, **1992**, 893.

[2] X.A. Guo, K.C. Sturge, A.D. Hunter, M.C. Williams, *Macromolecules*, 27, **1994**, 7825.

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

[4] A.D. Hunter, R. Chukwu, B.D. Santarsiero, S.G. Bott, J.L. Atwood, *J. Organomet. Chem.*, 526, **1996**, 1.

Mono- and disubstituted products were prepared in this fashion.

The reaction of the iron complex [FeCp(CO)$_2$(η^2-propene)]Cl in a diethyl ether suspension with phenyl lithium gave [FeCp(CO)$_2$(phenyl)][5] while the reaction of [FeCp(CO)(PPh$_3$)]Br with phenyl lithium afforded [FeCp(CO)(PPh$_3$)(phenyl)]. Replacement of one of the carbonyl ligands by a triphenylphosphine moiety was performed in order to stabilize the incipient carbon-metal σ-bond.

The [1,4-{FeCp(CO)$_2$}$_2$(μ-phenylene)] complex was studied experimentally and theoretically with respect to delocalization effects. After using Fenske-Hall calculations on this disubstituted phenylene complex as well as several other organic models, Richardson and Hall[6] questioned the claims made by Hunter *et al*[7] regarding delocalization through a quinoidal bridge, which he based on spectroscopic evidence. They asserted that π-delocalization effects are unimportant in this compound. Sponsler[8] reported an in-depth theoretical study of delocalization effects on metal centres connected by conjugated bridges. Several diiron[9] and dirhenium[10] complexes with different conjugated systems were investigated.

Derivatives of five-membered heterocycles in which transition metals are connected to the α-carbons of the heterocyclic ring, have not received much attention in literature. Few of these complexes contain more than one metal fragment directly bonded to the heteroaromatic ring system. A small number of σ-2-furyl complexes is known in the literature compared to (2-thienyl)metal complexes, which are more abundant because of their relevance as model compounds for desulfurization processes. Typical examples of σ-2-furyl complexes are

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[5] K.R. Aris, J.M. Brown, K.A. Taylor, *J. Chem. Soc., Dalton Trans.*, **1974**, 2222.

[6] N.A. Richardson, M.B. Hall, *Organometallics*, 12, **1993**, 1338.

[7] G.B. Richter-Addo, A.D. Hunter, *Inorg. Chem.*, 28, **1989**, 4063.

[8] M.B. Sponsler, *Organometallics*, 14, **1995**, 1920.

[9] N. Le Narvor, C. Lapinte, *J. Chem. Soc., Chem. Commun.*, **1993**, 357.

[10] Y. Zhou, J.W. Seyler, W. Weng, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.*, 115, **1993**, 8509.

[Au(PPh$_3$)2-furyl(CH$_3$)$_2$], [Pt(cod)(2-furyl)$_2$], [Pt(cod)Cl(2-furyl)][11] and [ZrCp$_2$(2-furyl)$_2$][12]. Onitsuka *et al*[13] prepared [Pt(PBu$_3$)$_2$(2-thienyl)$_2$] as well as 2,5-thienylene-bridged diplatinum complexes and found that these bimetallic complexes have d_π-p_π interaction between two platinum atoms through the thienylene bridge. They extended this study to include bithiophene as bridging ligand. The reactivity of these and similar complexes towards isocyanide were investigated[14], based on the unique reactivity of μ-ethynediyl complexes of palladium and platinum with isocyanide[15]. Synthesis of the 2-thienyl and 2,5-thienylene platinum compounds were accomplished *via* a 2-trimethylstannylthiophene[11c] and a 2,5-bis(trimethylstannyl)thiophene[16] precursor (figure 5.2). Nickel and palladium complexes were prepared in a similar fashion.

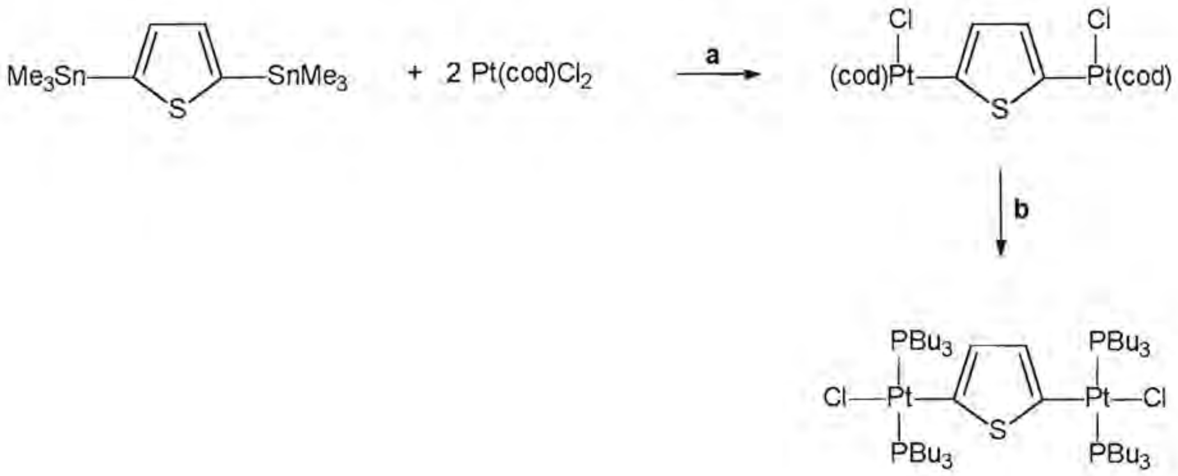

Figure 5.2 Synthesis of 2,5-thienylene diplatinum complexes

Reagents and conditions: (**a**) CH$_2$Cl$_2$, reflux 4 h; (**b**) 4PBu$_3$, CH$_2$Cl$_2$, RT, 4h

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[11] (a) S. Komiya, S. Ozaki, A. Shibue, *J. Chem. Soc., Chem. Commun.*, **1986**, 1555. (b) C. Eaborn, K.J. Kevin, A. Pidcock, *J. Chem. Soc., Dalton Trans.*, **1978**, 357. (c) J. Müller, C. Friedrich, *J. Organomet. Chem.*, 377, **1989**, C27.

[12] G. Erker, R. Petrenz, C. Krüger, F. Lutz, A. Weiss, S. Werner, *Organometallics*, 11, **1992**, 1646.

[13] K. Onitsuka, K. Murakami, K. Matsukawa, K. Sonogashira, T. Adachi, T. Yoshida, *J. Organomet. Chem.*, 490, **1995**, 117.

[14] S. Kotani, K. Shiina, K. Sonogashira, *J. Organomet. Chem.*, 429, **1992**, 403.

[15] K. Onitsuka, T. Joh, S. Takahashi, *J. Organomet. Chem.*, 464, **1994**, 247.

[16] C. van Pham, R.S. Macomber, H.B. Mark, H. Zimmer, *J. Org. Chem.*, 49, **1984**, 5250.

These reactions were carried out according to the method employed by Müller and Brune[17] for the preparation of disubstituted phenyl platinum complexes. Evidence of metal-metal communication[18] through the conjugated ring system prompted further studies of thiophene and similar compounds. Upon treating the 2,5-thienylene diplatinum complexes with *p*-tolyl isocyanide at elevated temperatures, one molecule of isocyanide inserted into each Pt-C bond (figure 5.3)[13].

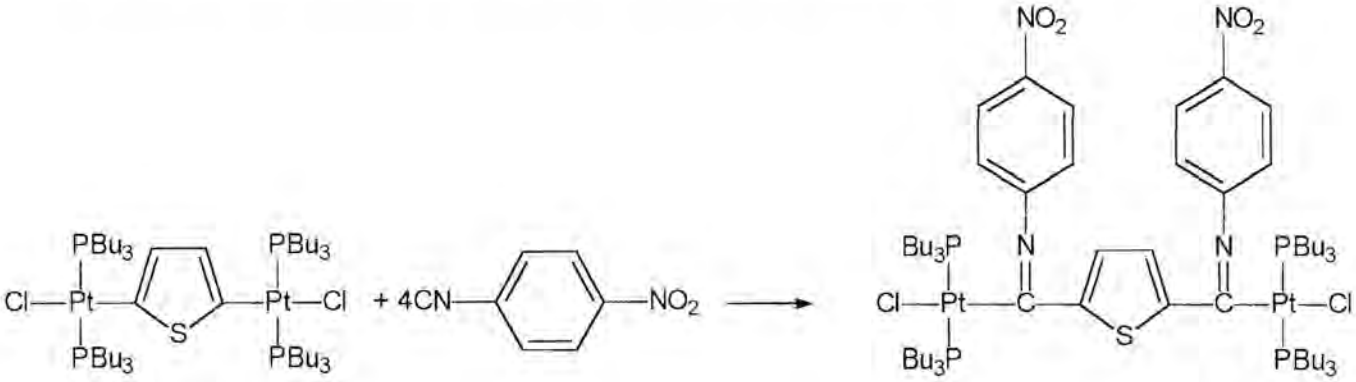

Figure 5.3 Reaction of 2,5-thienylene diplatinum complexes with isocyanide

Rauchfuss *et al*[19] embarked on the study of developing the chemistry of complexes with multiple thienyl ligands. Justification for this research was found in the rich chemistry of polyaryl metal complexes and it was suggested that, since thiophene is more reactive than benzene towards electrophiles and also more acidic, the polythienyl ligands should display novel reactivity. Known metallocene complexes of the type [MCp$_2$(2-thienyl)$_2$] include the transition metals Ti, Zr, Hf, Nb and W[20].

Angelici *et al*[21] synthesized [ReCp(PPh$_3$)(NO)thiophene]$^+$ to explore reactions of S-coordinated thiophenes, which undergo C-H cleavage to yield thienyl complexes. [ReCp(PPh$_3$)(NO)thiophene]$^+$ reacts with potassium hydroxide in methanol to afford [ReCp(PPh$_3$)(NO)2-thienyl].

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[17] W.D. Müller, H.A. Brune, *Chem. Ber.*, 119, **1986**, 759.

[18] U. Bayer, H.A. Brune, *Z. Naturforsch., Teil B*, 38, **1983**, 632.

[19] P.R. Stafford, T.B. Rauchfuss, S.R. Wilson, *Inorg. Chem.*, 34, **1995**, 5220.

[20] V.A. Knizhnikov, Yu.A. Ol'dekop, *J. Gen. Chem. USSR (Engl. Transl.)*, 55, **1985**, 1385.

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

Silylthiophenes have recently received considerable attention due to several reasons. Firstly they have been recognized as starting materials for the preparation of polythiophenes[22]. Furthermore, the presence of a trimethylsilyl group on the 2-position serves as a protecting group towards metallation[23] directed at the 3-position specifically. 2-Trimethylsilylthiophene was synthesized by Deans and Eaborn[24], while the 2,5-bis(trimethylsilyl)thiophene was prepared by Sauvajol (65% yield)[25] as well as by Van Pham (89% yield)[16] but by using different silylation methods. Both complexes were synthesized *via* the appropriate bromothiophene precursor. Although many studies of polycarbosilanes have appeared in literature, their germanium backbone analogues have been neglected until recently. The polymer [2,5-(dimethylgermyl)thiophene]$_n$ was prepared by Barrau *et al*[26] by poly-condensation between 2,5-dilithiothiophene and dichlorodimethylgermanium (80% yield). The formation of [2,5-bis(chlorodimethylgermyl)thiophene] (20% yield) was also observed in the same reaction.

Nesmeyanov and co-workers reported the syntheses of σ-complexes of manganese pentacarbonyl with furan, benzofuran and thiophene[27]. The monosubstituted σ-complexes of perchlorothiophene with nickel, iron and manganese derivatives have also been synthesized previously[28]. Iron complexes of the type [FeCp(CO)$_2$R], with R = 2-thienyl, 2-furyl, 5-methyl-2-furyl and 4,5-benzo-2-furyl were synthesized by the initial reaction of Na[FeCp(CO)$_2$] with 2-thiophenecarbonyl chloride (in the case of the thiophene product), followed by photochemical decarbonylation of these acyl complexes to yield the target products[29] (figure 5.4).

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[22] H. Masuda, Y. Taniki, K. Kaeriyama, *Synth. Met.*, 55, **1993**, 1246.

[23] D. Häbich, F. Effenberger, *Synthesis*, **1979**, 841.

[24] F.B. Deans, C. Eaborn, *J. Chem. Soc.*, **1959**, 2903.

[25] J.L. Sauvajol, C. Chorro, J.P. Lère-Porte, R.J.P. Corriu, J.J.E. Moreau, P. Thépot, M. Wong Chi Man, *Synth Met.*, 62, **1994**, 233.

[26] J. Barrau, G. Rima, A. Akkari, J. Satge, *Inorg. Chim. Acta*, 260, **1997**, 11.

[27] A.N. Nesmeyanov, K.N. Anisimov, N.E. Kolobova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1356, **1964**, 2247.

[28] M.D. Rauch, T.R. Criswell, A.K. Ignatovicz, *J. Organomet. Chem.*, 13, **1968**, 419.

[29] A.N. Nesmeyanov, N.E. Kolobova, L.V. Goncharenko, K.N. Anisimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1, **1976**, 153.

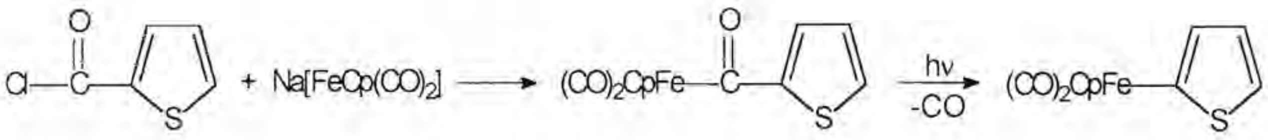

Figure 5.4 Synthesis of σ-iron heterocyclic complexes

Rauchfuss *et al*[30] prepared this same [FeCp(CO)$_2$(2-thienyl)] complex and studied its reaction with Fe$_3$(CO)$_{12}$. The expected thiaferrole complex was obtained, whereby an unusual synthetic route to multimetallic compounds is represented. This study was conducted in connection with research done on the activation and desulfurization of thiophene and benzothiophene by iron carbonyls.

2. Synthesis of iron complexes of Thiophene

The synthesis of iron complexes incorporating thiophene and derivatives thereof as bridging ligands was contemplated. Several different synthetic routes were explored and employed to try and synthesize these target molecules. The study was then to be extended to include other transition metals, for instance molybdenum, employing the most successful procedure for the syntheses of these complexes.

The first synthetic route employed was the synthesis *via* a dilithio intermediate, a similar method used by Lapinte *et al*[31] in synthesizing compounds consisting of long carbon chains capped with FeCp(CO)$_2$-metal moieties. The thiophene ligand was dilithiated using n-butyl lithium and TMEDA in a hexane solution at elevated temperatures. Upon reaction of 2,5-dilitiothienylene with FeCp(CO)$_2$I, two products were isolate, firstly the yellow mono [FeCp(CO)$_2$(2-thienyl] complex, previously prepared by Nesmeyanov *et al*[29], and secondly the orange coloured [2,5-{FeCp(CO)$_2$}$_2$thienylene] complex, **31**. This product was documented in a review article[32] but to

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[30] A.E. Ogilvy, M. Draganjac, T.B. Rauchfuss, S.R. Wilson, *Organometallics*, 7, **1988**, 1171.

[31] F. Coat, C. Lapinte, *Organometallics*, 15, **1996**, 477.

[32] T.B. Rauchfuss, *Prog. Inorg. Chem.*, 39, **1991**, 259.

our knowledge the data has not yet been published. The structure of this complex is shown in the paper but until now not recorded in the Cambridge database. No details of the synthesis was given. Both the mono- and the bis complexes were formed in low yields.

The analogous reaction using 3,6-dimethylthieno[3,2-b]thiophene instead of thiophene, afforded four products (figure 5.5).

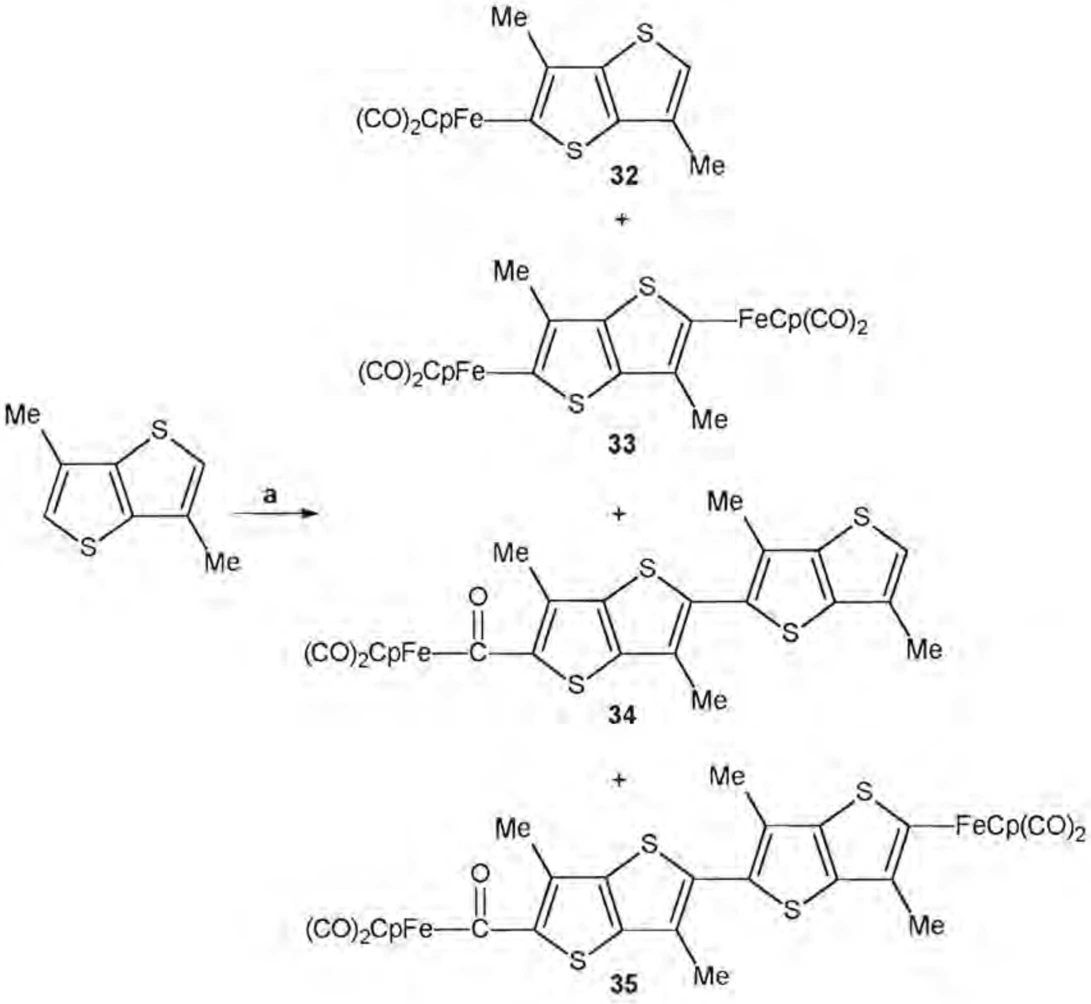
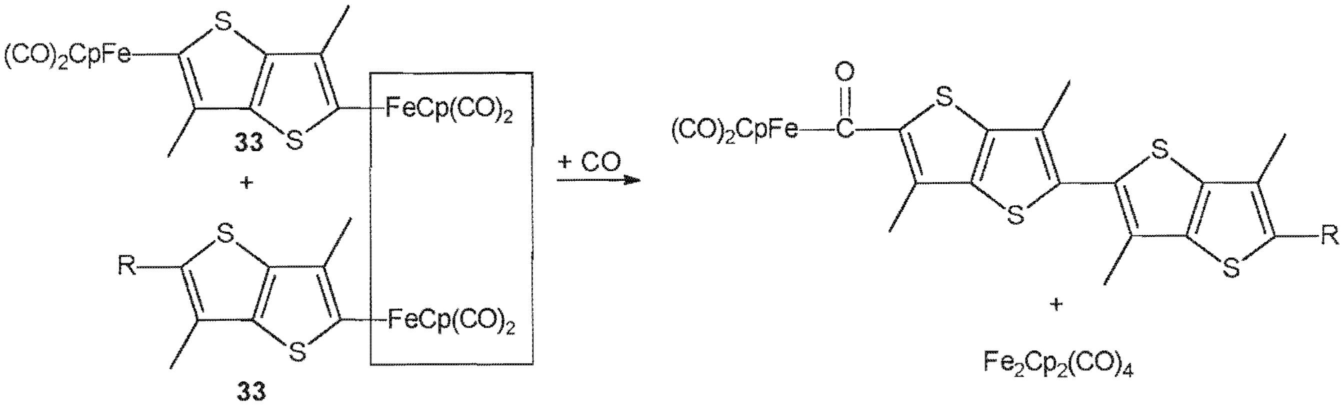


Figure 5.5 Synthesis of complexes **32-35**
Reagents: **a**(i) 2 eq. n-BuLi (ii) FeCp(CO)$_2$I

Again the mono-iron complex, **32**, as well as the bis complex, **33**, were formed, but the formation of two more products, complexes **34** and **35**, in which C-C coupling reactions are involved, is also observed. The suggested mechanism for the formation of these two products is outlined in figure 5.6. The bis complex **33** is unstable and very reactive and we therefore conclude that it facilitated the formation of complexes **34** and **35**. It comprises the reaction of a diiron complex **33** and a mono-iron complex **32** to form complex **34** and the reaction between two bis-iron complexes **33** to form complex **35**. These reactions are thermodynamically favoured by the formation of the iron dimer [{FeCp(CO)$_2$}$_2$]. The insertion of a carbonyl group stabilizes the Fe-thienyl bond and thus the molecule. This proposed mechanism is supported by the presence of the dimer [{FeCp(CO)$_2$}$_2$] in the final reaction mixture. The same observation regarding the stability of these complexes were made as for the thiophene analogues. This reaction was also performed using the metal complex [MoCp(CO)$_2$Cl], but no organometallic products were formed during the reaction.



R = H **34**
R = FeCp(CO)$_2$ **35**

Figure 5.6 Reaction route for the formation of complexes **34** and **35**

It was obvious from the yields of the reaction products that these reactions had not gone to completion. It was suggested that the reason for the low reactivity between the two reagents could be ascribed to the relative strength of the Fe-I bond. By substituting the iodine ligand for a more labile leaving group on the metal, a higher yield of target products was envisaged. Therefore it was contemplated to repeat the reactions, but instead of reacting the lithio species with [FeCp(CO)$_2$I], [FeCp(CO)$_2$(O$_3$SCF$_3$)] was used, containing a triflate leaving group. This method, however, proved to be unsuccessful since only the mono-iron complex was obtained for both ligands.

The iron complex Na[FeCp(CO)$_2$], prepared[33] from sodium amalgam and [{FeCp(CO)$_2$}$_2$], was reacted with 2,5-dibromothiophene and 2,7-dibromo-3,6-dimethylthieno[3,2-*b*]thiophene, respectively, at -78°C. This preparation method was successfully employed by Hunter *et al*[4] for the syntheses of iron complexes with N-heterocycles. Unfortunately the target products were not afforded but only the starting materials were reclaimed. The same observation was made on repeating this reaction with Na[MoCp(CO)$_2$].

In an attempt to stabilize the bis-iron complexes prepared *via* the lithio precursors, a test reaction was performed on the mono-iron complex **32**. Tertiary phosphine ligands are known to be strong donors of electronic charge and thus triphenylphosphine was chosen as a suitable ligand in substituting a carbonyl group. It was anticipated that the phosphine ligand would strengthen the iron-thienyl bond. A mixture of complex **32** and triphenylphosphine in hexane/ether (1:1) was irradiated for 30 minutes at 20°C. Only decomposition occurred and no evidence for the formation of a phosphine complex was observed.

Since the stability of the target products was one of the primary issues, the modification of the metal starting material [FeCp(CO)$_2$I] was proposed. By incorporating the triphenylphosphine ligand into this metal complex and then reacting it with the lithio species, an enhanced stability of the products was foreseen. The reaction was effected similar to the reaction with [FeCp(CO)$_2$I], but in this case no reaction product was isolated. This was again attributed to the relative strength of the Fe-I bond.

A new approach towards the synthesis of disubstituted iron complexes of thiophene derivatives was decided on, based on literature reports by Lo Sterzo *et al*[34]. They recounted the preparation of σ-metallaacetylides by palladium-catalyzed formation of metal-carbon bonds. The general procedure constitutes the coupling of halogen-containing transition metal moieties to mono- and bis[(trimethylstannyl)acetylides] in the presence of catalytic amounts of palladium. The 2,5-bis(trimethylstannyl)thiophene and the novel 2,7-bis(trimethylstannyl)-3,6-dimethylthieno[3,2-b]thiophene (complex **37**) were prepared in order to apply this method to our ligand systems.

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[33] A.D. Hunter, A.B. Szigety, *Organometallics*, 8, **1989**, 2670.

[34] E. Viola, C. Lo Sterzo, F. Trezzi, *Organometallics*, 15, **1996**, 4352.

Complex **36**, the mono 2-(trimethylstannyl)-3,6-dimethylthieno[3,2-*b*]thiophene complex, formed as a byproduct in the preparation reaction of complex **37**. The planned synthetic route for preparation of the iron complexes is outlined in figure 5.7.

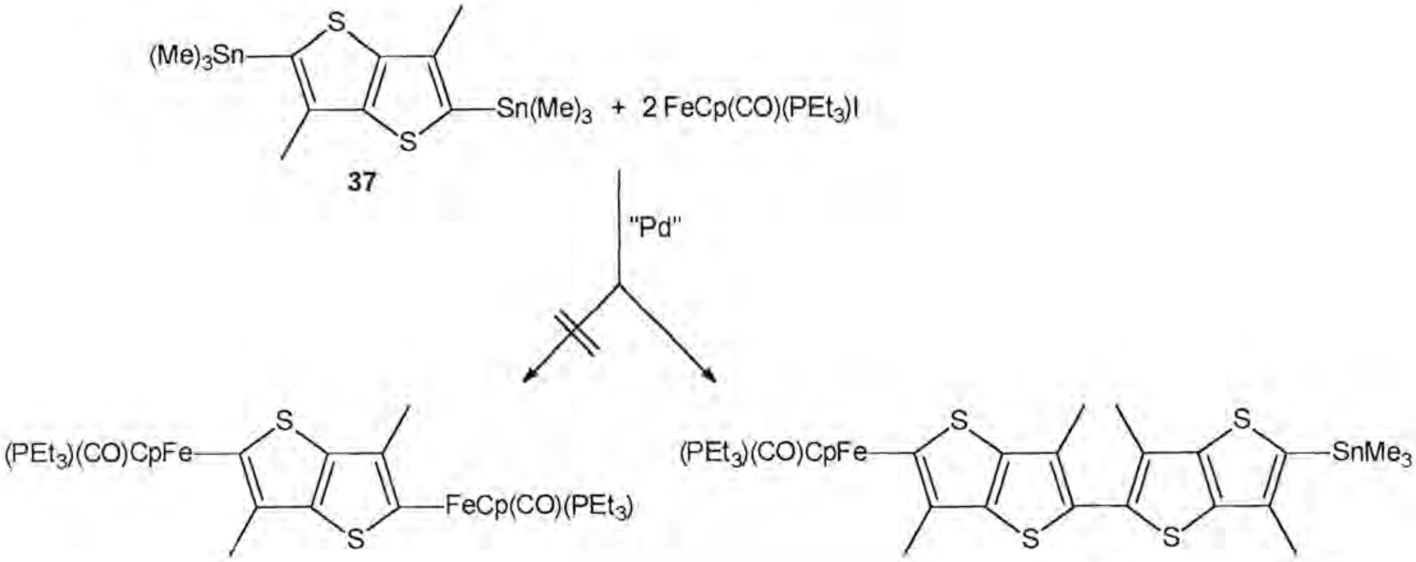

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Figure 5.7 Proposed preparation of diiron complexes

After completion of the reactions for both ligands, it was only possible to isolate and characterize one product, complex **38**, formed in the reaction of [FeCp(CO)$_2$I] with 2,7-bis(trimethylstannyl)-3,6-dimethylthieno[3,2-*b*]thiophene (complex **37**). This product was formed similar to the formation of complexes **34** and **35** and by the substitution of one of the trimethylstannyl groups by an iron metal fragment. Other products were also observed, but unfortunately their yields were too low to be able to isolate and characterize.

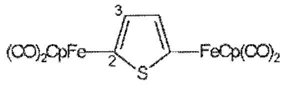
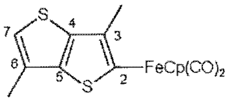
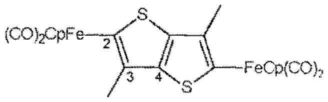
2.1 Spectroscopic characterization of novel complexes

The new iron complexes of the thiophene derivatives were characterized using ^{1}H NMR, ^{13}C NMR, infrared spectroscopy and mass spectrometry. Unfortunately many of the compounds were highly unstable and unsatisfactory ^{13}C NMR data were obtained due to decomposition. It was interesting to note that the thiophene complexes were seemingly more stable than their 3,6-dimethylthieno[3,2-*b*]thiophene counterparts, which is contrary to the trend observed for the carbene complexes where the complexes with the condensed rings were more stable than the analogous thiophene complexes. Pauson suggested that the Fe-C_{arene} bond is stabilized by the effect of the condensed ring[35]. This same trend was observed by Nesmeyanov *et al*[29], who observed the stability of the [FeCp$(CO)_2$(2-benzofuryl)] complex compared to the iron complexes containing five-membered heterocyclic ligands.

2.1.1 ^{1}H NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform as solvent unless otherwise specified. The ^{1}H NMR data for complexes **31-33** are summarized in table 5.1, while table 5.2 contains the data of complexes **34** and **35**. The data of complexes **36-38** are reported in table 5.3.

Table 5.1 ^{1}H NMR data of complexes 31, 32 and 33

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **31**		 **32**		 **33**	
	δ	J	δ	J	δ	J
H3	6.83 (s)	-	-	-	-	-
H4	6.83 (s)	-	-	-	-	-
H7	-	-	6.68 (q)	1.0	-	-
Me3	-	-	2.31 (s)	-	2.25 (s)	-
Me6	-	-	2.27 (d)	1.0	2.25 (s)	-
Cp	4.95 (s)	-	5.01 (s)	-	4.95 (s)	-

From the peaks observed on the spectra of the three complexes it is clear that ^{1}H NMR spectroscopy does not provide exclusive means for the characterization of these products. The protons observed do, however, indicate that both the metal fragment as well as the ligand are present in all of the complexes. The data for [FeCp$(CO)_2$(2-thienyl)][29] were found to be: 6.59 ppm

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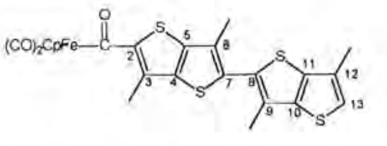
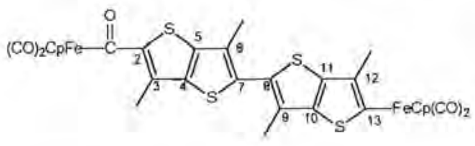
[35] P.L. Pauson, A.R. Quazi, B.W. Rockett, *J. Organomet. Chem.*, 7, **1967**, 325.

(H3), 6.84 ppm (H4), 7.18 ppm (H5) and 4.86 ppm (Cp).

The position of the Cp-ring on all three spectra is very similar although a more downfield shift is observed in the case of the mono-iron complex **32**. For this complex a quartet splitting pattern is found for the proton on the 7-position. This is due to long-range coupling with the methyl protons on the 6-position. For this methyl group a doublet is then also observed, instead of the expected singlet and the coupling constant of 1.0 Hz is calculated, correlating well with other four-bond couplings observed in literature[36].

Table 5.2 **^{1}H NMR data of complexes 34 and 35**

Proton	Chemical shifts (δ, ppm)	
	 **34**	 **35**
	δ	δ
H13	7.13 (s)	-
Me3	2.55 (s)	2.52[a] (br, s)
Me6	2.54 (s)	2.52 (br, s)
Me9	2.36 (s)	2.34 (br, s)
Me12	2.33 (s)	2.34 (br, s)
Cp	5.00 (s)	5.02 (br, s)

[a] Overlap of signals occur, broad bands observed

The spectra of the two complexes are, as expected, very similar. The methyl protons are little affected by changing form a mono complex to a dinuclear complex, since their values are very comparable for the two complexes. The spectrum of complex **35** is, however, affected by the coordination of a second metal moiety in that broad, undefined peaks are observed compared to the high resolution of the mono-nuclear complex. Interesting to note is the stability of the complex

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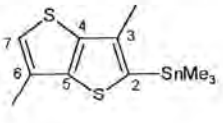
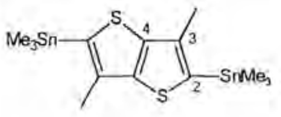
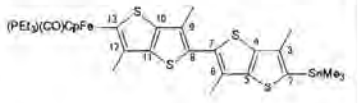
[36] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Metoden in der organische Chemie*, Georg Thieme Verlag, Stuttgart, **1984**.

even though the metal is directly bonded to the ring system and carbonyl insertion did not take place to stabilize this second metal moiety. Previously it was shown in our laboratories that this second metal alkyl bond is stabilized by a carbonyl group inserted into the metal alkyl bond on the other side of a conjugated spacer[37].

Table 5.3 ^{1}H NMR data of complexes 36, 37 and 38

Proton	Chemical shifts (δ, ppm) and Coupling constants (J, Hz)					
	 **36**		 **37**		 **38**	
	δ	J	δ	J	δ	J
H7	6.93 (s)	-	-	-	-	-
Me3	2.38 (s)	-	2.37 (s)	-	2.61 (s)	-
Me6	2.34 (s)	-	-	-	2.57 (s)	-
Me9	-	-	-	-	2.36 (s)	-
Me12	-	-	-	-	2.32 (s)	-
Sn$\mathbf{Me_3}$	0.42 (d)	56.1	0.40 (d)	55.8	0.05 (d)	56.8
Cp	-	-	-	-	5.28 (s)	-
P($\mathbf{CH_2}CH_3$)$_3$	-	-	-	-	1.23 (m)	-
P($CH_2\mathbf{CH_3}$)$_3$	-	-	-	-	0.84 (t)	6.3

Doublets are encountered on the spectra of complexes **36**, **37** and **38** for the methyl protons of the trimethylstannyl groups. These doublets are ascribed to coupling of these protons with the tin nucleus. A large coupling constant is observed for this coupling, which corresponds well with literature values[38].

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[37] T.A. Waldbach, P.H. van Rooyen, S. Lotz, *Organometallics*, 12, **1993**, 4250.

[38] H. Friebolin, *Basic One- and Two-Dimensional NMR Spectroscopy*, VCH Verlag, Weinheim, **1993**, p.104.

2.1.2 ^{13}C NMR spectroscopy

The ^{13}C NMR data of complexes **31**, **32**, **34**, **36** and **37** are given in table 5.4.

Table 5.4 ^{13}C NMR data of complexes 31, 32, 34, 36 and 37

Carbon	Chemical shifts (δ, ppm)				
	31	**32**	**34**	**36**	**37**
	δ	δ	δ	δ	δ
C2	150.0	145.8	n.o.	145.4	147.6
C3	140.7	142.8	136.7	136.8	136.5
C4	140.7	n.o.	n.o.	142.4	134.9
C5	150.0	n.o.	n.o.	134.7	134.9
C6	-	136.3	135.9	122.1	136.5
C7	-	129.6	n.o.	130.1	147.6
C9	-	-	132.1	-	-
C12	-	-	125.3	-	-
C13	-	-	130.4	-	-
Me3	-	17.3	17.3	16.3	16.4
Me6	-	14.8	15.7	14.7	16.4
Me9	-	-	15.2	-	-
Me12	-	-	14.6	-	-
Cp	85.5	85.8	85.9	-	-
$M(CO)_2$	215.2	214.4	213.9	-	-
$SnMe_3$	-	-	-	-8.25	-8.33

Recording of ^{13}C NMR spectra proved to be problematic since the complexes were unstable at room temperature and even more so in solution. Decomposition occurred in several cases and made the unambiguous assignment of resonance peaks impossible. The fact that nearly all the carbons in the structure of the complexes are quaternary carbons, made the situation even worse. For complexes **33**, **35** and **38** only the distinguishable chemical shift values will be reported. Resonance peaks (ppm) were observed on the spectrum of **33** as follows: 214.2 ($M(CO)_2$), 85.8

(Cp), 17.2 (Me3, Me6). The resonance peaks on the spectrum of complex **35** were found at the following chemical shift values (ppm): 213.7 ($M(CO)_2$), 85.7 (Cp), 17.4 (Me3), 14.7 (Me6), 14.1 (Me9), 15.6 (Me12).

2.1.3 Infrared Spectroscopy

The infrared data of complexes **31-35** and complex **38** are outlined in table 5.5. All the spectra were recorded in dichloromethane as solvent.

Table 5.5 Infrared data of complexes 31, 32, 33, 34, 35 and 38

Band	Stretching vibrational frequency (ν_{CO}, cm^{-1})					
	31	**32**	**33**	**34**	**35**	**38**
$A_1^{(1)}$	2025	2026	2023	2029	2053, 2028	1941
$A_1^{(2)}$	1972	1974	1972	1978	2007, 1978	-
C=O	-	-	-	1655	1656	-

Two bands were observed for the $M(CO)_2$ moieties while the inserted carbonyl band was observed at a characteristic value of 1656 cm^{-1} for both products containing this group.

2.1.4 Mass spectrometry

The fragmentation patterns of complexes **31**, **32**, **34**, **35**, **36** and **37** are presented in table 5.6. The molecular ion peak was observed on all the spectra except for the spectrum of complex **35**. The fragmentation pattern of these iron complexes constitute the elimination of the carbonyl groups of the metal moiety, followed by the loss of the inserted carbonyl (if present) and the loss of the cyclopentadienyl ring.

Table 5.6 Fragmentation patterns of complexes 31, 32, 34, 35, 36 and 37

Complex	Fragment ions (I, %)
31	435.8 (50) M^+; 407.8 (44) M^+ - CO; 379.8 (98) M^+ - 2CO; 351.8 (20) M^+ - 3CO; 323.8 (96) M^+ - 4CO; 258.8 (56) M^+ - 4CO - Cp; 193.9 (19) M^+ - 4CO - 2Cp; 83.0 (26) M^+ - 4CO - 2Cp -2Fe
32	343.9 (42) M^+; 316.0 (14) M^+ - CO; 287.9 (100) M^+ - 2CO; 222.9 (7) M^+ - 2CO - Cp; 167.0 (33) M^+ - 2CO - Cp - Fe
34	538.2 (36) M^+; 510.2 (4) M^+ - CO; 482.1 (100) M^+ - 2CO; 454.1 (8) M^+ - 3CO; 389.1 (2) M^+ - 3CO - Cp
35	573.9 (9) M^+ - 5CO; 509.3 (22) M^+ - 5CO - Cp; 443.2 (70) M^+ - 5CO - 2Cp
36	333.5 (38) M^+; 317.5 (93) M^+ - Me; 302.4 (30) M^+ - 2Me; 287.3 (9) M^+ - 3Me; 169.0 (100) M^+ - 3Me - Sn
37	494.5 (45) M^+; 479.5 (100) M^+ - Me; 449.4 (25) M^+ - 3Me; 419.3 (11) M^+ - 5Me; 404.2 (6) M^+ - 6Me

The molecular ion peak is present on the spectra of all the complexes, except complex **35** where the highest peak has a m/z value of 539.9. This peak is associated with the fragment where loss of all five carbonyl groups has occurred.

2.1.5 X-ray Crystallography

A single crystal X-ray diffraction determination confirmed the structure of complex **37**. The crystals were afforded from a dichloromethane:hexane (1:1) solution. Complex **37** crystallized as colourless cubic crystals. Figure 5.8 represents a ball-and-stick plot of this structure. Selected bond lengths and angles are given in table 5.7.

The bond angles around the sp^2-hybridized C(1) carbon atom are distorted from the normal value of 120°. This is evident when considering the bond angles C(2)-C(1)-Sn and S(1)-C(1)-Sn of 130.3(3)°and 117.6(2)°, respectively. This phenomenon is attributed to the presence of the methyl substituents on the arene ring, causing steric interaction with the methyl groups of the metal fragment. The result is the deformation of the molecule where the metal moiety is bent towards the sulfur atom of the ring.

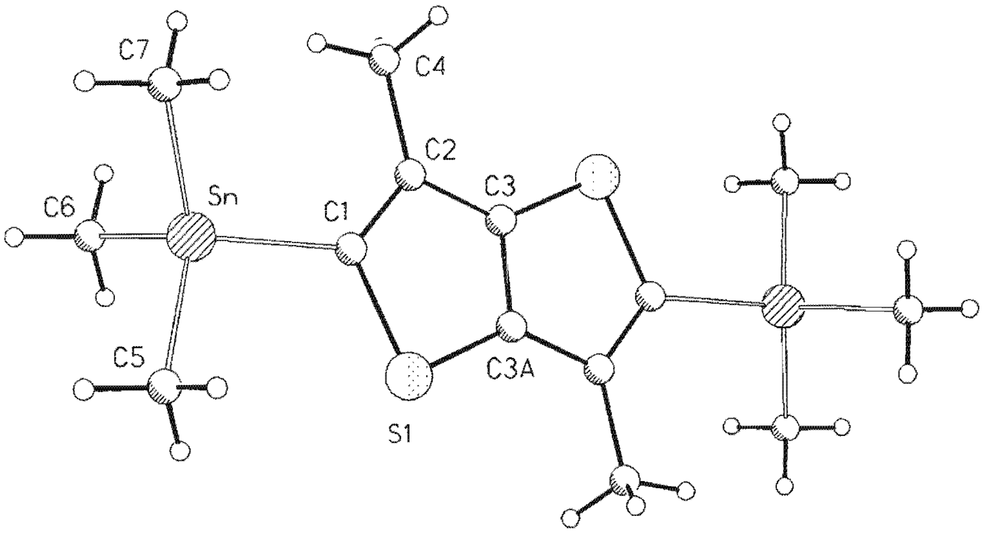

Figure 5.8 Ball-and-stick plot of complex **37**

Table 5.7 **Selected bond lengths and angles of complex 37**

37	Bond lengths (Å)	37	Bond angles (°)
Sn-C(1)	2.152(3)	C(3)#1-S(1)-C(1)	92.50(16)
S(1)-C(1)	1.757(3)	C(2)-C(1)-S(1)	111.8(2)
C(1)-C(2)	1.369(5)	C(1)-C(2)-C(3)	111.3(3)
C(2)-C(3)	1.438(5)	C(3)#1-C(3)-C(2)	114.7(4)
C(2)-C(4)	1.513(5)		
C(3)-C(3)#1	1.395(7)		
C(3)-S(1)#1	1.730(4)		

The metal moiety is pseudotetrahedral, evident from the bond angles around the tin atom the bond angles of C(7)-Sn-C(6) 109.9(2)°, C(7)-Sn-C(1) 112.4(2)°, C(6)-Sn-C(1) 107.0(1)°, C(7)-Sn-C(5) 110.1(2)°, C(6)-Sn-C(5) 111.4(2)° and C(1)-Sn-C(5) 105.9(2)° are marginally different from the normal value of 109° for tetrahedral arrangements. The Sn-C(thienyl) bond length is the same (2.15 (1) Å) as those recorded for the same bonds in Sn(thienyl)$_4$[39] and the 2.14 (1) Å recorded

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[39] A. Karipides, A.T. Reed, D.A. Haller, F. Hayes, *Acta Cryst. B*, 33, **1977**, 950.

for the analogous $Sn(phenyl)_4$[40]. These distances are similar to the average bond length of 2.14 Å found for Sn-C(Me) bonds. The Sn-C(1) bond length of 2.152(3) Å can not be compared to Sn-C bond lengths of organotin halides. The Sn-C bond length in $SnMe_2F_2$[41] and $SnMe_2Cl_2$[42] is 2.08 Å and 2.21 Å respectively. The variation in Sn-C bond lengths can be correlated with the electronegativity and size of the halogens.

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[40] V.K. Belsky, A.A. Simonenko, V.O. Reikhsfeld, L.E. Saratov, *J. Organomet. Chem.*, 244, **1983**, 125.

[41] E.O. Schlemper, *Inorg. Chem.*, 5, **1966**, 507, 511.

[42] A.G. Davies, *J. Chem. Soc. (A)*, **1970**, 2862.

6

Conclusion

1. General

The synthesis of binuclear complexes with conjugated spacer units was put forward as the first stage in preparing complexes specifically tailored for metal-metal communication and charge transfer for application in materials. The synthesis of stable binuclear complexes containing different end-capped metal moieties was envisaged as the eventual objective and can be seen as an extension of this study. The synthesis of the conjugated spacer units proved to be the more challenging part of the syntheses in this study, since the Fischer carbene method employed in the preparation of the novel carbene complexes has already been extensively studied and applied in literature. Metallation of the heteroaromatic substrates was readily accomplished and alkylation of the acyllated intermediate salts was effected effortlessly. Unfortunately the formation of byproducts such as the monocarbene complexes, due to incomplete metallation, and the decomposition products, due to the instability of the biscarbene complexes, influenced the yields of the binuclear complexes and thus the stability of these and similar complexes requires further investigation.

The stabilities of the novel complexes were not formally investigated, but the rates of decomposition of the different complexes in solution and on exposure to air were used as a criterion. It was found that the stability of the complexes increased on increasing the number of condensed thiophene fragments in the ring system. For instance, the molybdenum biscarbene complex of thiophene decomposed overnight in an inert atmosphere, stored below 0°C, while the analogous biscarbene complex containing a dithienothiophene ligand was air-stable for two days before decomposing. For the iron complexes, the opposite trend was observed. Complexes containing thiophene units were more stable and accessible than thienothiophene analogues. The stability of the different metal complexes was found to follow the following trend: W > Cr > Mo.

2. Electronic spectra

Three intense bands are present on the UV-spectrum of thiophene in the gas phase, at 240 nm, 207 nm and 188 nm. Two bands, at 215 nm and 231 nm, are observed on the spectrum of thiophene in solution. Substituents on the ring have an influence on the position of these bands, depending on the ring position of the substituent. As the number of conjugated thiophene units increases[1], the maxima of the absorption bands shift to longer wavelengths and the intensity of the absorbance increases with the lengthening of the thiophene annelation. This trend was also observed for the elongation of a C≡C bridging ligand[2] as well as for oligothiophenes. On increasing the number of thiophene moieties from one to three, an energy difference of *ca.* 100 nm was observed[3]. Four bands can be distinguished on the spectrum of thieno[3,2-*b*]thiophene, at 253 nm, 261 nm, 270 nm and 280 nm. On the spectrum of dithieno[3,2-*b*:2',3'-*d*]thiophene three bands are distinguished at 282 nm, 292 nm and 304 nm.

The UV-spectra of a few of the novel complexes were recorded in dichloromethane. The electronic data of the series **22**, **23** and **24** and the series **13** and **27** are produced in table 6.1 and the electronic spectrum of complex **23** is presented in figure 6.1. All the complexes exhibit strong ligand-based absorption bands between 223 and 245 nm. Intense characteristic absorption bands with λ_{max} in the range 330 to 390 nm are assigned to the thiophene-based π-π* transitions. Coordination to metal fragments shift these bands to higher wavelengths, indicating interaction of the metal carbene π-system with that of the thiophene substituent. The energies of the π-π* transitions in the thiophene are reduced. For example, compare the bands in the range 282-304 nm for thienothiophene with a range of 320-388 nm observed for complex **23**. Also, bands are more intense in the spectra of the biscarbene complexes as the corresponding bands for the monocarbene complexes. The energy of the transition shifts to higher energy as the number of thienyl fragments in the complexes increases. This is demonstrated in going from **13** to **24** to **27**. The absorption band at lowest energy is assigned to a d-p metal-to-ligand charge transfer

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[1] Y. Mazaki, K. Kobayashi, *Tetrahedron Lett.*, 30, **1989**, 3315.

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

[3] Y. Zhu, D.B. Millet, M.O. Wolf, S.J. Rettig, *Organometallics*, 18, **1999**, 1930.

transition. Since the colours of the different complexes are characteristic to the number of metal moieties coordinated to the ligand, it is not surprising that the values of this transition are very similar for the different types of complexes. Biscarbene complexes are all purple coloured for Cr, W and Mo complexes and purple-brown for Mn complexes and the absorption band is observed in the range 550 to 570 nm. This phenomenon also applies to the orange-red monocarbene complexes of Cr, W and Mo, with the absorption energy ranging from 460 to 493 nm in these complexes.

Table 6.1 **UV data of complexes 13, 22, 23, 24 and 27**

Complex	**Colour**	**Ligand π-π* transition (λ, nm)**	**Metal-ligand transition (λ, nm)**
22	Orange-red	373	493
23	Purple	340, 358	565
24	Orange-pink	358	505
13	Orange	349	463
27	Orange	373	490

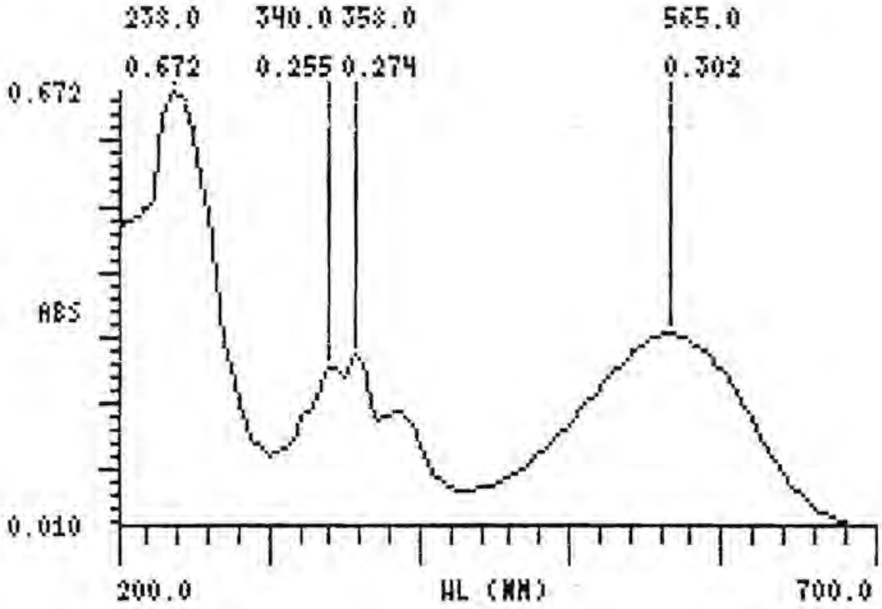


Figure 6.1 UV-spectrum of complex **23**

3. Structural features of the novel complexes

On scrutinizing the structural geometries of the complexes with thiophene, thienothiophene and dithienothiophene units, it seems as if the conformation where the metal fragment is positioned on the opposite side of the sulfur atom in the ring is preferred and a crab-like structure is observed for biscarbene complexes. This geometry was encountered for the structures of complexes **1**, **19**, **22**, **23** and **27**. The opposite conformation, where the metal fragment is directed towards the sulfur atom in the ring, was only found for complexes containing a 3,6-dimethyl[3,2-*b*]thiophene ligand, *i.e.* complexes **8**, **9**, **11**, **12**, **16** and **18**. It was suggested that steric influences of the methyl substituents on the ring prevented the positioning of the metal moiety on that side of the ligand.

On comparing the crystal data of all the different structures, it is evident that the heteroaromatic ligand is planar for all the complexes and it is thus possible to facilitate the delocalization of electron density through the π-system of the ligand. The torsion angles presented in table 6.2 confirm the planarity of the ring system, with small distortions observed for some of the complexes. These distortions are mostly observed in the structures of the biscarbene complexes and the decomposition products. The greatest deviation in the planarity of the ring itself is obtained for complex **19**, a decomposition product, with a value of 5.3°. In biscarbene complexes metal-metal communication through this delocalized system seems plausible.

For the monocarbene complexes **1**, **8** and **11** the metal atom, carbene carbon and arene ring are all exactly coplanar. In the case of the biscarbene complexes, distortion of the metal atom out of the carbene-arene plane ranges from 10° to 25°, with the greater deviations observed in complexes containing 3,6-dimethylthieno[3,2-*b*]thiophene. These distortions may be due to the position of the metal moiety on the same side as the sulfur atom in the ring, which is possibly not the preferred position of the metal fragment, as was suggested earlier. It is however forced into this orientation by the steric methyl substituents on the ring, occupying the space preferred by the metal moiety. The greatest deviation is again observed in complex **19**, where the metal is bent out of the plane at an angle of 31.2°.

Table 6.2 Magnitude of torsion angles in structures

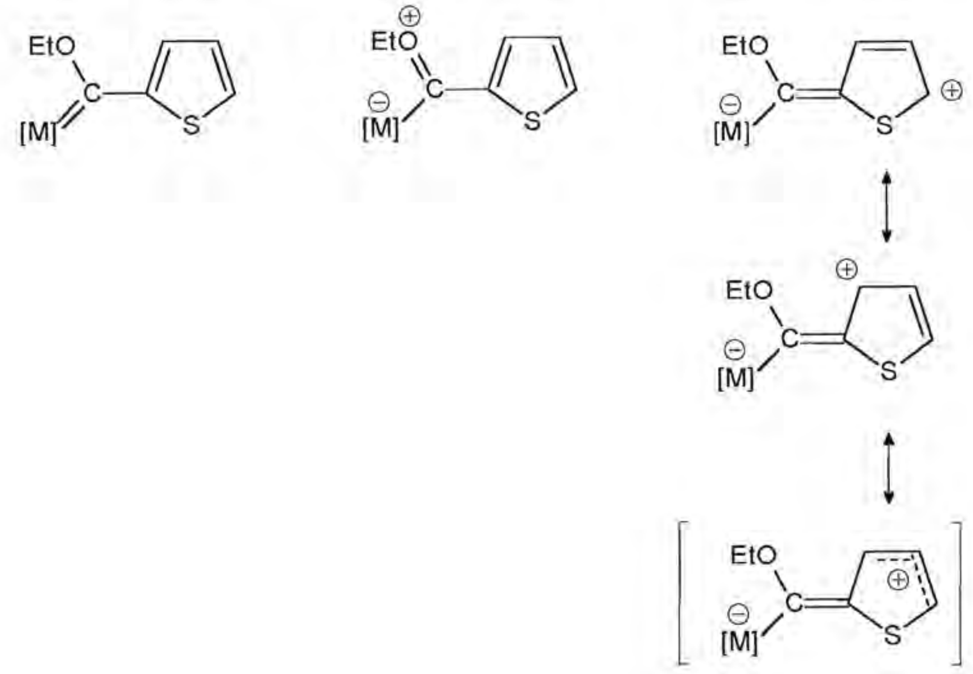
Complex	Torsion angle (°)						
	M-C1-C2-S	M-C1-C2-C3	C1-C2-C3-C4	S1-C5-C4-S2	C3-C4-C5-C6	S2-C7-C6-S3	C5-C6-C7-C8
1	180.0	0.0	180.0	-	-	-	-
8	0.0	180.0	180.0	180.0	180.0	-	-
9	24.6	152.5	176.5	-	-	-	-
11	0.0	180.0	180.0	180.0	180.0	-	-
12	25.3	152.0	176.6	-	-	-	-
16	8.3	173.8	179.7	178.1	178.1	-	-
18	19.8	157.6	177.5	-	-	-	-
19	148.8	28.4	174.7	179.1	176.8	-	-
22	168.1	11.5	178.4	178.6	179.4	178.4	179.4
23	166.0	10.6	176.3	179.0	176.7	177.9	175.5
27	178.3	2.0	179.1	179.7	179.2	177.0	176.3

Further evidence for the delocalization of the electron density in the heteroaromatic ring can be found in the lengthening of the C-C bonds of the ring system. This phenomenon is more prominent for biscarbene complexes than for the monocarbene or decomposition products. In going from one (thiophene) to two (thienothiophene) to three (dithienothiophene) condensed thiophene rings, it is interesting to note that the ring directly coordinated to the carbene moiety is the most affected by the delocalization effect while the second and third thiophene units are less affected. Bond lengths for the other rings indicate more localized bonding which are also more comparable in length to those of the free thiophene. Contributing resonances are outlined in figure 6.2. From the resonance structures of the complexes in figure 6.2 it is evident that the delocalization effect of the electron density in the ring will influence the bond length of the C(2)-C(3) bond the most. This is confirmed on the structural data of all the complexes (table 6.3). It is interesting to note that this effect is more enhanced for the monocarbene complexes and the decomposition products. The average bond length for this bond in the structures of the three ring systems is 1.35 Å. The decrease in bond length of the C(3)-C(4) bond in the complexes compared to the free ligand is observed in only a few cases but these differences are too insignificant to fully justify the existence of this resonance structure.

Table 6.3 **C(2)-C(3) bond distances**

Complex	C(2)-C(3) bond (Å)	Complex	C(2)-C(3) bond (Å)
1	1.380(8)	**18**	1.394(7)
8	1.413(6)	**19**	1.384(4)
9	1.393(4)	**22**	1.401(9)
11	1.402(8)	**23**	1.396(11)
12	1.399(10)	**27**	1.400(11)
16	1.410(8)		

Thiophene:



Thienothiophene:

Dithienothiophene:

Figure 6.2 Resonance structures showing delocalization in thiophenes

In conclusion: It is possible to synthesize and fully characterize biscarbene complexes with condensed thiophene spacer units. Spectroscopic and structural features of this new complexes reveal thiophene involvement with the metal fragments *via* the carbene carbon atoms. Insight into the stability of the complexes on variation of the number of rings in the spacer is valuable information for future design and studies. Comparison with oligothiophene spacer units in similar complexes is a worthwhile expansion of this study and an in-depth investigation into the role of the sulfur atoms in the rings to enhance the charge transfer phenomenon along the chain is essential. These complexes represent a different variation of the "molecular wire" concept as it is now part of a band structure between two end poles. The unique features of activated sites in the new biscarbene complexes open various opportunities for novel syntheses in organic chemistry. Also, as a probe in well-known carbene reactions such as the Dötz and other reactions , it could afford interesting intermediates involving metallacycles which could aid in unraveling the mechanisms of these processes.

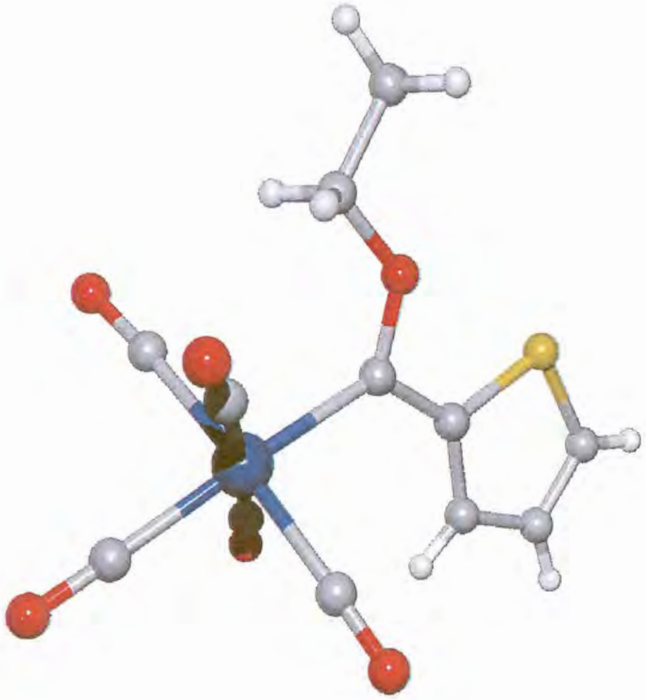


Figure 6.3 Crystal structure of complex **1**

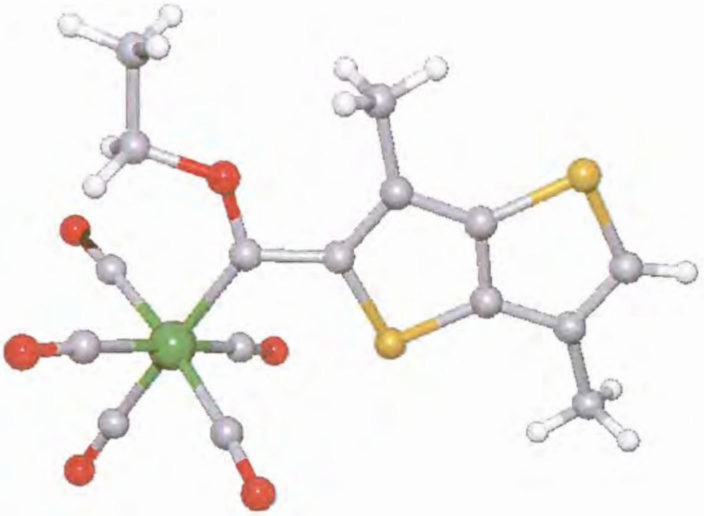


Figure 6.4 Crystal structure of complex **8**

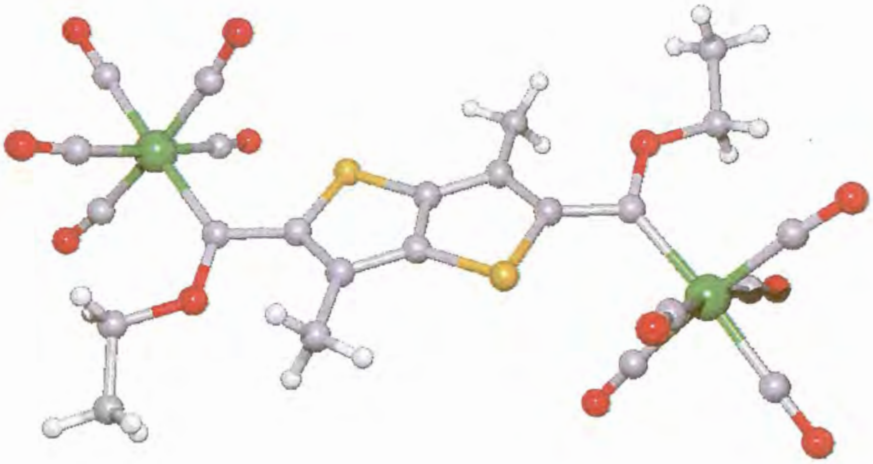


Figure 6.5 Crystal structure of complex **9**

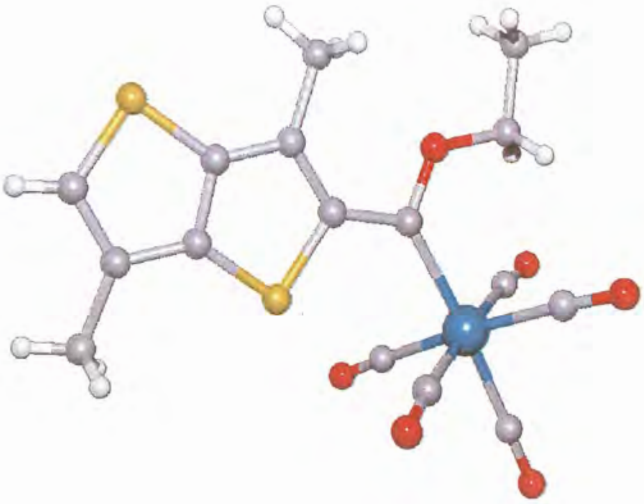


Figure 6.6 Crystal structure of complex **11**

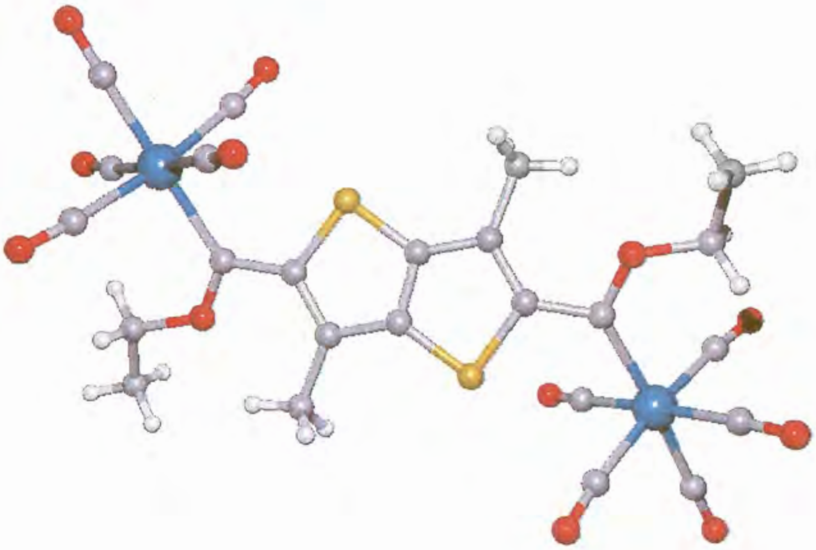


Figure 6.7 Crystal structure of complex **12**

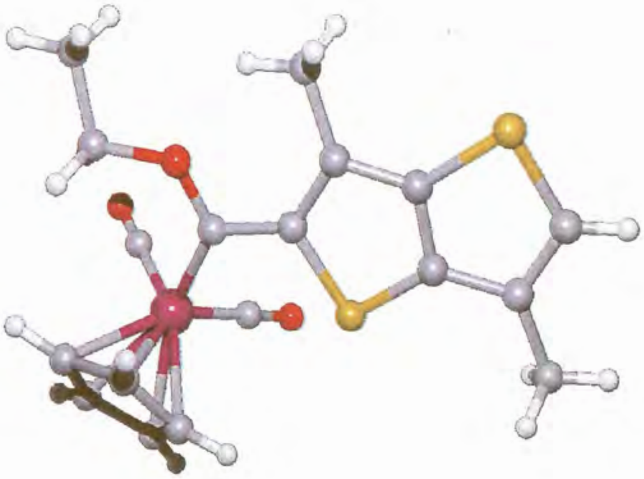


Figure 6.8 Crystal structure of complex **16**

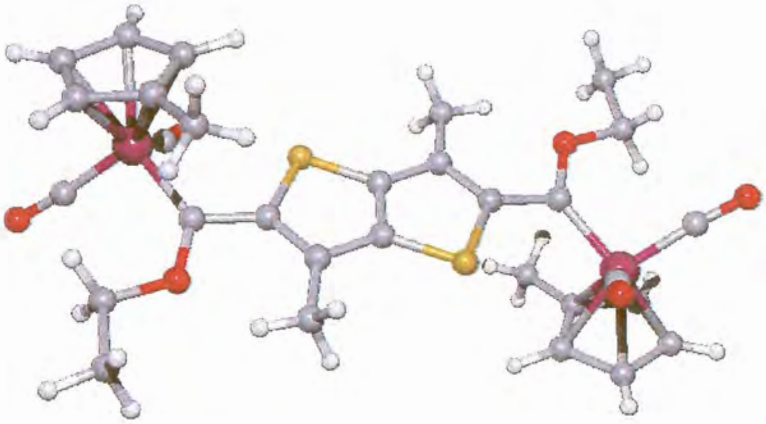


Figure 6.9 Crystal structure of complex **18**

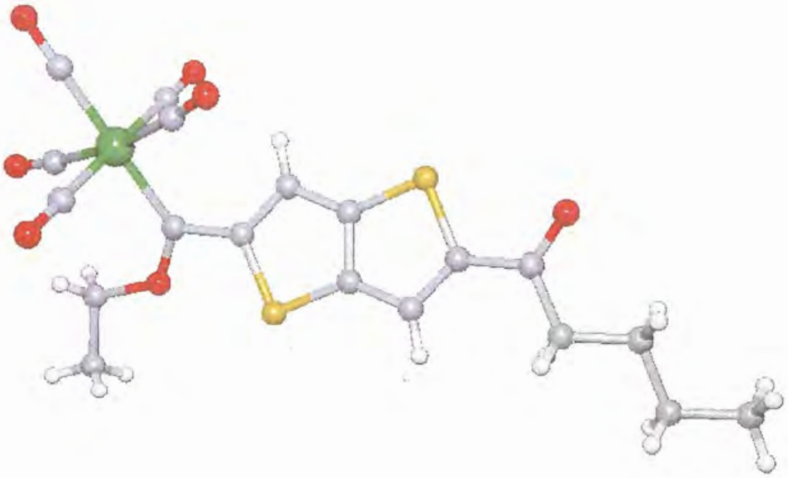


Figure 6.10 Crystal structure of complex **19**

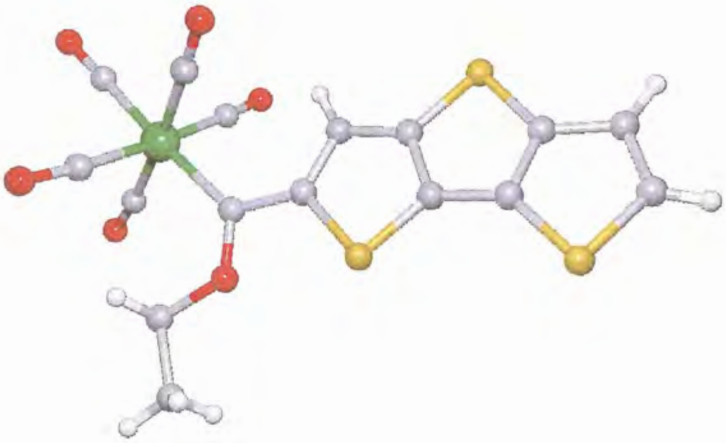


Figure 6.11 Crystal structure of complex **22**

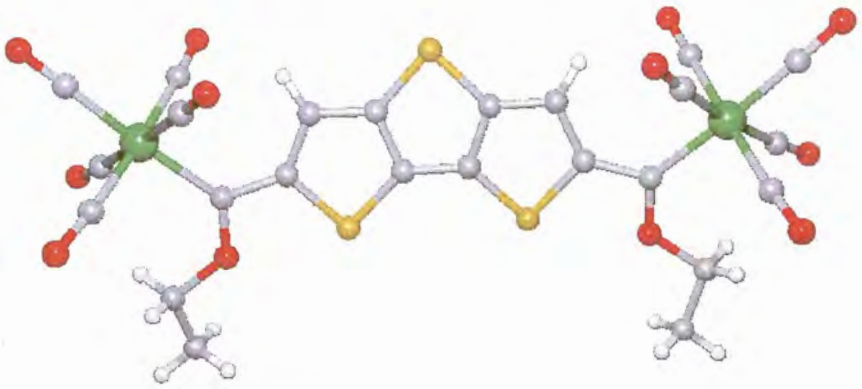


Figure 6.12 Crystal structure of complex **23**

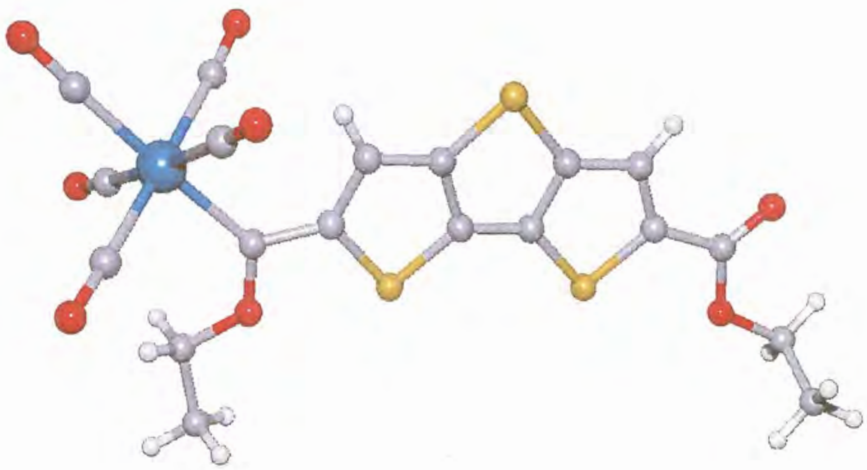


Figure 6.13 Crystal structure of complex **27**

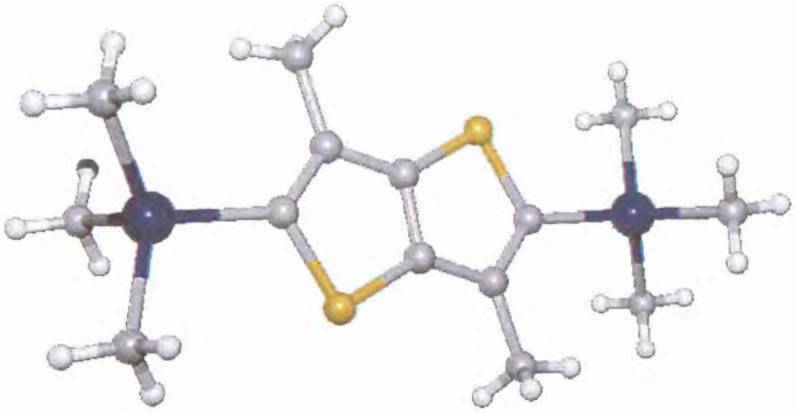


Figure 6.14 Crystal structure of complex **37**

7

Experimental

1. General

All reactions were performed in an inert atmosphere of either nitrogen or argon by using standard Schlenk techniques and vacuum-line. Solvents were dried and distilled under nitrogen prior to use. Column chromatography was carried out under nitrogen using either silica gel (particle size 0.063-0.200 nm) or neutral aluminium oxide as resin. Most chemicals were used directly without prior purification. Thiophene was purified as described by Spies and Angelici[1]. Trimethylamine N-oxide was azeotropically distilled from benzene and stored under argon.

1.1 Preparation of starting compounds

The following compounds were prepared using known literature methods: 3,6-Dimethylthieno[3,2-*b*]thiophene[2], 2,3,5-tribromothiophene[3], 3-bromothiophene[4], ethyl(3-thienothio)acetate[5], ethyl(2-formyl-3-thienothio)acetate[6], thieno[3,2-*b*]thiophene carboxylic acid, thieno[3,2-*b*]thiophene[4], cyclopentadienyliron dicarbonyl iodide[7], triethyl oxonium

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[1] G.H. Spies, R.J. Angelici, *Organometallics*, 6, **1987**, 1902.

[2] K.S. Choi, K. Sawada, H. Dong, M. Hoshino, J. Nakayama, *Heterocycles*, 38, **1994**, 143.

[3] L. Brandsma, H.D. Verkruijsse, *Synthetic Comm.*, 18, **1988**, 1763.

[4] S. Gronowitz, T. Raznikiewicz, *Org. Synth. Coll.*, 5, **1973**, 149.

[5] Y.L. Goldfarb, V.P. Litvinov, S.A. Ozolin, *Izv. Akad. Nauk. SSR, Otd. Khim Nauk*, **1965**, 510.

[6] A. Bugge, *Chem. Scand.*, 22, **1968**, 66.

[7] R.B. King, F.G.A. Stone, *Inorg. Synth.*, 7, **1963**, 110.

tetrafluoroborate[8], 3,3'-dithienyl sulfide[9], 2,5-bis(trimethyltin)thiophene[10] and dithieno[3,2-*b*;2',3'-*d*]thiophene[11]. Cyclopentadienyliron triethylphosphino iodide was prepared by two separate syntheses. The first method[12] comprised the irradiation of cyclopentadienyliron dicarbonyl iodide in toluene in the presence of triethyl phosphine. The second synthesis was effected according to a method described by Moreno *et al*[13], using cyclopentadienyliron dicarbonyl iodide and trimethylamine N-oxide in THF in the presence of triethyl phosphine. It was concluded that the second preparation method afforded the highest yield of product.

1.2 Characterization of complexes

1.2.1 NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform, unless stated otherwise, using the chloroform peak as standard on a Bruker ARX-300 spectrometer.

1.2.2 Infrared spectroscopy

Infrared spectra were recorded on a BOMEM FT-IR spectrophotometer using dichloromethane or hexane as solvent.

1.2.3. Mass spectrometry

Mass spectra were recorded at 70 eV on a Finnigan Mat 8200 instrument using the electron impact method.

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[8] H. Meerwein, *Org. Synth.*, 46, **1966**, 113.

[9] L. Brandsma, H.D. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer-Verlag, Berlin Heidelberg, **1987**, p.162.

[10] C. van Pham, R.S. Macomber, H.B. Mark, H. Zimmer, *J. Org. Chem.*, 49, **1984**, 5250.

[11] F. de Jong, M.J. Janssen, *J. Org. Chem.*, 36, **1971**, 1645.

[12] P.M. Treichel, D.A. Komar, *J. Organomet. Chem.*, 206, **1981**, 77.

[13] C. Moreno, M. Macazaga, R. Medina, D.H. Farrar and S. Delgado, *Organometallics*, 17, **1998**, 3733.

1.2.4 X-ray crystallography

Data collection and structure determinations were done by Dr. Helmar Görls, University of Jena, Germany. Experimental details for the X-ray analyses, listing of the experimental crystallographic parameters and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters are available from the author on request.

2. Synthesis of Organometallic compounds

2.1 Thiophene carbene complexes

2.1.1 Synthesis of molybdenum complexes 1, 2, 3, 4 and 5

16.8 ml (26.8 mmole) of n-butyl lithium (15% solution in hexane) was added to a solution of 0.99 ml (12.4 mmole) of thiophene and 3.7 ml (24.7 mmole) of TMEDA in 50 ml of hexane at room temperature. The mixture was refluxed for 30 minutes during which time the lithium chloride salt precipitated as a white solid. This suspension was cooled to 0°C and 30 ml of THF was added. The mixture was then further cooled to -20°C and 5.99 g (22.7 mmole) of $Mo(CO)_6$ was added gradually. The reaction was kept at this temperature for 15 minutes, stirring vigorously, and then allowed to rise to room temperature. Stirring was continued for another hour, during which time the colour of the reaction mixture changed to a dark red-brown. After completion of the reaction, the solvent was evaporated *in vacuo*. 4.55 g (24.7 mmole) of triethyl oxonium tetrafluoroborate was dissolved in 20 ml of dichloromethane. This was added to the residue of the reaction mixture at -20°C and the solution, purple-coloured, was stirred for an hour while the temperature was allowed to rise to RT. The mixture was filtered through silica gel with dichloromethane and the solvent removed under reduced pressure. Column chromatography was used to purify the mixture of carbene products. Hexane was employed as starting eluent and the polarity was gradually increased by adding dichloromethane to separate the different compounds. Four compounds were isolated. The first yellow-orange product (yield: 1.53 g; 32%; mp.: 155°C dec.) was identified as the monocarbene complex **1**, while the second purple product (yield: 1.41; 17%) was characterized as the biscarbene complex **2**. This product decomposed with time to form the red decomposition product **3**, yield: 0.67 g (12%). The third product , also purple-coloured, was identified as complex **4**, yield: 2.08 g (20%). The last compound, isolated using pure dichloromethane as eluent, was red and identified as complex **5**, yield:1.38 g (18%). The biscarbene complex **2** can be decomposed more rapidly on stirring in acetone or THF.

2.2 Aminolysis reactions of complex 1

2.2.1 Reaction with NH_3

0.55 g (1.5 mmole) of the molybdenum monocarbene complex **1** was dissolved in 50 ml of diethyl ether. Ammonia was bubbled through the solution for 5 hours. The solvent was removed under reduced pressure and the residue purified using column chromatography. Two bands were separated: unreacted starting complex **1** (yield: 0.23 g; 41%) and a yellow product **6**, (yield: 0.24 g; 46%).

2.2.2 Reaction with 1,4-phenylene diamine

0.55 g (1.5 mmole) of the molybdenum monocarbene complex **1** was dissolved in 50 ml of diethyl ether. A solution of 0.33 g (3.0 mmole) of 1,4-phenylene diamine in 10 ml of THF was added while stirring. The mixture was stirred for 24 hours. The solvent was removed under reduced pressure and the crude product purified on a silica column. Two bands were distinguished. The first yellow-orange band yielded the starting material **1**, (yield: 0.29 g; 51%). The second yellow product isolated was identified as the aminocarbene complex **7**, yield: 0.28 g (42%).

2.3. 3,6-Dimethylthieno[3,2-b]thiophene and Thieno[3,2-*b*]thiophene carbene complexes

2.3.1 Synthesis of chromium complexes 8, 9 and 10

0.67 g (4.0 mmole) of DMTT was dissolved in 50 ml of hexane. 1.2 ml (8.0 mmole) of TMEDA and 5.5 ml (8.8 mmole) of n-butyl lithium were added at room temperature. The mixture was refluxed for 45 minutes and then cooled to 0°C. Lithium chloride precipitated as a white solid. After the addition of 50 ml of THF, 1.76 g (8.0 mmole) of $Cr(CO)_6$ was added and the suspension stirred for an hour. The colour of the reaction changed to dark brown. After completion of the reaction, the solvent was removed *in vacuo*. 1.50 g (8.1 mmole) of triethyl oxonium tetrafluoroborate was dissolved in 20 ml of dichloromethane and this was added to the cooled reaction residue (-20°C) in dichloromethane. Immediately the colour change to a purple solution was observed. Stirring was maintained for a further hour while the temperature was allowed to reach room temperature. The mixture was then filtered, the solvent removed and the remainder purified on a silica gel column. Three products were isolated. The first was the orange monocarbene complex **8**, yield: 0.55 g (33%), mp.:173.4 - 176.8°C. The second purple complex was identified as the biscarbene complex **9**, yield: 1.25 g (47%). The third red-orange compound was characterized as **10**, yield: 0.23 g (12%).

2.3.2 Synthesis of tungsten complexes 11, 12 and 13

0.34 g (2.0 mmole) of DMTT was dissolved in 30 ml of hexane. 2.8 ml (4.4 mmole) of n-butyl lithium and 0.6 ml (4.0 mmole) of TMEDA were added to this solution at room temperature. The same procedure was followed as for the chromium analogue with the addition of 1.4 g (4.0 mmole) of $W(CO)_6$. For alkylation 0.74 g (4.0 mmole) of triethyl oxonium tetrafluoroborate was used. On purification using column chromatography, three bands separated. The first monocarbene complex **11**, was isolated as an orange solid with a yield of 0.45 g (41%); mp.:187.2 - 189.4°C. The second purple band, the biscarbene complex **12**, had a yield of 0.67 g (36%) while the third red-orange band was identified as (**13**), yield: 0.11 g (9%).

2.3.3 Synthesis of molybdenum complexes 14 and 15

The dilithio species, prepared according to the method described in **2.3.1**, was treated with $Mo(CO)_6$ (1.1 g, 4.0 mmole) at -20°C. The reaction mixture was stirred for 2 hours, while the temperature gradually rose to RT. The solvent was removed *in vacuo*. 0.74 g (4.0 mmole) of triethyl oxonium tetrafluoroborate in 50 ml of dichloromethane was added to the reaction residue and an immediate colour change from orange to purple was observed. Column chromatography yielded two products. The first orange product was identified as the monocarbene complex **14**, yield: 0.34 g (37%) while the second purple complex was the biscarbene complex **15**, yield: 0.32 g (21%). Several other complexes, in very low yields, were formed in this reaction but it was impossible to isolate or purify them.

2.3.4 Synthesis of manganese complexes 16, 17 and 18

(i) $Mn(C_5H_5)(CO)_3$

The reaction was carried out according to the general method described in **2.3.1** with the addition of 5.5 ml (8.8 mmole) of n-butyl lithium and 1.2 ml (8.1 mmole) of TMEDA to a solution of 0.67 g (4.0 mmole) of DMTT in 50 ml of hexane. 1.63 g (8.0 mmole) of $Mn(C_5H_5)(CO)_3$ was added to the dimetallated species. The reaction was effected with the addition of 1.5 g (8.0 mmole) of triethyl oxonium tetrafluoroborate and the subsequent purification on a silica gel column. Two products were isolated: the first reddish-brown monocarbene complex **16** (yield: 0.43 g; 27%) and the second purple-brown biscarbene complex **17** (yield: 1.49 g; 59%).

(ii) $Mn(C_5H_4Me)(CO)_3$

The metallation of DMTT was performed according to the method described in **2.3.1**, using 0.67 g (4.0 mmole) of DMTT. 0.92 g (8.0 mmole) of $Mn(C_5H_4Me)(CO)_3$ was added to the dilithiated species and alkylation was done with 1.5 g (8.0 mmole) of triethyl oxonium tetrafluoroborate. Column chromatography yielded mainly the biscarbene complex **18**, yield: 1.64 g (62%).

2.3.5 Synthesis of chromium complexes 19 and 20

Thieno[3,2-*b*]thiophene (0.56 g, 4.0 mmole) was dissolved in 30 ml of hexane. THF (100 ml) was added together with 1.2 ml (8.0 mmole) of TMEDA and 5.5 ml (8.8 mmole) of n-butyllithium. The mixture was refluxed for 45 minutes and cooled to 0°C after which 100 ml of THF was added. 1.7 g (8.0 mmole) $Cr(CO)_6$ was introduced and the mixture was stirred for an hour at room temperature. The solvent was evaporated and 1.5 g (8.0 mmole) triethyl oxonium tetrafluoroborate, dissolved in 30 ml of dichloromethane, was added at -30°C. The mixture was stirred for 15 minutes in the cold and for a further 45 minutes at room temperature after which it was filtered and the solvent evaporated. The residue was column chromatographed with a hexane: dichloromethane (1:1) solution to yield two products. The first purple-pink product was identified as **19**, yield: 0.79 g, 42% . The second orange product was characterized as **20** with a yield of 0.34 g, 14%.

2.4. Dithieno[3,2-b: 2',3'-d]thiophene carbene complexes

2.4.1 Synthesis of tungsten complex 21

3,3'-Dithienyl sulfide (0.79 g; 4.0 mmole) was dissolved in 30 ml of hexane. 5.5 ml (8.8 mmole) of n-butyl lithium and 1.2 ml (8.0 mmole) of TMEDA were added to this solution at room temperature. After refluxing the mixture for 45 minutes, it was cooled to 0°C and 20 ml of THF was added. Tungsten hexacarbonyl (1.4 g, 4.0 mmole) was introduced at -20°C with vigorous stirring and this was continued for one hour while the temperature was allowed to reach room temperature. The solvent was evaporated *in vacuo* and the residue dissolved in 50 ml of dichloromethane. Alkylation was effected with triethyl oxonium tetrafluoroborate (1.5 g, 8.0 mmole), which was dissolved in 30 ml of dichloromethane and added at -20°C. Stirring was maintained for one hour , the mixture was filtered through silica gel and the solvent removed. The green product, complex **21**, was isolated using column chromatography, with a yield of 1.26 g (52%).

2.4.2 Synthesis of chromium complexes 22, 23 and 24

0.19 g (1.0 mmole) of DTT was dissolved in 30 ml of hexane. 1.4 ml (2.2 mmole) of n-butyl lithium and 0.3 ml (2.0 mmole) of TMEDA were added to this solution at room temperature. This mixture was refluxed for 45 minutes and then cooled to 0°C. Lithium chloride precipitated from the yellow solution as a white solid. 30 ml of THF was added and the suspension was cooled even further to -40°C. 0.44 g (2.0 mmole) of $Cr(CO)_6$ was added and the colour of the mixture turned to red-brown. The temperature of the reaction was allowed to rise to room temperature while the mixture was stirred vigorously. After an hour the solvent was removed *in vacuo* and a solution of 0.4 g (2.0 mmole) of triethyl oxonium tetrafluoroborate in 50 ml of dichloromethane was added to the cooled residue (-20°C). After the addition of the alkylating agent, as room temperature was reached, the colour changed to dark purple. The mixture was filtered, the solvent removed. Three products were isolated using column chromatography. The first orange product was characterized as the monocarbene complex **22**, yield: 0.15 g (32%); mp. 181.5 - 183.7°C, while the second blue-purple product was identified as the biscarbene complex **23**, yield: 0.27 g (39%). The third product had a red-purple colour and was characterized as the decomposition product **24**, yield: 0.11 g (22%).

2.4.3 Synthesis of tungsten complexes 25, 26 and 27

1.4 ml (2.2 mmole) of n-butyllithium and 0.3 ml (2.0 mmole) of TMEDA were added to a solution of 0.19 g (1.0 mmole) of DTT in 30 ml of hexane. The reaction was effected in the same manner as described for the chromium analogue in **2.4.2.** with the addition of 0.70 g (2 mmole) tungsten hexacarbonyl and subsequent alkylation with 0.4 g (2.0 mmole) triethyl oxonium tetrafluoroborate.

Three products were isolated with column chromatography. The first orange product was identified as the monocarbene complex **25**, yield: 0.24 g (42%). The second purple was the biscarbene complex **26** which was formed in a yield of 0.25 g (26%). The third product had an brown-orange colour and was characterized as the decomposition product **27**, yield: 0.19 g (30%).

2.4.4 Synthesis of molybdenum complexes 28, 29 and 30

0.19 g (1.0 mmole) of DTT was dissolved in 30 ml of hexane after which 1.4 ml (2.2 mmole) of n-butyllithium and 0.3 ml (2.0 mmole) were added. The same reaction procedure was followed as described in **2.4.2** for the dilithiation of DTT. The addition of 0.53 g (2.0 mmole) of $Mo(CO)_6$ led to a dark brown colour change of the reaction mixture. Quenching the reaction with 0.4 g (2.0 mmole) triethyl oxonium tetrafluoroborate resulted in a purple-pink colour for the final reaction solution. Three products were purified on a column and isolated in the following order: the orange monocarbene complex **28**, yield: 0.13 g (26%); the purple biscarbene complex **29**, yield: 0.27 g (35%) and the pink-purple complex **30**, yield: 0.34 g (31%).

2.5. Alkyl complexes of Thiophene derivatives

2.5.1 Synthesis of iron complex 31

Dilithiation of thiophene was accomplished by adding 17.0 ml (27.3 mmole) of n-butyllithium and 3.7 ml (24.8 mmole) of TMEDA to a solution of 0.99 ml (12.4 mmole) of thiophene in 50 ml of hexane and refluxing the mixture for 30 minutes. The reaction mixture was cooled to 0°C, 30 ml of THF was added and it was further cooled to -20°C. 6.9 g (22.7 mmole) of $FeCp(CO)_2I$

was added with vigorous stirring which was maintained for a further two hours while the temperature was allowed to gradually raise until room temperature was reached. After filtration through silica gel and anhydrous sodium sulphate, the solvent was removed and the residue purified using column chromatography. Four bands were distinguished on the column. The first yellow band was identified as the mono-iron complex previously synthesized by Nesmeyanov *et al*[14]. The second brown product was the starting compound $FeCp(CO)_2I$. The third red band was isolated and identified to be the iron dimer complex $[FeCp(CO)]_2$. The fourth orange compound was characterized as the diiron complex **31**, yield: 1.13 g (21%). This compound is very polar and could only be collected by using pure dichloromethane as eluent.

2.5.2 Synthesis of iron complexes 32, 33, 34 and 35

Dimetallation of 3,6-dimetylthieno[3,2-*b*]thiophene was accomplished by dissolving 0.34 g (2.0 mmole) of the ligand in 30 ml of dry diethyl ether and adding 1.4 ml (2.2 mmole) of n-butyl lithium while cooling the mixture on an ice bath. The mixture was stirred for two hours at this temperature and for a further 30 minutes at room temperature. The reaction mixture was cooled to -40°C after which 0.6 g (2.0 mmole) of $[FeCp(CO)_2I]$ was added. The reaction was stirred for 15 minutes at this temperature and for a further two hours at room temperature. Filtration through silica gel and the subsequent evaporation of the solvent *in vacuo* afforded a brown residue. Six products were isolated using column chromatography. The first organic product isolated was the starting material, DMTT, yield: 0.03 g (8%). The second yellow product was characterized as the mono iron complex **32**, yield: 0.13 g (19%). The third brown product was identified as the iron starting material $[FeCp(CO)_2I]$, yield: 0.16 g (27%). The following two orange-yellow products were found to be complexes **34** and **35**, which were isolated with yields of 0.17 g (16%) and 0.16 g (11%), respectively. The sixth orange product, complex **33**, was isolated using dichloromethane as eluent. This product was formed in a yield of 0.12 g (12%) and was characterized as the diiron complex.

2.5.3 Synthesis of tin complexes 36 and 37

Dilithiation of DMTT was effected as described in **2.3.1**. The reaction was performed using 0.674 g (4.0 mmole) of DMTT. The solution containing the dilithiated species was cooled to -

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[14] A.N. Nesmeyanov, N.E. Kolobova, L.V. Goncharenko, K.N. Anisimov, *Izv. Akad. Nauk, SSSR, Ser. Khim.*, 1, **1976**, 153.

40°C and 1.594 g (8.0 mmole) of $SnMe_3Cl$ was added. The mixture was stirred at this temperature for 15 minutes and a further two hours at room temperature. The solvent was removed *in vacuo*. 100 ml of water was added to the residue and extracted with three 30 ml portions of diethyl ether. The ether extracts were combined, dried over sodium sulphate and filtered. After evaporation of the solvent, the residue was washed with hexane after which an oily residue remained. All the hexane extracts were combined, the solution was concentrated and the product left to crystallize. Complex **37** crystallized as colourless, cubic crystals from this solution, yield: 1.50 g (76%). The oily residue left in the initial flask was distilled and the mono tin complex, **36**, was afforded as a colourless oil, yield: 0.28 g (21%).

2.5.4 Synthesis of iron complex 38

Complex **37** (0.99 g; 2.0 mmole) and $[FeCp(CO)(PEt_3)I]$ (1.6 g; 4.0 mmole) were dissolved in 20 ml of DMF. The palladium catalyst $Pd(CH_3CN)_2Cl_2$ (0.025 g; 0.1 mmole) was added to the solution and the mixture was stirred for 12 hours at room temperature. Complex **38** was isolated using column chromatography (yield: 0.37 g; 24%), after collecting the green iron starting material.