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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 metals¹. 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 derivatives². 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 1964³. 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.

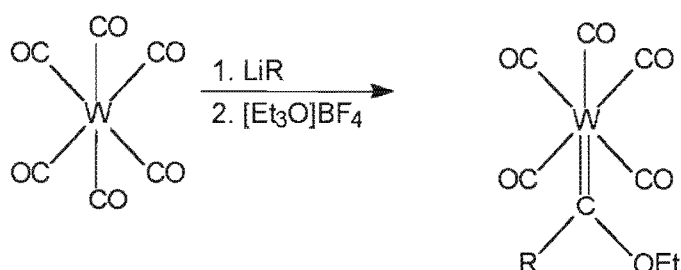


Figure 1.1 An example of a Fischer carbene complex

The second type is the Schrock 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.

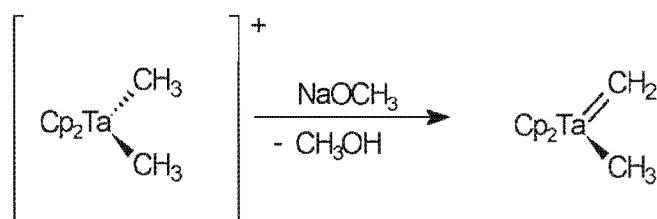


Figure 1.2 An example of a Schrock-carbene complex

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 topic⁴, 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.

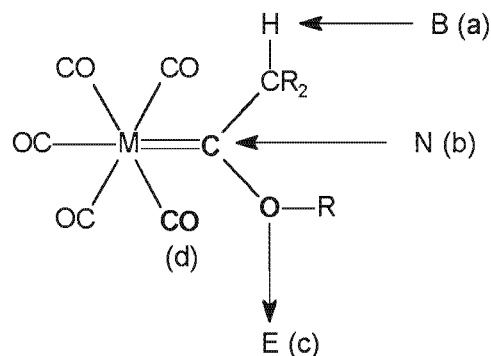


Figure 1.3 Reactivity of Fischer carbene complexes

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

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. Kreisssl, 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. (e) 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}.

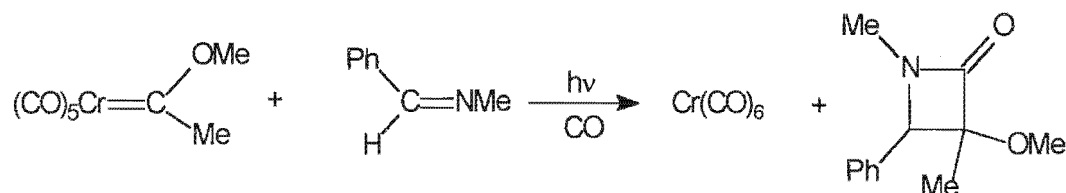


Figure 1.4 Employing a carbene complex to synthesize a β -lactam

Carbene complexes have been employed in carbon-carbon bond formation in organic synthesis⁸. 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 phenyl⁹, naphthyl¹⁰, furyl- and thienyl¹¹ substituted carbene ligands have been reacted with various alkynes to give substituted naphthol, phenanthrene, benzofuran and benzothiophene ligands π -coordinated to a tricarbonylchromium fragment.

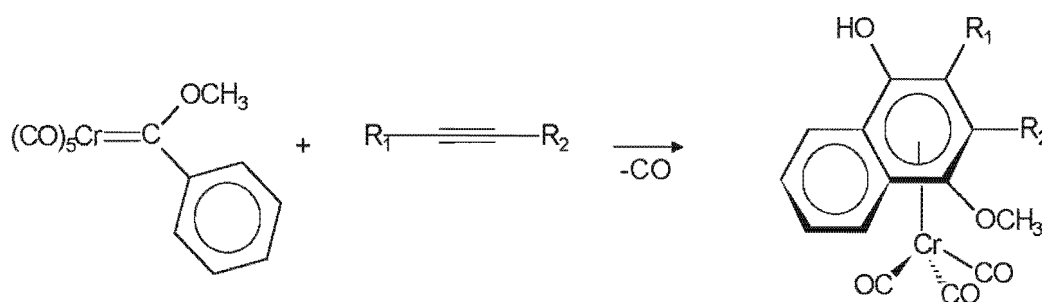


Figure 1.5 Reaction of carbene with alkyne

⁵ L.S. Hegedus, *Acc. Chem. Res.*, 28, **1995**, 299.

⁶ M.A. Sierra, L.S. Hegedus, *J. Am. Chem. Soc.*, 111, **1989**, 2335.

⁷ C.A. Merlic, D. Xu, S.I. Khan, *Organometallics*, 11, **1992**, 412.

⁸ K.H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 23, **1984**, 587.

⁹ K.H. Dötz, I. Pruskil, *Chem. Ber.*, 111, **1978**, 2059.

¹⁰ K.H. Dötz, *Angew. Chem. Int. Ed. Engl.*, 14, **1975**, 644.

¹¹ K.H. Dötz, W. Kuhn, *J. Organomet. Chem.*, 252, **1983**, C78.

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 $\text{Cr}(\text{CO})_3$ moiety. The unsubstituted ring of the naphthol ligand and the $\text{C}(\text{OCH}_3)$ unit of the second ring originate from the carbene ligand, while the $\text{C}(\text{OH})$ 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 ligands¹².

Carbene complexes also play important roles as intermediates in olefin metathesis¹³. Grubbs *et al*¹⁴ synthesized ruthenium(II) carbene complexes of the type *trans*- $[\text{Ru}=\text{CHCH}=\text{CPh}_2(\text{PPh}_3)_2\text{Cl}_2]$, to catalyze the polymerization of highly strained cyclic olefins.

1.2 Cumulene and related complexes

Carbene complexes with cumulated double bonds of the form $\text{M}=(\text{C})_n\text{R}_2$ (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 properties¹⁵. Transition metal complexes of this structural type have been proposed as one-dimensional molecular wires¹⁶ and exhibit both liquid crystalline¹⁷ and nonlinear optical properties (NLO)¹⁸. The maximum chain length achieved

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.

¹³ C.P. Casey, *J. Am. Chem. Soc.*, **96**, **1974**, 7808.

¹⁴ S.T. Nguyen, L.K. Johnson and R.H. Grubbs, *J. Am. Chem. Soc.*, **114**, **1992**, 3974.

¹⁵ H. Lang, *Angew. Chem. Int. Ed. Engl.*, **33**, **1994**, 547.

¹⁶ (a) J.S. Schumm, D.L. Pearson, J.M. Tour, *Angew. Chem. Int. Ed. Engl.*, **33**, **1994**, 1360. (b) M.D. Ward, *Chem. Soc. Rev.*, **1995**, 121.

¹⁷ (a) A.M. Giroud-Godquin, P.M. Maitlis, *Angew. Chem. Int. Ed. Engl.*, **30**, **1991**, 375. (b) M. Altmann, U.H.F. Bunz, *Angew. Chem. Int. Ed. Engl.*, **34**, **1995**, 569. (c) L. Oriol, J.L. Serrano, *Adv. Mater.*, **7**, **1995**, 248.

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 only¹⁹. Since then, a few reports describing the syntheses of similar compounds, including group 6 metal complexes, have appeared²⁰. However, complexes containing even-numbered carbon chains seem to be restricted to the ruthenium-butatrienyldiene complex prepared by Lompfrey and Selegue²¹. Theoretical calculations²² 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_α ²³, while the protonation of vinylidenes to carbynes reflects the ease of addition of electrophiles to C_β ²⁴.

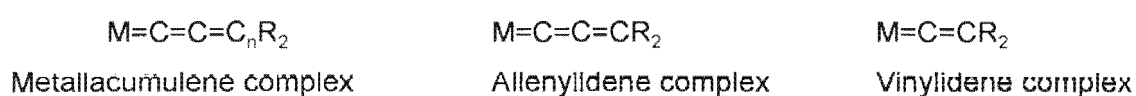


Figure 1.6 Cumulene complexes

Allenylidene complexes have been known since 1976²⁵, 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

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.

²¹ J.R. Lompfrey, J.P. Selegue, *Organometallics*, **12**, **1993**, 616.

²² N.M. Kostic, R.F. Fenske, *Organometallics*, **1**, **1982**, 974.

²³ D. Touchard, N. Pirio, P.H. Dixneuf, *Organometallics*, **14**, **1995**, 4920.

²⁴ C. Kelly, N. Lugan, M.R. Terry, G.L. Geoffroy, B.S. Haggerty, A.L. Rheingold, *J. Am. Chem. Soc.*, **114**, **1992**, 6735.

²⁵ (a) H. Berke, *Angew. Chem. Int. Ed. Engl.*, **15**, **1976**, 624. (b) E.O. Fischer, H.J. Kalder, A. Franck, F.H. Köhler, G. Huttner, *Angew. Chem. Int. Ed. Engl.*, **15**, **1976**, 623.

²⁶ S. Takahashi, Y. Takai, H. Morimoto, K. Sonogashira, *J. Chem. Soc., Chem. Commun.*, **1984**, 3.

straightforward method employed by Selegue and co-workers²⁷. This synthesis comprises the reactions of alkyn-3-ols with metal complexes eg. $[\text{RuCpCl}(\text{PR}_3)_2]$ 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. iron²⁸, rhodium²⁹ and ruthenium³⁰ derivatives. The same method is now directed towards the building of bimetallic systems with allenylidene ligands³¹ or bridges³².

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 Stang³³ and Bruce³⁴. Complexes containing these species are likely intermediates in coupling of alkynes to give enynes³⁵ or butatrienes³⁶, and in the synthesis of unsaturated ketones from alkynes and allylic alcohols³⁷.

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

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. Kovacic, M. Laubender, H. Werner, *Organometallics*, 16, **1997**, 5607. (c) D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, *Organometallics*, 17, **1998**, 3844.

³⁰ T. Braun, P. Steinert, H. Werner, *J. Organomet. Chem.*, 488, **1995**, 169.

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

³² H.P. Xia, G. Jia, *Organometallics*, 16, **1997**, 1.

³³ P.L. Stang, *Acc. Chem. Res.*, 15, **1982**, 348.

³⁴ M.I. Bruce, *Chem. Rev.*, 91, **1991**, 197.

³⁵ C. Bianchini, M. Peruzzini, P. Frediani, *J. Am. Chem. Soc.*, 113, **1991**, 5453.

³⁶ Y. Wakatsuki, H. Yamakazi, N. Kumegawa, T. Satoh, J.Y. Satoh, *J. Am. Chem. Soc.*, 113, **1991**, 9604.

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

recently attracted much interest in view of their new material properties³⁸ and as model systems for surface carbides in heterogeneous catalysis³⁹. 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 support³⁹, most of the complexes synthesized contain an acetylenic $\mu-C\equiv C$ bridge. The cumulenic structure $M=C=C=M$ was only observed in a few titanium and tantalum complexes.

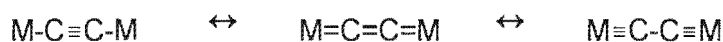


Figure 1.7 Resonance structures for the MC_2M species

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 complexes⁴¹ 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-worker⁴².

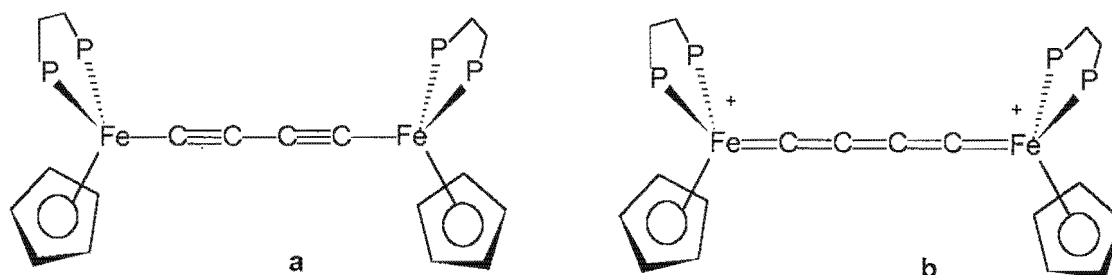


Figure 1.8 (a) Polyynic structure and (b) oxidized structure

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.

⁴¹ M. Brady, W. Weng, J.A. Gladysz, *J. Chem. Soc., Chem. Comm.*, 1994, 2655.

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

The complex with the highest number of carbon atoms in the chain, $[\{\text{ReCp}^*(\text{PPh}_3)(\text{NO})\}_2(\mu\text{-C}_{20})]$ was recently synthesized by Gladysz and co-workers⁴³. The longest polyynene 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-workers⁴⁵.

Complexes containing two different transition metal building blocks, linked by C_n bridges ($n=1-5$), have only recently become accessible¹⁵. Synthesis of these compounds, particularly for those containing organometallic substituents, turned out to be remarkably easy⁴⁶. These complexes were proposed as a new class of one-dimensional molecular wires¹⁶. Very few compounds have been synthesized with an odd number of carbons in the C_n chain⁴⁷. Only one C_3 bridged complex has been structurally characterized, namely $[\{\text{ReCp}^*(\text{PPh}_3)(\text{NO})\}(\mu\text{-C}_3)\{\text{MnCp}(\text{CO})_2\}]$. 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 cumulenenic forms dominate over the alkyne-carbyne forms⁴⁸.

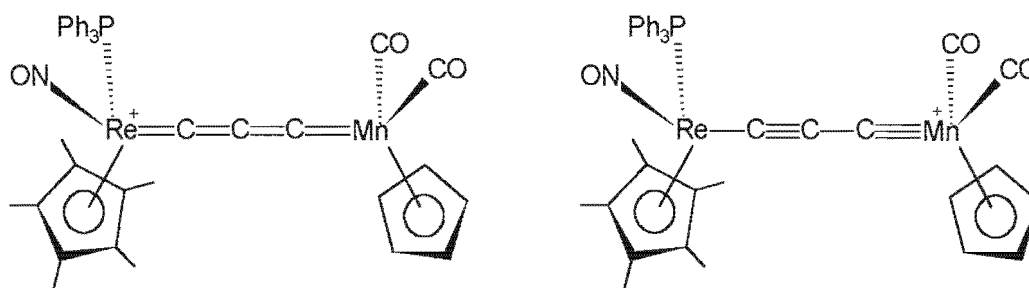


Figure 1.9 Valence structures of C_3 bridged chain with different metal fragments

⁴³ B. Bartik, R. Dembinski, T. Bartik, A.M. Arif, J.A. Gladysz, *New J. Chem.*, 21, **1997**, 739.

⁴⁴ T.B. Peters, J.C. Bohling, A.M. Arif, J.A. Gladysz, *Organometallics*, 18, **1999**, 3261.

⁴⁵ A. Sakurai, M. Akita, Y. Moro-oka, *Organometallics*, 18, **1999**, 3241.

⁴⁶ (a) W. Beck, W. Knauer, C. Robl, *Angew. Chem. Int. Ed. Engl.*, 29, **1990**, 293. (b) W. Weng, J.A. Ramsden, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.*, 115, **1993**, 3824. (c) J.W. Seyler, W. Weng, J. Zhou, J.A. Gladysz, *Organometallics*, 12, **1993**, 3802.

⁴⁷ P. Belanzoni, N. Re, A. Sgamellotti, C. Floriani, *J. Chem. Soc., Dalton Trans.*, **1998**, 1825.

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 reported⁵⁰. 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 ion⁵¹ (figure 1.10), 4,4'-bipyridine⁵² and related heteroaromatic groups⁵³.

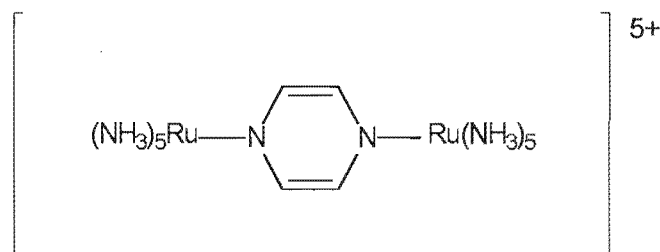


Figure 1.10 The Creutz-Taube ion

Sponsler and co-workers⁵⁴ have recently reported the first examples of delocalized mixed-valence

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

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

⁵¹ C. Creutz, H. Taube, *J. Am. Chem. Soc.*, 95, 1973, 1086.

⁵² S. Woitellier, J.P. Launay, C. Joachim, *Chem. Phys.*, 131, 1989, 481.

⁵³ S. Boyde, G.F. Strouse, W.E. Jones, T.J. Meyer, *J. Am. Chem. Soc.*, 112, 1990, 7395.

⁵⁴ B.A. Etzenhauser, M.D. Cavanaugh, H.N. Spurgeon, M.B. Sponsler, *J. Am. Chem. Soc.*, 116, 1994, 2221.

$\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ complexes containing butadienediyl bridges (figure 1.11), prepared by one-electron oxidation of the corresponding $\text{Fe}^{\text{II}}/\text{Fe}^{\text{II}}$ complexes. Since then several mixed valence complexes of this type have been synthesized, eg. a $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ complex prepared by Moreira and co-workers⁵⁵.

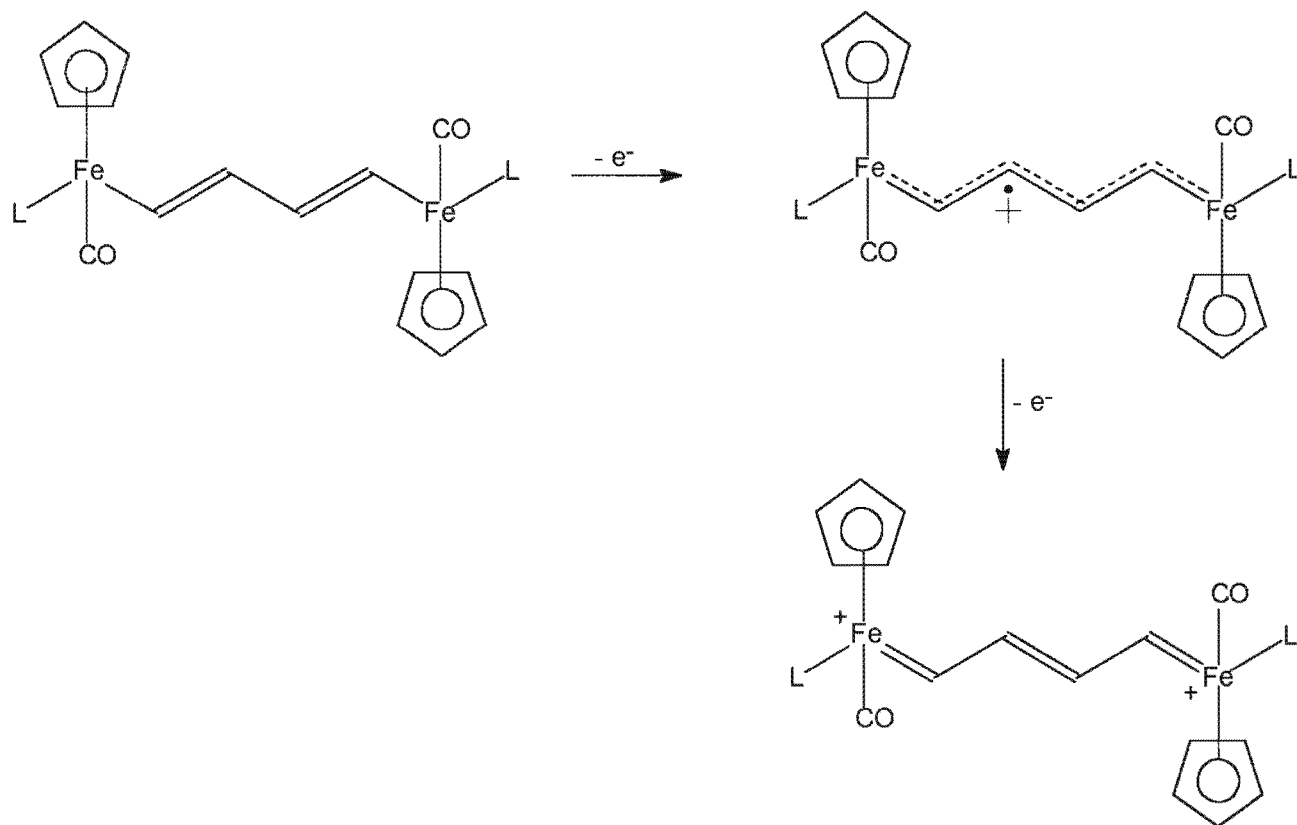


Figure 1.11 $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ complexes containing butadienediyl bridges

Organometallic complexes in which two metal-containing fragments are bridged by arene⁵⁶ or heteroarene ligands⁵⁷ have enjoyed considerable attention recently since they serve as models for the repeating units in related organometallic polymers⁵⁸. 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

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.

⁵⁷ R. Chukwu, A.D. Hunter, B.D. Santarsiero, *Organometallics*, 10, 1991, 2141.

⁵⁸ R. McDonald, K.C. Sturge, A.D. Hunter, L. Shilliday, *Organometallics*, 11, 1992, 893.

to 9,10-C₁₄H₈⁵⁹, 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 polymers⁶⁰. The two metal centers do indeed interact and they transfer significant electron density to the arene ring. Hunter and co-workers⁶¹ 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 fuels⁶² and the coordination chemistry of these compounds has received recent attention because of its relevance to the metal-catalyzed hydrodesulfurization of the fossil fuels⁶³. A mechanism for the hydrodesulfurization was proposed by Angelici and co-workers⁶⁴ 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 eV), it is found that thiophene is slightly more nucleophilic than benzene. *Ab initio* calculations⁶⁵ 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

⁵⁹ A.D. Hunter, D. Ristic-Petrovic, J.L. McLernon, *Organometallics*, 11, **1992**, 864.

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

⁶¹ A.D. Hunter, A.B. Szigety, *Organometallics*, 8, **1989**, 2670.

⁶² W.L. Orr and C.M. White, Eds., *Geochemistry of Sulfur in Fossil fuels*, American Chemical Society, Washington, D.C., **1990**.

⁶³ B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic processes*; McGraw-Hill; New York, **1979**.

⁶⁴ J. Chen, L.M. Daniels and R.J. Angelici, *J. Am. Chem. Soc.*, 113, **1991**, 2544.

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

found in literature⁶⁶.

Oligomers of thiophene are also compounds of current interest because many of them show photo-enhanced biological activities⁶⁷, while α -polymerization of thiophene produces crystalline, electroconductive polythiophenes⁶⁸. 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 polymers⁶⁹, electron acceptors⁷⁰, hydrogen-poor heterocycles⁷¹, organic conductors or superconductors⁷² and materials with non-linear optical properties⁷³. 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 $\{\text{Ru}(\text{NH}_3)_5\}^{2+/3+}$ 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 bridge⁷⁴.

⁶⁶ (a) R.J. Angelici, *Coord. Chem. Rev.*, 105, 1990, 61; (b) T.A. Waldbach, P.H. van Rooyen, S.Lotz, *Angew. Chem. Int. Ed. Engl.*, 32, 1993, 710; (c) J. Chen, V.G. Young and R.J. Angelici, *J. Am. Chem. Soc.*, 117, 1995, 6362; (d) J. Chen and R.J. Angelici, *Organometallics*, 26, 1989, 3424.

⁶⁷ (a) J. Lam, H. Breter, T. Arnason and L. Hansen, *Chemistry and Biology of Naturally-occurring Acetylenes and Related Compounds*, Eds. Elsevier, Amsterdam, 1988. (b) S-W. Lai, M.C.W. Chan, K-K. Cheung, S-M. Peng, C-M. Chi, *Organometallics*, 18, 1999, 3991.

⁶⁸ J. Nakayama and T. Konishi, *Heterocycles*, 27, 1988, 1731.

⁶⁹ (a) S. Musmanni and J.P. Ferraris, *J. Chem. Soc., Chem. Comm.*, 1993, 172. (b) J. Yao, D.Y. Son, *Organometallics*, 18, 1999, 1736.

⁷⁰ D. Lorcy, K.D. Robinson, Y. Okuda, J.L. Atwood and M.P. Cava, *J. Chem. Soc., Chem. Commun.*, 1993, 345.

⁷¹ K. Yui, H. Ishida, Y. Aso, T. Otsubo, F. Ogura, A. Kawamoto and J. Tanaka, *Bull. Chem. Soc. Jpn.*, 62, 1989, 1547.

⁷² O. Kobayashi, *Phosphorus Sulfur*, 43, 1989, 187.

⁷³ (a) N.J. Long, *Angew. Chem. Int. Ed. Engl.*, 34, 1995, 21. (b) R.A. Ham and D. Bloor, *Organic Materials for Non-linear Optics*, The Royal Society of Chemistry, Cambridge, Special Publication No. 91, 1991. (c) I.S. Lee, H. Seo, Y.K. Chung, *Organometallics*, 18, 1999, 1091.

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 molecule¹. The coordination of transition metals to thiophene moieties has been extended to include bithiophene⁷⁵, 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 synthesized⁷⁶, 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 hexacarbonyl⁷⁷ 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.

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.

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 biscarbene 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 fuels¹. 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 synthesized². Few S-bound complexes have been isolated, for example $[\text{Ru}(\text{NH}_3)_5\text{T}]^{2+}$, $[\text{FeCp}(\text{CO})_2\text{T}]^+$, $[\text{FeCp}(\text{NCMe})_2(2,5\text{-Me}_2\text{T})]^+$ and $[\text{W}(\text{CO})_3(\text{PCy}_3)_2\text{T}]^3$. 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 $[\text{Os}_3(\text{C}_4\text{H}_4\text{S})\text{H}_2(\text{CO})_9]$, a complex exhibiting the η^2 -

¹B.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 Hockett and Angelici⁵, who prepared the complex $[\text{IrCp}^*\text{T}]$. Several η^5 -coordinated complexes can be found in literature, e.g. $[\text{Cr}(\eta^5\text{-T})(\text{CO})_3]$ 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.

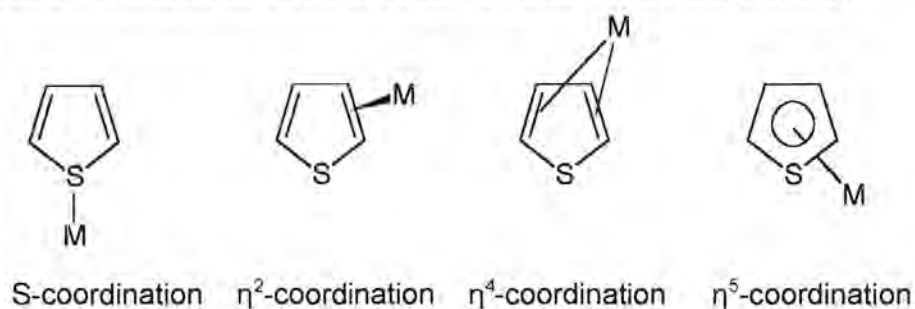


Figure 2.1 Coordination modes of thiophene to one transition metal

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 $[\text{Fe}(\text{CO})_3\{\mu\text{-}\eta^2\text{-S-T}\}\text{Re}(\text{CO})_2\text{Cp}^*]$ ⁷. Angelici *et al* recently synthesized the first thiophene complexes coordinated to three metal centres namely the complexes $\{\mu_3\text{-}\eta^4\text{-S,S}\}[\text{IrCp}(2,5\text{-Me}_2\text{T})][\text{Mo}_2(\text{CO})_4\text{Cp}_2]$ ⁸ and $\{\mu_3\text{-}\eta^4\text{-S,S}\}[\text{IrCp}(2,5\text{-Me}_2\text{T})][\text{Fe}_2(\text{CO})_7]$ ⁹, both exhibiting the $\{\mu_3\text{-}\eta^4\text{-S,S}\}$ -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 $\eta^1:\eta^5$ -coordination mode of thiophene has received considerable attention in our laboratories

⁵ S.C. Hockett, 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 $[\text{Pt}(\eta^1\text{-C}_4\text{H}_3\text{S})\text{L}_2\{(\mu\text{-}\eta^1:\eta^5\text{-C}_4\text{H}_3\text{S})\text{Cr}(\text{CO})_3\}]^{10}$ and $[\text{Mn}(\text{CO})_5\{\mu\text{-}\eta^1:\eta^5\text{-C}_4\text{H}_3\text{S}\}\text{Cr}(\text{CO})_3]^{11}$. The latter complex was found to undergo a metal exchange reaction in solution¹².

The C-S bond cleavage is observed in a base-catalyzed reaction where the iridium in $[\text{IrCp}^*(\eta^4\text{-2,5-Me}_2\text{T})]$ inserts into a C-S bond of the η^4 -thiophene to give the ring-opened iridathiabenzene $[\text{IrCp}^*(\text{C,S-2,5-Me}_2\text{T})]$, a six-membered ring. This iridathiabenzene ring reacts with various metal carbonyls to yield η^6 -coordinated complexes of the type $[\text{IrCp}^*\{\eta^6\text{-}(\text{C,S-2,5-Me}_2\text{T})\}\text{ML}_3]$, (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 moieties¹⁴. Russian workers have described the preparation of the compound $[\text{FeCp}(\text{CO})_2(\text{C}_4\text{H}_3\text{S})]^{15}$, which was reacted with $\text{Fe}_3(\text{CO})_{12}$ to yield a trimetallic thiaferrole complex¹⁶.

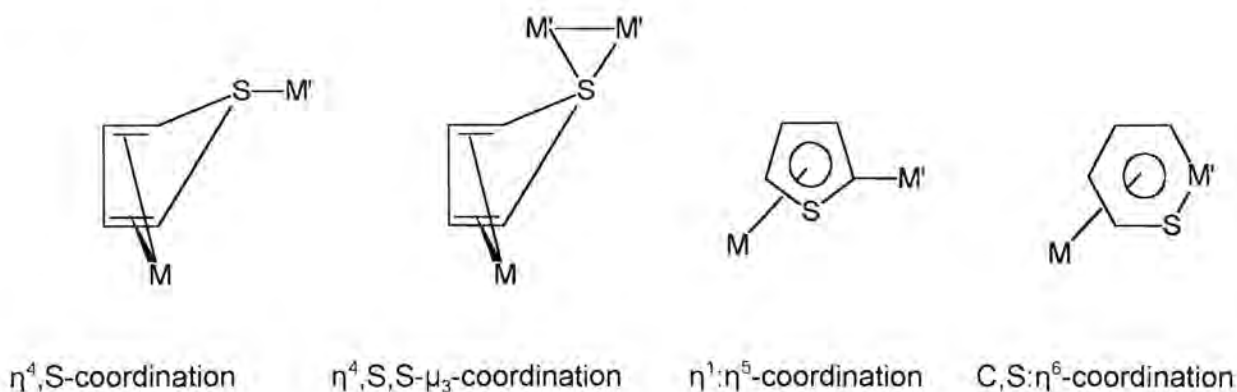


Figure 2.2 Coordination modes of thiophene to more than one transition metal

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 Maasböl¹⁷, $[\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$, is also the first example of a carbene complex containing an aromatic substituent. Shortly after this discovery, the structural data of the complexes $[\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$ and $[\text{Cr}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$ 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 recognized¹⁹ (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 $[\text{W}(\text{CO})_5\text{C}(\text{Ph})\text{Ph}]$ carbene complex, which could be synthesized from the complex $[\text{W}(\text{CO})_5\text{C}(\text{OEt})\text{Ph}]$ ²⁰. The complexes $[\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$ and $[\text{Cr}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]$ together with the $[\text{MnCp}(\text{CO})_2\text{C}(\text{OMe})\text{Ph}]$ carbene complex were synthesized to investigate the electrophilic activity of the carbonyl ligands. To determine whether carbene complexes can accommodate dinuclear metal carbonyl complexes,

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 known²², 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 oxygen²³.

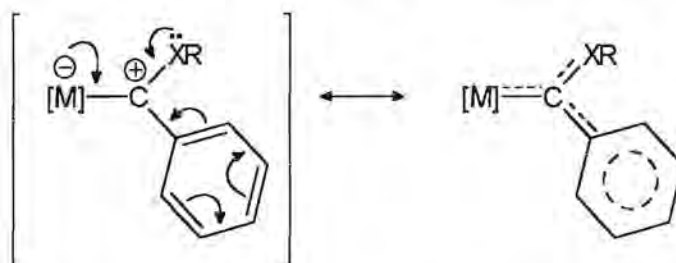


Figure 2.3 π -delocalized network around carbene carbon in arene carbene complex

Connor and Jones²⁴ 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-workers²⁶ 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).

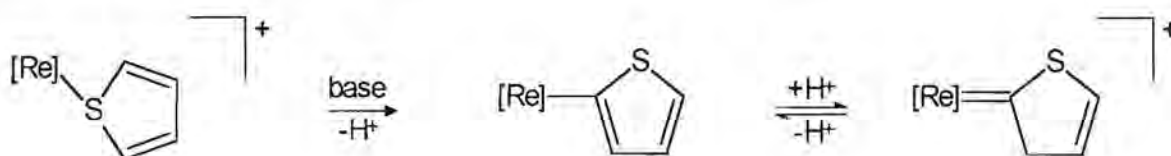


Figure 2.4 Formation of 2-thienylidene carbene complex

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.

The precursor $[\text{ReCp}(\text{NO})(\text{PPh}_3)\text{thiophene}]^+$ undergoes deprotonation by a strong base to give the 2-thienyl complex $[\text{ReCp}(\text{NO})(\text{PPh}_3)(2\text{-thienyl})]$. 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 recently²⁷. 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 $[\text{FeCp}(\text{CO})_2\text{Cl}]$ 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 isothiazolylidene complexes are unique since the nucleophilic heteroatom is situated γ to the coordinated carbon atom.

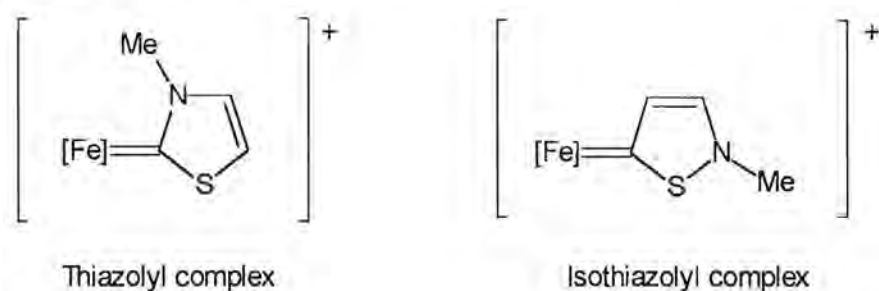


Figure 2.5 Thiazolyl and isothiazolyl carbene complexes

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 1991³¹. 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

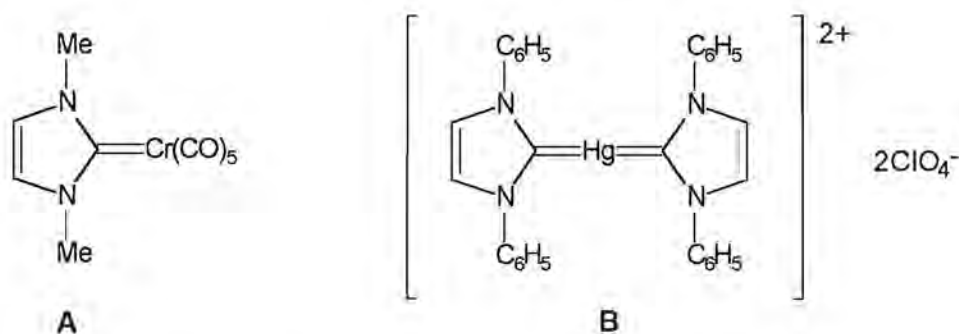


Figure 2.6 First N-heterocyclic carbene complexes

2.2 Biscarbene complexes

Fischer³³ 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

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. Röhl, 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 ligand³⁴. 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 twisted³⁵.

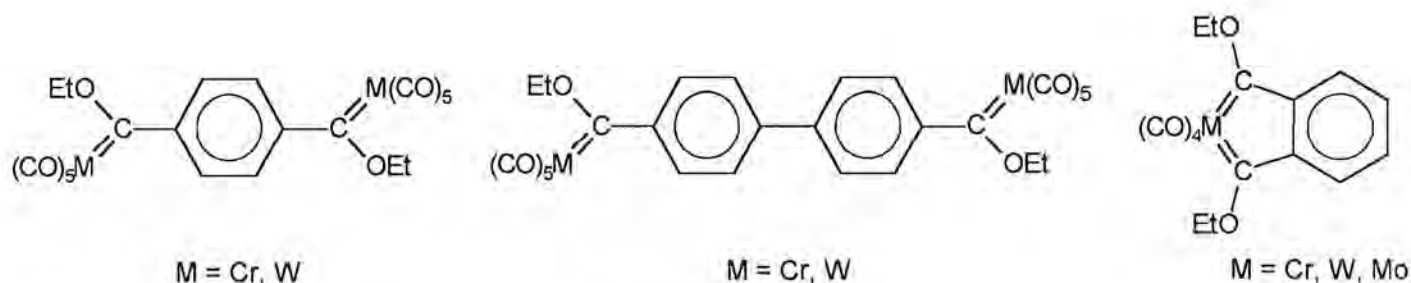


Figure 2.7 Phenylene biscarbene complexes

Synthesis of the biscarbene complex of tungsten with anthracene as bridging unit³⁶ 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.

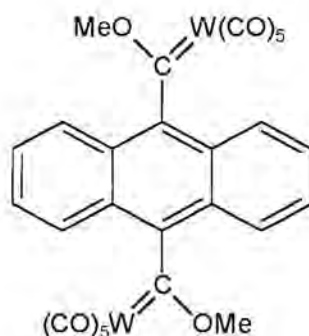


Figure 2.8 Bimetallic biscarbene complex with anthracene as bridging unit

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 prepared³⁷ 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

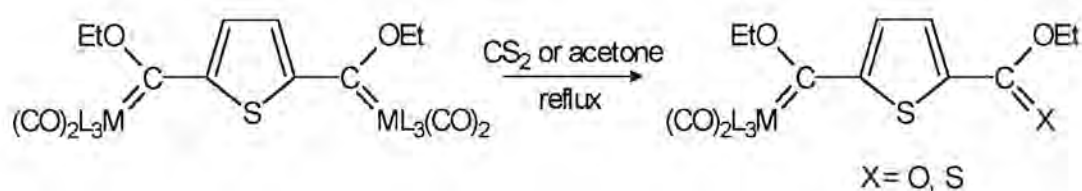


Figure 2.9 Decomposition of biscarbene complexes

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.

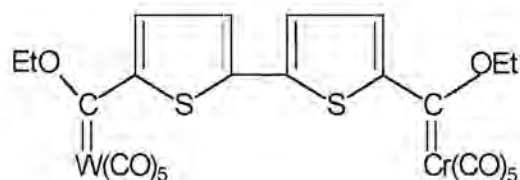


Figure 2.10 Biscarbene complex containing two different metal moieties

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 $[M(CO)_5\{\mu-T\}M(CO)_5]$ ($M = Cr, W$) were recognized³⁷, 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 complexes³⁸ 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 synthesized³⁷, it was envisaged to prepare the molybdenum analogues of these complexes to compare stabilities of the different products. According to Fischer³⁹ 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*-butyllithium⁴⁰. 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

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. Verkruisje, *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 $\text{Mo}(\text{CO})_6$ 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.

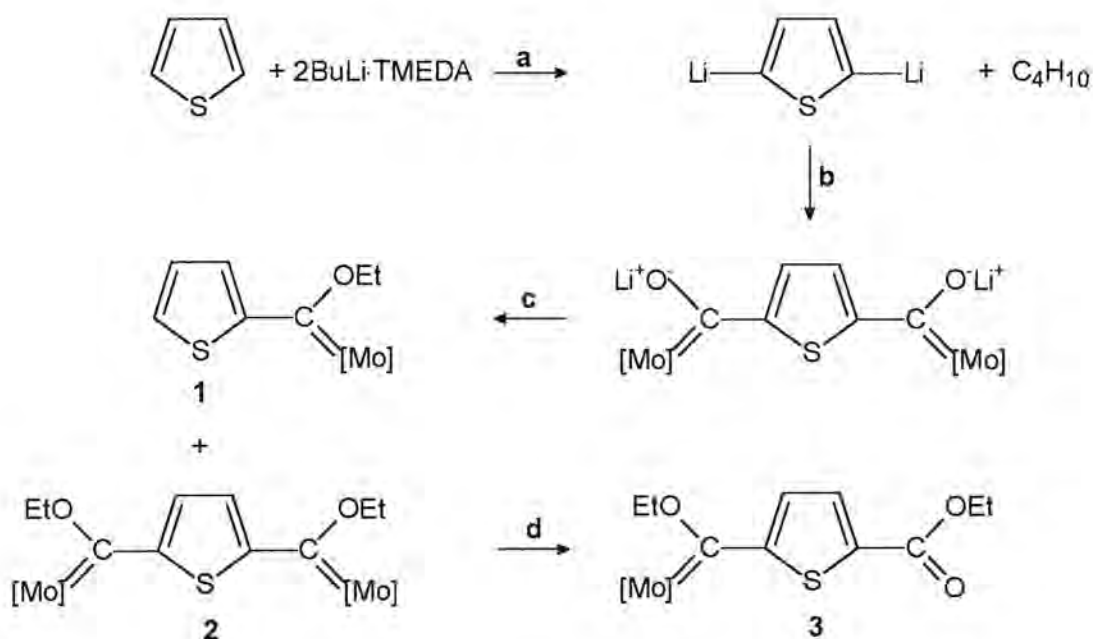


Figure 2.11 Procedure for preparation of carbene complexes

Reagents: (a) Hexane, reflux; (b) 2 eq. $\text{Mo}(\text{CO})_6$, THF, -20°C ; (c) 2 eq. $[\text{Et}_3\text{O}][\text{BF}_4]$, 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 reported⁴¹. 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 O₂ (c) with complex **4**. (compare step d figure 2.11)

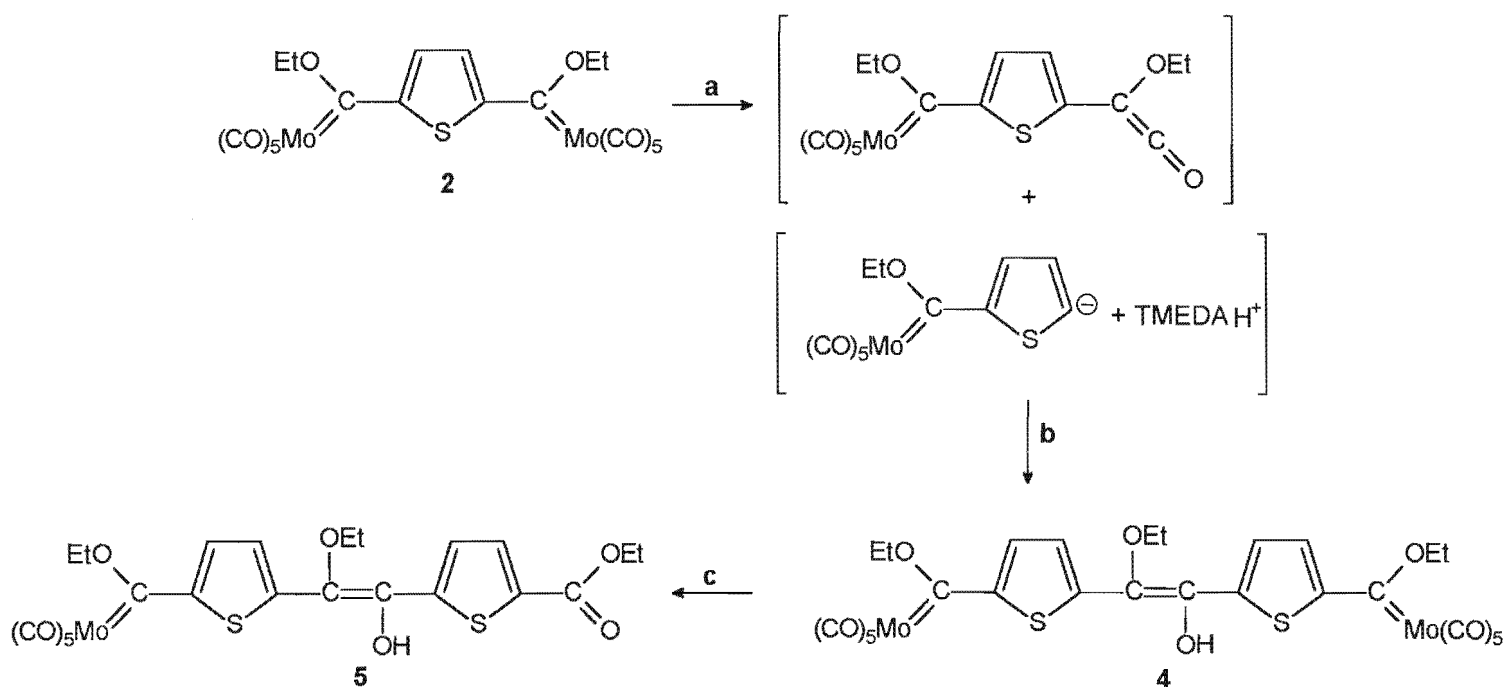


Figure 2.12 Proposed mechanism for the formation of complexes **4** and **5**

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.

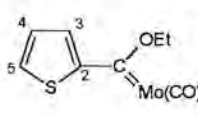
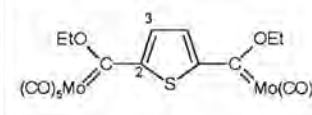
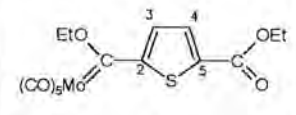
3.1 Spectroscopic characterization of novel carbene complexes

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 ^1H NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform as solvent unless otherwise specified. The ^1H 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 ^1H 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 H4⁴². 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 Gronowitz⁴³. 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.

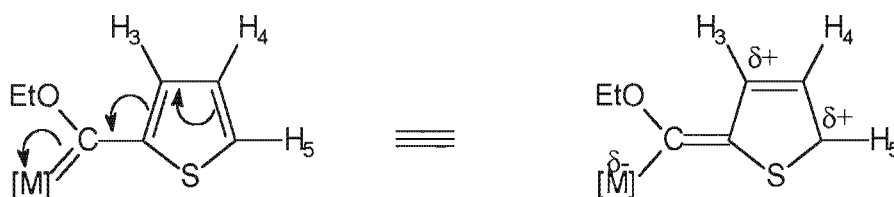


Figure 2.13 Draining of electrons in monocarbene complex

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.

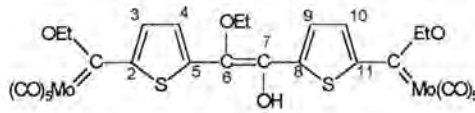
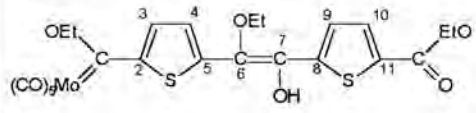
⁴² R.J. Abrahams, J. Fischer, P. Loftus, *Introduction to NMR Spectroscopy*, John Wiley and Sons, 1988.

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



Figure 2.14 Draining of electrons in biscarbene complexes

Table 2.2 ¹H 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.

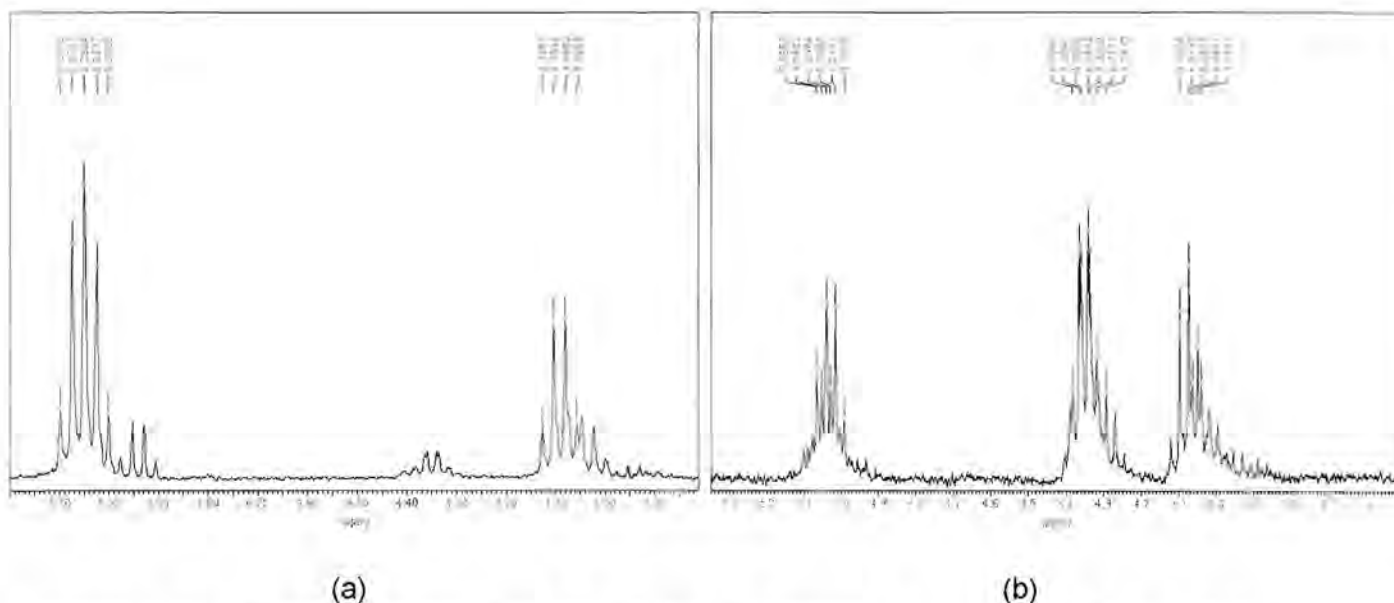


Figure 2.15 Methylene proton region on the ^1H NMR spectra of complexes (a) **4** and (b) **5**

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.

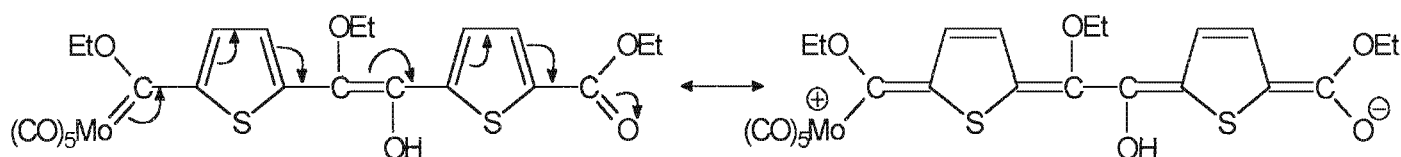


Figure 2.16 π -delocalization in complex **5**

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 (OCH₂CH₃); 15.5, 15.1, 14.9 (OCH₂CH₃).

Table 2.3 ¹³C 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
OCH ₂ CH ₃ -M	77.8	78.3	78.2
OCH ₂ CH ₃ -O	-	-	61.9
OCH ₂ CH ₃ -M	15.1	15.0	15.0
OCH ₂ CH ₃ -O	-	-	14.2
M(CO) ₅	206.1 (<i>cis</i>) 212.8 (<i>trans</i>)	205.6 (<i>cis</i>) 212.9 (<i>trans</i>)	205.7 (<i>cis</i>) 212.7 (<i>trans</i>)
C=O	-	-	206.1

Chemical shift values of carbene carbon atoms fluctuate in a very broad range starting at 200 ppm, for aminocarbene complexes⁴⁴, to 400 ppm, for some silicon complexes⁴⁵. 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-furyl²⁴. This decrease is in accordance with the

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.

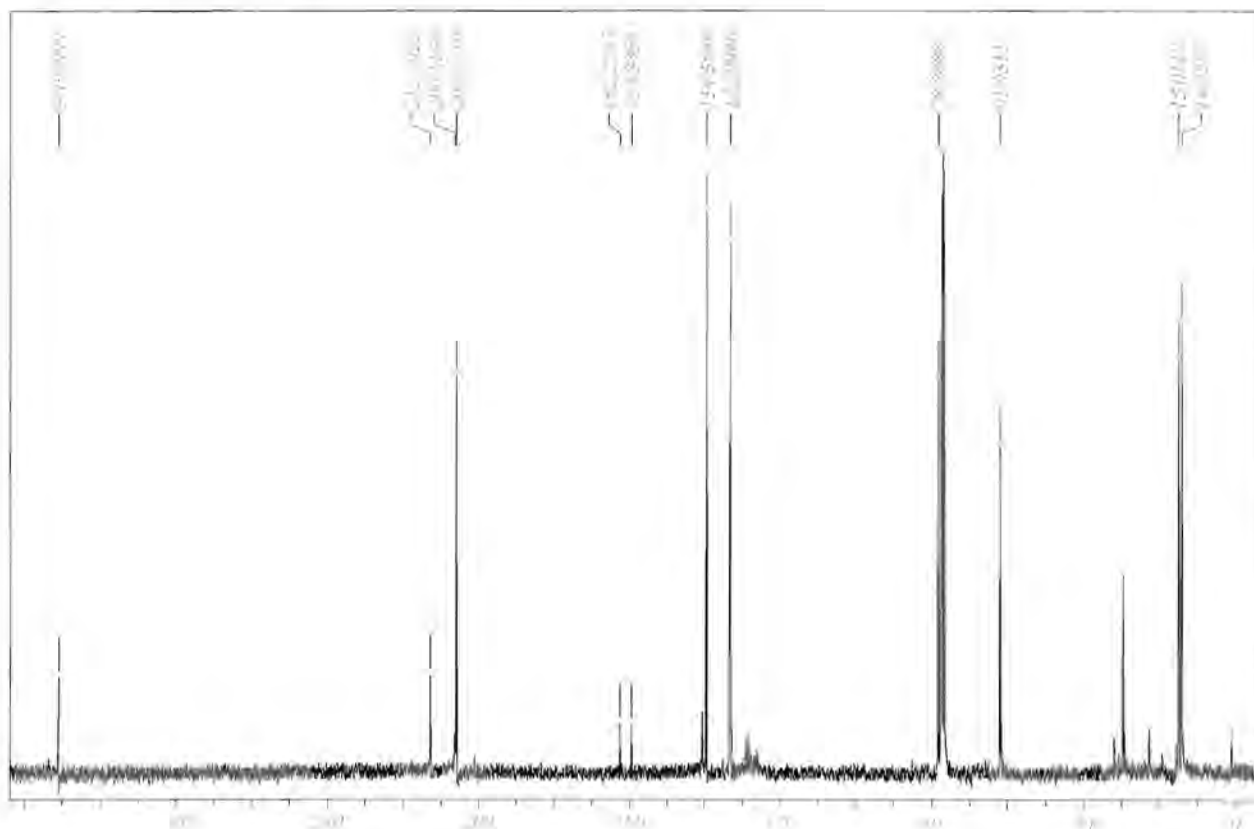


Figure 2.17 ^{13}C NMR spectrum of complex **3**

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 $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ 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) $M^+ - \text{CO}$; 321.9 (32) $M^+ - 2\text{CO}$; 293.8 (33) $M^+ - 3\text{CO}$; 265.8 (69) $M^+ - 4\text{CO}$; 237.9 (100) $M^+ - 5\text{CO}$; 208.9 (76) $M^+ - 5\text{CO} - \text{CH}_2\text{CH}_3$
2	669.3 (24) M^+ ; 613.2 (10) $M^+ - 2\text{CO}$; 585.0 (15) $M^+ - 3\text{CO}$; 557.2 (15) $M^+ - 4\text{CO}$; 501.2 (79) $M^+ - 6\text{CO}$; 473.1 (49) $M^+ - 7\text{CO}$; 445.2 (73) $M^+ - 8\text{CO}$; 417.2 (54) $M^+ - 9\text{CO}$; 389.0 (73) $M^+ - 10\text{CO}$; 360.0 (49) $M^+ - 10\text{CO} - \text{CH}_2\text{CH}_3$, 331.1 (54) $M^+ - 10\text{CO} - 2\text{CH}_2\text{CH}_3$; 303.0 (42) $M^+ - 11\text{CO} - 2\text{CH}_2\text{CH}_3$; 275.0 (100) $M^+ - 12\text{CO} - 2\text{CH}_2\text{CH}_3$
3	450.4 (4) M^+ ; 422.4 (5) $M^+ - \text{CO}$; 394.3 (6) $M^+ - 2\text{CO}$; 366.3 (5) $M^+ - 3\text{CO}$; 338.4 (12) $M^+ - 4\text{CO}$; 310.3 (43) $M^+ - 5\text{CO}$; 281.1 (27) $M^+ - 5\text{CO} - \text{CH}_2\text{CH}_3$; 253.1 (11) $M^+ - 6\text{CO} - \text{CH}_2\text{CH}_3$; 155.1 (54) $\text{C}_7\text{H}_7\text{O}_2\text{S}^+$; 139.1 (22) $\text{C}_7\text{H}_7\text{OS}^+$

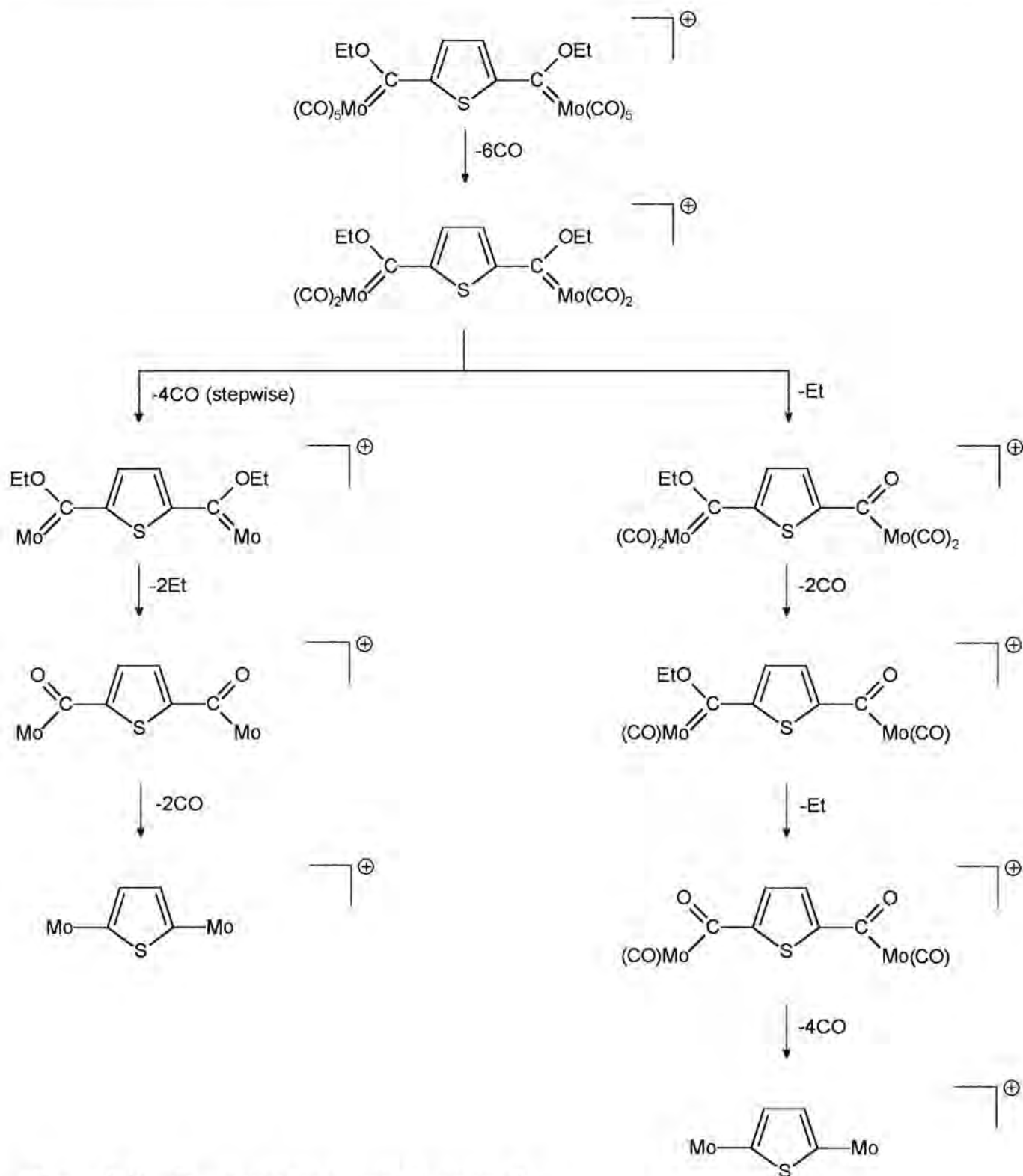


Figure 2.18 Fragmentation pattern of complex 2

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.

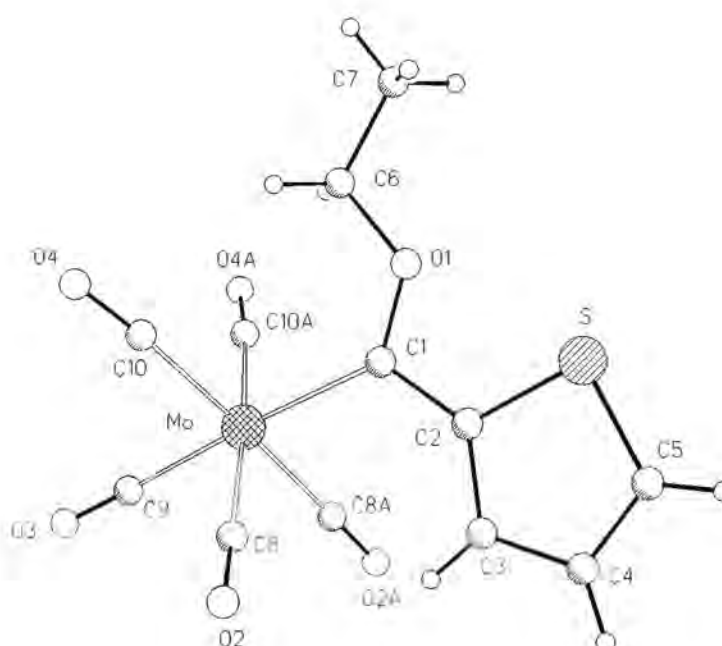


Figure 2.19 Ball-and-stick plot of complex **1**

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).

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 sp²-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 sp²-hybridized carbon atom but are typical for alkoxy carbene complexes. This deformation of the complex may be attributed to steric as well as electronic factors⁴⁷.

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

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)₅C(OEt)p-Tol] I the M-C(carbene) bond length was calculated as 2.189 Å⁴⁸ and for [(μ-O){Mo(CO)₅C(Ph)OZrCp₂}]₂ II the M-C(carbene) bond length was calculated as 2.195 Å⁴⁹.

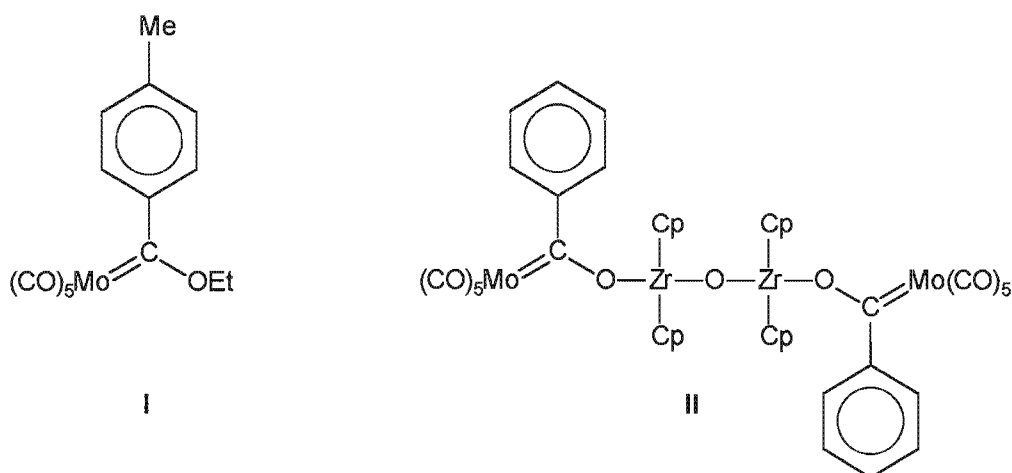


Figure 2.20 Structures of reference complexes I and II

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.

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 Fischer⁵¹. 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 $[W(=CC_6H_4Me-4)Cp(CO)_2]$ reacts with hydrogen chloride to form the acyl complex $[W(\eta^2-C(O)CH_2C_6H_4Me-4)Cp(CO)Cl_2]$ ⁵², the same reagent with $[W(=CNEt_2)Cp(CO)_2]$ affords the aminomethylene complex $[W(=CHNEt_2)CpCl(CO)_2]$ ⁵³. Fillipou⁵⁴ recently obtained similar results for chromium.

Unfortunately the aminolysis of alkoxy carbene 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

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 $\text{Cr}(\text{CO})_5^{2-}$ with tertiary amides in the presence of chlorotrimethylsilane. The reaction is believed to proceed via nucleophilic addition of $\text{Cr}(\text{CO})_5^{2-}$ 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.

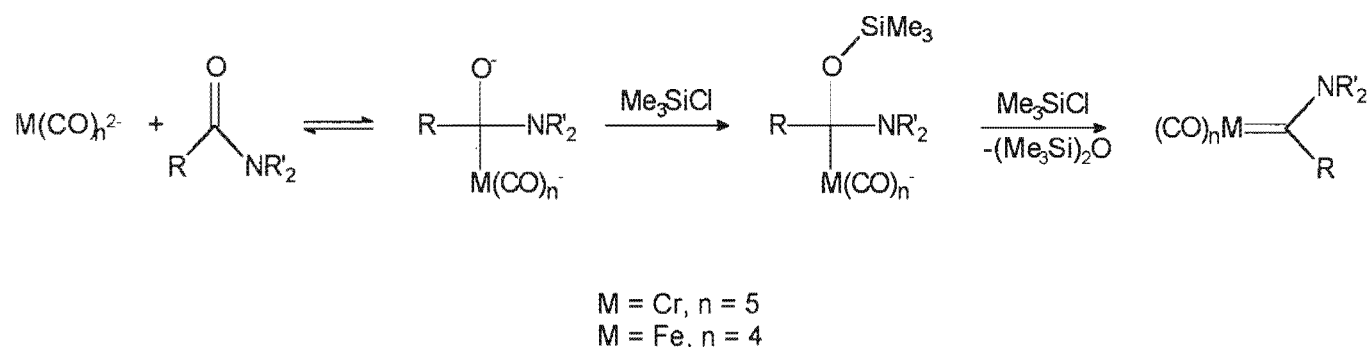


Figure 2.22 Synthesis of aminocarbene complexes

This method has recently been utilized to prepare iron aminocarbene complexes lacking α -hydrogens⁵⁶. This study has been extended to include the preparation of (μ -bis(aminocarbene)dimetal complexes of chromium and iron⁵⁷ 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 analogues⁵⁸.

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

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 aminoindenes⁵⁹, while N-acylation⁶⁰ 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 -lactams⁶¹ and α -amino acid esters⁶².

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 complexes⁶³.

The two amines used in the reactions were ammonia (NH₃) 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. Werner⁶⁴ 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.

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.

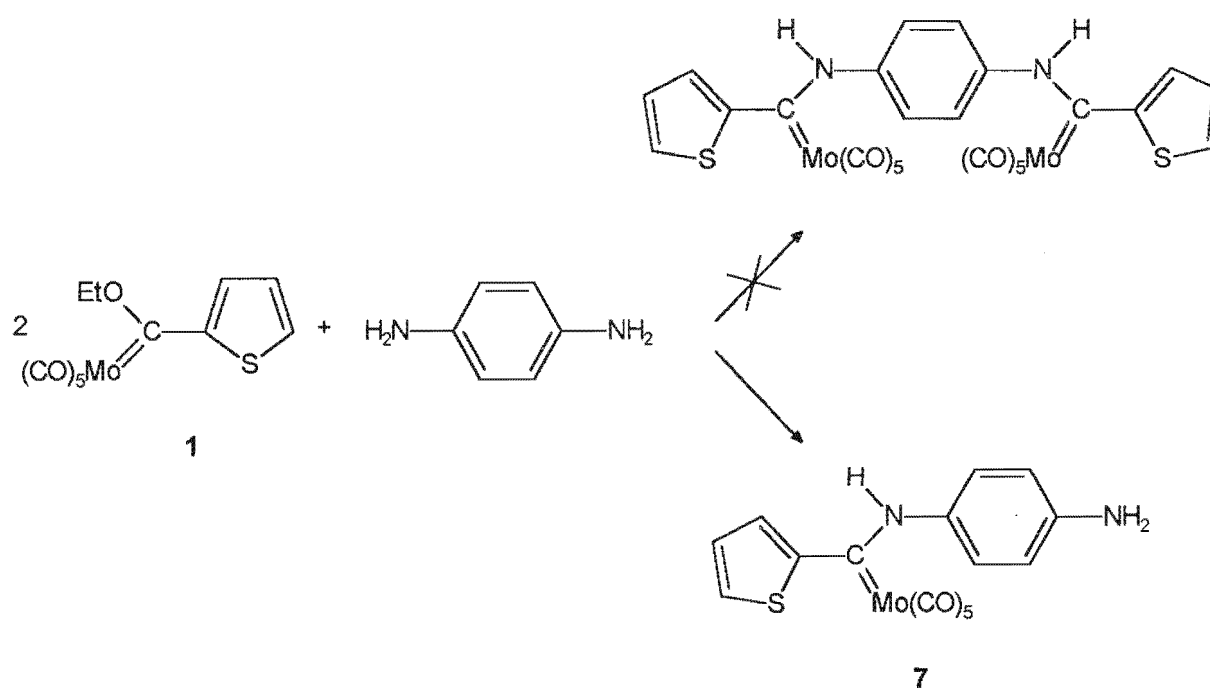


Figure 2.23 Reaction of **1** with 1,4-phenylene diamine

Similar results were obtained by Fischer *et al*⁶⁵. They reacted the carbene complex $[\text{Cr}(\text{CO})_5\text{C}(\text{OCH}_3)_2\text{CH}_3]$ 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

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 ethereal solutions.

4.2 Spectroscopic characterization of novel aminocarbene complexes

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

4.2.1 ^1H NMR spectroscopy

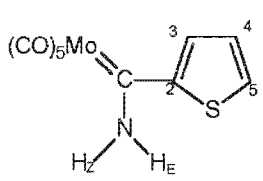
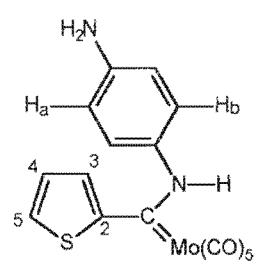
The proton NMR data of the two complexes are summarized in table 2.7. In the spectrum of **6** two different broad peaks are observed for the two NH_2 protons. The Z-proton is more downfield than the E-proton³⁴. The two NH_2 proton peaks appear downfield, which is consistent with the double bond character 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 bonds⁶⁷. However, the metal-carbon bond has less double bond character in complexes **6** and **7** because of competitive back-donation. Since $-\text{NH}_2$ is a much better π -donor than $-\text{OEt}$, 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 ^1H 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.

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 ^1H 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 NH₂ because of the presence of the electron donating NH₂ 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 ¹³C NMR spectroscopy

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

Table 2.8 ¹³C 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 (<i>cis</i>) 213.0 (<i>trans</i>)	206.6 (<i>cis</i>) 214.0 (<i>trans</i>)

On comparing the ¹³C 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 A₁⁽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

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).

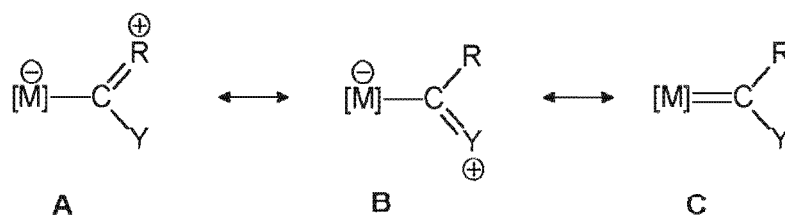


Figure 2.24 Limiting structures for carbene complexes

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) $M^+ - \text{CO}$; 292.9 (15) $M^+ - 2\text{CO}$; 264.9 (18) $M^+ - 3\text{CO}$; 237.0 (29) $M^+ - 4\text{CO}$; 209.0 (55) $M^+ - 5\text{CO}$; 111.0 (39) $\text{C}_5\text{H}_5\text{SN}^+$; 83.0 (6) $\text{C}_4\text{H}_5\text{S}^+$
7	440.0 (0.04) M^+ ; 412.2 (0.3) $M^+ - \text{CO}$; 356.1 (0.4) $M^+ - 3\text{CO}$; 328.1 (0.2) $M^+ - 4\text{CO}$; 300.0 (0.7) $M^+ - 5\text{CO}$; 202.1 (100) $\text{C}_{11}\text{H}_{10}\text{SN}_2^+$; 201.1 (61) $\text{C}_{11}\text{H}_9\text{SN}_2^+$; 108.1 (19) $\text{C}_5\text{H}_2\text{SN}^+$

3

Carbene complexes of Thienothiophene

1. General

The interest in thiophenes as molecules with potential electro-optical properties for use as molecular devices¹ was recently extended to thieno[3,2-*b*]thiophenes². 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 Friedmann³ 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 Horton⁴ 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 Jacobson⁵ prepared II in 1% yield by heating a mixture of citric acid and P₂S₃. Thieno[3,4-*b*]thiophene (III), an unstable compound at room temperature⁶, was prepared by Cava and Pollack⁷ 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 tetravalent sulfur. Derivatives of this isomer were synthesized by Cava

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 Pollack⁸ while the unsubstituted compound could not yet be isolated.

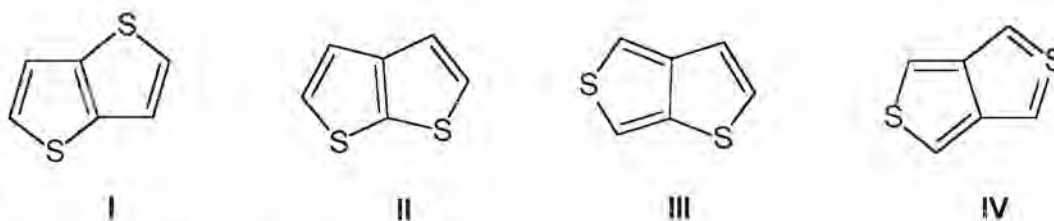


Figure 3.1 Isomers of thienothiophene

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 IV¹¹. 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°C¹². Electron donor substituents do not have the same effect, since 4,6-dimethylthieno[3,4-*b*]thiophene is an unstable compound¹³. From reactivity studies done on heterocycles it is clear that it is difficult to define quantitatively the reactivity of a given

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.

position¹⁴. This is due to the high polarisability of the molecule. Reactivity of the thienothiophenes was investigated by Archer and Taylor¹⁵. 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 planned¹⁶. 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 tellurium¹⁷ 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 fashion¹⁸. 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 photosolvolyis¹⁹. Guest ethanol molecules in the clathrate crystals reacted photochemically with the diol host compounds to cause photosubstitution

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.



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 $\text{Cr}(\text{CO})_3$ -moiety and the lone-pair of electrons on the S-atom to bond to a $\text{Cr}(\text{CO})_5$ -fragment²⁰. This utilizes the aromatic electrons of one ring while the other ring is left with a S-coordinated sulfur atom and an olefin.

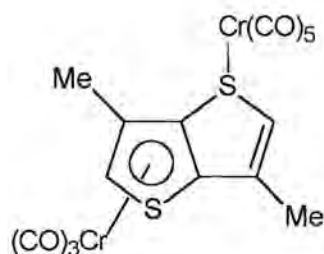


Figure 3.3 Binuclear σ, π -complex of 3,6-dimethylthieno[3,2-*b*]thiophene

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-workers²¹ and was prepared in 50% overall yield. The synthetic route is depicted in figure 3.4.

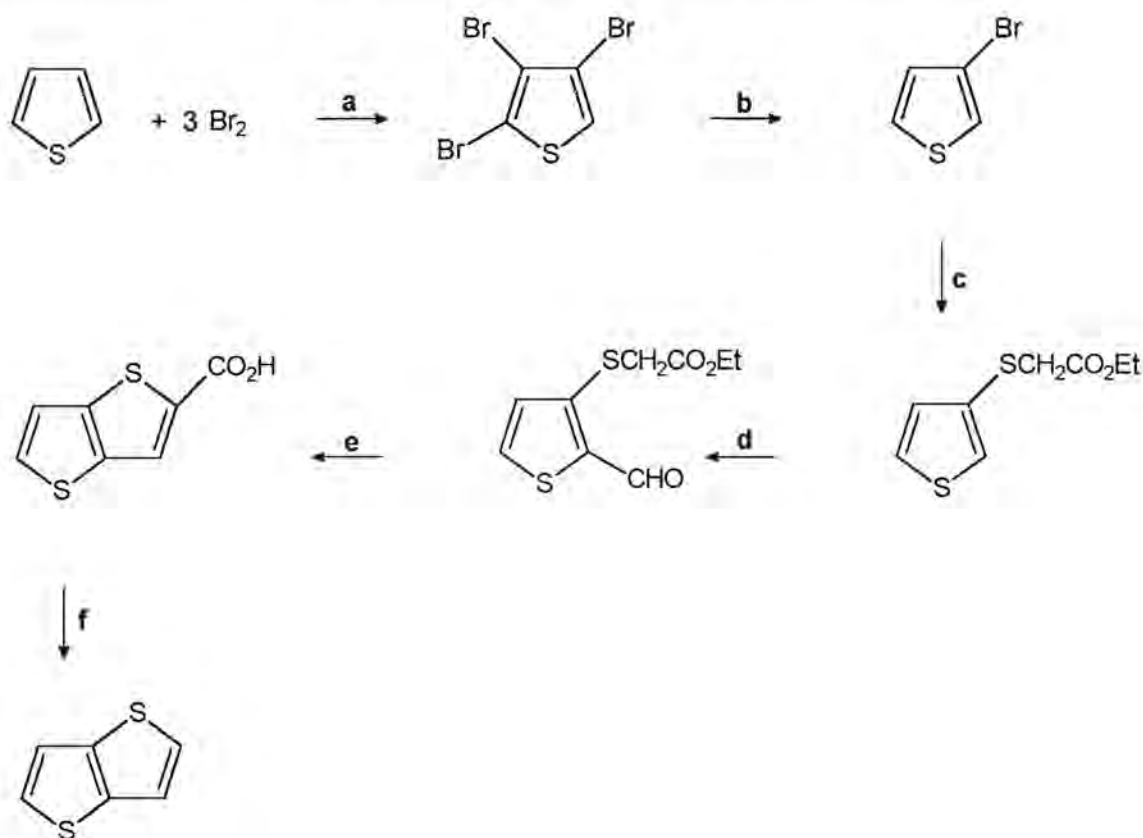


Figure 3.4 Reagents: (a) Et₂O, 48% HBr, 75°C; (b) Zn, CH₃COOH, reflux; (c) n-BuLi, -70°C, S₈, BrCH₂CO₂Et; (d) POCl₃, DMF; (e) NaOMe, MeOH, heat; (f) Quinoline, Cu powder, heat

Synthesis of 2,3,5-tribromothiophene was effected according to the method described by Brandsma and Verkruisje²² 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-

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

²² L. Brandsma, H.D. Verkruisje, *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*]thiophene²¹.

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'h²⁵ 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).

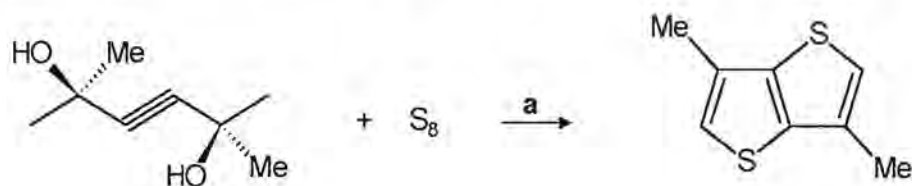


Figure 3.5 Reagents: (a) Benzene, 200°C, 12h

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.

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 Bugge²⁶. 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_3OBF_4 . Following this procedure, 3,6-dimethylthieno[3,2-*b*]thiophene was reacted with the metal complexes $\text{Cr}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{MnCp}(\text{CO})_3$ and $\text{Mn}(\text{MeCp})(\text{CO})_3$ 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.

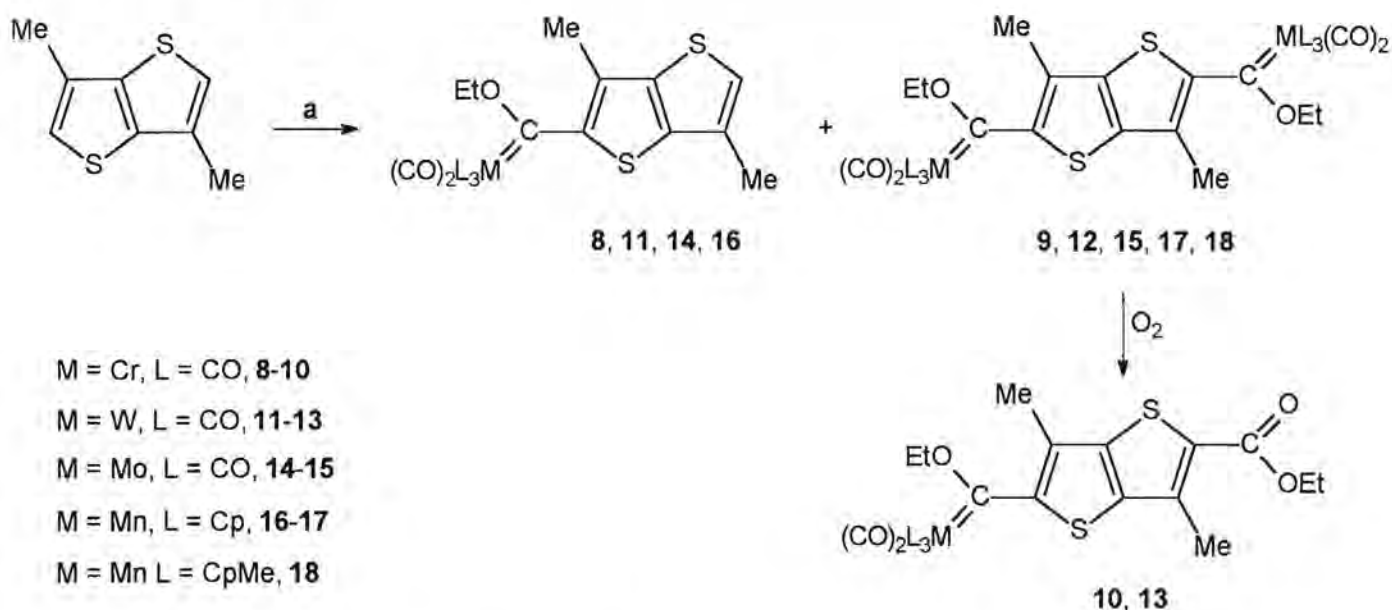


Figure 3.6 Synthesis of complexes **8-18**

Reagents: **a** (i) 2 eq. *n*-BuLi (ii) $\text{ML}_3(\text{CO})_3$ (iii) Et_3OBF_4

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

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 $[\text{MnCp}(\text{CO})_3]$ 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 $[\text{Cr}(\text{CO})_5\text{C}(\text{OEt})\text{Bu}]$ 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 $[\text{MnCp}(\text{CO})_3]$ 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 $[\text{Mn}(\text{MeCp})(\text{CO})_3]$. 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 $[\text{Cr}(\text{CO})_6]$ 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.

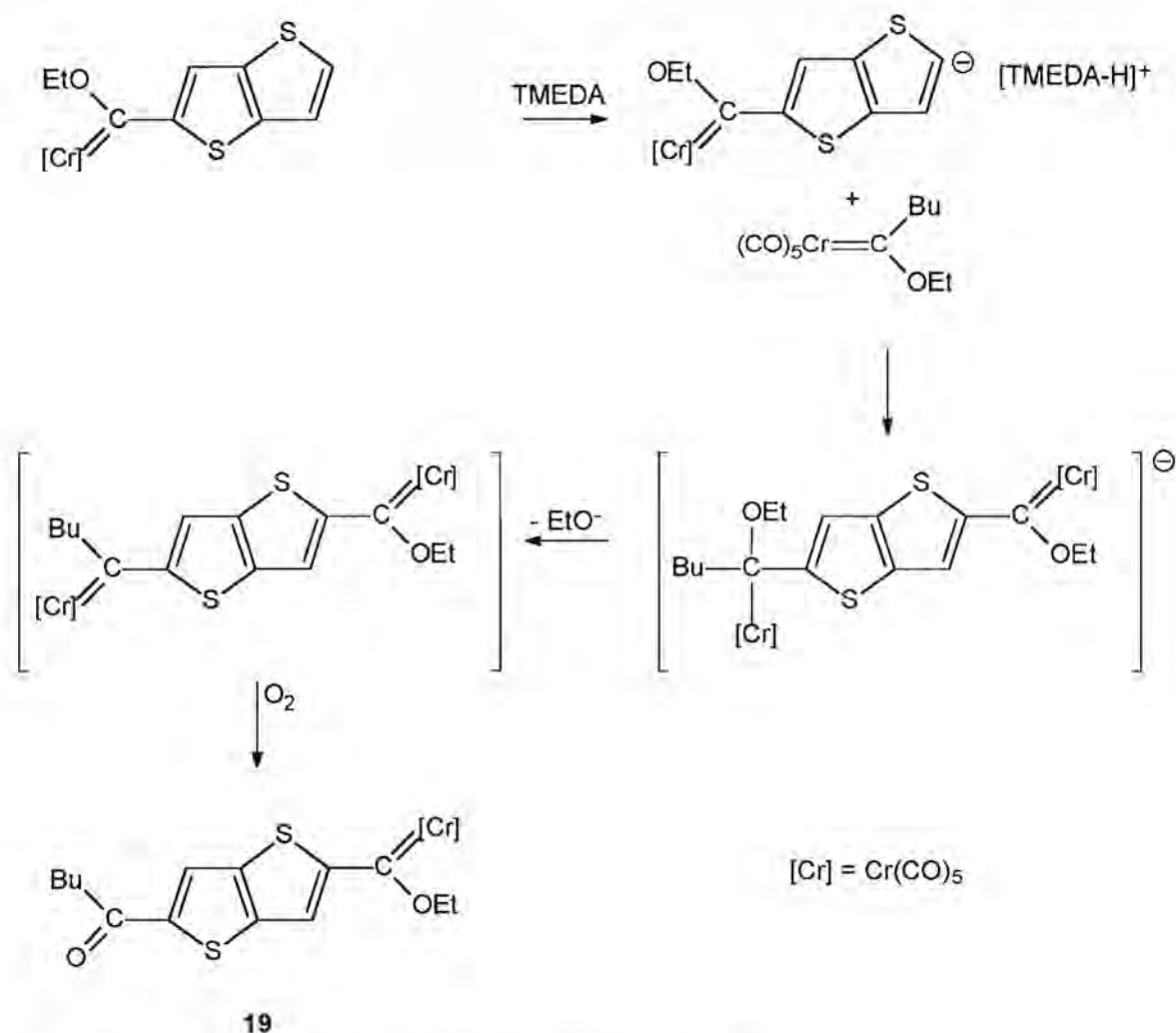


Figure 3.7 Proposed mechanism for the formation of **19**

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.

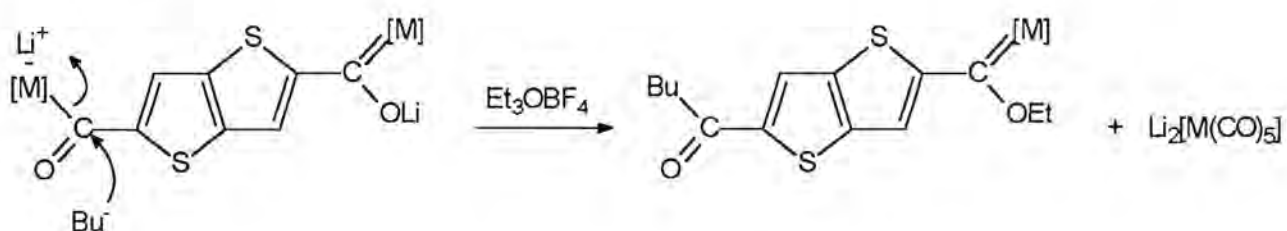


Figure 3.8 Formation of complex **19** via a bis-acylated intermediate

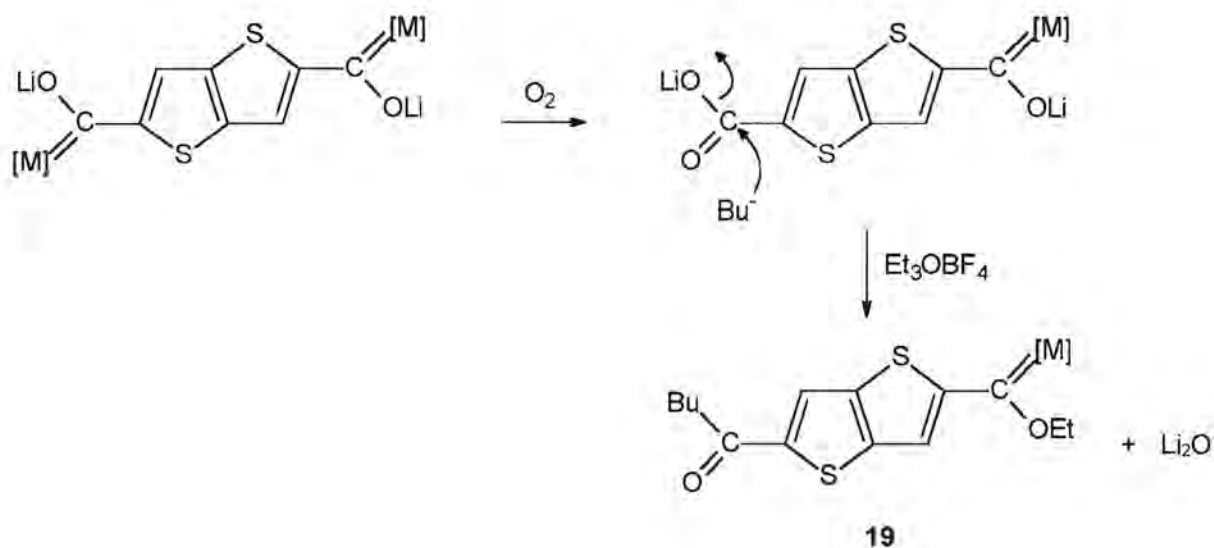


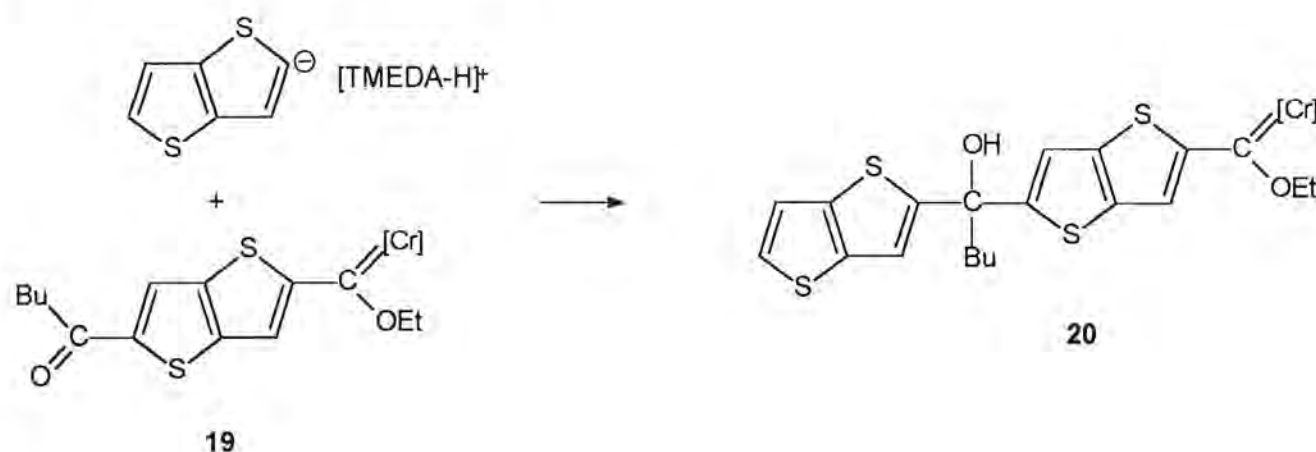
Figure 3.9 Formation of complex **19** via selective oxidation

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 $\text{Cr}(\text{CO})_6$ 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 $[\text{TMEDA-H}]^+$ species (figure 3.10).

Figure 3.10 Formation of complex **20**



3.1 Spectroscopic characterization of novel carbene complexes

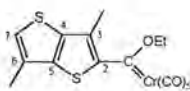
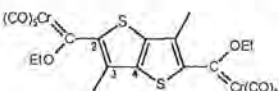
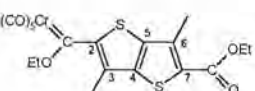
Complexes **8-20** were characterized spectroscopically using NMR and IR spectroscopy and mass spectrometry. The structures of compounds **8**, **9**, **11**, **12**, **16**, **18** and **19** were confirmed with X-ray crystallography.

3.1.1 ^1H NMR spectroscopy

All NMR spectra were recorded in deuterated chloroform as solvent unless otherwise specified. The ^1H 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 C6². The ¹H NMR spectrum of thieno[3,2-*b*]thiophene was recorded in CDCl₃ and two doublets at 7.55 ppm (H2 and H7) and 7.24 ppm (H3 and H6) were observed.

Table 3.1 ¹H 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 $J_{\text{H-H}}^4$ 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, $J = 7.0$).

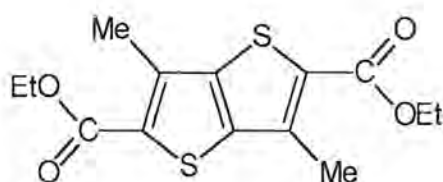
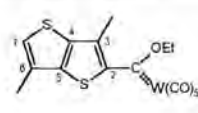
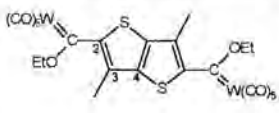
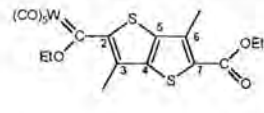


Figure 3.11 The bis(ethylester) of 3,6-dimethylthieno[3,2-*b*]thiophene

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 ¹H 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	-	-	-	-
OCH ₂ CH ₃ -M	5.02 (q)	7.1	5.04 (q)	7.1	5.03 (q)	7.2
OCH ₂ CH ₃ -O	-	-	-	-	4.36 (q)	7.2
OCH ₂ CH ₃ -M	1.69 (t)	7.1	1.72 (t)	7.1	1.70 (t)	7.2
OCH ₂ 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.

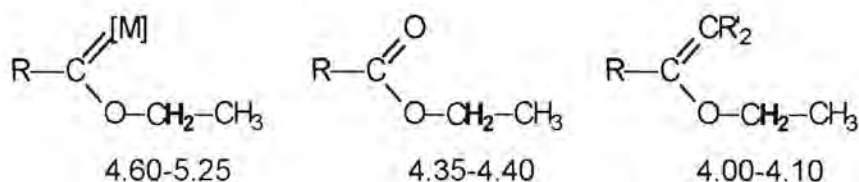


Figure 3.12 Characteristic positions of the methylene protons (ppm) on ¹H NMR spectra

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 ^1H NMR data of complexes **14** and **15**

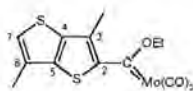
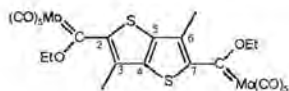
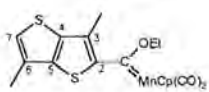
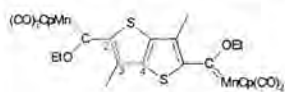
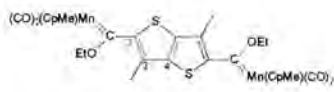
Proton	Chemical shifts (δ , ppm) and Coupling constants (J, Hz)			
	 14		 15	
	δ	J	δ	J
H7	7.21 (s)	-	-	-
$\text{OCH}_2\text{CH}_3\text{-M}$	5.08 (q)	7.0	5.13 (q)	7.1
$\text{OCH}_2\text{CH}_3\text{-M}$	1.69 (t)	7.1	1.73 (t)	7.1
Me3	2.50 (s)	-	2.52 (s)	-
Me6	2.41 (s)	-	2.52 (s)	-

Table 3.4 ^1H 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)	-	-	-	-	-
$\text{OCH}_2\text{CH}_3\text{-M}$	4.67 (q)	6.9	4.67 (q)	7.0	4.74 (q)	6.7
$\text{OCH}_2\text{CH}_3\text{-M}$	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 ligand²⁷. 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

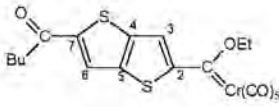
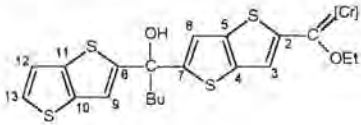
On the spectrum of **18**, two singlet resonances are observed for the Cp protons while only one singlet is found on the spectra of **16** and **17**, since the Cp group of **18** is substituted with a methyl group on one position and thus gives rise to two non-equivalent groups of two protons. The electron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

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

almost identical.

Table 3.5 ^1H 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
$\text{OCH}_2\text{CH}_3\text{-M}$	5.21 (q)	7.0	5.14 (q)	7.1
$\text{OCH}_2\text{CH}_3\text{-M}$	1.69 (t)	7.0	1.65 (t)	7.1
$\text{C(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	2.93 (t)	7.3	2.91 (t)	7.3
$\text{C(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1.74 (t)	7.5	1.75 (t)	7.3
$\text{C(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1.42 (t)	7.5	1.43 (t)	7.3
$\text{C(O)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	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*]selenophene²⁸.

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
$\text{OCH}_2\text{CH}_3\text{-M}$	76.4	76.6	76.4
$\text{OCH}_2\text{CH}_3\text{-O}$	-	-	61.4
$\text{OCH}_2\text{CH}_3\text{-M}$	15.6	15.5	15.6
$\text{OCH}_2\text{CH}_3\text{-O}$	-	-	14.4
Me3	18.6	17.6	17.7
Me6	14.7	17.6	15.0
$\text{M}(\text{CO})_5$	216.8 (<i>cis</i>) 222.8 (<i>trans</i>)	216.3 (<i>cis</i>) 223.6 (<i>trans</i>)	216.7 (<i>cis</i>) 223.3 (<i>trans</i>)

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 ^1H 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 $\text{M}(\text{CO})_5$ peaks on the different spectra, *i.e.* the $\text{Cr}(\text{CO})_5$ chemical shift values are at the highest chemical shift values and the $\text{W}(\text{CO})_5$ 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 $\text{W} > \text{Mo} > \text{Cr}$. 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 $\text{M}(\text{CO})_5$ 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.

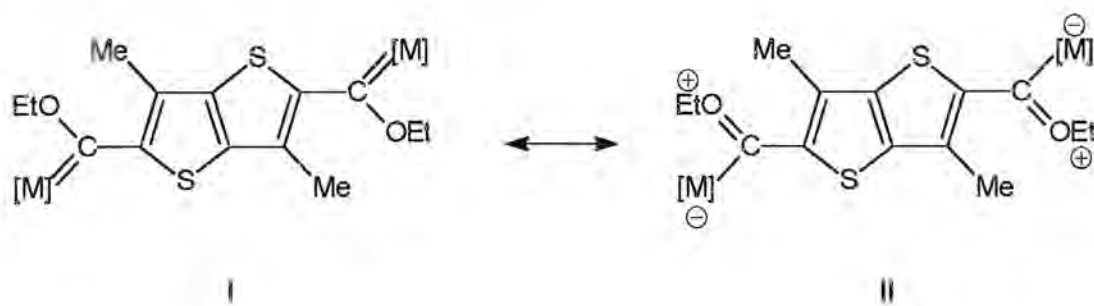


Figure 3.13 Resonance structures I and II

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
$\text{OCH}_2\text{CH}_3\text{-M}$	79.0	79.6	79.5	78.2	78.8
$\text{OCH}_2\text{CH}_3\text{-O}$	-	-	61.5	-	-
$\text{OCH}_2\text{CH}_3\text{-M}$	15.4	15.3	15.2	15.5	15.5
$\text{OCH}_2\text{CH}_3\text{-O}$	-	-	14.2	-	-
Me3	18.9	18.4	18.4	18.8	18.2
Me6	14.6	18.4	14.8	14.7	18.2
$\text{M}(\text{CO})_5$	197.8 (<i>cis</i>) 201.9 (<i>trans</i>)	197.3 (<i>cis</i>) 202.2 (<i>trans</i>)	197.8 (<i>cis</i>) 202.3 (<i>trans</i>)	206.1 (<i>cis</i>) 212.6 (<i>trans</i>)	205.7 (<i>cis</i>) 212.7 (<i>trans</i>)

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
$\text{OCH}_2\text{CH}_3\text{-M}$	72.3	72.7	72.9
$\text{OCH}_2\text{CH}_3\text{-M}$	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
$\text{M}(\text{CO})_2$	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 $\text{M}(\text{CO})_2$ peak is observed downfield from the values obtained for $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}, \text{Mo}$) 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
$\text{OCH}_2\text{CH}_3\text{-M}$	75.7	75.7
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	43.0	38.7
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	25.5	27.0
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	22.8	22.4
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	13.9	13.8
$\text{OCH}_2\text{CH}_3\text{-M}$	15.1	15.1
$\text{M}(\text{CO})_5$	217.5 (<i>cis</i>) 223.5 (<i>trans</i>)	217.5 (<i>cis</i>) 223.7 (<i>trans</i>)
$\text{C}=\text{O}$	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

^aFirst 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	
$\text{Cr}(\text{CO})_5\text{C}(\text{OEt})\text{T}$	2063	1987	1961	1950	29
$\text{Cr}(\text{CO})_5\text{C}(\text{OEt})\text{Ph}$	2062 ^a	1963	1954	1942	31
$\text{W}(\text{CO})_5\text{C}(\text{OEt})\text{T}$	2070	1977	1952	1944	30
$\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}$	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 $[\text{Cr}(\text{CO})_5\text{C}(\text{OEt})\text{T}]^{29}$ 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 $[\text{W}(\text{CO})_5\text{C}(\text{OEt})\text{T}]^{30}$ 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

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, $[\text{Cr}(\text{CO})_5\text{C}(\text{OEt})\text{Ph}]^{31}$ and $[\text{W}(\text{CO})_5\text{C}(\text{OMe})\text{Ph}]^{32}$, 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 thienothieryl substituent.

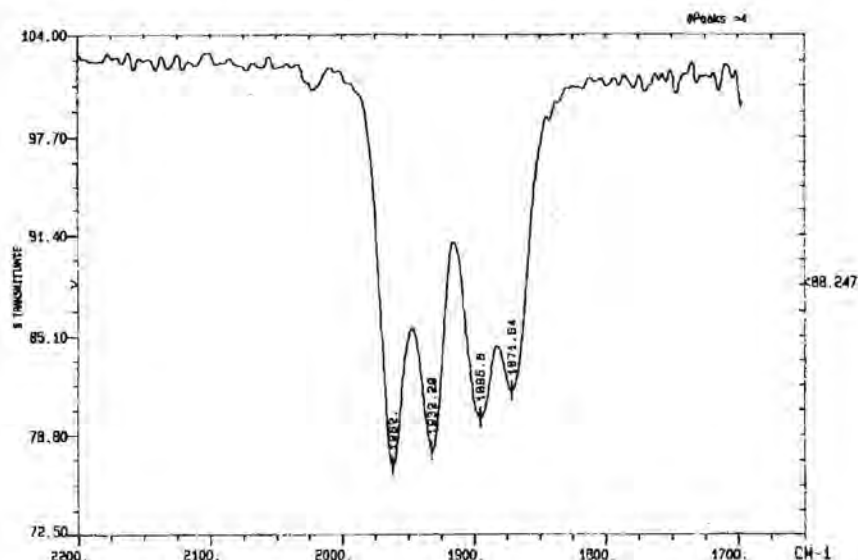


Figure 3.15 Carbonyl region on the infrared spectrum of complex 17

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

^aValues 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

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 $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OMe})\text{Ph}\}]^{33}$, $[\text{MnCp}(\text{CO})_2\{\text{C}(\text{OEt})\text{Ph}\}]^{34}$, $[\text{Cr}(\eta^5\text{-Ar})(\text{CO})_2\{\text{C}(\text{OMe})\text{Ph}\}]^{35}$ and $[\text{MnCp}(\text{CO})_2\{\eta^2\text{-C}_2\text{H}_4\}]^{36}$.

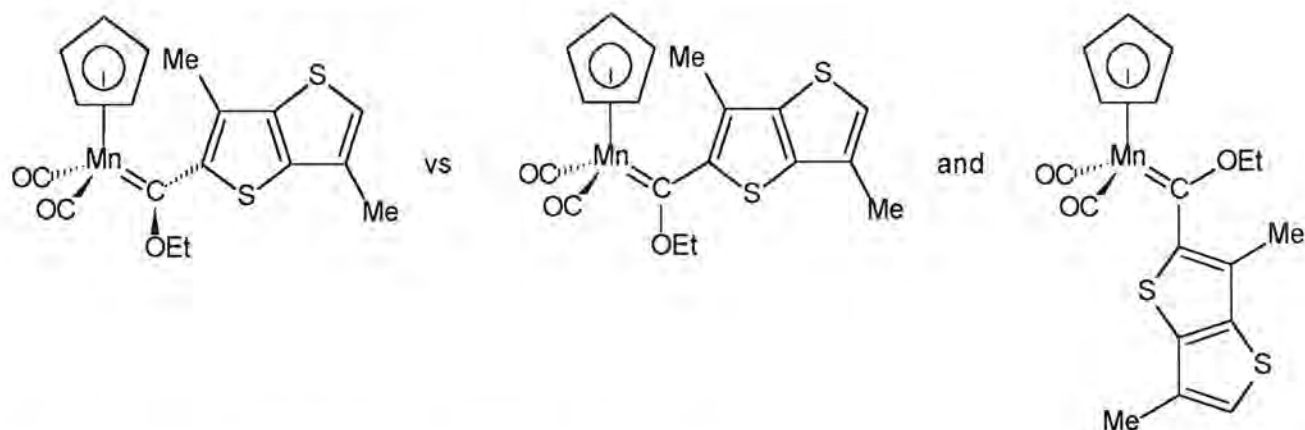


Figure 3.16 Conformational isomers of complex 16

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

^aValues recorded in dichloromethane

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 ₂ CH ₃ ; 286.9 (100) M ⁺ - 3CO - CH ₂ CH ₃ ; 221.9 (37) M ⁺ - 3CO - CH ₂ CH ₃ - Cp; 167.0 (34) C ₈ H ₇ S 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 ₂ CH ₃ ; 463.5 (66) M ⁺ - 5CO - CH ₂ CH ₃ ; 434.4 (15) M ⁺ - 5CO - 2CH ₂ CH ₃ ; 406.3 (44) M ⁺ - 6CO - 2CH ₂ CH ₃ ; 341.2 (13) M ⁺ - 6CO - 2CH ₂ CH ₃ - Cp; 287.2 (15) M ⁺ - 6CO - 2CH ₂ CH ₃ - Cp - Mn; 222.1 (5) M ⁺ - 6CO - 2CH ₂ CH ₃ - 2Cp - Mn; 167.1 (9) C ₈ H ₇ S ₂ ⁺
18	660.5 (7) M ⁺ ; 604.4 (73) M ⁺ - 2CO; 548.3 (100) M ⁺ - 4CO; 519.2 (11) M ⁺ - 4CO - CH ₂ CH ₃ ; 491.2 (36) M ⁺ - 5CO - CH ₂ CH ₃ ; 462.2 (6) M ⁺ - 5CO - 2CH ₂ CH ₃ ; 434.5 (25) M ⁺ - 6CO - 2CH ₂ CH 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 ₂ CH ₃ ; 275.1 (7) M ⁺ - 6CO - CH ₂ CH 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**

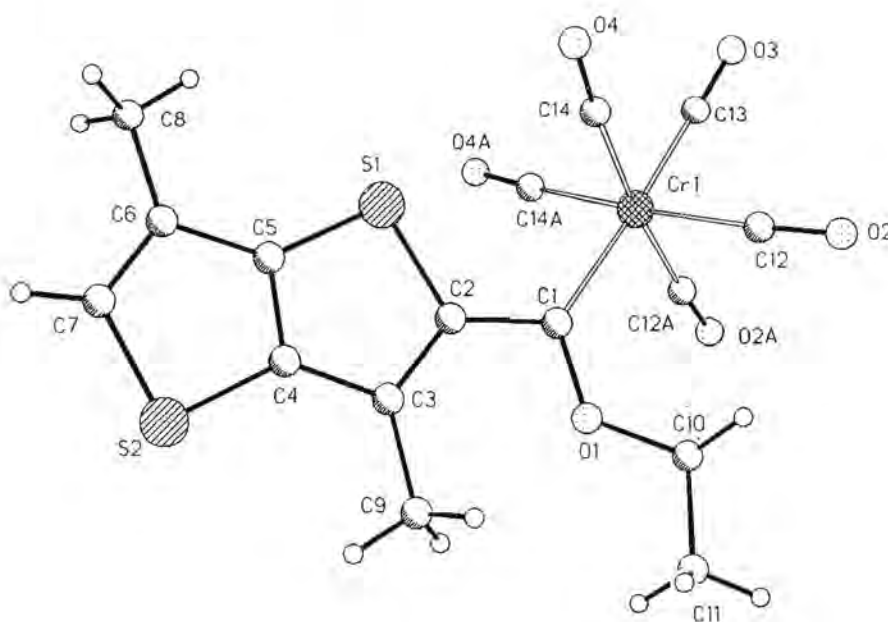


Figure 3.17 Ball-and-stick plot of complex **8**

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°.

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 $94.5(1)^\circ$ 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 metals³⁸.

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

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.

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(sp²)-C(sp²) single bond (1.46 Å) and a C(sp²)-C(sp²) 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) ₅ C(OMe)Ph	2.04(3)	1.33(2)	1.46	1.47(4)	38(a)
Cr(CO) ₅ C(OEt)Me	2.05(1)	1.31(1)	-	1.51(1)	40
Cr(CO) ₅ C(OH)Ph	2.05(1)	1.32(1)	-	-	41
Cr(CO) ₅ C[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

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

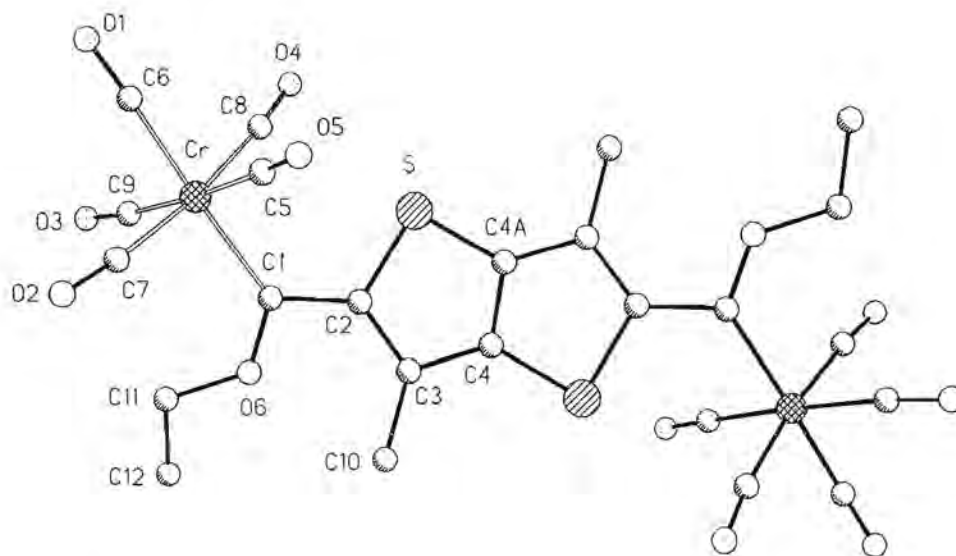


Figure 3.18 Ball-and-stick plot of complex 9

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 $\text{Cr}(\text{CO})_5$ 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 spacer²⁷. 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 atoms⁴⁴. The *cis*-carbonyl

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(sp²) single bonds and C(sp²) 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

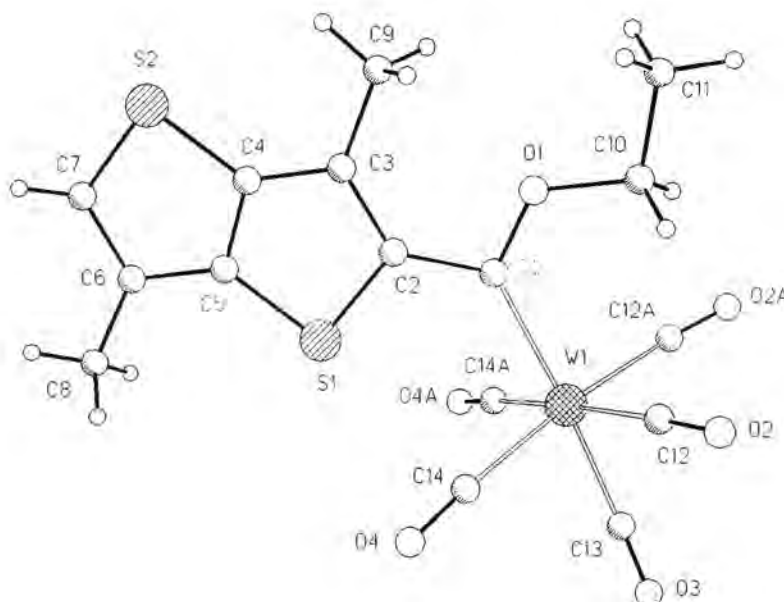


Figure 3.19 Ball-and-stick plot of complex 11

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

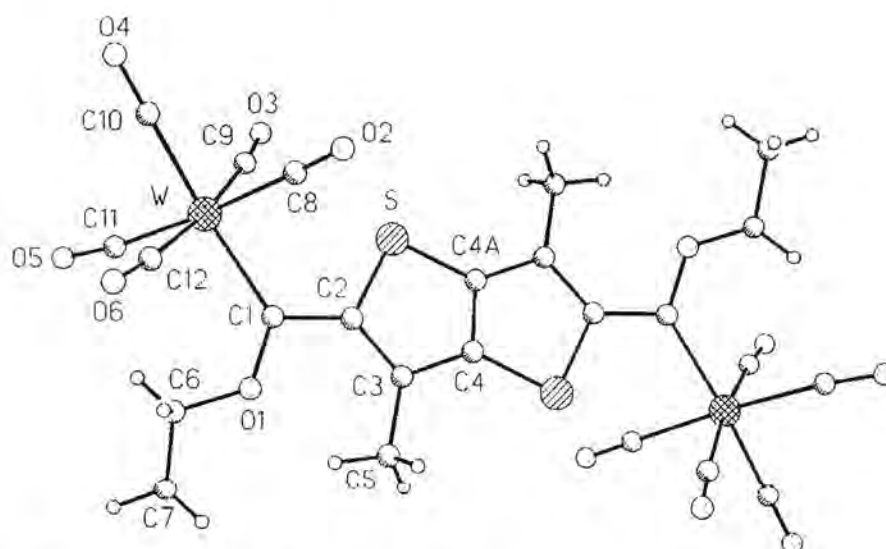


Figure 3.20 Ball-and-stick plot of complex 12

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) ₅ C(OMe)Ph	2.05	1.31	1.43	1.49	45
W(CO) ₅ C(Ph)Ph	2.15(1)	-	-	1.45(2), 1.51(2)	46
[(W(CO) ₅ C(OEt)) ₂ T]	2.15(1)	1.33(1)	1.47(1)	1.46(1)	47
[(W(CO) ₅ C(OMe)) ₂ (anthracendiyl)]	2.16(1)	1.31(1)	-	1.50(1)	48

3.1.5.5 Crystal structure of complex 16

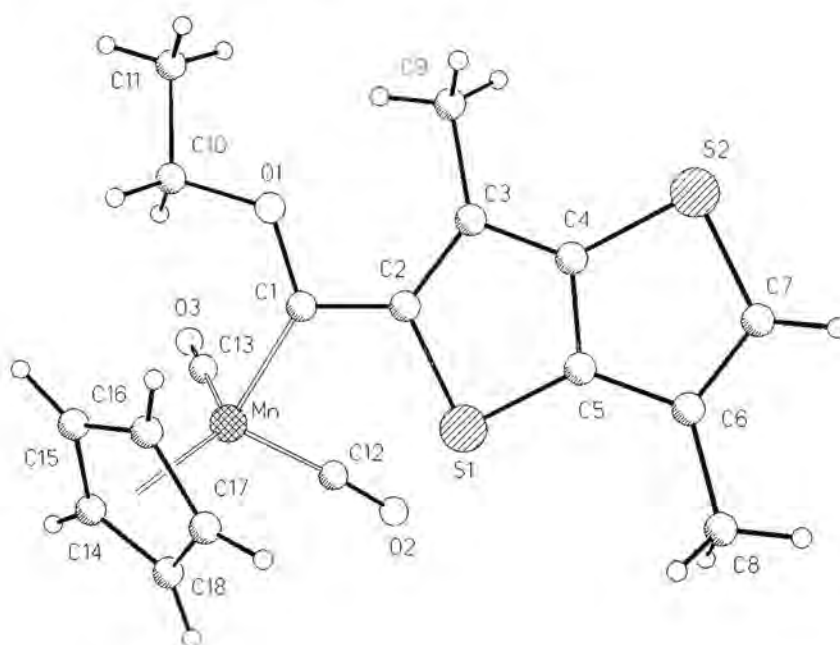


Figure 3.21 Ball-and-stick plot of complex 16

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

⁴⁶ C.P. Casey, T.J. Burkhardt, C.A. Bunnell, 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 $129.6(5)^\circ$ and $112.3(4)^\circ$, 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 thiophene²⁷ 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

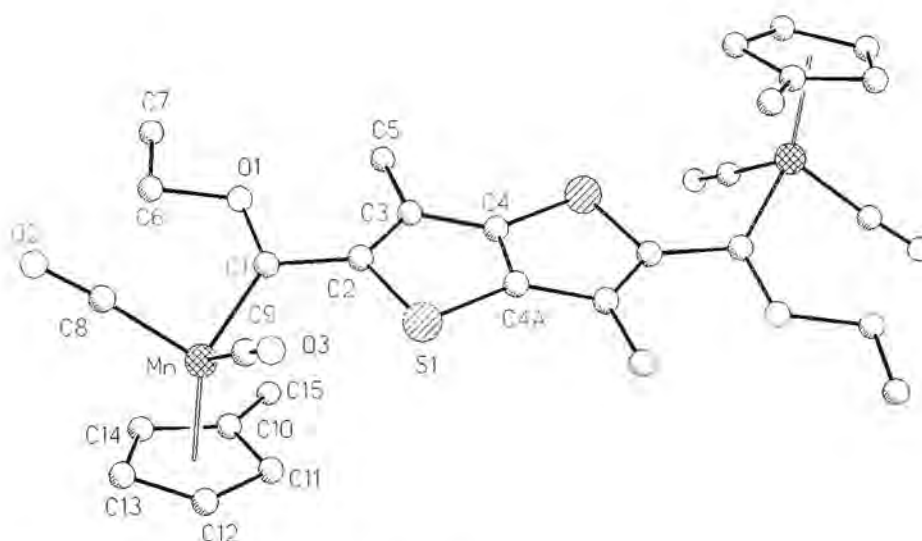


Figure 3.22 Ball-and-stick plot of complex 18

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 $\text{MnCp}(\text{CO})_2$ fragment. Although this conformation is electronically the more unfavourable^{36c}, 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).

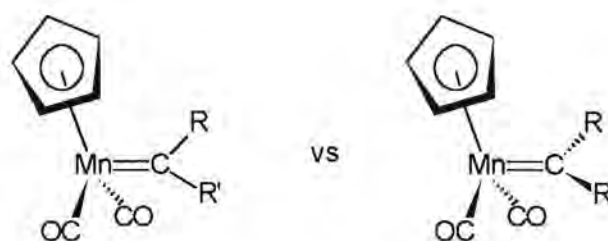


Figure 3.23 Conformations of $\text{MnCp}(\text{CO})_2$ carbene complexes

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) ₂ C(OMe)menthyl	1.89(2)	1.33(2)	1.53(2)	49
MnCp(CO) ₂ C(OEt)Ph	1.87(1)	1.36(2)	1.54(2)	38c
MnCp(CO) ₂ C(Ph)Ph	1.89(2)	-	-	38c
[μ-O{MnCp(CO) ₂ CPh} ₂]	1.85(2), 1.88(5)	-	-	50

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

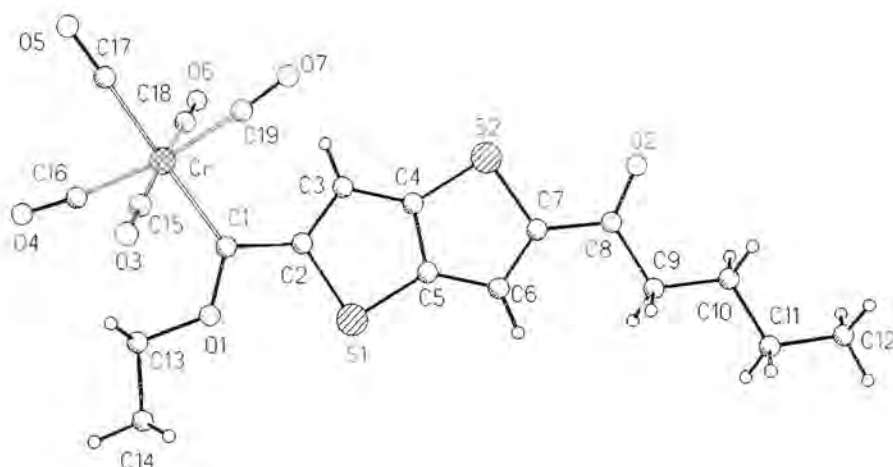


Figure 3.24 Ball-and-stick plot of complex 19

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 complexes²⁷.