THIOPHENE BIMETALLIC CARBENE COMPLEXES

by

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“It was the best of times, it was the worst of times;
it was the age of wisdom, it was the age of foolishness;
it was the epoch of belief, it was the epoch of incredulity;
it was the season of Light, it was the season of Darkness;
we had everything before us, we had nothing before us;
we were all going direct to Heaven, we were all going direct the other way.”

A Tale of Two Cities, Charles Dickens

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Acknowledgments

I would hereby like to make use of the opportunity to express my sincerest gratitude to the following people who played an important role throughout the entire course of this study:

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Prof R Vleggaar for his continued assistance, interest and support during the absence of my supervisor.

Last but not in the least all my friends and family for the moral support and for bearing with me throughout the tough times; for this, I thank you.

Yvette
August 1996

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Summary

The syntheses of σ,σ-bimetallic biscarbene- and σ,π-bimetallic monocarbene complexes, as well as the reactivity of the former, were investigated. The metal carbonyls $Cr(CO)_6$, $W(CO)_6$, $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$ and $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ were reacted with dilithiated thiophene to synthesize the novel σ,σ-bimetallic biscarbene complexes: $(CO)_2L_3M\{C(OEt)C_4H_2SC(OEt)\}ML_3(CO)_2$, where M = Cr, W, Mn; L = CO; $L_3 = \eta^5\text{-}C_5H_4Me$, $\eta^5\text{-}C_5H_5$. With dilithiated 2,2'-methylene dithiophene; $(CO)_2L_3M\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}ML_3(CO)_2$, were obtained. These complexes were fully characterized and formulations were confirmed by crystal structure determinations for the former. Spectroscopic data indicate the thiophene rings to act as sources of electron density which stabilize the electrophilic carbene carbons.

Treatment of monolithiated $(\eta^5\text{-thiophene})Cr(CO)_3$ with hexacarbonyls afforded in addition to the expected σ,π-bimetallic monocarbene complexes, $(\eta^1\text{:}\eta^5\text{-}C_4H_3SC(OEt)M(CO)_5)Cr(CO)_3$, the complexes $(\eta^1\text{:}\eta^5\text{-}C_4H_3SC(O(CH_2)_4OEt)M(CO)_5)Cr(CO)_3$ and $M\{C(O(CH_2)_4OEt)C_4H_3S\}(CO)_5$, where M = Cr, W. The formation of the latter two types is most unexpected and indicates that π-coordination of $Cr(CO)_3$ to thiophene plays an important electronic and steric role which leads to an unique pathway in which a THF-ring is opened and incorporated into the carbene functionality. The σ,π-bimetallic monocarbene complex of $(\eta^6\text{-benzo[b]thiophene})Cr(CO)_3$ was synthesized to enable a comparison with the former. Monolithiation of $(\eta^6\text{-benzo[b]thiophene})Cr(CO)_3$ occured in the 2-position of the thiophene ring and $(\eta^1\text{:}\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$ was afforded in a quantitative yield, thereby proving that π-coordination to the benzene ring is stronger and more distant from the σ-bonded metal fragment. Related THF-incorporated complexes were not formed in this reaction.

The stability of the thienylene biscarbene complexes at various temperatures, in different solvents and under two different inert atmospheres, led to the characterization of the following classes of complexes: **I**: $(CO)_2L_3M\{C(OEt)C_4H_2SC(O)OEt\}$; **II**: $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2SC(O)OEt\}(CO)_5$; **III**: $(CO)_2L_3M\{C(OEt)C_4H_2SC(S)OEt\}$; **IV**: $M\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)OEt\}_2C_4HS\}L_3(CO)_2$; **V**: $Cr\{C(OEt)C_4H_2SC(O)C(O)C_4H_2SC(O)OEt\}(CO)_5$. **I** was obtained from the decomposition in acetone under nitrogen and was presumably formed in the reaction between the carbene moiety and oxygen which had diffused into the system, as no proof of an oxygen transfer from acetone could be found. **II** was isolated from the analogous decomposition under argon, thus indicating that the complete elimination of oxygen from a better equiped system would lead to the formation of new and different types of oligomeric products. **III** was afforded by the reaction in CS_2, with the exception of **IV**, which was yielded, for the chromium biscarbene in CS_2, as well as, hexane. **V** was isolated from the decomposition in hexane. The result of these studies

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indicates that as opposed to monocarbene complexes, biscarbene complexes displayed enhanced reactivity and the reaction conditions control conversion.

The reaction of the thienylene chromium and tungsten biscarbenes with hex-3-yne yielded analogous monocarbene products, $M\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$, lacking a π-coordinated $Cr(CO)_3$. This is a surprising result for tungsten as the expected product should be the cyclopentathienyl complex. The result suggests an alternative mechanism for the Dötz reaction and a possible reaction route is proposed. The reaction of biphenyl acetylene, however, afforded the expected cyclopentathienyl complex, $M\{C(OEt)CCHCC(Ph)C(Ph)CH(OEt)CS\}(CO)_5$, in two isomeric forms. The analogous chromium reaction gave the related cyclopentathienyl product, as well as, the expected benzothienyl complex, as two isomers, with $Cr(CO)_3$ π-coordinated to either the benzene- or thiophene ring , and the end product lacking the $Cr(CO)_3$-fragment. The isolation of the alkyne inserted intermediate, $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)C(Ph)$-$C(Ph)\}Cr(CO)_5$, emphasises that the stabilization of intermediates by coordination to more than one metal fragment, highlights the value of bimetallic systems in studying reaction mechanisms.

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Opsomming

Die sintese van σ,σ-bimetaal biskarbeen- en σ,π-bimetaal monokarbeen komplekse, asook die reaktiwiteit van eersgenoemde is ondersoek. Die metaalkarboniele $Cr(CO)_6$, $W(CO)_6$, $Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$ en $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ is met dubbel gelitieerde tiofeen gereageer om die nuwe σ,σ-bimetaal biskarbeen komplekse: $(CO)_2L_3M\{C(OEt)C_4H_2SC(OEt)\}ML_3(CO)_2$ te sintetiseer, met M = Cr, W, Mn; L = CO; $L_3 = \eta^5\text{-}C_5H_4Me$, $\eta^5\text{-}C_5H_5$. Met dubbel gelitieerde 2,2'-metileen ditiofeen is $(CO)_2L_3M\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}ML_3(CO)_2$ verkry. Hierdie komplekse is ten volle gekarakteriseer en formulerings van eersgenoemde is deur kristalstruktuur bepalings gestaaf. Spektroskopiese data dui daarop dat die tiofeen ringe as bronne van elektrondigtheid optree, wat die elektrofiele karbeen koolstowwe stabiliseer.

Behandeling van mongelitieerde $(\eta^5\text{-tiofeen})Cr(CO)_3$ met heksakarboniele het nie net die verwagte σ,π-monokarbeen komplekse, maar ook die komplekse $(\eta^1{:}\eta^5\text{-}C_4H_3SC(O(CH_2)_4OEt)M(CO)_5)Cr(CO)_3$ en $M\{C(OCH_2)_4OEtC_4H_3S\}(CO)_5$, met M = Cr, W, gelewer. Die vorming van die laaste twee tipes is onverwags en toon dat π-koördinasie van $Cr(CO)_3$ aan tiofeen 'n belangrike elektroniese en steriese rol speel wat tot 'n unieke roete lei, waartydens 'n THF-ring oopgemaak word en in die karbeen funksionaliteit ingebou word. Die $(\eta^6\text{-benso[b]tiofeen})Cr(CO)_3$ σ,π-bimetaal monokarbeen kompleks is gesintetiseer met die doel om met eersgenoemde te vergelyk. Monolitiëring van $(\eta^6\text{-benso[b]tiofeen})Cr(CO)_3$ het in die 2-posisie van die tiofeenring plaasgevind en $(\eta^1{:}\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$ is met 'n kwantitatiewe opbrengs gevorm, daardeur is getoon dat π-koördinasie aan die benseen sterker en verder verwyder is, vanaf die σ-gebonde metaalfragment. Verwante THF-ingevoegde komplekse is nie tydens hierdie reaksie gevorm nie.

Die stabiliteit van die tiënileen biskarbeen komplekse by verskillende temperature, in verskillende oplosmiddels en onder twee verskillende inerte atmosfere, het tot die karakterisering van die volgende klasse verbindings gelei: **I**: $(CO)_2L_3M\{C(OEt)C_4H_2SC(O)OEt\}$; **II**: $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2S\text{-}C(O)OEt\}(CO)_5$; **III**: $(CO)_2L_3M\{C(OEt)C_4H_2SC(S)OEt\}$; **IV**: $M\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)OEt\}_2C_4H_2]\}\text{-}L_3(CO)_2$; **V**: $Cr\{C(OEt)C_4H_2SC(O)C(O)C_4H_2SC(O)OEt\}(CO)_5$. **I** is verkry vanaf die ontbinding in asetoon onder stikstof en is waarskynlik gevorm tydens die reaksie tussen die karbeen funksionaliteit en suurstof wat in die sisteem ingediffundeer het, aangesien geen bewyse van 'n suurstofoordrag vanaf asetoon gevind kon word nie. **II** is geïsoleer vanaf die analoë ontbinding onder argon, wat dus toon dat die algehele eliminasie van suurstof vanuit 'n beter toegeruste sisteem tot die vorming van nuwe en verskillende oligomeriese produkte. **III** is gelewer tydens die reaksie in CS_2, met die uitsondering van **IV**, wat gevorm is vir die chroom biskarbeen in CS_2, asook in heksaan. **V** is geïsoleer vanaf die ontbinding in heksaan. Die resultaat van hierdie studie toon dat in teenstelling met die monkarbeen komplekse, biskarbeen komplekse verhoogde reaktiwi-

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teite toon en dat die reaksiekondisies omsettings beheer.

Die reaksie van die tiënileen chroom en wolfram biskarbene met heks-3-yn het analoë monokarbeen produkte, $M\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$, waarvan die π-gekoördineerde $Cr(CO)_3$ ontbreek, gelewer. Hierdie is 'n verbasende resultaat vir wolfram, aangesien die verwagte produk die siklopentatiëniel kompleks sou moes wees. Die resultaat stel 'n alternatiewe meganisme vir die Dötz reaksie voor en 'n moontlike roete word voorgestel. Die reaksie met bifenielasetileen, gee egter die verwagte siklopentatiëniel kompleks, $M\{C(OEt)CCHCC(Ph)C(Ph)CH(OEt)CS\}(CO)_5$, as twee isomeriese vorms. Die analoë chroom reaksie lewer die verwante siklopentatiëniel produk, sowel as die verwagte bensotiëniel kompleks, as twee isomere, met $Cr(CO)_3$ π-gekoördineerd aan hetsy die benseen- of tiofeenring, en die eindproduk sonder die $Cr(CO)_3$-fragment. Die isolering van die alkyningevoegde intermediêr, $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)C(Ph)C(Ph)\}Cr(CO)_5$, beklemtoon dat die stabilisering van intermediêre deur koördinering aan meer as een metaalfragment, beklemtoon die waarde van bimetaal sisteme tydens die bestudering van reaksiemeganismes.

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List of Abbreviations

Ar	:	Aryl substituent
br	:	broad
Bu	:	butyl
BT	:	Benzothienyl / Benzothiophene
Bz	:	Benzene
C(Ph)(H)NNC(Ph)H	:	Benzalazine
Cp*	:	η^5-C_5Me_5
Cp	:	η^5-C_5H_5
d	:	doublet
DBT	:	Dibenzothiophene
DCM	:	Dichloromethane
dq	:	doublet of quartets
dt	:	doublet of triplets
DPPE	:	*N, N'*-Diphenyl-1,4-phenylenediamine
DME	:	1,2-Dimethoxyethane
DMSO	:	Dimethylsulphoxide
EPR	:	Electron Paramagnetic Resonance Spectroscopy
Et	:	ethyl
η^n	:	number, n, of ring atoms bonded to the metal in a π-ring fashion
Fc	:	Ferrocenyl, (η^5-C_5H_5)Fe(η^5-C_5H_4)
HMPT	:	Hexamethylphosphoric triamide
IR	:	Infrared Spectroscopy
m	:	multiplet
MDT	:	2, 2'-methylene dithiophene
Me	:	methyl
MeCp	:	η^5-$C_5H_4CH_3$
MS	:	Mass spectra
NMR	:	Nuclear Magnetic Resonance Spectroscopy
n.o.	:	not observed
Pet. ether	:	Petroleum ether 40–60 °C
Ph	:	phenyl

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ppm : parts per million

q : quartet

R_{fn} : n, number of fluoro substituents

s : singlet

sh : shoulder

Th : Thienyl / Thiophene

THF : Tetrahydrofuran

TLC : Thin layer chromatography

TMS-Cl : Trimethylchlorosilane

TMEDA : Tetramethyl ethylene diamine

t : triplet

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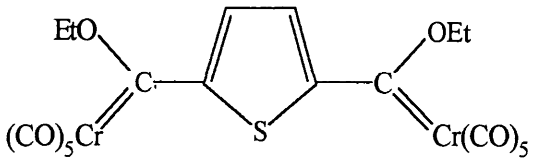
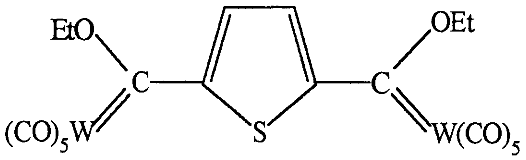
List of Compounds

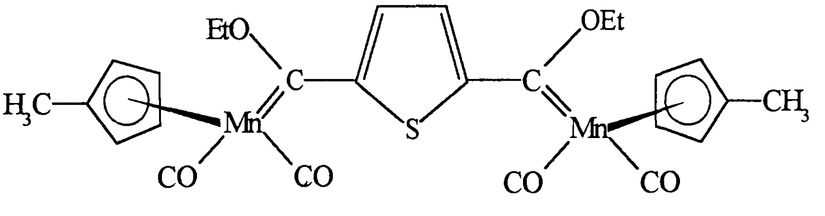
1: $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$



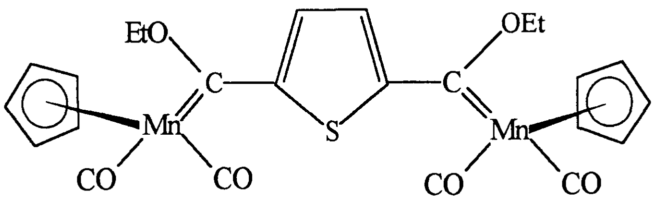
2: $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$



3: $(\eta^5\text{-}C_5H_4CH_3)(CO)_2Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(CO)_2(\eta^5\text{-}C_5H_4CH_3)$



4: $(\eta^5\text{-}C_5H_5)(CO)_2Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(CO)_2(\eta^5\text{-}C_5H_5)$



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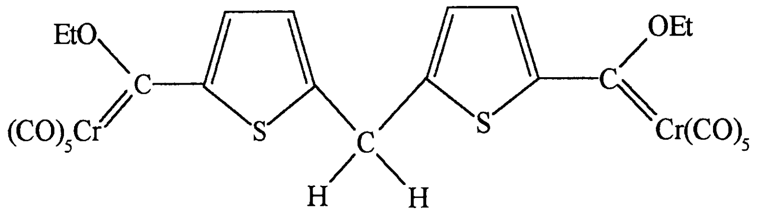
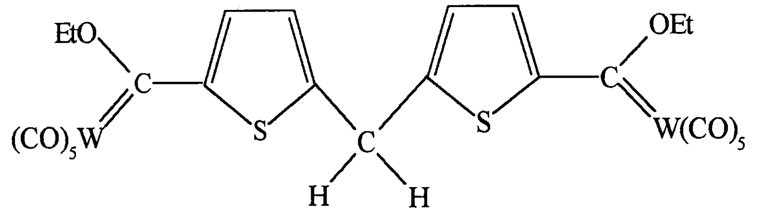
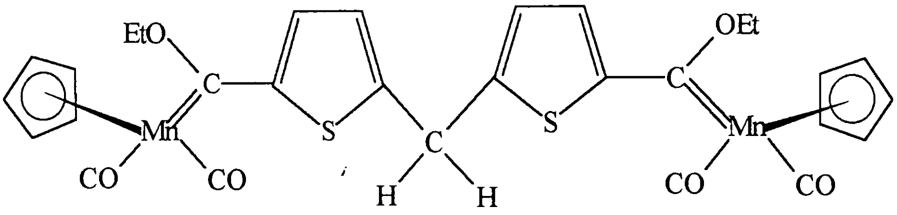
5: $(CO)_5Cr\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}Cr(CO)_5$



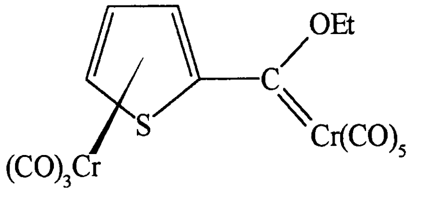
6: $(CO)_5W\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}W(CO)_5$



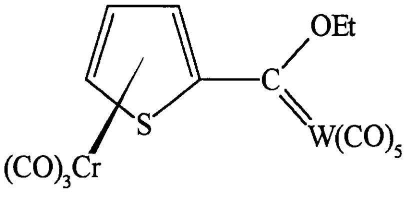
7: $(\eta^5\text{-}C_5H_5)(CO)_2Mn\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}Mn(CO)_2(\eta^5\text{-}C_5H_5)$



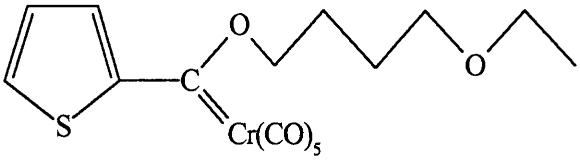
8: $(\eta^1:\eta^5\text{-}C_4H_3SC(OEt)Cr(CO)_5)Cr(CO)_3$



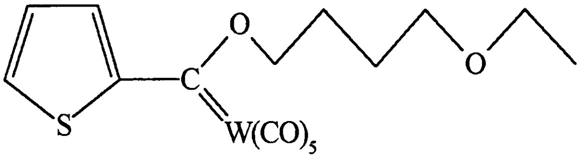
9: $(\eta^1:\eta^5\text{-}C_4H_3SC(OEt)W(CO)_5)Cr(CO)_3$



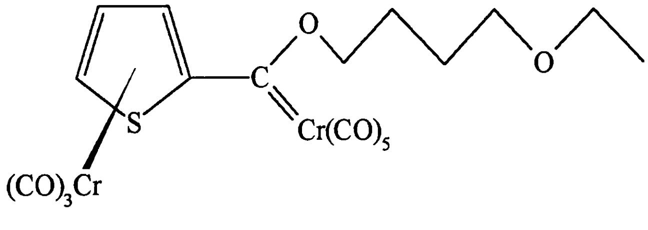
10: $Cr\{C(O(CH_2)_4OEt)C_4H_3S\}(CO)_5$



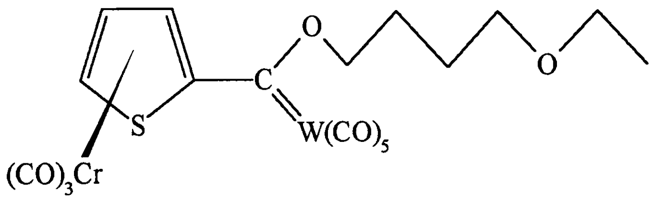
11: $W\{C(O(CH_2)_4OEt)C_4H_3S\}(CO)_5$



12: $(\eta^1:\eta^5\text{-}C_4H_3SC(O(CH_2)_4OEt)Cr(CO)_5)Cr(CO)_3$



13: $(\eta^1:\eta^5\text{-}C_4H_3SC(O(CH_2)_4OEt)W(CO)_5)Cr(CO)_3$



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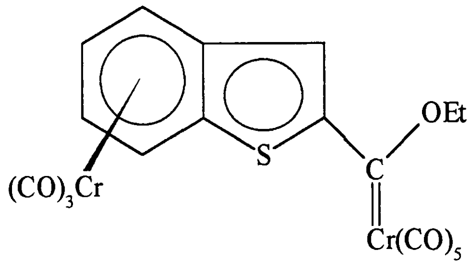
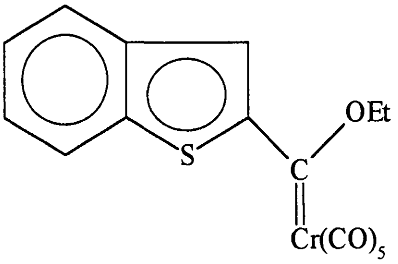
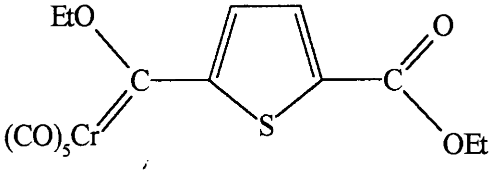
14: $(\eta^1:\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$



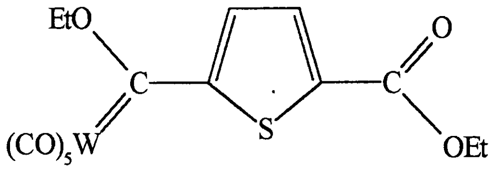
15: $Cr\{C(OEt)C_8H_5S\}(CO)_5$



16: $Cr\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$



17: $W\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$



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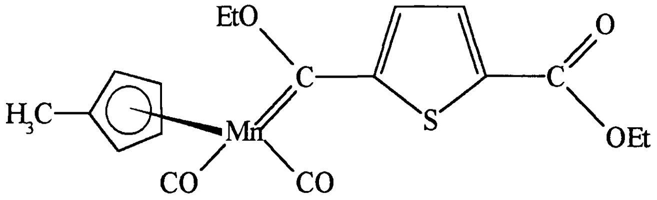
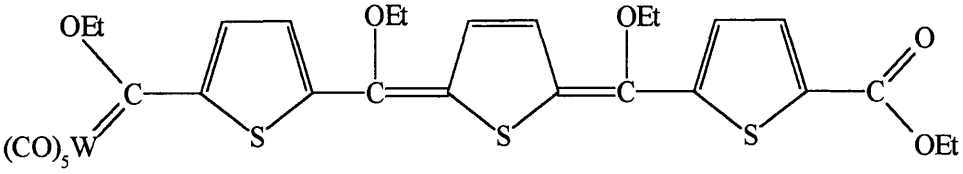
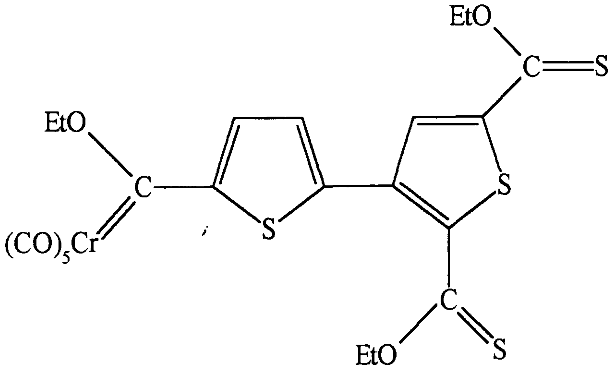
18: $Mn\{C(OEt)C_4H_2SC(O)OEt\}(\eta^5\text{-}C_5H_4CH_3)(CO)_2$



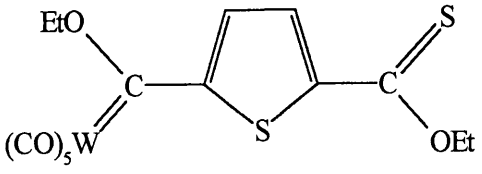
19: $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2SC(O)OEt\}(CO)_5$



20: $Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)OEt\}_2C_4HS]\}(CO)_5$



21: $W\{C(OEt)C_4H_2SC(S)OEt\}(CO)_5$



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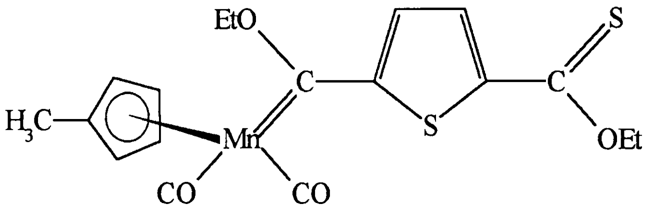
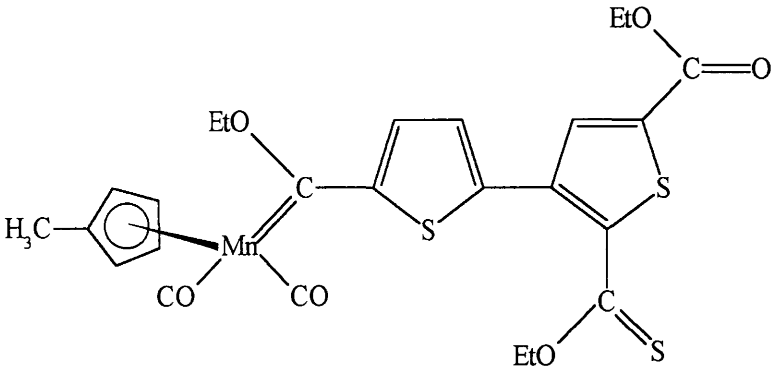
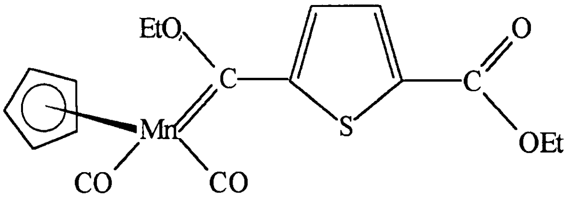
22: $Mn\{C(OEt)C_4H_2SC(S)OEt\}(\eta^5\text{-}C_5H_4CH_3)(CO)_2$



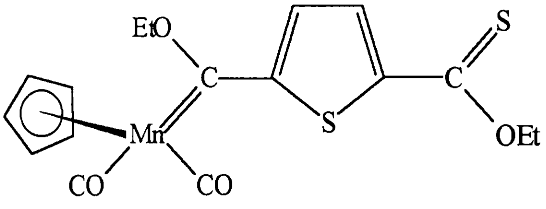
23: $Mn\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)OEt\}\{C(O)OEt\}C_4HS)]\}(\eta^5\text{-}C_5H_4CH_3)(CO)_2$



24: $Mn\{C(OEt)C_4H_2SC(O)OEt\}(\eta^5\text{-}C_5H_5)(CO)_2$



25: $Mn\{C(OEt)C_4H_2SC(S)OEt\}(\eta^5\text{-}C_5H_5)(CO)_2$



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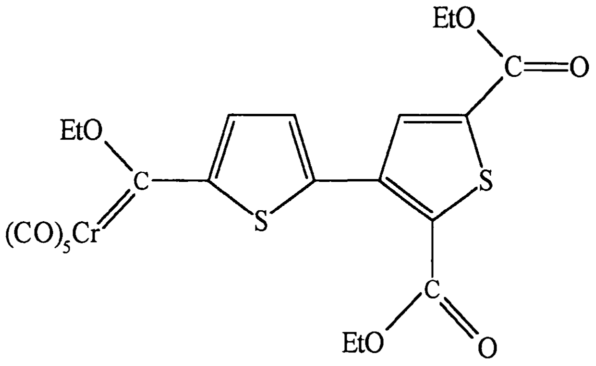
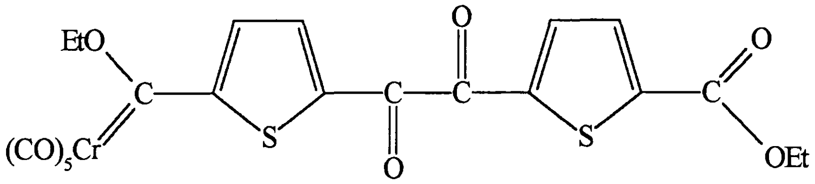
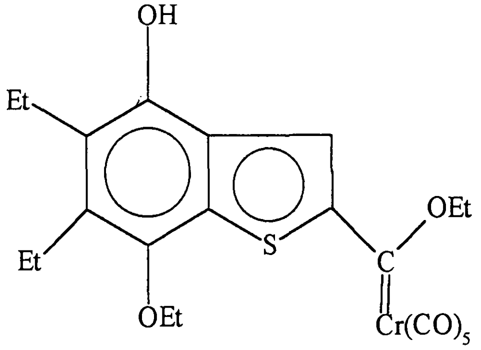
26: $\mathrm{Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(O)OEt\}_2C_4HS]\}(CO)_5}$



27: $\mathrm{Cr\{C(OEt)C_4H_2SC(O)C(O)C_4H_2SC(O)OEt\}(CO)_5}$



28: $\mathrm{Cr\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5}$



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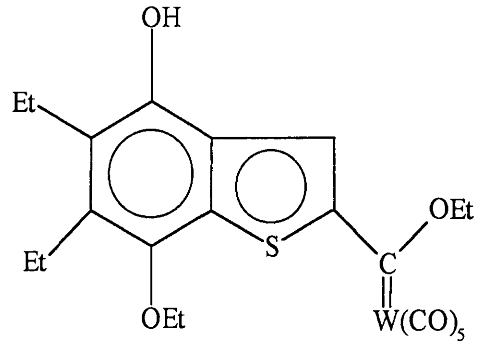
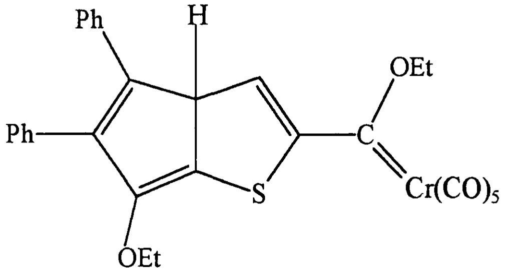
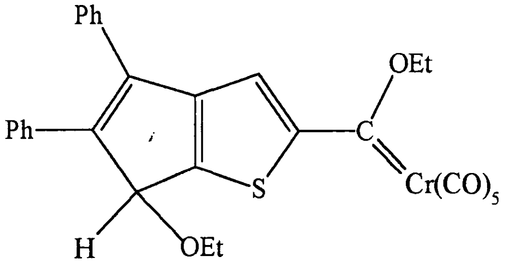
29: $W\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$



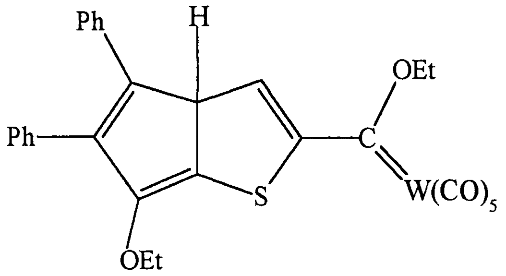
30a: $Cr\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$



30b: $Cr\{C(OEt)CCHCC(Ph)C(Ph)CH(OEt)CS\}(CO)_5$



31a: $W\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$



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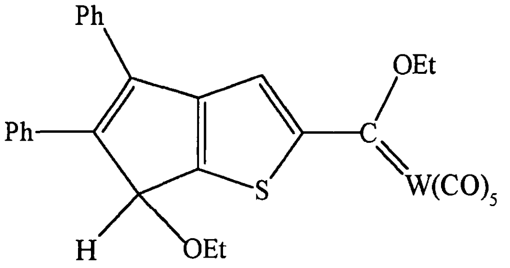
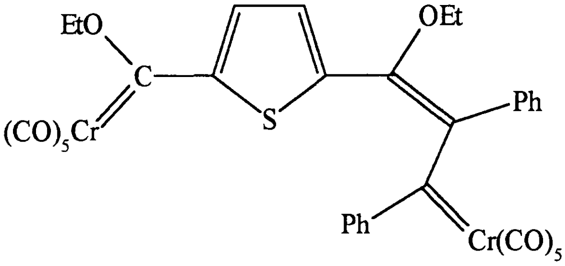
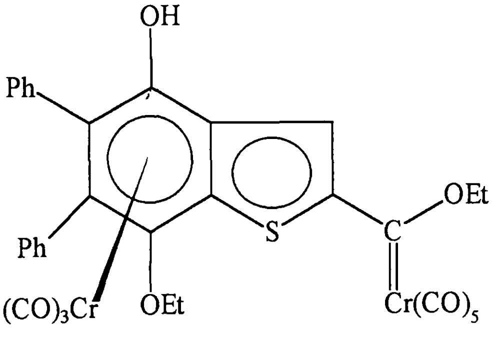
31b: $W\{C(OEt)CCHCC(Ph)C(Ph)CH(OEt)CS\}(CO)_5$



32: $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)C(Ph)C(Ph)\}Cr(CO)_5$



33a: $\{\eta^1{:}\eta^6\text{-}SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3$



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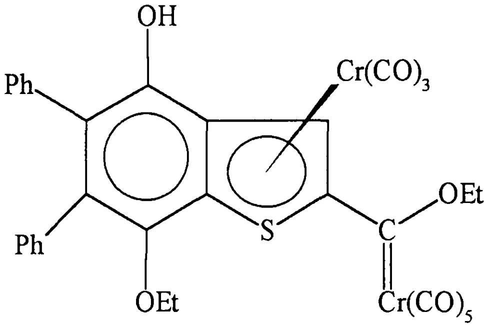
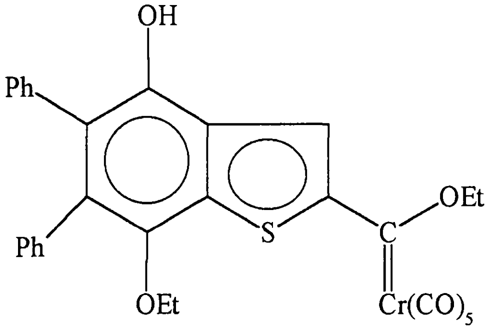
33b: $\{\eta^1{:}\eta^5\text{-SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)}_5\}\text{Cr(CO)}_3]$



34: $\text{Cr}\{\text{C(OEt)CCHCC(OH)C(Ph)C(Ph)C(OEt)CS}\}\text{(CO)}_5$



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1 Introduction

1.1 General Introduction

Fundamental research in organometallic chemistry has been stimulated by the industrial application of especially catalytic reactions.[1] In the area of application of organotransition metal chemistry to organic synthesis where reactions are mostly stoichiometric as opposed to catalytic, new and efficient synthetic methodologies are being developed. Extraordinary regio- and stereoselectivities are exhibited in many of these transformations and complexes are designed to control the stereochemistry of conversions.[2]

The rapid development that has taken place in this field of chemistry is clearly demonstrated by carbene complexes, examples of which are now known for almost all transition metals.[2] These compounds are not only suitable as carbene-transfer agents but also undergo interesting reactions, eg. cycloadditions with other ligands in the metal coordination sphere. The manipulation of these requires techniques no more complicated than those for Grignard reactions. However, only a few examples of conjugated biscarbene complexes or bimetallic complexes with σ,σ-coordinated bridging carbene ligands or with σ,π-coordinated bridging monocarbene ligands have been reported.[3]

Thiophene is a remarkable molecule with pseudo-aromatic character and displays diverse coordination abilities towards transition metals.[4] Thiophene is also an excellent conductor exhibiting superior charge distribution properties when found in polymeric chains.[5] Studies relating to the hydrodesulphurization of thiophene revealed much of thiophene activation by transition metals.[6]

Renewed emphasis has been placed on the design and synthesis of materials with polymeric, conducting and optical properties.[7] Commercialization of organic materials as polymers, polymers with conducting properties, liquid crystals or devices with nonlinear optical properties have stimulated widespread interest in the preparation of organometallic compounds exhibiting these features.[8] The incorporation of transition metals into polymer main chains promises to give access to speciality materials displaying unusual and

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attractive electrical, optical magnetic and preceramic properties. Two important features which are required of such materials are π-conjugation and metal communication within or *via* the unique ligand.

Another area that is receiving increasing interest is the activation of organic substrates by more than one transition metal.[3, 9] In the past two decades, cluster synthesis and cluster reactivity have developed into surface chemistry whereby organic transformations are now being studied on the surfaces of metals.[1, 2] However studies relating to metal-metal communication through organic substrates and not *via* metal-metal bonds, are only now beginning to receive attention.[7] Systematic studies into substrate activation by two or more independent and totally different transition metals have been hampered by the lack of availability of sound synthetic methods.[3]

1.2 Mononuclear Complexes with Unsaturated Metal-to-Carbon Double Bonds

1.2.1 Carbene Complexes

Complexes containing formal metal-to-carbon double bonds, the so-called carbene complexes have been isolated since as early as 1915[10] but were recognized as such only 55 years later.[11] The first stable transition metal carbene complex was prepared by Fischer and Maasböl in 1964.[12] Today two bonding extremes for carbene complexes are known,[2c] the first being Fischer carbene complexes, which are electrophilic carbene complexes of transition metals like chromium, molybdenum, tungsten, iron, ruthenium, rhenium and manganese, Figure 1.1 (a). These are readily synthesized by the reaction of the air stable, crystalline metal carbonyls with a range of organolithium reagents. These carbene complexes have a very rich chemistry and undergo reactions at several sites. The second type, the Schrock carbene complexes, are nucleophilic carbene complexes and represent the opposite extreme of reactivity and bonding from the electrophilic carbene complexes. These are often formed by metals in high oxidation states (often d^0) with strong donor ligands, such as alkyl or cyclopentadienyl, and no acceptor ligands. The carbene ligand is often simply a methylene or alkylidene substituted methylene $=CR_2$ group, Figure 1.1 (b).

Figure 1.1 (a) Fischer Carbene Complexes; (b) Schrock Carbene Complexes

Transition metal carbene complexes have become increasingly more important as starting materials for the synthesis of organic compounds or as precursors for new organometallic complexes.[2b] These metal carbene complexes are known to undergo a variety of reactions; (i) reactions with nucleophiles (eg. aminolysis and related reactions, formation of ylide complexes, addition of carbon- and transition metal nucleophiles), (ii) addition-rearrangement reactions (eg. metal-heteroatom bond formation, modification of the carbene side chain, formation of metal π-complexes), (iii) substitution reactions (eg. substitution of a non-carbene- or carbene ligand), (iv) reactions with transition metal nucleophiles, (v) reactions with electrophilic reagents (synthesis of neutral and cationic transition metal carbyne complexes, rearrangement to carbyne complexes), (vi) oxidation and reduction reactions and (vii) carbene transfer reactions (intermetallic transfer, cyclopropanation, synthesis of heterocycles, insertion reactions).[2b, d]

1.2.2 Cumulene- and Related Complexes

Metallacumulenes, $M(C)_nCR_2$ constitute a new class of organometallic compounds containing a carbon-rich unsaturated chain with a M=C linkage, Figure 1.2 (a). As unsaturated molecules they have the potential for the access to metal containing copolymers exhibiting useful material properties.[13] The M=C bonds offers useful applications in the fields of organometallic, as well as, organic synthesis. Vinylidene complexes (R=H) represent the simplest unsaturated carbene complexes of this class of compounds and contain in addition to a metal-to-carbon double bond, one carbon-to-carbon double bond, $MCCR_2$, Figure 1.2 (b). Excellent review articles on vinylidene complexes by Stang[14]and Bruce[15] are available. Vinylidene complexes are prepared by one of the following methods; from (i) 1-alkynes, (ii) metal acetylides, (iii) deprotonation of carbyne complexes, (iv) acyl complexes, (v) vinyl complexes, (vi) olefines, (vii) disubstituted alkynes, (viii) vinylidene ligand transfer and (ix) modification of the vinylidene ligand.

Allenylidene complexes differ from vinylidene complexes, in that these complexes contain two carbon-to-carbon double bonds in addition to the metal-to-carbon double bond, $MCCCR_2$[16, 17], Figure 1.2 (c). Although the first allenylidene complexes were discovered in 1976[18 a - b] and despite their potential in synthesis due to their cumulene and M=C functionalities, the chemistry of these complexes is only now beginning to be explored. The use of allenylidenes is, however, limited by the lack of general methods of preparation. They are generally obtained *via* (i) transformation of alkenyl- and alkynylcarbene complexes[18a, 19] and (ii) coordination of a C_3 skeleton dianion, either $[C{\equiv}CC(R)_2O]^{2-}$ or $Li_2C_3Ph_2$[7]. The most straightforward method of access appears to be the method employed by Selegue and co-workers[20] which comprises the reactions of alkyne-3-ols with metal complexes eg. $[RuCpCl(PR_3)_2]$ in polar media that lead to the formation of hydroxyvinylidene intermediates, which spontaneously dehydrate *in situ* to yield allenylidene complexes.

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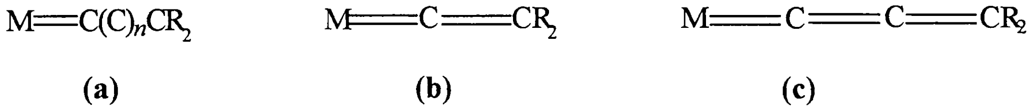

Figure 1.2 (a) Metallacumulenes; (b) Vinylidene Complexes; (c) Allenylidene Complexes

1.3 Binuclear Complexes with Unsaturated Metal-to-Carbon Double Bonds

1.3.1 Novel Carbon Compounds Containing "Naked" C_n Units

During recent years, however, a new class of compounds exhibiting unique properties for application in materials[8] and as model systems for surface carbides in heterogeneous catalysis[21] has become significant. These are compounds in which linear carbon chains C_n (n = 1-5) bridge either similar or different metal fragments, Figure 1.3. Compounds containing "naked" C_n units (n = 1, 2, 4), bridging similar transition metal building blocks, have already been documented.[8, 22] However, complexes with C_n (n = 1 - 5) which link different transition metal complex building blocks have only recently become accessible.[21, 23]. The isolation of these compounds reveals that the highly reactive carbon units C_n (n = 1-5) can be stabilized by suitable terminal building groups. The synthesis of these new compounds particularly those containing organometallic substituents is surprisingly simple. The modification of the alkyne precursors offers a fascinating perspective for the preparation of novel organic chains. In a wider sense it is also conceivable that alkyne-containing metal complexes with conjugated carbon bridges between different terminal groups could find potential application as signal transformers in nonlinear optical materials and perhaps even as molecular wires. Finally, applications in the field of material sciences may also be possible in which the inherent mechanical stability of the C_n-chains plays an essential role.

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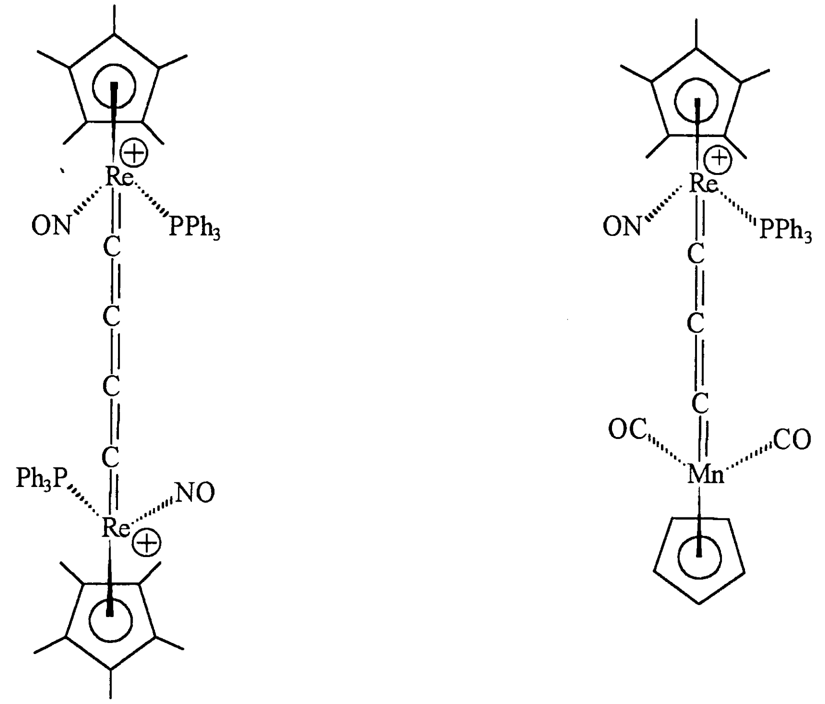


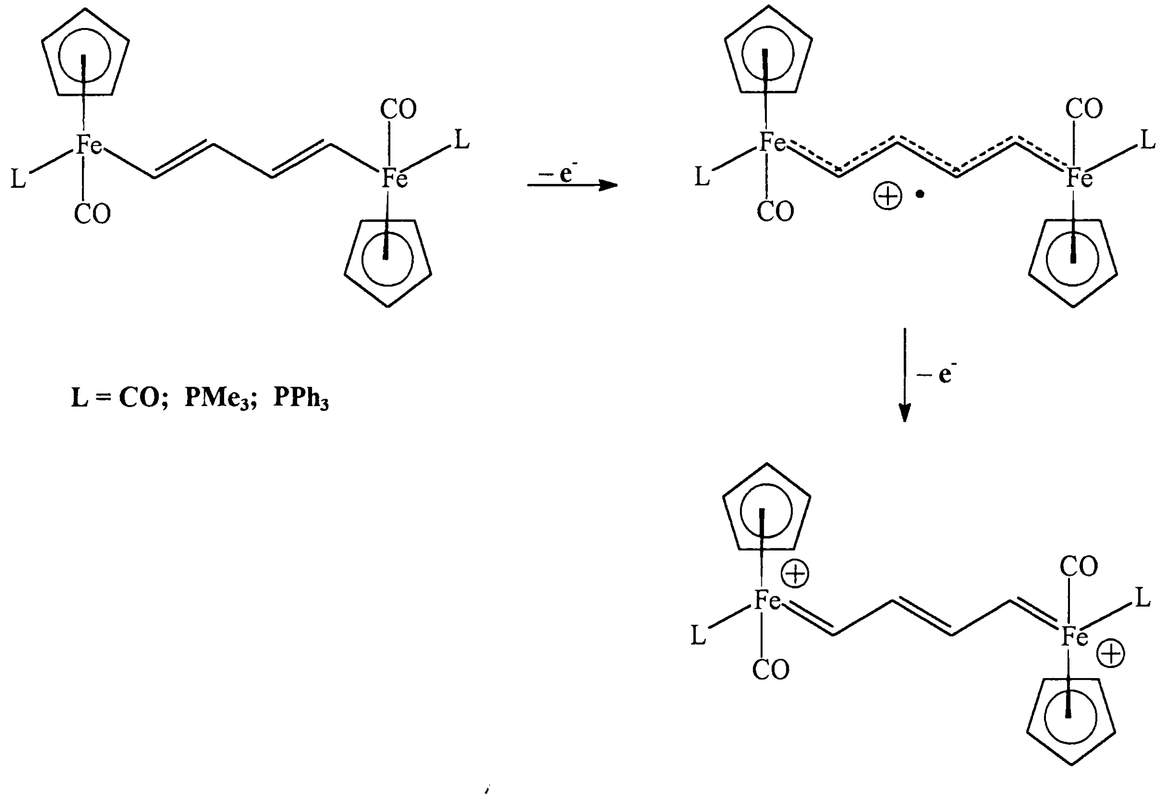
(a) **(b)**

Figure 1.3 Examples of Compounds with Linear Carbon Chains (a) Similar or (b) Different Metal Fragments

1.3.2 Conjugated Bridging Ligands

Related to the above are the bridged mixed valence complexes of iron, which have been isolated by Lapinte *et al.*[24] In these complexes the two metal building blocks differ due to the odd-electron delocalization on the two metal centres, over the bridging ligand, which in these complexes are not comprised of linear carbon chains only, but also contain a conjugated ring, (benzene ring). These complexes constitute examples of polymetallic derivatives in which intramolecular long-distance electron transfer occurs and thus also have potential application in the fields of solid state chemistry, and the emerging field of molecular electronics.

Polyene segments are widely recognized for their ability to allow long-distance electronic coupling through π-delocalization. The first transition-metal mixed valence complexes with polyenediyl bridges were reported by Sponsler *et al.*[25] These delocalized mixed-valence Fe^{II}/Fe^{III} complexes with butadienediyl bridges were prepared by the one-electron oxidation of the corresponding Fe^{II}/Fe^{II} complexes $[CpFe(CO)(L)]_2(\mu$-CHCHCHCH), where L = CO, PMe_3 or PPh_3, Scheme 1.1. The phosphine analogues were prepared by the photochemical substitution of the complex containing L = CO. These complexes are members of the multistage redox systems, $X(CHCH)_nX$, a general class from which many organic examples have been characterized.[26]



L = CO; PMe_3; PPh_3

Scheme 1.1

Another related class of complexes are the enyne and vinylalkenylidene complexes which were synthesized by Casey and co-workers.[27] These complexes, however, differ somewhat in that they contain one transition metal building block only, which is coordinated to either the enyne or the alkylidene.

1.4 Complexes with π-Coordinated Ring Ligands

At first many examples of novel sandwich and half-sandwich complexes were synthesized and characterized, concentrating on synthetic strategies and structural features.[3, 9] The ring ligands involved may be isolated double bonds such as in cyclooctadiene or conjugated π-rings such as cyclopentadienyl, benzene, etc., or increasingly more important pseudo-aromatic five or six membered rings containing a heteroatom. More

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recently, however, attention has shifted to the activation of simple unsaturated organic substrates by transition metals and the resulting electronic and steric properties are being exploited to facilitate unique conversions and to synthesize novel compounds. In this respect regio controlled- and stereospecific syntheses have proven to be valuable assets in modern organic chemistry.[28] Metal complexes have now become a part of the tools available to the organic chemist for designing and accomplishing the synthesis of target compounds. Also, in the quest for materials with exceptional properties the possibility of distributing the charge from a metal *via* π-arene ring ligands onto other fragments appears very attractive and presently considerable effort is being inserted into this field of chemistry.

It is possible to introduce a second metal fragment as a substituent of the π-bonded ring ligand and study the effects of metal-activation on the bridging ligand in both the σ- and π-frame of the common ligand. The σ-bonded metal fragment, when bonded directly or *via* a conjugated spacer will be in direct contact with the π-bonded metal fragment *via* π-resonance effects. Recently it was discovered in our laboratories that this type of communication in $(\eta^1:\eta^5\text{-}C_4H_3SMn(CO)_5)Cr(CO)_3$ leads to an unprecedented metal exchange process whereby the Mn and Cr exchange coordination sites.[28]

1.5 Synthesis and Application of Transition Metal Carbene Complexes from Metallated Thiophene

In this study we decided to embark on a course of synthesizing bimetallic σ,σ-biscarbene and σ,π-monocarbene complexes. Although we are also interested in metal-metal communication through π-delocalization of bimetallic compounds *via* bridging, the advantages of activating organic substrates by more than one metal centre for synthetic purposes is the foremost aim of this study. Ligand activation may be of a local nature and with a specific objective, as is the case when no direct path for electronic contact between metal centres exists. On the other hand, when a conjugated link is employed, activation may be of a co-operative nature and lead to enhanced activation of the substrate. Furthermore, two metal centres could lead to the stabilization and trapping of an otherwise unstable intermediate, hence making characterization possible, and thereby offering insight into the relevant reaction mechanism, as well as, an opportunity to improve and exploit synthetic aspects of the reaction.

It is well-known that thiophene can be either singly or doubly lithiated with relative ease at low temperatures, which makes it ideally suited in the synthesis of Fischer type mono- or biscarbene complexes.[29]

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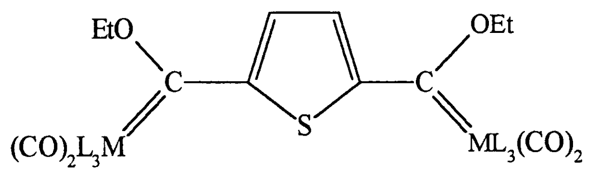
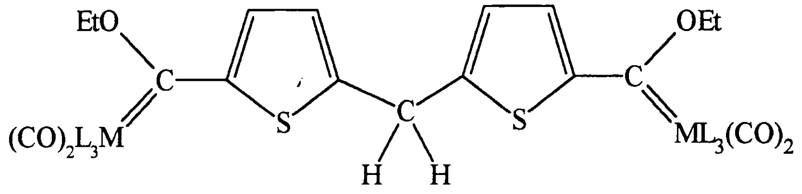
The above mentioned considerations thus prompted an investigation, firstly, into the synthesis of three different types of Fischer carbene complexes with thiophene. The first type are the σ,σ-bimetallic biscarbene complexes, in which thienylene acts as a conjugated π-system to enable direct contact between the two metal carbene functionalities, Figure 1.4. These complexes were successfully prepared employing the metal carbonyls $Cr(CO)_6$, $W(CO)_6$, $Mn(MeCp)(CO)_3$ and $MnCp(CO)_3$, and were subsequently studied.



M = Cr, W, Mn
L = CO
L_3 = MeCp, Cp

Figure 1.4 σ,σ-Bimetallic Thienylene Biscarbene Complexes

The second type are σ,σ-bimetallic biscarbene complexes of 2,2'-methylene dithienyl, (MDT), in which the two thiophene units cannot act as a conjugated π-system to afford communication between the two metal functionalities, but in which ligand activation may be of a localized nature, Figure 1.5. These complexes were successfully prepared for the metal carbonyls $Cr(CO)_6$, $W(CO)_6$ and $MnCp(CO)_3$.



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

Figure 1.5 σ,σ-Bimetallic MDT Biscarbene Complexes

The third type of carbene complexes to be synthesized are the σ,π-bimetallic monocarbene complexes of thiophene and benzothiophene, Figure 1.6 (a) and (b). With this the effect on the carbene environment by π-conjugation to two different types of aromatic rings, (thiophene ring or benzene ring) is investigated, to determine whether this will affect the formation of carbene complexes in any way. The aromatic ring was π-coordinated to $Cr(CO)_3$ and the monocarbene complexes of thiophene were synthesized for $Cr(CO)_6$

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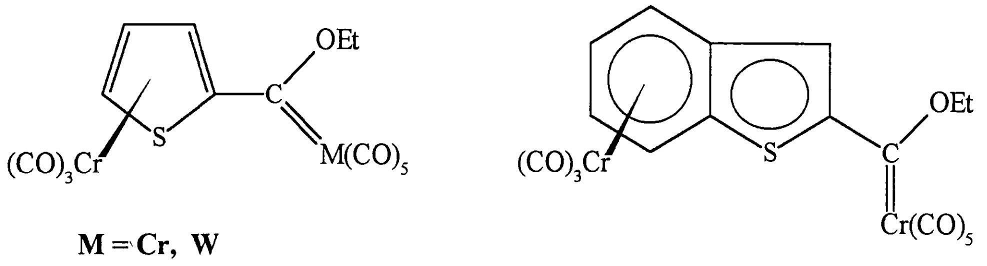
and $W(CO)_6$. The monocarbene complex of benzothiophene was synthesized for $Cr(CO)_6$ only, for comparison.



(a) (b)

Figure 1.6 (a) σ,π-Bimetallic Thienyl Carbene Complexes; (b) σ,π-Bimetallic Benzothienyl Carbene Complex

The second main objective of this study was therefore, to test the reactivity of the new σ,σ-bimetallic biscarbene complexes of thiophene. Two main types of reactions were considered, the first being decomposition patterns of the biscarbene complexes, in which the stability of these carbene complexes in different solvents and at different temperatures was investigated. For this purpose solvents like acetone, carbon disulphide and hexane were employed. The studies in acetone were done at room temperature, whereas those in carbon disulphide and hexane were done at elevated temperatures. The second type of reaction investigated was the reaction with alkynes, in this study the alkynes, hex-3-yne and biphenyl acetylene were employed. The objective again being the comparison of reactivities with monocarbene complexes and an attempt to possibly isolate an intermediate of this well-known reaction.[2b, d] If successful, the latter would represent another method of studying reaction mechanisms and in the process highlight the use of bimetallic systems.

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2 σ,σ-Bimetallic Biscarbene Complexes

2.1 Introduction

Various types of metallic complexes, in which metal-to-carbon double bonds are present have been synthesized, some of these being the bimetallic complexes, shown in Figure 2.1. These include complexes in which two metal-to-carbon double bonds, involving two different carbon atoms and one metal nucleus are present, *i e* a mononuclear biscarbene complexes, **I**.[1] Biscarbene complexes can also contain two metal-to-carbon double bonds, involving a single carbon atom and two metal nuclei, **II**.[2] A third type of biscarbene complexes contain two separate carbene ligands as part of a common ligand, **III**,[5, 7, 9] (see Table 2.1 for examples). In the latter two types the metal atoms can be similar or dissimilar. Bimetallic complexes which contain a metal-to-carbon double bond (on a carbene carbon atom), as well as, a transition metal bonded to the oxygen of the carbene carbon, **IV**, have also been isolated.[3]

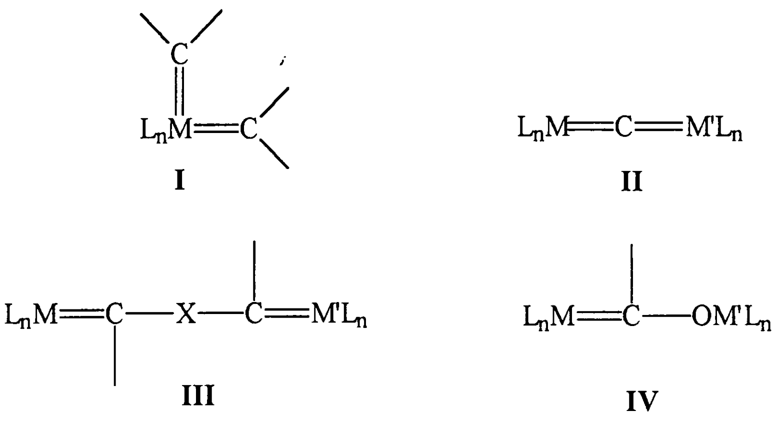

Figure 2.1 Carbene Complexes

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Table 2.1 Selected Bimetallic Biscarbene Complexes Containing Bridging Ligands

M and L in Biscarbene Complex	Bridging Ligand
$Cr(CO)_5$ [17]	$=C(OEt)CH=CH$-*p*-C_6H_4-$CH=CHC(OEt)=$
$Cr(CO)_5$ [5d]	$=C(OEt)$biphenylene-4,4'-diyl-$C(OEt)=$
$Cr(CO)_5$ [5d]	$=C(NEt_2)-C(Me)=C(OEt)$-biphenylene-4,4'-diyl- $C(OEt)=C(Me)-C(NEt_2)=$
$Cr(CO)_5$ [8]	$=C(OMe)$-1,6-methano[10]annulene-2,7-diyl- $C(OMe)=$
$Cr(CO)_5$ [5a]	$=C(OEt)-CH=\overline{C-C^+(NEt_3)-C}=CH-C(OEt)=$
$Cr(CO)_5$ [13]	$=C(OMe)CH_2CH_2CH(Me)C(OMe)=$
$Cr(CO)_5$ [9]	$=C(OEt)$-*p*-C_6H_4-$C(OEt)=$
$Cr(CO)_5$ [19]	$=C(Me)O-(CH_2)_n-O-C(Me)=$ ($n = 2, 3, 4$ and 10)
$Cr(CO)_5$ [9]	$=C(OEt)CH(Ph)CH(Ph)C(OEt)=$
$Cr(CO)_5$ [18]	$=C(NEt_2)-O-C(p-C_6H_4Me)=$
$Cr(CO)_5$ and $W(CO)_5$ [18]	$=C(NEt_2)-O-C(Me)=$
$W(CO)_5$ [9]	$=C(OEt)CH(Ph)CH(Ph)C(OEt)=$
$W(CO)_5$ [9]	$=C(OEt)$-*p*-C_6H_4-$C(OEt)=$
$W(CO)_5$ [7]	$=C(OEt)$-anthracene-9,10-diyl-$C(OEt)=$
$Cr(CO)_5$ and $W(CO)_5$ [30]	$=C(OEt)C_4H_2S-C_4H_2SC(OEt)=$
$Cr(CO)_5$ [14]	$=C(OMe)CH_2CH_2C(OMe)=$
$Mn(C_5H_4Me)(CO)_2$ [11]	$=C(OEt)-CHR-CHR-C(OEt)=$ ($R = H$; CH_3)
$Mn(C_5H_4Me)(CO)_2$ [11]	$=C(OEt)-CH=CH-C(OEt)=$
$Mn(C_5H_4Me)(CO)_2$ [11]	$=CN(Ph)C(H)PhCHCHC(H)Ph\{N(Ph)C\}=$
$Re(C_5Me_5)(NO)(PPh_3)^+$ [5c]	$=C=C=C=C=$
$FeC_5H_5(Ph_2PCH_2PPh_2)^+$ [5b]	$=CH-CH=CH-CH=$
$Mo(C_5H_5)(CO)_2$ [5f]	$=C(NEt_2)C(NEt_2)=$

Although many bimetallic complexes in which the two metal centres are connected by an acetylene bridge, $L_nM-C{\equiv}C-ML_n$ or an ethylene bridge, $L_nM-C(X)=C(X)-ML_n$,[4] are known, there are as yet not many examples

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of bimetallic biscarbene complexes in which the bridging ligand is a conjugated system, $L_nM{=}CX(CR{=}CR)_x$-$CX{=}ML_n$.[5] Table 2.1 shows some examples of bimetallic biscarbene complexes which have been synthesized in recent years, some of which contain conjugated π-systems as bridging ligands.

Transition metal complexes comprised of one carbene ligand bonded to a single transition-metal fragment have been extensively studied. It was, therefore envisaged that the biscarbene bimetallic analogues, which consist of two carbene ligands (similar or dissimilar) bonded to two transition metal fragments (similar or dissimilar), could exhibit reactivities which are equally extensive and interesting.

2.2 Bimetallic Biscarbene Complexes

2.2.1 Carbene Complexes from Dimetallated Substrates

Most bimetallic biscarbene complexes are synthesized by the classic Fischer method using dilithiated organic substrates and metal carbonyl complexes of transition metals like chromium, tungsten, molydenum, manganese, iron, rhenium, cobalt etc. Quenching of the bisacylate anions is normally done with Meerwein-type oxonium salts.[6] Many interesting new bimetallic biscarbene complexes eg., the complex, μ-9,10-anthracenediyl{bis(methoxycarbene)pentacarbonyltungsten}, have been prepared by employing the classic Fischer method[7], see Figure 2.2. 9,10-Dibromoanthracene was metallated and reacted with $W(CO)_6$ followed by the subsequent methylation with magic methyl, ($MeOSO_2CF_3$).

It is evident from Table 2.1 that a number of biscarbene bimetallic complexes of chromium, tungsten, molybdenum, manganese and iron have been prepared and characterized, however, the investigation into the chemistry of these complexes has only recently been started. Neidlein and and co-workers[8] synthesized new Fischer carbene complexes of 1,6-methano[10]annulene and investigated the reaction of these complexes with several alkynes under benzo-annulation conditions, to form new benzoquinones, hydroquinones and protected hydroquinones.

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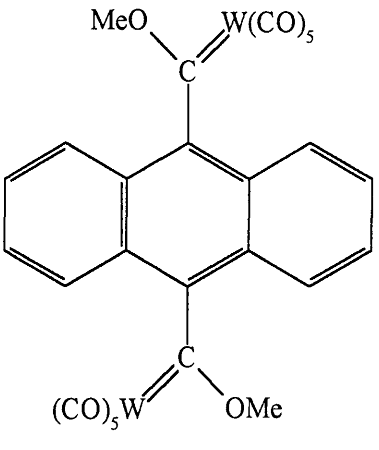
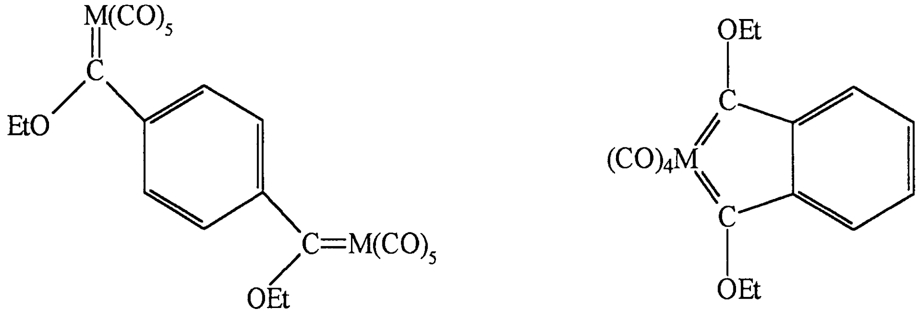


Figure 2.2 Bimetallic Biscarbene Complex, μ-9,10-anthracenediyl{Bis(methoxycarbene)pentacarbonyltungsten}

The synthesis of mono- and binuclear biscarbene complexes of chromium, tungsten and molybdenum and the subsequent reactions of these complexes were studied by Fischer and co-workers.[9] It was found that the reaction of *p*-phenylenedilithium yielded the μ-(*p*-phenylene)bis[ethoxycarbenepentacarbonylmetal] complexes, $(CO)_5MC(OEt)$-*p*-C_6H_4-$C(OEt)M(CO)_5$, where M = Cr, W. The analogous reaction of *o*-phenylenedilithium with metal hexacarbonyls afforded the expected mononuclear 1,4-chelated biscarbene complexes, $(CO)_4M\{C(OEt)$-*o*-C_6H_4-$C(OEt)\}$, where M = Cr, Mo or W, see Figure 2.3. On the other hand it was found that 1,2-dilithio-1,2-diphenylethane gave a mixture of mononuclear, $(CO)_4M\{C(OEt)CH(Ph)$-$CH(Ph)C(OEt)\}$, and binuclear $(CO)_5MC(OEt)CH(Ph)CH(Ph)C(OEt)M(CO)_5$ biscarbene complexes, where M = Cr or W. The reaction of the biscarbene complexes, $(CO)_5MC(OEt)$-*p*-C_6H_4-$C(OEt)M(CO)_5$ with borontrihalides BX_3 yielded the corresponding *trans*-halogenocarbyne complexes, $X(CO)_4M{\equiv}C$-C_6H_4-$C{\equiv}M$-$(CO)_4X$.



M = Cr or W

M = Cr, Mo,W

Figure 2.3 Biscarbene Complexes with a Phenylene Substituent

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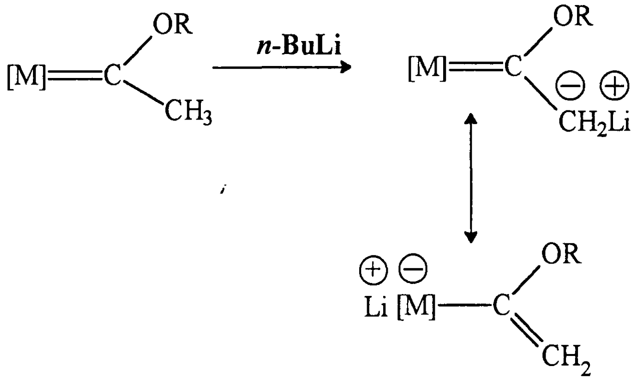
Lappert *et al*[10] extended the classic Fischer procedure, using a lithium or magnesium reagent of a dicarbanion, to give brigded biscarbene bimetallic complexes. Convenient candidate reagents for this purpose were o-$C_6H_4(CH_2MgCl)_2$ (or its chloride-free equivalent) and o-$C_6H_4[CH(SiMe)_3Li(TMEDA)]_2$. The hexacarbonyls, $M(CO)_6$, (M = Cr or W), were reacted with the bifunctional magnesium reagent $Mg[o\text{-}(CH_2)_2\text{-}C_6H_4]\text{-}(THF)_n$ to give the bimetallic complex, $M(CO)_5\{C(O)CH_2\text{-}o\text{-}C_6H_4CH_2C(O)\}M(CO)_5Mg(THF)_n$, M = Cr, $n = 3$; M = W, $n = 4$. A molybdenum analogue was similarly obtained (as for M = Cr). Both of the magnesium complexes (M = Cr or W) upon acid hydrolysis and the treatment of the dichloromethane extract with $[Et_3O][BF_4]$ yielded the appropriate bimetallic biscarbene complex $M(CO)_5\{C(OEt)CH_2\text{-}o\text{-}C_6H_4CH_2\text{-}C(OEt)\}M(CO)_5$, M = Cr or W. The similar reaction of the dimolybdenum magnesium complex gave decomposition products, consistent with the much lower thermal stability of carbene complexes of Mo than those of Cr or W.

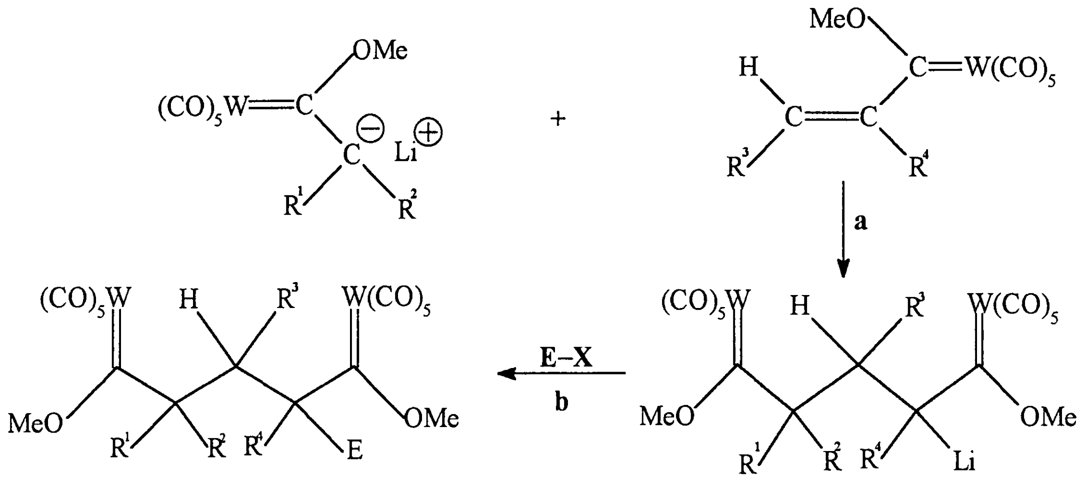
2.2.2 Biscarbene Complexes from Connecting Alkyl Substituents

It is a well established fact that hydrogen atoms α to the carbene carbon atom in Fischer type carbene complexes are acidic and can be removed upon treatment with strong bases to form carbene anions[11] or enolates, as illustrated by Scheme 2.1.



Scheme 2.1

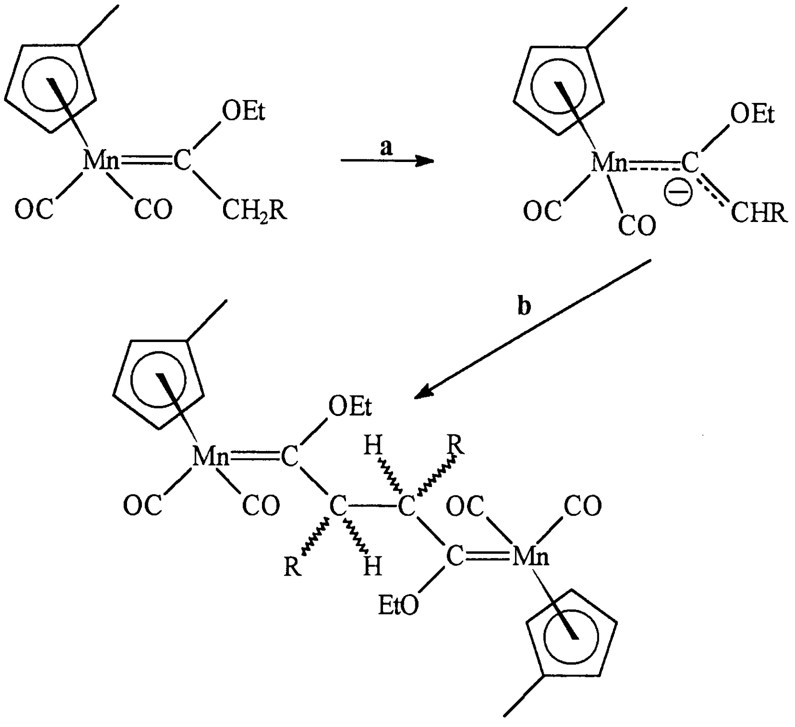
A new, general route to the synthesis of Fischer biscarbene ditungsten complexes has been reported by Macomber *et al.*[12, 13] The approach to the synthesis of the complexes, $(CO)_5MC(OMe)(CH_2)_3C(OMe)\text{-}M(CO)_5$, (M = Cr, W), involved the conjugate addition of substituted α-lithio carbene anions, (obtained by treating the corresponding carbene complexes, $(CO)_5MC(OMe)Me$ with n-butyllithium at -78 °C), to various α,β-unsaturated tungsten carbene complexes. The resulting α-lithio acylates were quenched with various electrophillic reagents, to afford good yields of the desired compounds. The method has since been extended to prepare the biscarbene complexes shown in Scheme 2.2 and some aminocarbene derivatives.



Reagents: (a) THF, -30°C to -78°C; (b) 1. CH_2Cl_2, -78 °C, 2. E-X = M_3e SiCl, C_2H =CHC$_2$H Br, $PhCH_2Br$, CH_3OSO_3, CF_3, HCl

Scheme 2.2

It has furthermore been found that the carbene anions resulting from the *in situ* deprotonation of MeCp(CO)$_2$MnC(OEt)CH$_2$R, (where R = H, Me) and MeCp(CO)$_2$MnCN(Ph)CH(Ph)CH$_2$ undergo oxidative coupling in the presence of copper salts to produce the corresponding neutral bridging biscarbene dimanganese complexes {MeCp(CO)$_2$Mn}$_2${μ-C(OEt)CH(R)CH(R)C(OEt)} and {MeCp(CO)$_2$Mn}$_2${μ-CN(Ph)C(Ph)HCHCHC(Ph)N(Ph)C}.[11] Subsequent treatment of the former biscarbene dimanganese complex with butyllithium (double deprotonation) followed by a carbon-carbon coupling reaction induced by copper(II)chloride led to the formation of the μ-vinylcarbene dimanganese complex, {MeCp(CO)$_2$Mn}$_2$-{μ-C(OEt)CHCHC(OEt)}. Scheme 2.3 presents a general reaction of this type. The controlled reduction of the latter compound led to the formation of a Mn^0/Mn^I mixed valence complex which was characterized by EPR spectroscopy.



Reagents: (a) *n*-BuLi, -60 °C; (b) 1. CuI, 2. O_2, -78 °C

Scheme 2.3

Beck and co-workers[14] found that the oxidative coupling of $[(CO)_5CrC(OCH_3)CH_2]^-Li^+$ and $[FcCOCH_2]^-K^+$, with $AgBF_4$ gives the dinuclear neutral complexes $(CO)_5CrC(OMe)CH_2CH_2C(OMe)Cr(CO)_5$ and $FcCOCH_2CH_2COFc$ in good yield. The double deprotonation of both of these neutral complexes with *n*-BuLi or KH respectively, affords dianionic species which are oxidized to the conjugated complexes, $(CO)_5CrC(OCH_3)CHCHC(OCH_3)Cr(CO)_5$ and FcC(O)CH=CHC(O)Fc. The addition of the dianion $[(CO)_5CrC(OCH_3)HCHC(OCH_3)Cr(CO)_5]^{2-}(Li^+)_2$, to the cationic electrophiles $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+[BF_4]^-$ and $[Re(CO)_5(\eta^2\text{-}C_2H_4)]^+[BF_4]^-$ leads to nucleophilic attack on the cyclohexadienyl ring and the formation of tetranuclear diastereomers.

Pentacarbonyl(alkoxyalkylcarbene)chromium complexes are well-known, usefull substrates in organic synthesis.[15] In the reaction of the anion of the carbene complex $(CO)_5CrC(OMe)Me$ with propylene oxide in the presence of $TiCl_4$ two products are yielded, one of which being the dimeric carbene complex as a by-product, Scheme 2.4. In this case the yields of both products are low and cannot be increased. Furthermore it was found that the reaction could not be applied as a general reaction in the synthesis of biscarbene complexes.[16]

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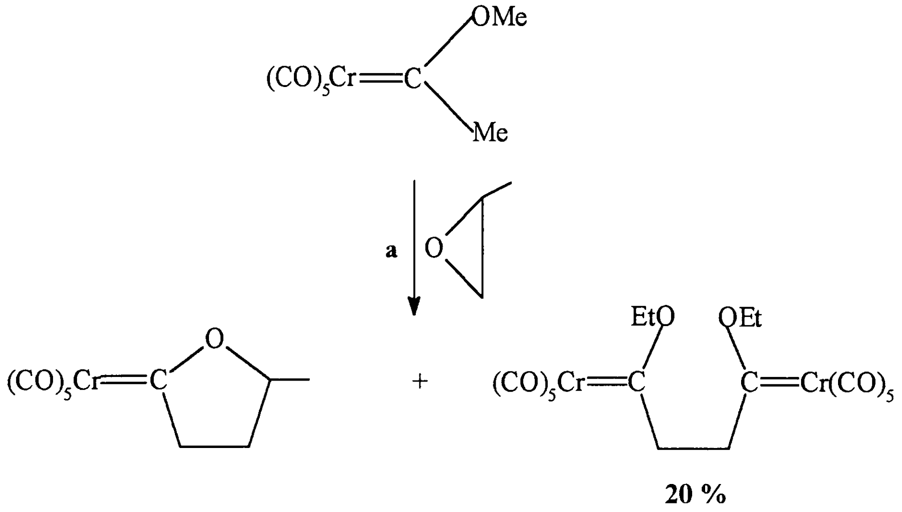

Reagents (a) 1. *n*- BuLi, 2. $TiCl_4$

Scheme 2.4

During the past few years it has become increasingly important to study and synthesize biscarbene complexes in which the two metal centers are in contact through a conjugated π-system. Aumann and Heinen[17] have explored this field and synthesized two carbene complexes, $(CO)_5CrC(OEt)CH{=}CH$-*m*-C_6H_4-$CH{=}CHC(O$-$Et)Cr(CO)_5$ and the analogous complex $(CO)_5CrC(OEt)CH{=}CH$-*p*-C_6H_4-$CH{=}CHC(OEt)Cr(CO)_5$, see Figure 2.4. The synthesis was performed by reacting the corresponding dialdehyde, (1,3-benzoldicarbaldehyde or 1,4-benzoldialdehyde) with two equivalents of the monocarbene complex ($(CO)_5CrC(OEt)CH_3$). The chromium atoms in the complex containing a *p*-substituted aryl as the bridging unit were found to be in contact with each other through a conjugated π-system. More recently Aumann *et al*[5a] investigated the reaction of pentacarbonyl(1-ethoxy(ethylidene))chromium and tetrachloro(cyclopropene) in the presence of triethyl amine. The reaction afforded the biscarbene complex, $(CO)_5CrC(OEt)CH\overline{CC^{+}(NEt_3)C}CHC(OEt)$-$Cr(CO)_5$, in which the carbene chromium units are connected by a conjugated and planar ammonium pentadienide bridge. The condensation involved the elimination of four equivalents of HCl and the formation of a hitherto unknown nitrogen ylide system, in which two carbene units are connected by an ammonium pentadienide bridge.[5a]

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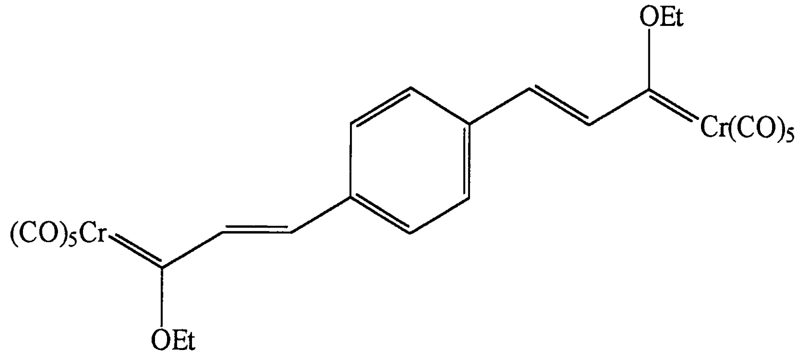

Figure 2.4 Bimetallic Biscarbene Complex containing a Conjugated π-system

2.2.3 Biscarbene Complexes by Connecting Alkoxy Substituents

The principle involved here is the alkylation of the oxygen, Figure 2.5, or in other words the nucleophilic attack by the oxygen on a coordinated carbocationic carbon atom.

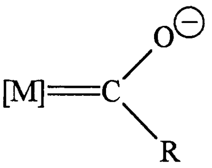

Figure 2.5 Metal Acylates as Nucleophiles

Examples containing chromium and tungsten are shown in Figure 2.6. The synthesis was done by the slow addition of a solution of the methoxy(diethylamino)carbene complex in dichloromethane to the tetramethylammonium salt of the $[(CO)_5MC(O)R]^-$ anion at - 78 °C, where M = Cr or W, and R = *p*-$C_6H_4CH_3$, CH_3.[18] The reaction yielded the bimetallic biscarbene complexes $(CO)_5CrC(NEt_2)OC(R)Cr(CO)_5$ and the mixed bimetallic biscarbene complex $(CO)_5CrC(NEt_2)OC(R)W(CO)_5$.

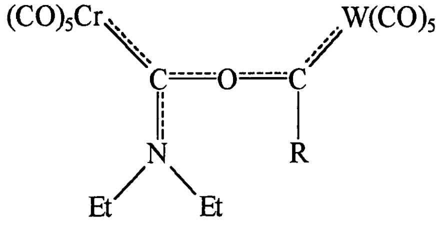

Figure 2.6 Mixed Bimetallic Biscarbene Complexes of Chromium and Tungsten

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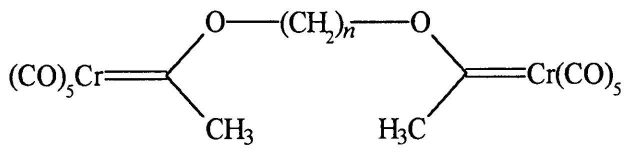
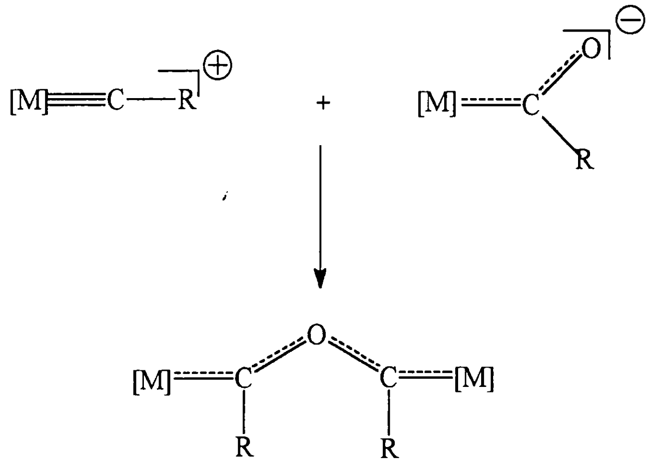
Dichromium alkoxycarbene complexes, bridged *via* the alkoxy groups, were synthesized in a straightfoward manner by the treatment of the corresponding acetoxycarbene complex with diols at low temperatures. This type of bimetallic biscarbene complex is shown in Figure 2.7, and was synthesized by Hegedus and co-workers[19] as precursors for the production of bis-dioxocyclam ligands.



$n = 2, 3, 4, 10$

Figure 2.7 Alkoxy Bridged Biscarbene Complex

Fischer *et al*[20] employed an interesting and unusual synthesis to prepare the symmetrical anhydrides of hydroxy(carbene) complexes of manganese and rhenium, $[\pi\text{-}C_5H_5(CO)_2MC(R)]_2O$, (M = Mn, Re; R = Ph, $C_6H_5CF_3$), Scheme 2.5. This was done by the reaction of the cationic carbyne complexes $[\pi\text{-}C_5H_5(CO)_2M\text{-}CR]BX_4$, with the corresponding metal carbonyl acylates $Li[\pi\text{-}C_5H_5(CO)_2MC(O)R]$. The complex, $[\pi\text{-}C_5H_5\text{-}(CO)_2MC(Ph)]_2O$, was also obtained by the controlled hydrolysis of $\pi\text{-}C_5H_5(CO)_2MnC(Br)C_6H_5$.[20]



Scheme 2.5

2.2.4 Carbon-Carbon Coupling Reactions

Of recent interest are the cycloaddition reactions of alkenylcarbene complexes. An organometallic analogue (involving benzalazine and vinylidene or carbyne complexes) of the "criss-cross" (2 + 3) cycloaddition reac-

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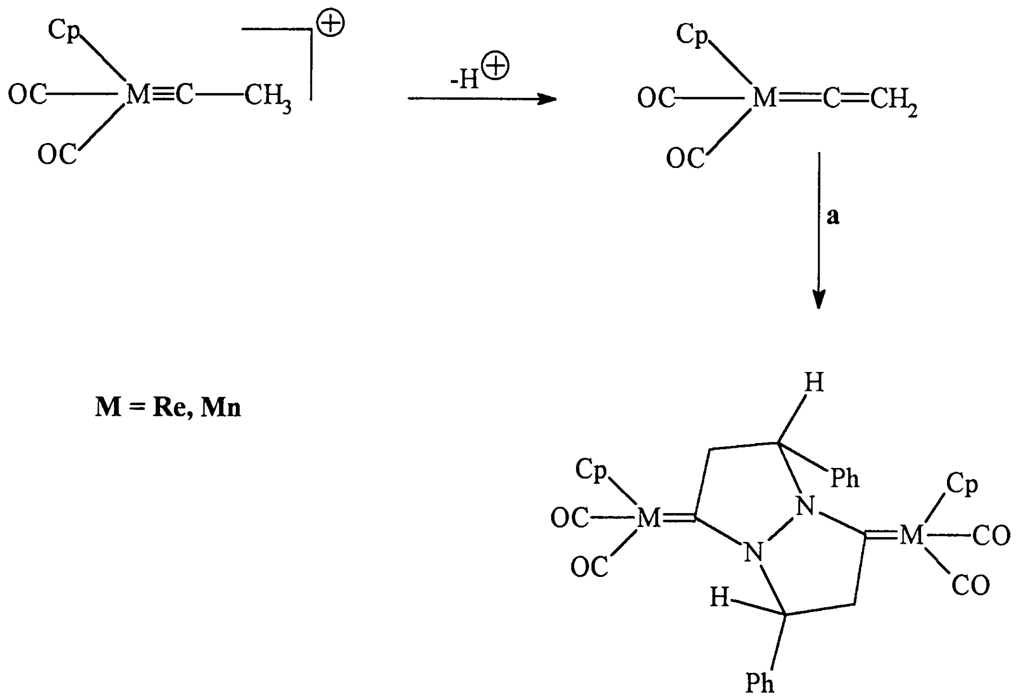
tion of electron rich azines with electron deficient alkenes has been reported by Geoffroy and co-workers.[21] The addition of benzalazine, C(Ph)(H)NNC(Ph)H, to the vinylidene complex $Cp(CO)_2Re{=}C{=}CH_2$ led to the formation of the "criss-cross" cycloaddition product $Cp(CO)_2Re{=}CCH_2C(Ph)(H)NNC(Ph)(H)CH_2C{=}Re(CO)_2Cp$. Similarly a reaction occurred between the carbyne complex, $[Cp(CO)_2Mn{\equiv}CCH_3]^+$ and benzalazine to give a manganese "criss-cross" cycloaddition product, see Scheme 2.6.



Reagents: (a) Benzalazine, C(Ph)(H)NNC(Ph)H

Scheme 2.6

A new biscarbene complex was isolated and fully characterized in the reaction of $(CO)_5Cr\{C(OEt)C{\equiv}CPh\}$ and ethyl diethoxyacrylate. The complex $(CO)_5Cr\{C(OEt)CHC(Ph)CC(Ph)CHC(OEt)OC\}Cr(CO)_5$ represents the coupling of a second alkynyl(alkoxy)carbene complex, with the intermediate, $[(CO)_5Cr\{CCC(Ph)CHC(OEt)O]^-$ which is formed *in situ* by a (4 + 2) cycloaddition reaction of alkynyl(alkoxy)carbene metal complexes and ethyl diethoxyacrylate, this complex represents the trapping of a carbanionic intermediate.[22]

Allenylidene complexes are active species in the catalytic cyclization-reconstructive addition of prop-2-ynyl alcohols with allyl alcohols and as reactive intermediates in the formation of Fischer-type unsaturated carbene complexes of the type alkenyl(alkoxy)- or polenyl(alkoxy)carbene complexes of chromium, tungsten and ruthenium. This property was exploited by Cardierno and co-workers[23] to afford novel unsaturated alky-

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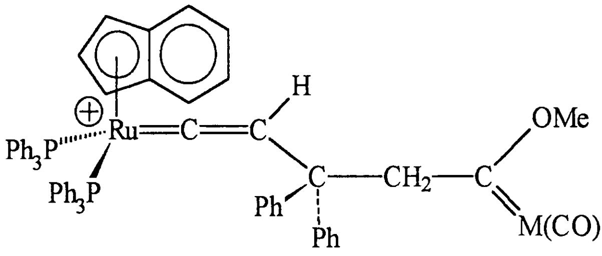
nyl ruthenium complexes obtained through Wittig processes *via* the alkynylphosphino complex [Ru(η^5-C_9H_7)(PPh_3)$_2${C≡CC(H)(Ph)}][PF_6] and to synthesize the first examples of bimetallic complexes containing difunctionalized hydrocarbon bridges of the type vinylidene-carbene, see Figure 2.8.



M = Cr, Mo, W

Figure 2.8 Vinylidene-carbene Complex

2.2.5 Synthesis of Bimetallic Bis(aminocarbene) Complexes

A very efficient method for the preparation of monocarbene complexes of chromium containing amino substituents is the reaction of $Cr(CO)_5^{2-}$ with tertiary amides in the presence of chlorotrimethylsilane.[24] This method has also been employed in the synthesis of iron aminocarbene complexes lacking α-hydrogens.[25] Recently it has been extended to the synthesis of bimetallic bis(aminocarbene) complexes.[26] The reactions of $Cr(CO)_5^{2-}$ and $Fe(CO)_4^{2-}$ with diamines like *N,N,N',N'*-tetramethylisophthalamide or the *N,N,N',N'*-tetramethylamide of pyridine-2,6-dicarboxylic acid in the presence of chlorotrimethylsilane readily gives the bis(aminocarbene) dichromium complexes, $(CO)_5Cr\{\mu\text{-}m\text{-}C(NMe_2)C_6H_4C(NMe_2)\}Cr(CO)_5$ and $(CO)_5Cr\{\mu\text{-}2,6\text{-}C(NMe_2)(C_5H_3N)C(NMe_2)Cr(CO)_5$, and the bis(aminocarbene) diiron complexes, $(CO)_4Fe\{\mu\text{-}m\text{-}C(NMe_2)C_6H_4C(NMe_2)\}Fe(CO)_4$ and $(CO)_4Fe\{\mu\text{-}2,6\text{-}C(NMe_2)(C_5H_3N)(C(NMe_2)\}Fe(CO)_4$, respectively, Scheme 2.7. Under the same conditions *N,N,N',N'*-tetramethylphalamide, binaphthyl bis(amide) and *N,N,N',N'*-tetramethylsuccinamide affords the monocarbene complexes, $(CO)_5Cr\{C(NMe_2)(2\text{-}(Me_2NC(O)C_6H_4)\}$, the binaphthyl derivative and $(CO)_5Cr\{C(NMe_2)CH_2CH_2C(O)NMe_2\}$, as products, **V** and **VI**, in Scheme 2.7. With the use of a 1:1 molar ratio of *N,N,N',N'*-tetramethylisophthalamide and $Cr(CO)_5^{2-}$, however, the monocarbene complex, $(CO)_5Cr\{C(NMe_2)\text{-}m\text{-}C_6H_4C(O)NMe_2\}$ is formed, which can be converted to the mixed chromium-iron bis(aminocarbene) complex, $(CO)_5Cr\{C(NMe_2)\text{-}m\text{-}C_6H_4C(NMe_2)\}Fe(CO)_4$, by the reaction with $Fe(CO)_4^{2-}$ and chlorotrimethylsilane.

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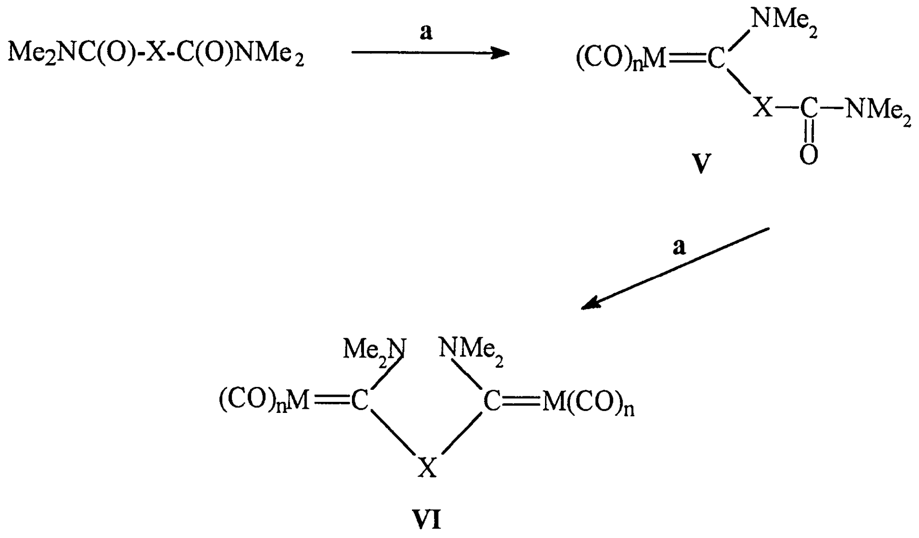


Reagents: (a) $M(CO)_n^-$, Me_3SiCl

Scheme 2.7

2.3 Carbene Complexes with Thiophene Substituents

The metallation of thiophene, to yield various organometallic complexes, has been known for quite some time[27], and was employed by Connor and Jones[28] to synthesize monocarbene complexes containing thienyl substituents. These have also been utilized in reactions with acetylenes to give benzothiophene dervatives.[29]

Thienyl carbene complexes of Cr and W were recently prepared with the objective of demonstrating the principle of protecting the electrophilic carbene carbon from nucleophilic attack.[30] The introduction of an anionic charge adjacent to a carbene unit serves this purpose and a variety of functionalized Fischer carbene complexes have become available using this method, Figure 2.9.

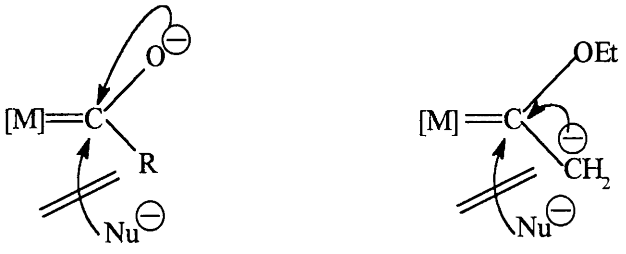
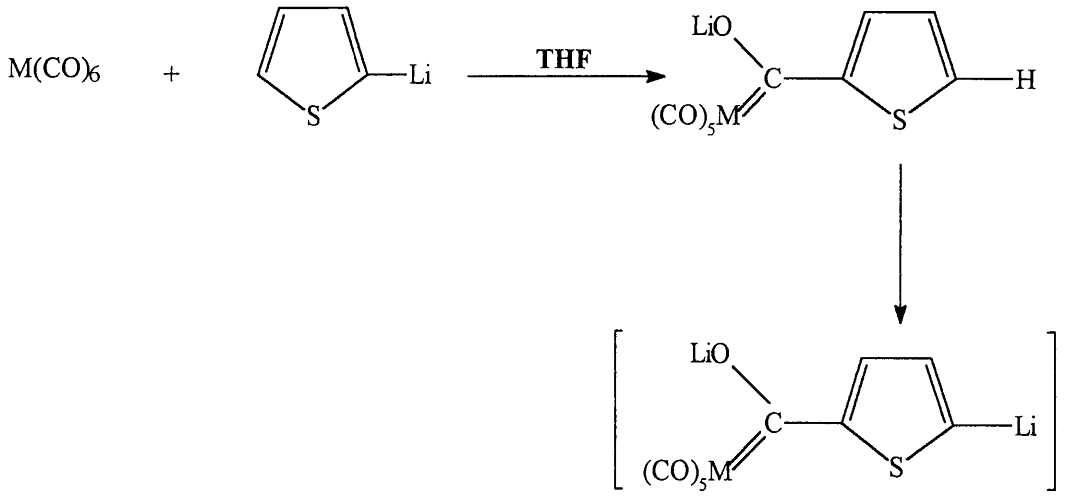


Figure 2.9 Anionic Protection of a Carbene Carbon Atom

This was demonstrated by the stepwise generation of the dianion, Scheme 2.8.



VII

Reagent: BuLi

Scheme 2.8

Isolation of the dianions, **VII** or further lithiation of the thienyl substituent in the 3-position failed. The treatment of, **VII** with organic electrophiles afforded substituted thienyl carbene complexes.

In comparison to this, the double metallation of thiophene in this study was employed to afford, after the subsequent reaction with two equivalents of a metal carbonyl, a dianionic bis(acyl-metallate) in a high yield. This intermediate was use to give biscarbene complexes which were fully characterized and studied, Figure 2.10.

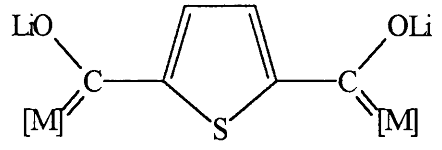


Figure 2.10 Bis(acyl-metallate) with Thienylene Bridge

After this study had already been completed a paper[31] appeared at the end of 1995 describing the synthesis of the related, mixed bimetallic biscarbene complex $(CO)_5Cr\{C(OEt)\text{-}2,2'\text{-dithienyl-}C(OEt)\}\text{-}W(CO)_5$, in which the dithienyl bridge links the two carbene moieties, Figure 2.11. A stepwise addition of the different metal carbonyls was employed and due to incomplete reactions, afforded, after alkylation

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with $[Et_3O][BF_4]$, mixtures of mono- and biscarbene complexes of W and Cr.

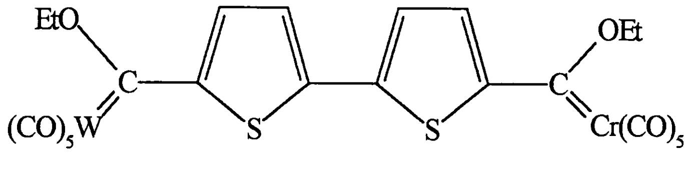

Figure 2.11 Mixed Bimetallic Biscarbene Complex, $(CO)_5Cr\{C(OEt)$-2,2'-dithienyl-$C(OEt)\}$-$W(CO)_5$

The heterobimetallic biscarbene complex was synthesized to test its potential as a species with second order non-linear optical properties. It was important to establish whether a 'push-pull' situation could be created, by using two different metal fragments, *via* the π-conjugated carbene-dithienyl-carbene bridge. No data to support or disprove this supposition was given in the communication. Before studying the effect of dithienylene linked bimetallic systems, it is important to systematically study the synthesis and properties of biscarbene complexes containing only one thienylene, connecting the two carbene units and extend from there to larger "polythienylene spacers" with and without π-conjugating features.

2.4 Synthesis of Bimetallic Thienylene Biscarbene Complexes

The approach to the synthesis of the bimetallic thienylene biscarbene complexes, $L_3(CO)_2M\{C(OEt)C_4H_2SC(OEt)\}ML_3(CO)_2$, **(1)** - **(4)**, where M = Cr and L = CO **(1)**; M = W and L = CO **(2)**; M = Mn and L_3 =MeCp **(3)**; M = Mn and L_3 = Cp **(4)** was that of the classic Fischer procedure. The general procedure for the synthesis is outlined in Scheme 2.9.

Thiophene is readily metallated by butyllithium in THF or diethyl ether. The dimetallation, however, is not possible in these solvents, since the solvent is attacked under forcing conditions. The addition of a strong polar co-solvent like HMPT does not lead to the introduction of an additional metal atom, but rather causes the ring to open due to deprotonation in the 3-position.[32] In the abscence of THF or diethyl ether the monomeric BuLi·TMEDA complex is capable of abstracting both the 2- and 5-proton of thiophene. The first deprotonation occurs at a relatively low temperature (-10 °C or lower), whereas the removal of the second proton is sufficiently fast at elevated temperatures. The rest of the reaction proceeds according to the classic mechanism for the synthesis of Fischer carbene complexes,[6] and will be described very briefly. It has been established that the carbon atom in coordinated CO should bear a larger positive charge than in free CO. One of the six equivalent CO groups, in $Cr(CO)_6$ and $W(CO)_6$, or

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for $MeCpMn(CO)_3$ and $CpMn(CO)_3$ one of the three equivalent CO groups, undergoes attack by the thiophene dianion (one dianionic moiety attacks two metal carbonyl complexes) to produce the dinuclear, dianionic bisacylate complex, in which the negative charges are stabilized and extensively delocalized to the remaining π-accepting, electron withdrawing carbonyl ligands. Treatment with alkylating agents such as triethyloxonium tetrafluoroborate in dichloromethane as solvent results in alkylation at the oxygen, producing the ethoxy carbene complexes **1** - **4**.

In order to accomplish the double deprotonation of thiophene two equivalents of butyllithium in addition to two equivalents of TMEDA had to be added to a solution of one equivalent of thiophene in hexane after which the temperature of the solution was elevated and refluxing maintained for 30 min. The addition of two equivalents of chromium-, tungsten hexacarbonyl, methylcyclopentadienyl tricarbonyl manganese or cyclopentadienyl tricarbonyl manganese at a much lowered temperature (-40 °C) afford the dilithium salt of the biscarbene complex. Quenching with two equivalents of triethyloxonium tetrafluoroborate yielded the neutral biscarbene complex.

A noteworthy observation was the fact that these reactions did not yield the desired biscarbene complexes **1**, **2**, **3** or **4** only, but a mixture of carbene complexes. The corresponding butyl- and monocarbene complexes $M(CO)_5\{C(OEt)\}Bu$[28] and $M(CO)_5\{C(OEt)C_4H_3S\}$[33], respectively were formed in relatively (5 - 20 %) low yields for the reactions of the chromium and tungsten hexacarbonyls. The manganese biscarbene complexes, **3** and **4**, on the other hand were obtained in higher yields (≈ 80 %) and as a result the by-products, which were present in low yields were not isolated or characterized. A possible explanation for the formation of a mixture of carbene complexes could be due to the fact that the reactions were done at mild conditions (low temperatures) and were therefore not fully driven to yield the major product, the biscarbene complex. Also the second deprotonation of an anionic intermediate is more difficult and incomplete. Double deprotonation did therefore not occur quantitatively and some monoanions of thiophene were also formed, which reacted with the metal carbonyls, hence producing the monocarbene complexes. Similarly the unreacted butyllithium also reacted with the metal carbonyls to yield the butylcarbene complexes after alkylation.

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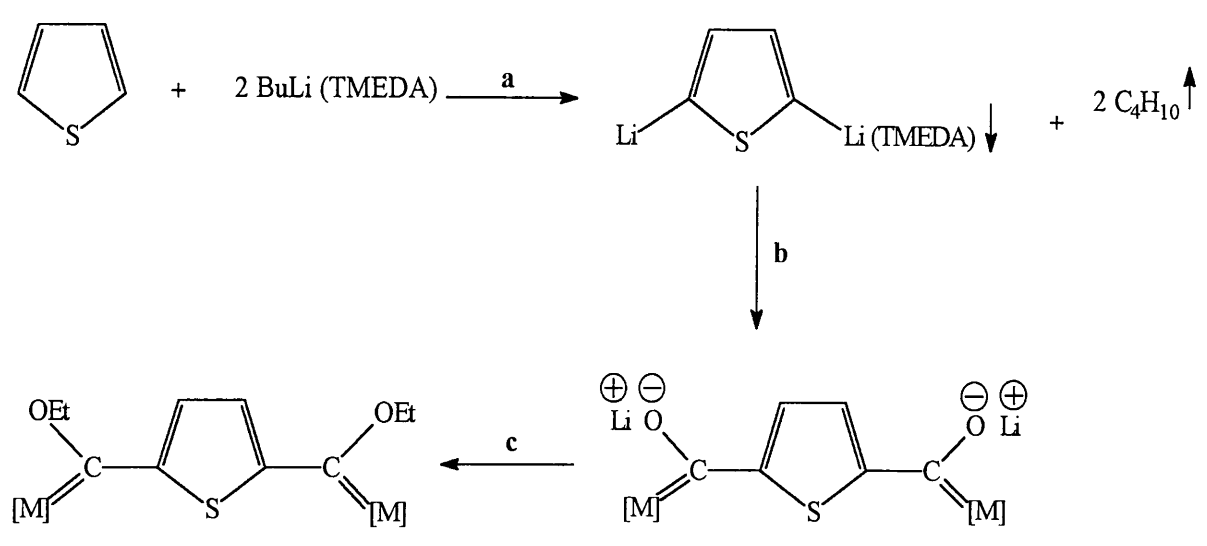
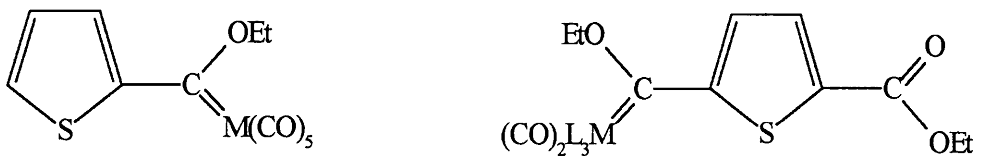


1 - 4

Reagents: (a) Hexane, reflux; (b) 2 equiv. $ML_3(CO)_3$, THF, –40°C; (c) 2 equiv. $[Et_3O][BF_4]$, CH_2Cl_2

Scheme 2.9

Whereas it is possible to alkylate the monoacylates in water with $[Et_3O][BF_4]$, the bisacylates on the other hand cannot be treated in this manner. The dianionic bisacylate reacts with water and subsequent alkylation and work up afford the monothienyl carbene complexes, **A** and **B**, as well as, new monocarbene complexes, **C**, Figure 2.12. The new monocarbene complexes, with an ester functionality in the 5-position, **C**, will be discussed in Chapter 4.



A, B **C**

M = Cr, (A) and M = W, (B); L = η^5-C_5H_5, η^5-$C_5H_4CH_3$

Figure 2.12 Monothienyl Carbene Complexes

It has been established that manganese carbonyl and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ (as well as the methyl derivative of the latter) are quite resistant to substitution reactions.[34] If one considers that the presence of ligands such as η^5-C_5H_5, (which is a poorer π-acceptor than three carbonyl ligands), CO and PR_3 allows for the synthesis of thermally stable compounds and that manganese has the formal oxidation state of +1, it can be considered that these factors promote better overlap between the metal and carbon orbitals implying

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increased bond strength, and thus a smaller positive charge on the CO carbon atom. It is therefore anticipated that the reactions involving the synthesis of complexes **3** and **4** will take longer, which is supported by the observation that a longer reaction time was indeed required for the formation of complexes **3** and **4**, compared to that needed for complexes **1** and **2**, (30 min compared to 10 min).

The complexes **1** and **2** could effortlessly be crystallized from a mixture of hexane and dichloromethane (ratio 2:1) to yield dark purple crystals. Whereas complex **4** could only be crystallized with some difficulty to afford reddish purple crystals, it was not possible to crystallize complex **3**. All of these complexes were found to be relatively stable in the solid state, as well as in solution, however, after some time even at low temperatures and in an inert atmosphere, decomposition to the different monocarbene complexes of the type **C** occured in both the solid state and in solution.

2.5 Spectroscopic Characterization of the Bimetallic Thienylene Biscarbene Complexes

The bimetallic thiophene biscarbene complexes, **1** - **4**, were fully characterized, by NMR-, infrared- and mass spectroscopy. Molecular formulations were based on all of the data. The ^{1}H NMR and ^{13}C NMR spectra for complex **3** were recorded at - 30 °C in order to improve the resolution and to obtain spectral data which could be fully interpreted. All NMR spectra were recorded in $CDCl_3$ as deuterated solvent. Confirmation of the molecular stuctures of **1** and **2** was obtained from single crystal X-ray structure determinations.

The system of numbering used for the protons and carbon atoms of the thienyl fragment, as shown by Figure 2.13 will consistently be used in the discussions, unless mentioned differently.

If one substituent only, is bonded to the thiophene ring the smaller number will be used for that carbon atom and in the case of a metal carbene substituent on the one side of the ring and a different non-metal substituent on the other side the lower number will be assigned to the carbon atom to which the carbene fragment is bonded.

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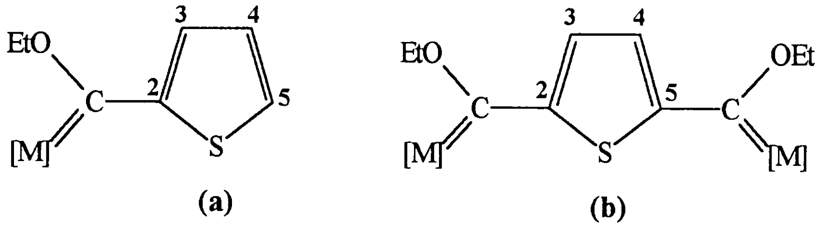

Figure 2.13 Atom Numbering in (a) Monothienyl Carbene Complexes, (b) Bisthienylene Carbene Complexes

2.5.1 ^{1}H NMR Spectroscopy

The coordination of an organic ligand to a metal fragment affects the resonance frequencies of the ligand nuclei in a characteristic way. This coordination shift, $\Delta\delta$, is defined as the chemical shift difference between that of the metal bonded ligand and the free ligand:[35]

$$\Delta\delta = \delta(\text{complex}) - \delta(\text{ligand})$$

Metal-bonded protons are generally regarded as hydridic and experience particularly strong shielding and thus show very large chemical shifts, $\Delta\delta$. The shielding of a proton increases with an increase in the atomic number for a group of metals. Protons which are bonded to metal-bonded carbon atoms display a much smaller span of chemical shifts. Protons at non-coordinated carbon atoms show very small coordination shifts, $\Delta\delta$.[35]

The ^{1}H NMR data obtained for the biscarbene complexes **1** - **4** are summarized in Table 2.2 and support the assigned molecular structures of the complexes. The ^{1}H NMR spectrum of complex **2** is presented by Figure 2.14 and is representative of the spectra for **1** - **4**. From the data in Table 2.2 and Figure 2.14 it is evident that the different metal atoms have an influence on the chemical shifts of protons and an indication of the general features and patterns of the chemical shifts of the protons in the spectra can be obtained. Spectroscopic data[36] have indicated that it is reasonable to replace the metal fragment in Fischer-type carbene complexes with an oxygen, thereby creating an ester. The biscarbene complexes **1** - **4**, treated similarly will transform into the diester, 2,5-$C_4H_2S\{C(O)OEt\}_2$, and it is anticipated that the NMR properties of **1** - **4** should roughly resemble that of the diester, (δ H3, H4 7.73 ppm).[36b]

Single resonances are observed for the symmetrically orientated thienyl protons H3, H4, with δ-values

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ranging from 8.06 ppm - 7.52 ppm in the spectra of the biscarbene complexes. The methylene protons of the ethoxy carbene substituent appear as quartets between 5.21 ppm and 4.97 ppm, while the methyl protons of the same ethoxy substituent are observed as triplets between 1.69 ppm and 1.57 ppm in the spectra of **1** - **4**. The chemical shifts for protons in the spectrum of **1** are downfield from the corresponding shifts in the spectrum of **2**, owing to more shielding of the protons by the metal nucleus in **2**.

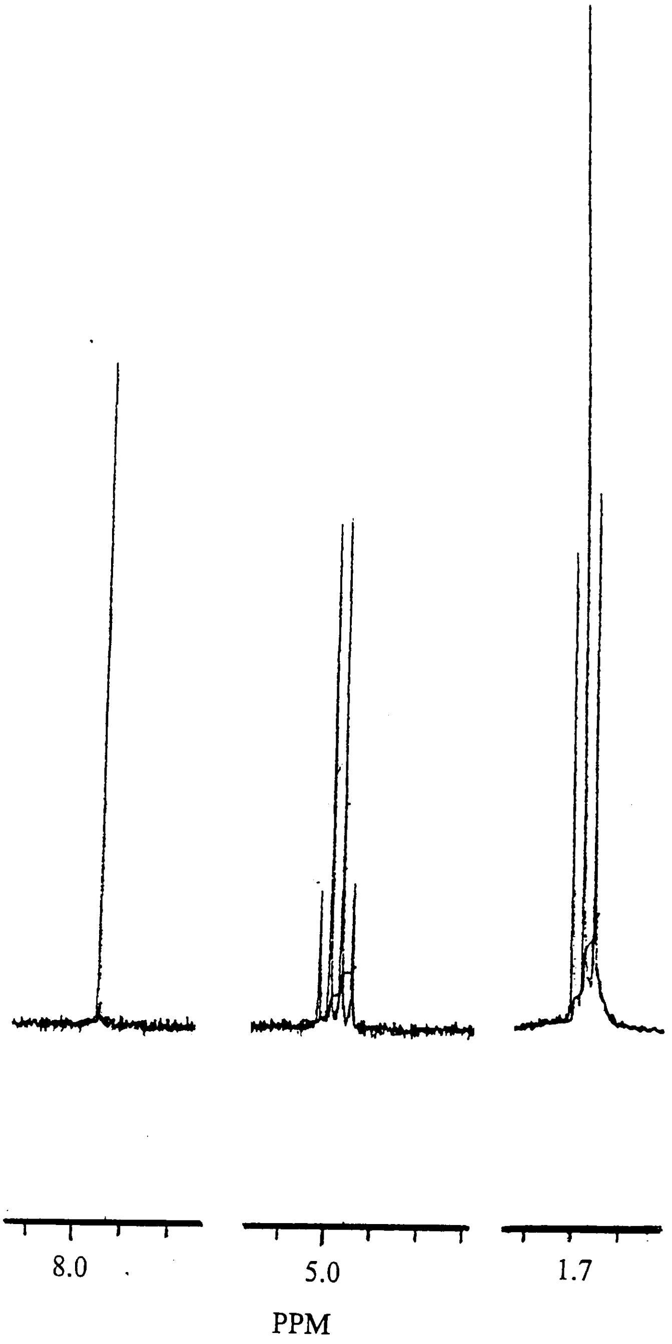

Figure 2.14 ^{1}H NMR Spectrum of $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$

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Table 2.2 ^{1}H NMR Data of the BimetallicThienylene Biscarbene Complexes

Assignment	**Complexes**							
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)							
	1		**2**		**3**		**4**	
Proton	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$
H3, H4 (thiophene)	8.06 (s)	—	7.95 (s)	—	7.65 (s)	—	7.52 (s)	—
$O\mathbf{CH_2}CH_3$	5.21 (q)	7.2	4.98 (q)	7.0	4.97 (q)	6.7	4.97 (q)	7.4
$OCH_2\mathbf{CH_3}$	1.69 (t)	7.1	1.68 (t)	7.1	1.57 (t)	6.8	1.57 (t)	7.0
$C_5\mathbf{H_5}$ (Cp)	—	—	—	—	—	—	4.61 (s)	—
$C_5\mathbf{H_4}CH_3$ (MeCp)	—	—	—	—	4.50 (s), (br) 4.36 (s), (br)	—	—	—
$C_5H_4\mathbf{CH_3}$ (MeCp)	—	—	—	—	1.75 (s)	—	—	—

The chemical shifts for the protons of free thiophene are at 7.20 ppm for H2 and H5 and at 6.96 ppm for H3 and H4.[37] The thienylene protons H3 and H4 in **1** - **4**, on the other hand display a single resonance. Bonded to the metal the electrophilic nature of the carbene moiety causes electron density to be drained from the double bonds of the thiophene ring, (hence from H3 and H4) to the metal nuclei, thus leading to deshielding of H3 and H4 which leads to downfield chemical shifts of approximately 1 ppm compared to free thiophene in the ^{1}H NMR spectrum. Figure 2.15 illustrates this phenomenon.

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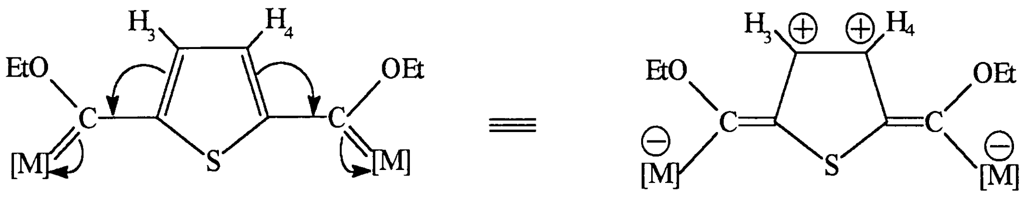

Figure 2.15 Draining of Electron Density from the Thienylene Ring in Thienylene Biscarbene Complexes

The thienylene protons in the ^{1}H NMR spectrum of the chromium and tungsten biscarbene complex with a 2,2'-dithienyl unit linking the carbene units, reported recently as a communication,[31] display chemical shifts of 7.45, 7.49, 8.09 and 8.17 ppm. Based on the data for **1** and **2**, the set of higher δ-values 8.17 (H3) and 7.49 (H4) are assigned according to the thienylene ring with the Cr-carbene substituent in the 2-position and 8.09 (H3) and 7.45 (H4) to the thienylene ring with the W-carbene substituent in the 2-position. Assuming that these assignments are correct, the chemical shifts of H3 are shifted only marginally downfield (0.1 ppm), compared to those in **1** and **2**. A comparison of H4 of the Cr, W biscarbene complex containing the 2,2'-dithienyl unit with H3 of **1** and **2** is senseless. Furthermore in this example metal fragments are connected *via* a carbene and dithienylene unit which is π-conjugated with the intention to distribute charge from one metal fragment to the other, ("push-pull"). A comparison of the ^{1}H NMR data reveals that this complex exhibits very little of such a phenomenon and that the two carbene units operate independently in withdrawing electron density from the thienyl rings. In fact, this seems to be the case on comparing the data of the ^{1}H NMR spectra of this compound with the monocarbene thienyl complexes below.

The chemical shifts, for the thienyl protons in the spectra of the monocarbene complexes, **A** and **B**, which were formed as by-products in the reactions to synthesize the corresponding biscarbene complexes, appear as follows: H3 8.23 ppm, H4 7.20 ppm and H5 7.68 ppm in the spectrum of **A**, H3 8.14 ppm, H4 7.20 ppm and H5 7.80 ppm in the spectrum of **B**. The assignment of H3, H4 and H5 were made according to Gronowitz.[38] Whereas the chemical shift of H3 is downfield in the spectra of **A** and **B** compared to where it appears in the spectra of **1** and **2**, the chemical shift for H4 is upfield. The reason for this becomes evident when the resonance structures (**IX** and **X**) resulting from the π-resonance effect are compared, as shown by Figure 2.16.

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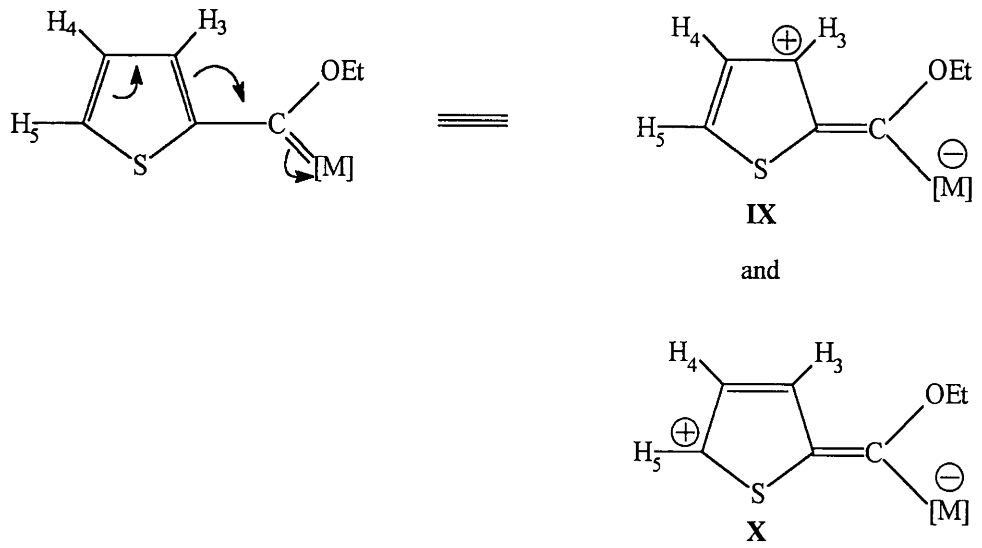

Figure 2.16 Draining of Electron Density from the Thienyl Ring in Complexes A and B

The ^{1}H NMR data correlate with the structures displaying positive charges on H3 and H5, with H4 unaffected. The resonance structures do not discriminate between H3 and H5, however, H3 being closer to the carbene carbon it will be more affected, *i e* δH3 > δH5 > δH4. Although the draining of electron density from the thienylene in the biscarbene complexes **1** - **4** is the combined withdrawing effect of two metal-carbene substituents the nett result is unfavourable. π-Resonance effects generate two positive charges on adjacent carbon atoms, resonance structure **VIII** in Figure 2.15. This result can only be altered if two different metal-carbene fragments with different electron withdrawing properties were linked *via* carbene units to the 2- and 5-positions of the thiophene. Polarization from the one metal fragment to the other is then possible . On a qualitative basis, the data reflects a situation where the thienylene ring in **1** and **2** is marginally more electron poor than in **A** and **B**. Electron density is withdrawn from the thiophene ring in both types of complexes. In comparison the chemical shifts for 2-$C_4H_3SC(O)OMe$[36b] are δH3 7.80, δH4 7.10 and δH5 7.55, which is similar to the case of the diester, and shifted upfield compared to **A** and **B**.

The presence of the methyl group on the Cp ring of compound **3** leads to two non-equivalent groups of two protons, and the cyclopentadienyl protons are present as two broad singlets in the spectrum of **3**. The electron donating methyl group causes shielding of the Cp protons, thus chemical shifts which appear upfield from those for an unsubstituted Cp ring. Electron density can also be distributed to the electro-

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philic carbene carbon through π-interaction with the ethoxy oxygen. Large downfield shifts of the methylene protons are consistent with the strong electron withdrawing properties of the $L_3(CO)_2MC(OEt)$-$C_4H_2SC(OEt)ML_3(CO)_2$ groups of **1** - **4**, Figure 2.17.

XI **XII**

Figure 2.17 Electron Withdrawal from Ethoxy Substituents

The chemical shifts of the methylene protons can thus be used as a probe to indicate the importance of the resonance structure **XII** in Figure 2.17 relative to the competing π-donating resonance effects of the thienylene substituent, (Figure 2.15) and the metal fragments shown by **XI** in Figure 2.17. The corresponding δ-values in the spectrum of **A** are observed at 5.16 ppm and 1.65 ppm respectively for these protons, similarly these appear at 4.99 ppm and 1.64 ppm respectively in the spectrum of **B**. These chemical shifts are similar in the spectra of **1** and **A**, as well as, in the spectra of **2** and **B**, which shows that these chemical shifts are fairly characteristic for a specific metal and insensitive to the number of carbene substituents. The chemical shifts of the thiophene protons on the other hand are determined by the number of carbene ligands and the nature of the transition metal involved.

The chemical shifts for the $-OCH_2CH_3$ group of other related bimetallic biscarbene complexes are given in Table 2.3 for comparison. The data of literature values of spectra recorded in other solvents can, however, not be compared directly.

On comparing the chemical shifts of the methylene and methyl protons of the ethoxy substituents of the examples in Table 2.3 with those of **1** and **2**, the following observation was made. When the biscarbene fragments are connected *via* a non-conjugating fragment, the resonances are shifted upfield compared to those of **1** and **2**. With conjugated phenyl and dienyl links the chemical shifts appear further downfield than the corresponding resonances of **1** and **2**. A final observation seems to indicate that the thienylene is a better π-donor group in **1** and **2** than the analogous phenyl fragments in Table 2.3 where π-conjugation exists.

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Table 2.3 ^{1}H NMR Chemical Shifts of Related Bimetallic Biscarbene Complexes

M	**Ref**	OCH_2CH_3	OCH_2CH_3	**Bridging Ligand**
		Chemical Shifts, δ (ppm)		
Cr[a]	10	5.05 (q)	1.44 (t)	$C(OEt)CH_2C_6H_4CH_2$-$C(OEt)$
W[a]	10	4.88 (q)	1.25 (t)	$C(OEt)CH_2C_6H_4CH_2$-$C(OEt)$
Cr[b]	9	5.20 (q)	1.75 (t)	C(OEt)-*p*-C_4H_6-C(OEt)
W[c]	9	5.10 (q)	1.70 (t)	C(OEt)-*p*-C_4H_6-C(OEt)
Cr, W[a]	30	Cr: 5.17 (q) W: 4.98 (q)	Cr: 1.68 (t) W: 1.66 (t)	C(OEt)-2,2'-C_4H_3S-C_4H_3S-C(OEt)
Cr[a]	17	5.28 (q)	1.70 (t)	C(OEt)CHCH-*p*-C_6H_4-CHCHC(OEt)

(a) $CDCl_3$, (b) CD_3COCD_3, (c) CD_2Cl_2

In the spectrum of the cyclopentadienyl manganese monocarbene complex, $Cp(CO)_2MnC(OEt)$-C(H)-C(H)(Ph),[39] the chemical shifts of the methylene and methyl protons of the ethoxy group appear at 4.78 ppm and 1.25 ppm, respectively and the chemical shift of the Cp protons is observed at 4.46 ppm. These corresponding chemical shifts appear further downfield in the spectrum of, **4**, as well as, in the spectrum of the methylcyclopentadienyl manganese complex, **3**. This difference can in part be attributed to the fact that different deuterated solvents were used to record the spectra, but can also be attributed to the action of two metal carbene functionalities in **3** and **4**, compared to one above. However, based on the data for mono- and biscarbene complexes of W and Cr with thienyl substituents, this seems unlikely.

2.5.2 ^{13}C NMR Spectroscopy

The ^{13}C NMR data of complexes **1** - **4** are summarized in Table 2.4. The chemical shifts for carbene carbon atoms in spectra range from 400 - 200 ppm. Deshielding of a similar magnitude is also encountered for carbenium ions it is therefore clear that the carbene carbon atoms in their respective metal complexes bear a partial positive charge. Within a group of metals shielding of the carbon nucleus bonded to the metal atom increases with increasing atomic number of the metal [eg.: $Cr(CO)_6$ 212 ppm, $Mo(CO)_6$ 202 ppm, $W(CO)_6$ 192 ppm].[35]

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Table 2.4 ^{13}C NMR Data of BimetallicThienylene Biscarbene Complexes

Assignment	**Complexes**			
	Chemical Shifts, (δ, ppm)			
Carbon Atom	**1**	**2**	**3**	**4**
C (carbene)	321.9	312.5	319.5	319.6
$M(CO)_2$	—	—	230.8	230.5
$M(CO)_5$, (*trans*)	223.7	202.7	—	—
$M(CO)_5$, (*cis*)	216.5	196.9	—	—
C2 and C5 (thiophene)	157.7	162.6	157.2	157.2
C3 and C4 (thiophene)	137.1	137.2	132.5	132.4
$\mathbf{C_5H_4}$R (R = H or CH_3); (Cp)	—	—	84.4 83.3	84.6
$\mathbf{OCH_2}CH_3$	77.4	79.0	73.9	74.0
$OCH_2\mathbf{CH_3}$	15.2	14.9	15.3	15.3
$C_5H_4(\mathbf{CH_3})$ (MeCp)	—	—	13.5	—

The carbene carbon atoms in **1** - **4** have chemical shifts of between 312 and 322 ppm. The spectrum of **1** displays a chemical shift which is the furthest downfield, whereas it is the furthest upfield in the spectrum of **2**. This is in accordance with the phenomenon that an increase in the atomic number of metals in the same group leads to an increase in the shielding of the carbon nucleus. The same observation is made for the carbonyl groups; in the spectrum of complex **1**; the chemical shifts for both of the *cis* and *trans* carbonyl groups are further downfield than for the corresponding carbon atoms in the spectrum of **2**. In the spectra of **3** and **4** the chemical shifts for the carbene carbon atoms are virtually at the same δ-value, as is the case for the carbonyl groups, which is understandable as these carbon nuclei are bonded to manganese atoms in both complexes. The chemical shifts (ppm) for the carbene carbon atom appears at 319.8 in the spectrum of **A**[40] and at 312.5 ppm in the spectrum of **B**, and for the carbonyl groups: δCO *cis* 218.7 and δCO *trans* 224.9 in the spectrum of **A**[40] and δCO *cis* 197.6 and δCO *trans* 205.0 in the spectrum of **B**. These δ values are in good agreement with values reported in literature, fairly insensitive to changes of substituents on ligands and are representative of the type of ligand and the metal.[41]

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The ^{13}C NMR chemical shifts for the carbon atoms in the spectrum of free thiophene appear as two signals, at 124.9 ppm for C2 and C5 and at 126.7 ppm for C3 and C4.[37] Similar as for chemical shifts in the ^{1}H NMR spectra, the ^{13}C chemical shifts for the coordinated thienylene group are downfield from those in the spectrum of free thiophene. This can be attributed to the deshielding of the ring carbon nuclei caused by the transfer of electron density from the ring to the metal carbene moieties.

The chemical shifts for the carbon atoms of thienyl appear as follows in the spectra of complexes **A** and **B**: C2 157.5 ppm, C3 135.8 ppm, C4 129.8 ppm and C5 141.5 ppm in the spectrum of **A**[40], C2 162.0 ppm, C3 135.9 ppm, C4 128.9 ppm and C5 141.4 ppm in the spectrum of **B**. The chemical shifts for C2 are virtually the same as in the spectra of **1** and **2**, although shifted marginally upfield in the spectra of **A** and **B**. The chemical shifts for C3 and C4 on the other hand, appear somewhat further upfield in the spectra of complexes **A** and **B**, especially that of C4, due to the absence of the second carbene moiety. The chemical shift for C3 is downfield from that of C4 as it is closer to the carbene moiety. The chemical shift for C5 appears downfield in the spectra of **1** and **2** compared to the spectra of **A** and **B**, due to the absence of the second carbene moiety in the latter. These results support conclusions made from the ^{1}H NMR data and is consistent with resonance structures in Figures 2.15 and 2.16.

The chemical shifts for the methylene- and methyl carbon atoms of the ethoxy group of the carbene moiety appear at 77.2 ppm and 15.5 ppm in the spectrum of **A**[40] and at 79.0 ppm and 14.9 ppm in the spectrum of **B**. These δ-values in the spectra of **1** and **2**, are virtually the same for **1** and **A**, as well as, for **2** and **B**, as is the case for the methylene protons in the ^{1}H NMR spectra.

The resonances of the carbene carbons in **3** and **4** appear at exactly the same chemical shift value of 319 ppm, which is also observed for the biscarbene complex $(MeCp)(CO)_2Mn\{C(OEt)CH{=}CHC(OEt)\}Mn(MeCp)(CO)_2$, which has a π-conjugated link between the carbene carbons and upfield compared to the 338 ppm recorded for $(MeCp)(CO)_2Mn\{C(OEt)CH_2CH_2C(OEt)\}Mn(MeCp)(CO)_2$ which does not contain an unsaturated carbon fragment connecting the carbenes.

Owing to the downfield shift of resonances associated with the thienyl ring in **1** and **2** in the ^{1}H and ^{13}C NMR transfer of electron density from the metal fragment *via* the carbene carbon to the ring was not considered to extend beyond the carbene carbon. Therefore, the resonance structure **XIII** in Figure 2.18 was not deemed important. Furthermore, the process shown in **XIV** whereby electron density is distributed from the sulphur atom to the metal fragments was not perceived as something that takes place independently, but, owing to the aromatic character of thiophene, included as part of the ring effect. This may be an oversimplification as the aromatic character may be altered significantly on transfering π-electron density to the substituents.

XIII **XIV**

Figure 2.18 Resonances Structures for 1 or 2

2.5.3 Infrared Spectroscopy

Carbonyl stretching vibrational frequencies, in comparison to M-C stretching frequencies can be regarded as being independent from other vibrations in the molecule. Therefore a qualitative correlation can be established between the position of the bands, *i e* the CO stretching vibrational frequencies and the CO bond order and bonding properties of other unique ligands. The stretching vibrational frequency for a free CO group is 2143 cm^{-1}, whereas it lies between 1850 and 2120 cm^{-1} for terminal carbonyl ligands[35], eg. in $Cr(CO)_6$, νCO = 2000 cm^{-1}. Different patterns for the bands in the carbonyl region in spectra are observed for metal carbonyl fragments and the number and intensities of the bands aid in the identification of the structure of a particular fragment. The adaptation of a method of local symmetry for the carbonyls and the assignment of symmetry symbols to vibrational modes and bands are available in literature.[42]

The infrared spectrosopic data for the bimetallic thiophene biscarbene complexes **1** - **4** are summarized in Table 2.5. Figure 2.19 shows the carbonyl regions in the infrared spectra of complexes **1** and **4**.

The band ($A_1^{(2)}$) is affected most by changes in electronic properties of the unique ligand of $M(CO)_5L$ and is found at lower wavenumbers for W compared to Cr complexes with the same ligands.

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

The wavenumber of the $A_1^{(2)}$ band in the spectrum of **2** is only marginally lower than that observed in the

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spectrum of **1**. In the spectra of **3** and **4** the wavenumbers for the A and A^1 bands differ only slightly from each other, but due to the fewer carbonyl ligands, appear far lower than those of **1** and **2**.

Table 2.5 Infrared Data of the Bimetallic Thienylene Biscarbene Complexes

Assignment		**Complexes**			
		Stretching Vibrational Frequency, (νCO, cm^{-1})			
		1	**2**	**3**	**4**
M(CO)$_5$	A$_1$$^{(1)}$	2054 2053	2074 2061	—	—
	B$_1$	1987 —	1985 —	—	—
	E	1953 1948	1952 1945	—	—
	A$_1$$^{(2)}$	1964 1948	1960 1945	—	—
M(CO)$_2$	A	—	—	1944 1932	1948 1935
	A^1	—	—	1893 1874	1896 1877

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

The stretching vibrational frequencies of the M(CO)$_5$ unit present in other biscarbene complexes are compared to those in the spectra of **1** and **2** in Table 2.6. The fragments designated **(i)**, **(ii)** and **(iii)** are compared.

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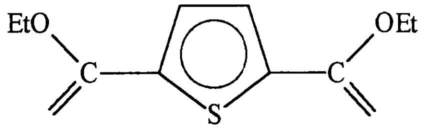
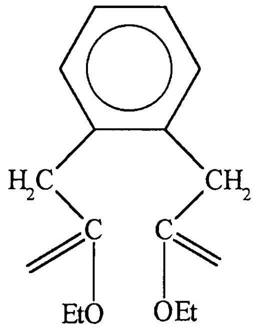
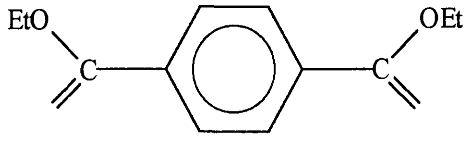


(i)



(ii)



(iii)

The wavenumbers of the vibrational stretching frequencies associated with $A_1^{(2)}$ are highest in the spectra of the biscarbene complexes which contain -CH_2-*o*-C_6H_4-CH_2-[10] and lowest for **1** and **2**. The complexes with the bridging unit -*o*-C_6H_4-[9], have $A_1^{(2)}$ bands of higher wavenumbers compared to **1** and **2**. Thus for the three examples the most electron density as reflected by the infrared data is found on the metal nuclei with the thienylene bridging unit, thus leading to an increase in the metal-carbonyl back bonding with the corresponding decrease in the C≡O bonding order, hence the lower wavenumbers.

Table 2.6 Stretching Frequencies for Bimetallic Biscarbene Complexes

Band	Stretching Vibrational Frequency, (νCO, cm^{-1})					
	i*		ii		iii	
M	Cr	W	Cr	W	Cr	W
	1	2				
$A_1^{(1)}$	2053	2061	2060	2068	2071	2070
$A_1^{(2)}$	1948	1945	1975	1975	1957	1938
E	1948	1945	1943	1940	1949	1932

Solvent: dichloromethane

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

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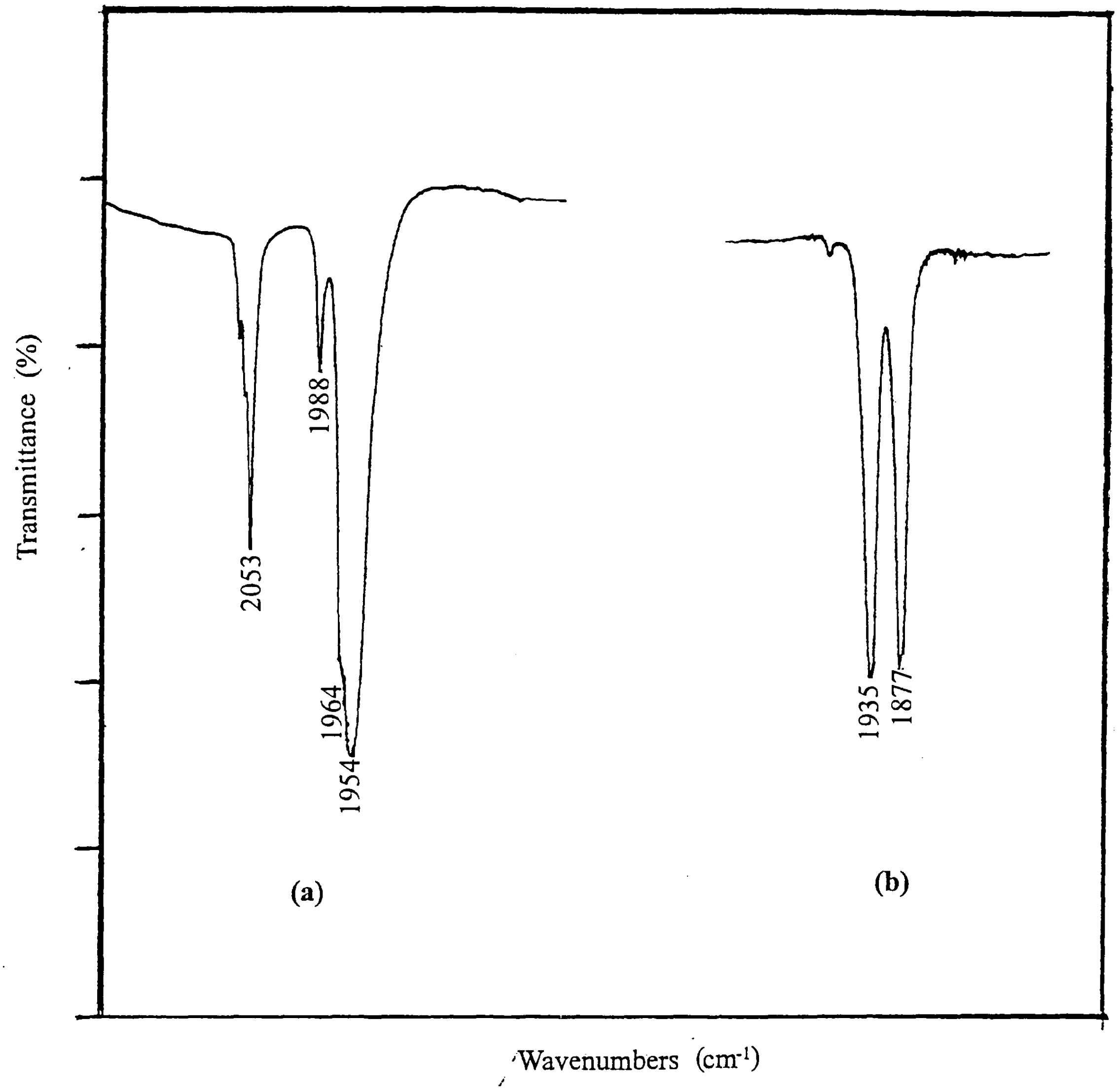

Figure 2.19 Carbonyl Regions in the Infrared Spectra of (a) $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$ and (b) $(CO)_2CpMn\{C(OEt)C_4H_2SC(OEt)\}MnCp(CO)_2$

The wavenumbers for the carbonyl stretching frequencies in the spectra of complexes **A** and **B**, recorded in hexane, are: $A_1^{(1)}$ 2050 cm^{-1}, B_1 1980 cm^{-1}, E 1946 cm^{-1} and $A_1^{(2)}$ 1957 cm^{-1} for **A**, and $A_1^{(1)}$ 2070 cm^{-1}, B_1 1977 cm^{-1}, E 1944 cm^{-1} and $A_1^{(2)}$ 1952 cm^{-1} for **B**. A comparison with the corresponding wavenumbers of **1** and **2** reveals that the stretching vibrational frequencies are at lower values which implies that the thienylene unit in **1** and **2** contributes to less electron density being placed on the two metal fragments compared to that, that the thienyl unit of **A** and **B** can place on one metal fragment.

A comparison of the infrared data in the carbonyl region with the mixed biscarbene complex[31] containing a connecting dithienylene unit was not possible as no assignments were made and the spectrum was recorded in Nujol.

2.5.4 Mass Spectroscopy

A molecular ion peak, M^+, was observed in the mass spectra for each of the complexes **1** - **4** and a general fragmentation pattern was recognized, as shown by Scheme 2.10. After the initial fragmentation of the carbonyl ligands the carbene moieties are fragmented in a stepwise manner. First an ethyl of an ethoxy group is fragmented which can be represented by the formation of a fragment ion with an acyl group. Fragment ions indicate that thereafter the ethyl of the second carbene moiety is lost in a similar fashion. The Cp ring remains bonded in **3** and **4** and is only fragmented after the carbene and carbonyl ligands.

Table 2.7 gives a summary of the most important peaks and fragment ions associated with these in the spectra of each of the biscarbene complexes.

The M^+ ions and fragmentation patterns obtained from the mass spectra of **1** - **4**, aided in the identification of the complexes and verification of the structures of these complexes.

Table 2.7 Fragment Ions and Peaks of the Thienylene Biscarbene Complexes

Complex	Fragment Ions, (%I)
1	580 (15) M^+; 300 (100) M^+ - 10 CO; 271 (11) M^+ - 10 CO - CH_2CH_3; 242 (13) M^+ - 10 CO - 2 CH_2CH_3; 186 (20) M^+ - 12 CO - 2 CH_2CH_3
2[a]	842 (10) M^+; 562 (20) M^+ - 10 CO; 533 (20) M^+ - 10 CO - CH_2CH_3; 504 (11) M^+ - 10 CO - 2 CH_2CH_3; 448 (10) M^+ - 12 CO - 2 CH_2CH_3
3	576 (21) M^+; 464 (24) M^+ - 4 CO; 435 (26) M^+ - 4 CO - CH_2CH_3; 406 (48) M^+ - 4 CO - 2 CH_2CH_3; 350 (16) M^+ - 6 CO - 2 CH_2CH_3
4	548 (21) M^+; 436 (80) M^+ - 4 CO; 407 (20) M^+ - 4 CO - CH_2CH_3; 378 (83) M^+ - 4 CO - 2 CH_2CH_3; 322 (32) M^+ - 6 CO - 2 CH_2CH_3

[a] Based on ^{183}W

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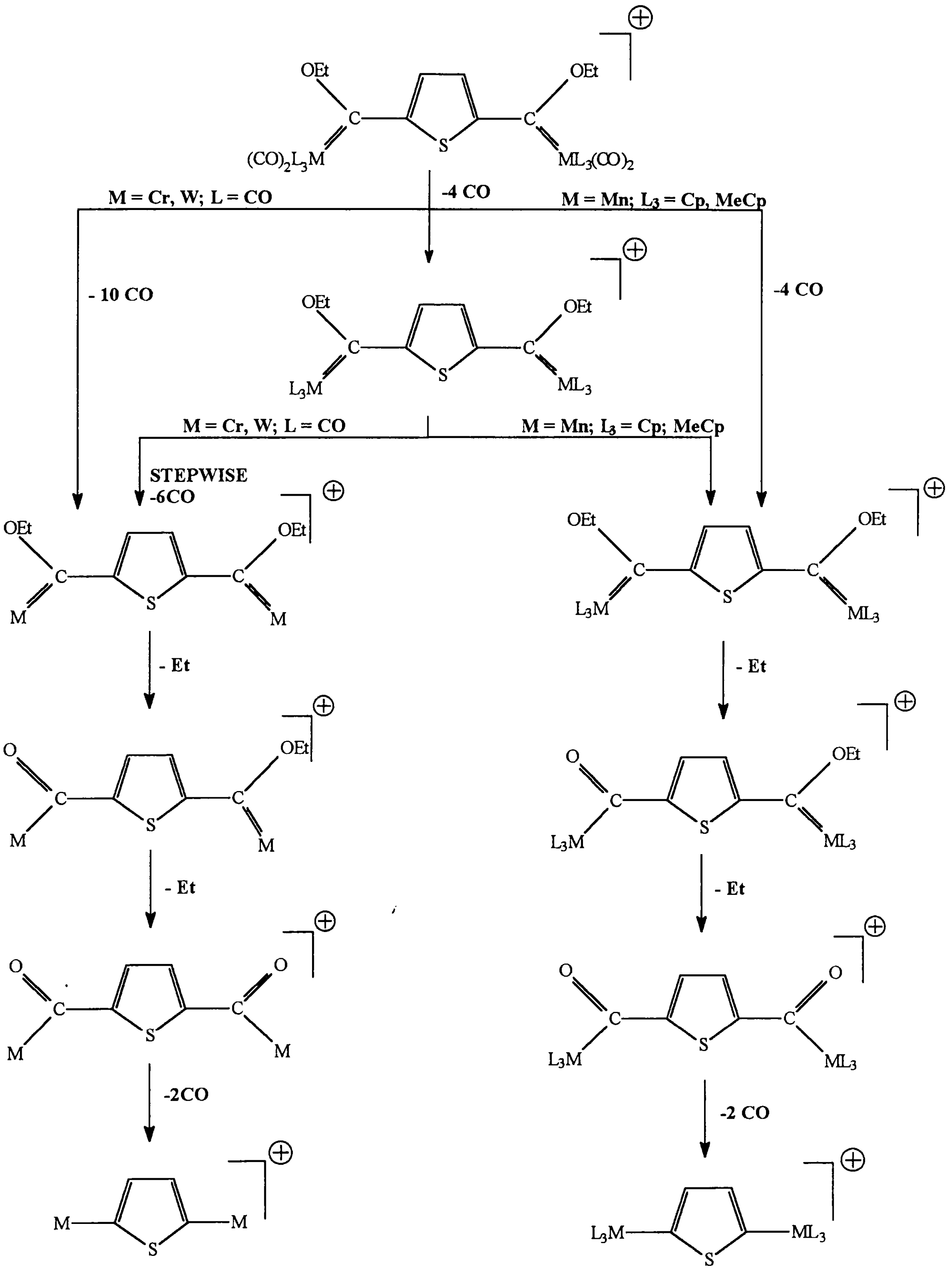

Scheme 2.10

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2.5.5 X-Ray Crystallography

Final confirmation of the structures of $(CO)_5M\{C(OEt)C_4H_2SC(OEt)\}M(CO)_5$, where M = Cr, **(1)** and M = W, **(2)**, was obtained in single crystal X-ray diffraction studies. Table 1 of Appendix 1 lists the crystallographic data of **1**, similarly it is listed in Table 1of Appendix 2 for **2**. Fractional coordinates for **1** are listed in Table 2 of Appendix 1 and for **2** in Table 2 of Appendix 2. Figures 2.20 and 2.21 represent the ORTEP[43] plots of the two structures. Relevant bond lenghts and angles are listed in Table 2.8. Important to note is that the numbering system for the carbon atoms in thiophene is not the same as that used for the spectroscopy, but that it has been adapted in order to facilitate the comparison of bond lengths and -angles of complexes 1 and 2, see Figures 2.20 and 2.21.

Single crystals of **1** and **2** were isolated from dichloromethane-hexane solutions and were suitable for X-ray diffraction studies. Complex **1** crystallized in the space group C2/c with a = 21.593(12), b = 10.235(3) and c = 22.531(12) Å, z = 8. Complex **2** crystallized in the space group P21/n with a = 14.731(1), b = 12.016(1), c = 15.087(2) Å, z = 4.

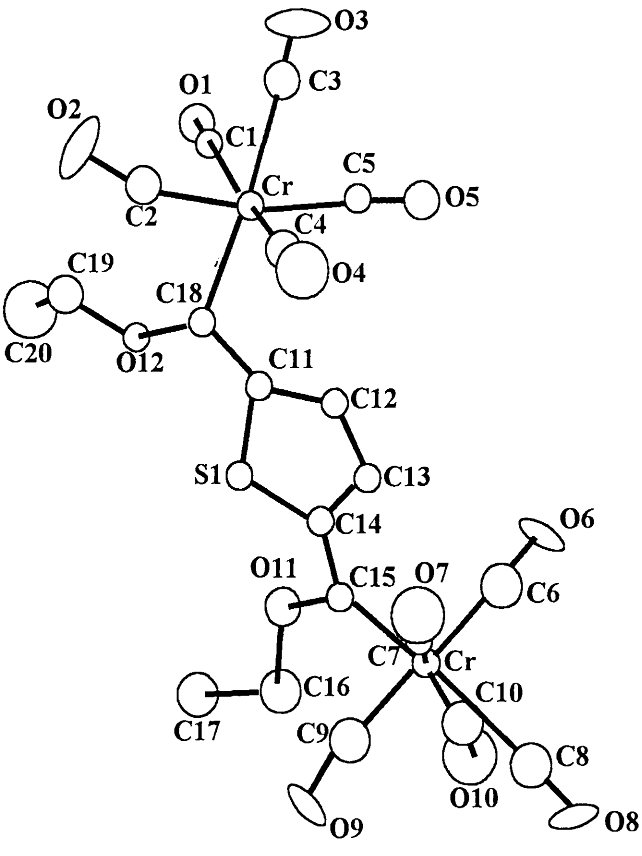

Figure 2.20 ORTEP Plot of $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$

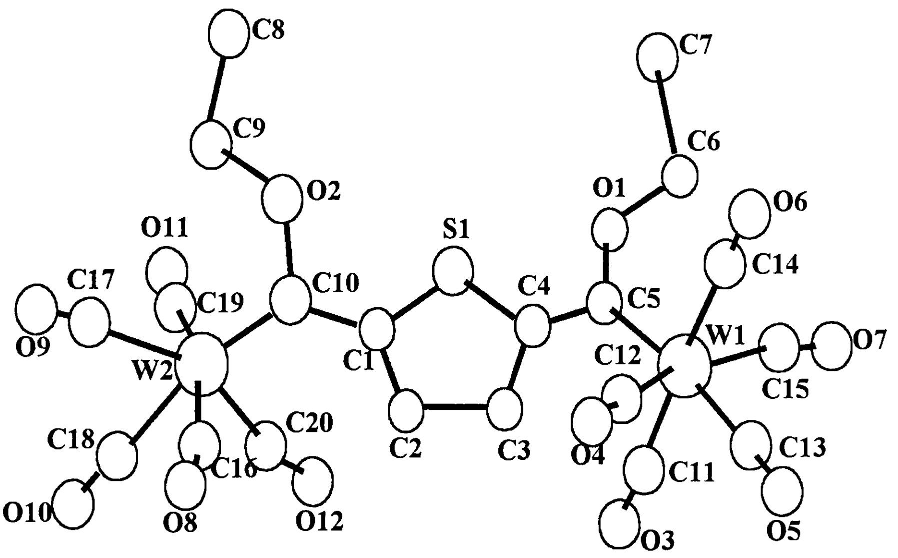

Figure 2.21 ORTEP Plot of $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$

The thienylene ring, carbene carbons and metals of **1** and **2** are planar, thus facilitating the distribution of electron density *via* π-conjugation. The $M(CO)_5$-fragments are on the same side of the thiophene ring *i e* on the side opposite to the sulphur of the ring. A plane of symmetry is found in the molecule and is perpendicular to the thienylene ring, intersects the sulphur and bisects the C12-C13 bond in **1** and the C2-C3 bond of the ring in **2**. The structures of **1** and **2** are remarkably similar, with the only difference the longer distances associated with the larger tungsten atom compared to the smaller chromium atom.

The bond lengths in free thiophene were determined as S-C(1) 1.714(1) Å, C(1)-C(2) 1.370(2) Å, C(2)-C(3) 1.424(2) Å, C(3)-C(4) 1.370(2) Å and C(4)-S 1.714(1) Å. The bond angles in free thiophene were determined as C(1)-S-C(4) 92.2(1)°, S-C(1)-C(2) 111.5(3)°, C(1)-C(2)-C(3) 112.5(3)° and C(2)-C(3)-C(4) 112.5(3)°.[44]

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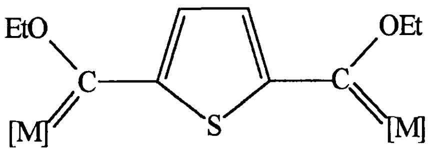
Table 2.8 Selected Bond Lengths and Angles in Complexes 1 and 2

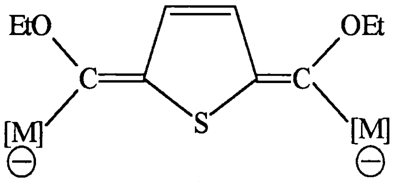
Bond Lengths	**(1) M = Cr**	**(2) M = W**
M(1)-C(Carbene)	2.040(5)	2.156(12)
M(2)-C(Carbene)	2.043(5)	2.154(11)
S-C(11) / S-C(1)	1.730(5)	1.738(10)
C(11)-C(12)/ C(1)-C(2)	1.385(6)	1.385(13)
C(12)-C(13) / C(2)-C(3)	1.388(6)	1.407(13)
C(13)-C(14) / C(3)-C(4)	1.371(6)	1.390(13)
C(14)-S / C(4) - S	1.732(5)	1.725(10)
C(14)-C(15) / C(4)-C(5)	1.496(6)	1.464(13)
C(11)-C(18) / C(1)-C(10)	1.456(6)	1.470(13)
C(15)-O(11) / C(5)-O(1)	1.319(5)	1.325(10)
C(18)-O(12) / C(10)-O(2)	1.330(6)	1.349(12)
Bond Angles		
C(11)-S-C(14) / C(1)-S-C(4)	92.3(2)	93.6(4)
C(12)-C(13)-C(14) / C(2)-C(3)-C(4)	112.6(5)	114.6(10)
S-C(11)-C(12) / S-C(1)-C(2)	109.3(4)	109.8(8)
C(11)-C(12)-C(13) / C(1)-C(2)-C(3)	114.8(5)	112.9(10)
S-C(14)-C(13) / S-C(4)-C(3)	111.0(4)	109.0(8)
M(1)-C(15)-C(14) / M(1)-C(5)-C(4)	124.3(4)	126.3(8)
M(2)-C(18)-C(11) / M(2)-C(10)-C(1)	125.3(4)	126.9(8)

On comparing the bond lengths in thiophene of the complexes **1** and **2** with those in free thiophene, all of these are longer in the complexes except for the C(2)-C(3) bond which is shorter in the complexes. Free thiophene displays carbon-carbon bonds which are more localized, *i e* more double bond character in C1-C2 and C3-C4 and more single bond character in C2-C3 than in **1** and **2**. Within experimental error all of the C-

C bond lengths of the thienyl ring of **1** and **2** are the same, indicating delocalization of electron density over the ring. This is represented by the structures **XV** and **XVI** in Figure 2.22. However, structure **XVI** is perhaps of less importance as it is not significantly supported by shorter C(carbene)-C(thienyl) bonds. These distances recorded in **1** or **2** are only slightly shorter than normal C-C single bonds, (1.51(3) Å).[45] The bond angles also differ from the corresponding angles in thiophene. These differences are an indication that the thiophene ring is somewhat more distorted in the complexes **1** and **2** than in free thiophene.



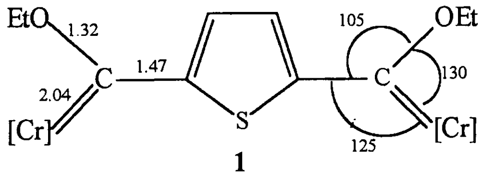
XV



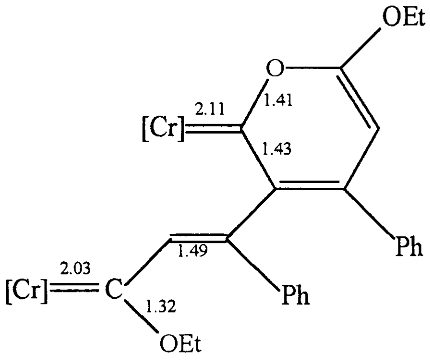
XVI

Figure 2.22 Delocalization of Electron Density in 1 and 2

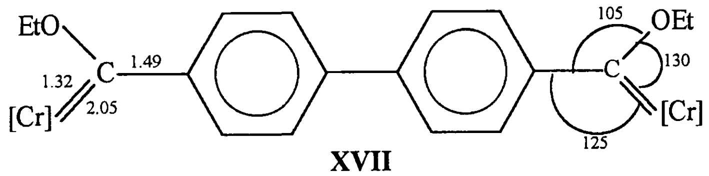
The metal carbene carbon distances of **1** and **2** fall within the range reported for alkoxy monocarbene complexes of Cr and W and represent middle to shorter values. For comparison the average distances and angles of **1** with **XVII**[22], **XVIII**[5d] and **XIX**[46] for Cr and of **2** with **XX**[5c], **XXI**[10] and **XXII**[7] for W are listed in Figure 2.23.



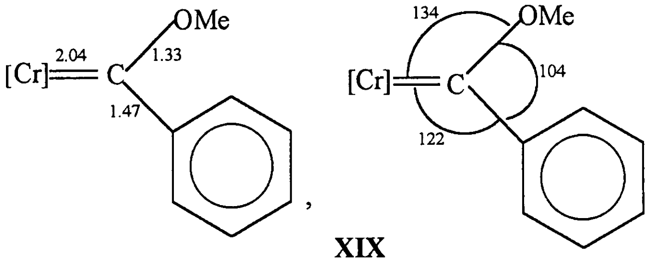
1



XVIII



XVII



XIX

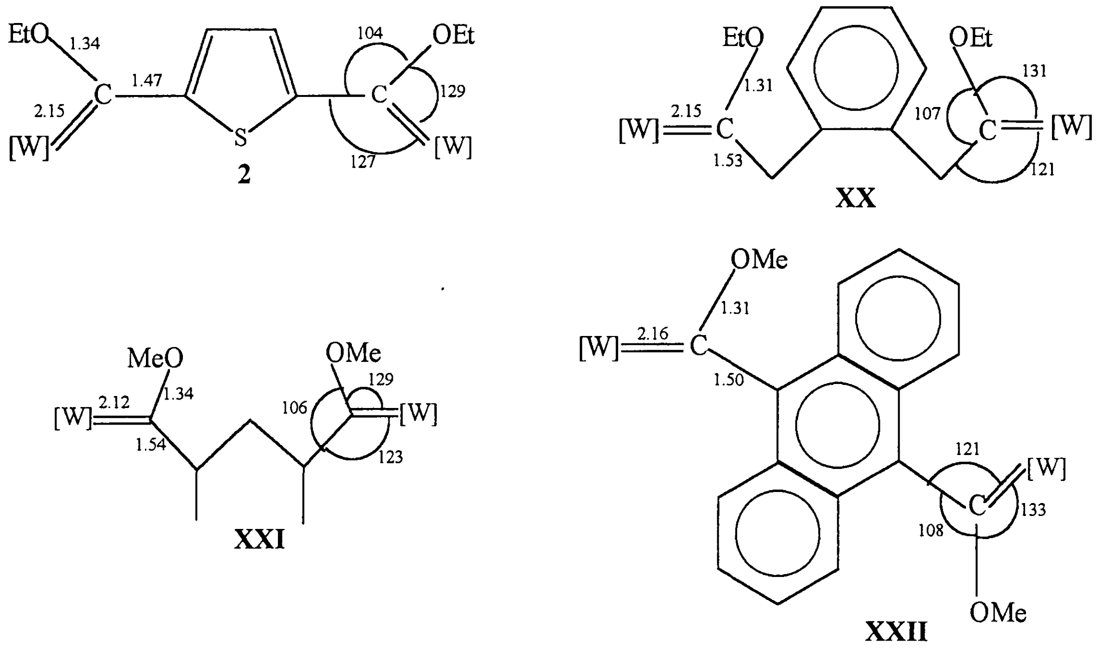


Figure 2.23 Selected Bond Distances and Angles of Related Structures

Bond distances associated with the carbene centre are remarkably similar, (distances to 1/100 Å, angles to 1 °) for all the examples shown. The only deviation is found in the structure of **XVIII** where angular deviations occur due to a six membered ring in one of the carbene units which results in a lengtening of the Cr-C(carbene) and C(carbene)-C(ring) distances. In fact, the comparison of **1** with the monocarbene complex **XIX** reveals that the carbene structural features are practically the same and that the introduction of a second carbene unit in **1** neither alters nor affects the geometry around the other carbene in any significant manner.

2.6 Synthesis of the Bimetallic Biscarbene Complexes of 2,2'-Methylene Dithienyl

Unlike thiophene the ligand 2,2'-methylene dithiophene (MDT) does not have a conjugated π-system through which the metal nuclei contained within the carbene moieties are in contact. It was, however, deemed interesting enough to synthesize biscarbene complexes of this ligand, in order to inspect the influences of a conjugated π-system in a biscarbene complex compared to the absence thereof.

The ligand MDT was prepared by a known method.[47] This method, in which zinc chloride is used as condensing agent, comprises the chloromethylation of thiophene. In the presence of zinc chloride and hydrochloric acid, thiophene reacts with a formaldehyde solution to form MDT. It is important that the reaction should be performed at between -7 and 0 °C, lest the yield of MDT is greatly reduced, as would be the case if the temperature rises above 0 °C. This is due to the fact that the amount of resin formed (at higher temperatures) increases and leads to poor yields of final products.

Unlike thiophene the double deprotonation of MDT is readily achieved with an excess of butyllithium in THF as solvent to yield the lithium acylates.[48] The double deprotonation of MDT is, however, greatly facilitated by the addition of the monomeric BuLi·TMEDA complex in the absence of THF with hexane as solvent. The reaction proceeds according to the same mechanism as described for the double deprotonation of thiophene.[49] In order to afford the double deprotonation of MDT a solution of MDT, butyllithium and TMEDA had to be refluxed for 30 min. The synthesis of the biscarbene complexes **5** - **7** was carried out by means of the classic Fischer procedure.[6] The conversion did, however, not proceed quantitatively, as a mixture of products was obtained. The separation of these products was done with extreme difficulty, employing repeated column chromatography with a non-polar solvent as eluting agent. Pure fractions of the biscarbene complexes could only be obtained after much effort. The other products could not be isolated in pure fractions and could therefore not be characterized with certainty. Some spectroscopic data indicated that the corresponding monocarbene complex was also synthesized in each reaction. Scheme 2.11 provides an outline of the route according to which the reaction to synthesize the bimetallic σ,σ-biscarbene complexes **5** - **7** proceeds, with $L_3(CO)_2M\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}M(CO)_2L_3$, M = Cr, L = CO (**5**); M = W, L = CO (**6**); M = Mn, L_3 = Cp (**7**).

The biscarbene complexes **5** - **7** were isolated as oils, which were fairly stable in an inert atmosphere. Complexes **5** and **6** are bright red in colour, whereas complex **7** has a more brownish red colour. The relative yields of these products were good.

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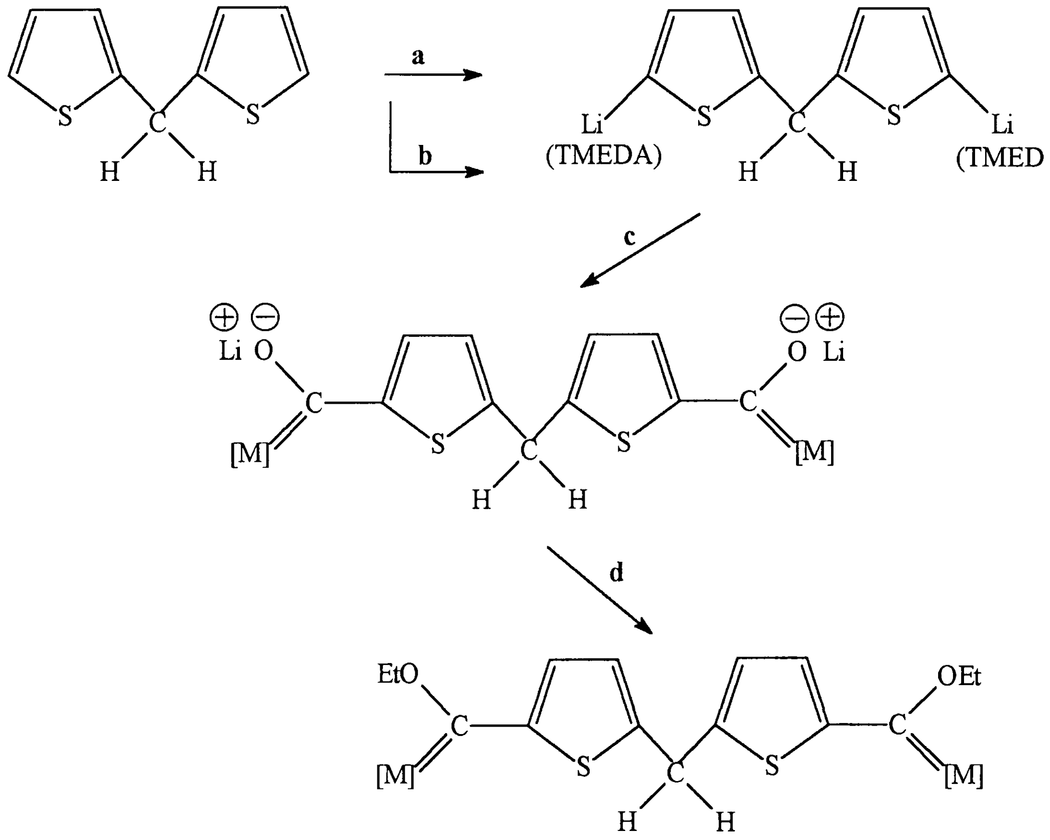


5 - 7

Reagents: (a) BuLi(TMEDA), hexane, reflux; (b) BuLi, THF, –5 to -10 °C, (c) THF, 2 equiv. $ML_3(CO)_3$, (d) 2 equiv. $[Et_3O][BF_4]$, CH_2Cl_2

Scheme 2.11

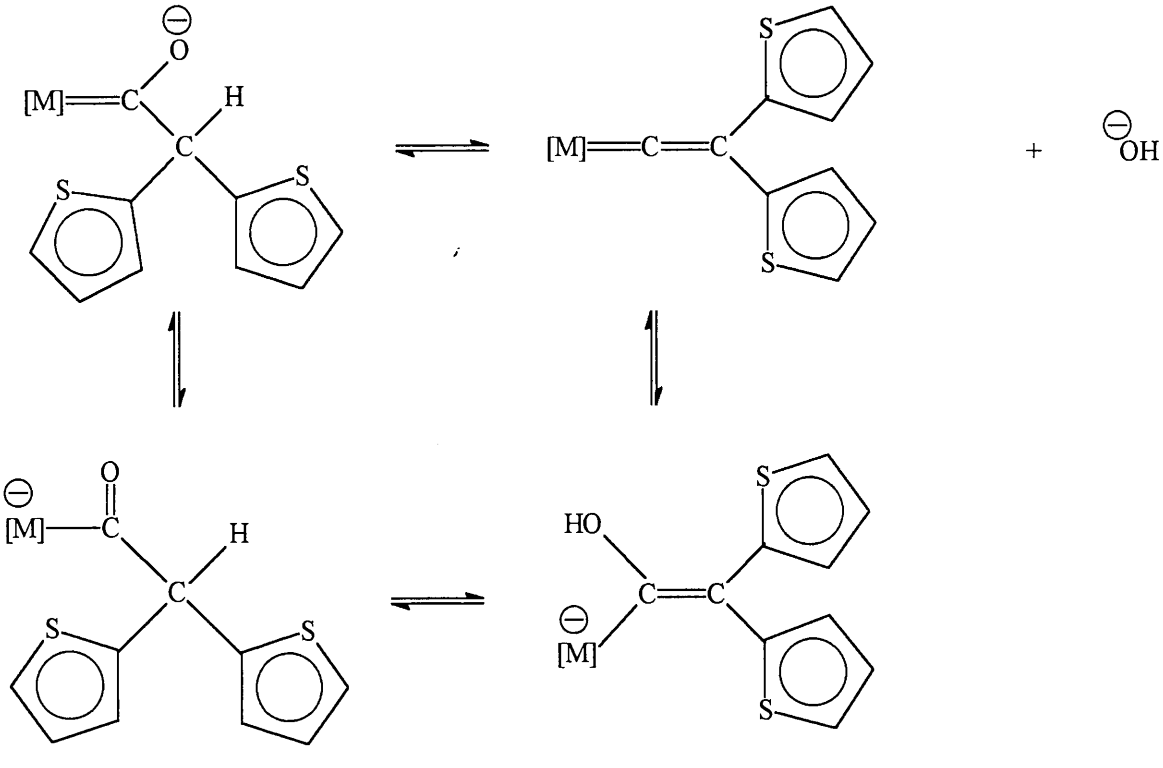
Metallation of the methylene carbon of MDT, *i e* C_α-lithiation of MDT, is a process which is in competition with the double metallation described above. In order to achieve C_α-lithiation, certain facts have to be taken into consideration. In view of the stronger stabilizing effects of the 2-thienyl group compared to that of a phenyl group on not only carbocations[50] but also carbanions[51], the C_α-protons of MDT would be more acidic than those of diphenylmethane ($pK_a = 32.8$) and even more acidic than those in dimethylsulfoxide ($pK_a = 35$). On the other hand, the C5-protons must be less acidic than in DMSO, even though these receive the heteroatom assistance of the adjacent sulphur atom for metallation.[48] Different methods have been proven to successfully lead to the deprotonation of methylene dithiophene at the C_α-position and the following results have been documented:[48]

(i) Treatment of MDT with sodium hydride or *n*-butyllithium in DMSO-THF (1/1 v/v) generated the desired metallated complex as shown by ^1H and ^{13}C NMR.

(ii) Lithium diisopropylamide (LDA) also effected the selective C_α-lithiation in THF in spite of possible directing properties by the sulphur atom.

(iii) The addition of 1.5 equivalents of TMEDA to *n*-butyllithium-THF showed a remarkable temperature dependence of the selectivity: C5-lithiation at - 60 °C, and C_α-lithiation at 0 °C. The more TMEDA is added the more the C_α-lithiation is favoured. The C_α-lithiation was resulted even at -60 °C in a 1 : 1 mixture of THF / TMEDA.

Bearing the above in mind, the C_α-lithiation was attempted by employing (iii). After the subsequent steps had been carried out, (addition of the metal carbonyl and quenching with triethyloxonium tetrafluoroborate at low temperatures), the desired monocarbene complexes, $L_3(CO)_2M\{C(OEt)C(Th)_2H\}$ were not obtained, but rather a mixture of compounds which appeared to be interesting, but could not successfully be separated, in order to make the characterization of these products possible. It appeared as if these products were continuously and spontaneously converting from the one to the other. The possible conversion of the acylate intermediate to a vinylidene complex is shown in Scheme 2.12. Both the hydroxyvinyl and the vinylidene complexes will be very reactive and unstable species under the prevailing reaction conditions.



Scheme 2.12

2.7 Spectroscopic Characterization of the Bimetallic MDT Biscarbene Complexes

The bimetallic biscarbene complexes **5** and **6** were spectroscopically characterized with ^{1}H NMR, ^{13}C NMR and infrared spectroscopy, the complex **7** was characterized with ^{1}H NMR and infrared spectroscopy. The spectroscopic data are summarized in Tables 2.9 - 2.11. No general fragmentation patterns could be obtained from the mass spectra of these complexes, a molecular ion peak could be obtained from the spectrum of **5**, (676 (5%)), only. The numbers allocated to the respective protons and carbon atoms as indicated in Figure 2.24 will be used throughout the discussion to ensure consistency and to facilitate the comparison with the thienyl and thienylene carbene complexes.

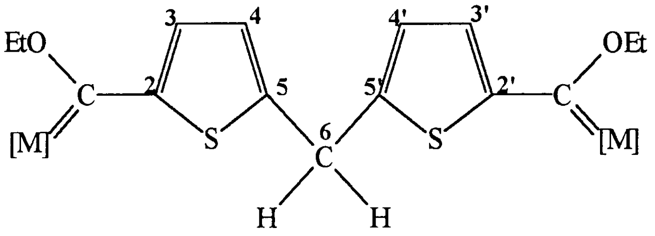


Figure 2.24 Atom Numbering in the MDT Biscarbene Complexes

2.7.1 ^{1}H NMR Spectroscopy

The ^{1}H NMR data for the various bimetallic MDT biscarbene complexes are summarized in Table 2.9. Figure 2.26 represents the ^{1}H NMR spectrum of complex **5**. The data is consistent with the formulation of the biscarbene complexes **5** - **7** and all the signals were assignable and of the correct intensities. All spectra were recorded at 20 °C in $CDCl_3$ as deuterated solvent. The spectrum obtained for **7**, gave enough information for the characterization of the compound, but it was not possible to calculate the coupling constants due to signal broadening. An attempt to improve the resolution at a much lower temperature (-20 °C), failed to give more information regarding the multiplicities of the signals.

The ^{1}H NMR spectrum of free MDT was recorded in $CDCl_3$ as solvent. These δ-values were detemined as: δ H2 H2' 7.18 ppm, δ H3 H3' 6.94 ppm, δ H4 H4' 6.91 ppm and H6 4.37 ppm.

Table 2.9 ^1H NMR Data of the Bimetallic MDT Biscarbene Complexes

Assignment	Complexes				
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)				
	5		6		7
Proton	δ	$^3J_{H-H}$	δ	$^3J_{H-H}$	δ
H4 H4'	7.05 (d)	4.1	7.03 (d)	4.1	6.88
H3 H3'	8.11 (d)	3.9	8.02 (d)	4.1	7.85
H6 (CH_2)	4.31 (s)		4.26 (s)		4.28
OCH_2CH_3	5.13 (q)	7.0	4.95 (q)	7.1	4.96
OCH_2CH_3	1.61 (t)	7.0	1.61 (t)	7.0	1.53
C_5H_5					4.53

The most important features of the ^{1}H NMR spectra of **5** - **7** are the resonances of the unsymmetrically orientated thienylene protons, H3 H3' and H4 H4' which are observed as doublets in the range of 8.11 - 6.88 ppm. A single resonance is observed for the methylene proton, H6 in the range of 4.26 - 4.31 ppm. Quartets are present at 5.13 - 4.95 ppm for the methylene protons and triplets at 1.61 - 1.53 ppm for the methyl protons of the carbene ethoxy substituent.

From Table 2.9 it is evident that the δ-values of the chemical shifts of the protons in **5** appear downfield from those of the corresponding protons present in the spectrum of **6**, due to more shielding by the tungsten nucleus.

The chemical shifts of the thiophene protons in the spectra of **5** - **7** are observed downfield from those for the corresponding protons in uncoordinated thiophene. Although MDT does not act as a conjugated π-bridging unit, through which the two metal nuclei are in contact, the π-system of each ring does lead to π-conjugation from the double bonds of the two independent thienylene rings which serve as electron donors. It is evident that electron density is transferred from the ring and hence from H3 H3' and H4 H4' to the carbene carbon atoms and onto the metal nuclei, thus leading to the deshielding of H3 H3' and H4 H4' and downfield chemical shifts.

From Table 2.9 it is evident that the chemical shifts of H3 H3' are downfield in the spectra of **5** - **7** from those for H4 H4', as well as, for the corresponding ones (H3 and H4) in the spectra of the thienylene biscarbene complexes, **1**, **2** and **4**. This is caused by the carbene substituent in position 2. When considering

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the monocarbene complexes, **A** and **B** the same tendency as for the complexes **5** - **7** should be observed, (*i e* downfield chemical shifts for H3, due to electron draining and hence deshielding of the ring by the carbene ligand, Figure 2.25. This is indeed the case with the chemical shifts of H3 H3' at 8.11 ppm and 8.02 ppm respectively for **5** and **6** which are like, the 8.23 ppm and 8.14 ppm respectively for **A** and **B**, downfield from the δ-values observed in the spectra of **1** and **2**, however significantly upfield from **A** and **B**. The chemical shifts of H4 H4', on the other hand appear upfield in the spectra of **5** and **6** from where these appear in **A** and **B**. The resonances of H4 H4' for **5** and **6**, as well as, H4 for **A** and **B** are significantly upfield compared to the δ-values in the spectra of **1** and **2**. This is simply due to the fact that H4 H4' are not subjected to the electron withdrawing properties of a second carbene moiety in **5** and **6**, as well as, H4 in **A** and **B** as is the case for **1** and **2**. The more upfield chemical shifts in the spectra of **5** and **6** compared to **A** and **B** could be due to the presence of the methylene group bonded to C5 C5', leading to better shielding of C4 C4' and hence H4 H4', causing upfield chemical shifts. On comparing the chemical shifts of H4 H4' with H4 in the spectra of the manganese complexes **7** and **4**, it is also found to be upfield in the spectrum of the first.

The chemical shifts of the protons of the methylene and methyl groups of the ethoxy substituent appear further upfield in the spectra of the MDT biscarbene complexes, **5** and **6**, from those in the spectra of **1** and **2**, indicating that less electron density is distributed to the carbene carbon from the metal and thienylene moieties of **5** and **6** compared to **1** and **2**, as illustrated in Figure 2.25. The corresponding chemical shifts also appear downfield in the spectra of **A** and **B**. The methylene and methyl protons of the ethoxy group appear at similar values for **4** and 7. The Cp protons of 7, on the other hand appear a little upfield from their position in the spectrum of **4**.

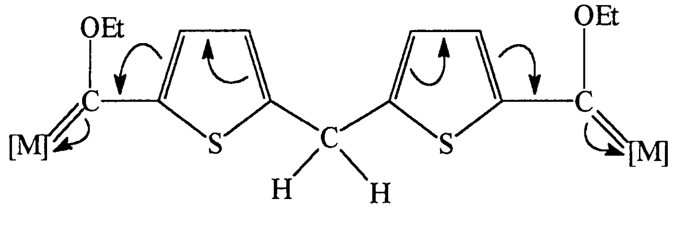

Figure 2.25 Distribution of Electron Density in 5 and 6

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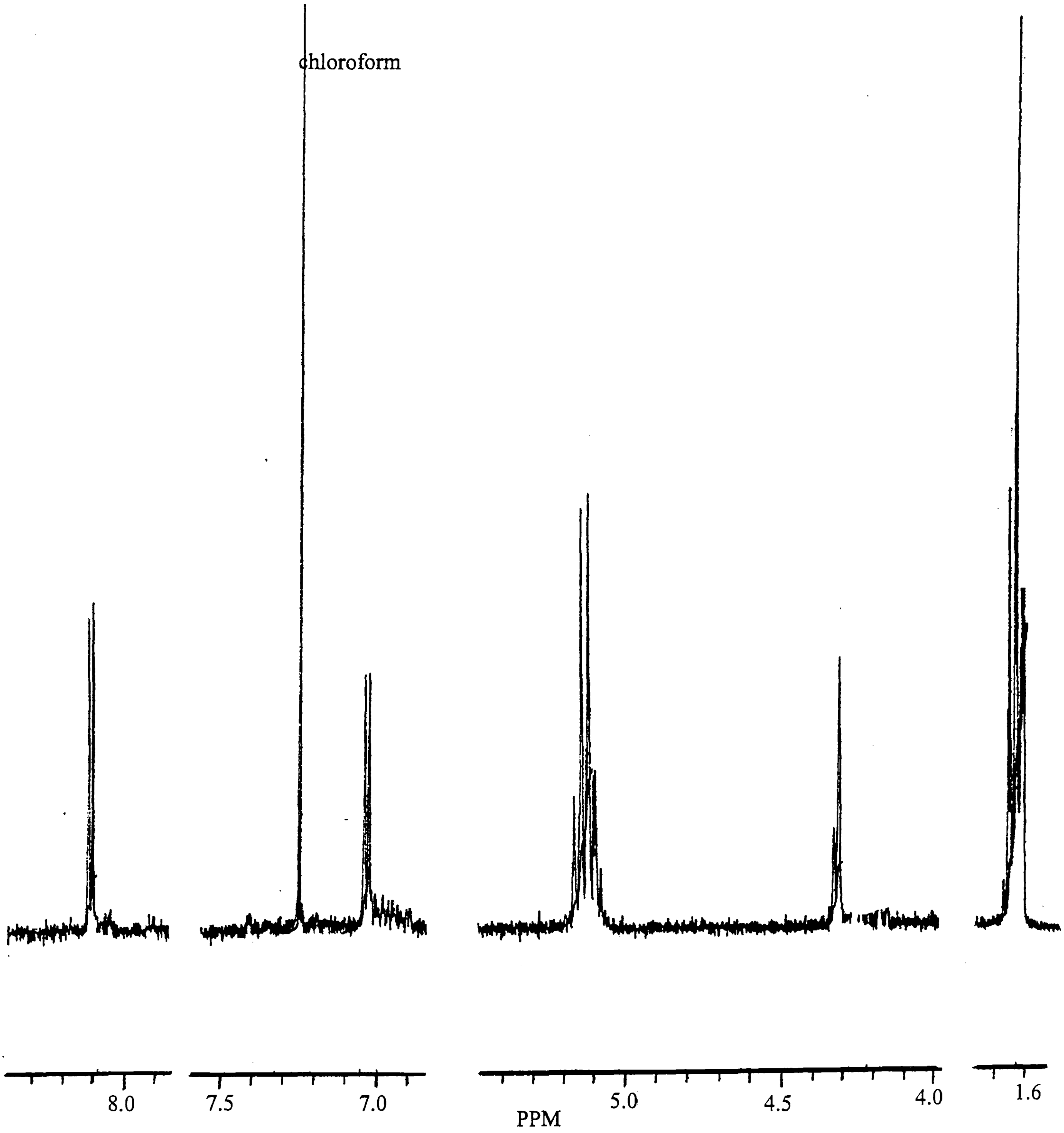

Figure 2.26 ^{1}H NMR Spectrum of $(CO)_5CrC(OEt)\{C_4H_2SCH_2C_4H_2S\}C(OEt)Cr(CO)_5$

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2.7.2 ^{13}C NMR Spectroscopy

The ^{13}C NMR data for complexes **5** and **6** are summarized in Table 2.10. The ^{13}C spectrum for uncoordinated methylene 2,2' dithiophene was recorded in $CDCl_3$ as solvent and the chemical shifts, (ppm) were determined as follows: C5 C5' 143.1, C4 C4' 126.5, C3 C3' 125.0, C2 C2' 123.8 and for the methylene carbon atom C6 at 35.0.

Table 2.10 ^{13}C NMR Data of the Bimetallic MDT Biscarbene Complexes

Assignment	**Complexes**	
	Chemical Shifts, δ, (ppm)	
Carbon Atom	**5**	**6**
C (carbene)	314.7	305.2 289.3
$M(CO)_5$, (*trans*)	223.2	202.4
$M(CO)_5$, (*cis*)	217.1	197.5
C2 C2'	157.2	157.1
C3 C3'	142.0	142.6
C4 C4'	128.2	128.3
C5 C5'	151.6	152.3
C6 (methylene)	31.4	31.9
$\mathbf{OCH_2}CH_3$	76.0	78.4
$OCH_2\mathbf{CH_3}$	15.1	14.9

The chemical shift of the carbene carbon of **6** appears upfield from the corresponding resonance of **5**. A second chemical shift appears for the carbene carbon at 289.3 ppm in the spectrum of **6**. The chemical shifts of the carbonyl groups appear downfield in the spectrum of **5** compared to the corresponding resonances of **6**. These δ-values are in good agreement with values reported in literature[41] and fairly insensitive to changes of substituents on the carbene ligand and are representative of the respective metal carbonyl fragment. The chemical shifts of the carbene carbons of **5** and **6** are slightly upfield from those in the spectrum of the monocarbene thienyl complexes, **A** and **B**, which are virtually the same. The difference in chemical shifts for the carbene carbon atoms can be accounted for by the fact that more electron density from the two thienylene rings is placed on the carbene carbon atoms in **5** and **6**, hence shielding, Figure 2.25.

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The chemical shifts for the MDT unit in the complexes **5** and **6**, compared to the chemical shifts for uncoordinated MDT are further downfield. For the monocarbene complexes, **A** and **B**, the chemical shifts for C2 of the thienylene ring are virtually the same in the spectra of complexes **1** and **5**, as well as, in the respective spectra of **2** and **6**. The chemical shifts of C3 C3' and C4 C4' in **5** and **6** when averaged are similar to the values obtained for C3 or C4 in **1** and **2** respectively. It is not clear why the chemical shift for C5 C5' in **5** and **6** is shifted so far downfield compared to the corresponding resonances in **A** and **B**, and why the resonances are closer to those in **1** and **2** than in **A** and **B**.

2.7.3 Infrared Spectroscopy

The infrared data for the biscarbene complexes **5** - **7** are summarized in Table 2.11. Figure 2.27 represents the infrared spectrum of **5**. All spectra were recorded in hexane as solvent.

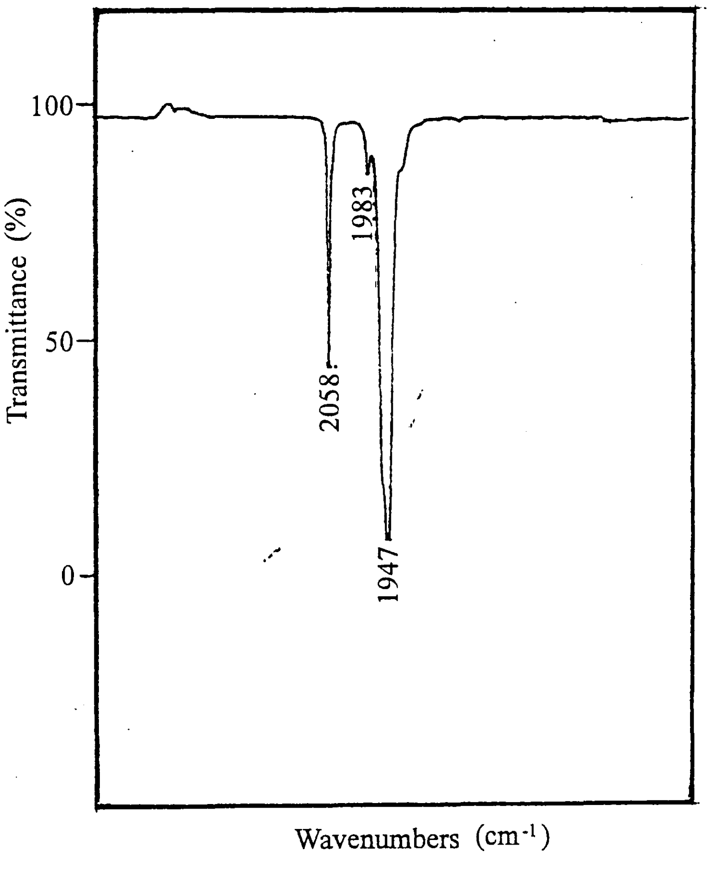

Figure 2.27 Carbonyl Region in the Infrared Spectrum of $(CO)_5CrC(OEt)\{C_4H_2SCH_2C_4H_2S\}$-$C(OEt)Cr(CO)_5$

Table 2.11 Infrared Data of the Bimetallic MDT Biscarbene Complexes

Assignment		Complexes		
		Stretching Vibrational Frequency, (νCO, cm^{-1})		
		5	6	7
$M(CO)_5$	$A_1^{(1)}$	2058	2066	
	B_1	1983	1975	
	E	1947	1941	
	$A_1^{(2)}$	1954 (sh)	1948	
$M(CO)_2$	A			1948
	A^1			1891

A comparison of the stretching frequencies of complexes **5** and **6** to those of complexes **1** and **2** is shown in Table 2.12

Table 2.12 Infrared Data of the Biscarbene Complexes 1, 2, 5 and 6

$M(CO)_5$	Cr (5)	W (6)	Cr (1)	W (2)
Band				
$A_1^{(1)}$	2058	2065	2064	2074
B_1	1983	1975	1987	1985
E	1947	1941	1953	1952
$A_1^{(2)}$	1954	1948	1964	1960

Solvent : hexane

The stretching frequencies of **1** and **2** are higher than those for **5** and **6** respectively, which reflects that less electron density is remains on the metal centre for **1** compared to **5** and for **2** compared to **6**. This is an indication that the two thienylene rings in MDT (which is not a conjugated π-system) are stronger donors of electron density compared to the conjugated bridging thienylene unit in **1** and **2**.

In conclusion it can thus be said than the ability of the bridging ligand to distribute electron density *via* the carbene to the metal nuclei influences the wavenumber of the bands in the spectrum of a metal carbonyl fragment and that the conjugated bridging thienylene unit donates less electron density than the bridging MDT unit which does not act as a conjugated system. This was also observed on comparing **1** and **2** with the

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monocarbene thienyl complexes **A** and **B**. The infrared data of **A** and **B** and **5** and **6** are similar when compared to that of **1** and **2**.

2.8 Summary

On comparing the chemical shifts in the ^{1}H NMR and ^{13}C NMR spectra of the thiophene- and MDT biscarbene complexes it is evident that there are definite differences in especially the chemical shifts of the thienyl ring atoms. The chemical shifts of C4 C4' and H4 H4' are upfield in the spectra of the MDT biscarbene complexes compared to the more downfield position in the spectra of the thiophene biscarbene complexes. Also a comparison of the wavenumbers in the infrared spectra of these complexes shows definite differences. The π-conjugated bridging thienylene unit does not donate as much electron density to the carbene moieties as the non-conjugated bridging ligand MDT or the monocarbene thienyl complexes. However, one should bear in mind that the latter two have one thienyl unit, per carbene which is attached, whereas two carbene ligands are served by one thienylene ring in **1** and **2**.

Good agreement among similar chemical shifts are found for all the new compounds and the spectral data confirm the presence of an alkoxy carbene ligand with a thienyl substituent. The NMR data also reveal the donation of electron density from the thiophene substituent to the carbene carbon for all the new complexes. Smaller variations in the data indicate that more electron density is transferred by the thienyl of the monocarbene thienyl complexes **A** and **B** compared to the unconjugated 2,2'-dithienyl unit in the biscarbene MDT complexes **5** and **6**. Reasons for this are not clear. However, most electron density is transferred by the conjugating thienylene in the biscarbene complexes **1** - **4**, but it must be remembered that the deshielding effect is caused by two electron withdrawing carbene substituents for only one thiophene ring.

From the infrared data it is evident that the order in which electron density is donated for the thiophene substituents is the following:

MDT ≥ thienyl > thienylene

It seems reasonable to conclude that the amount of electron density donated by thienyl can not be doubled by thienylene to two metal fragments and that the flow of electron density *via* π-interaction of thienylene to the two metal fragments is controlled by the carbene units and is limited by the resulting positive character on the thiophene ring.

The planarity of the thienylene ring, carbene unit and metal centre displayed in the structures of **1** and **2** holds promise for future work regarding π-delocalization and conducting properties with two electronically very

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different metal fragments at the ends. However, some concern exists on the linearity if larger spacers of this type are used. Of great interest is a structure determination and linearity of more than one thienylene spacer between the carbene units.

2.9 References

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3 σ,π-Bimetallic Monocarbene Complexes

3.1 Introduction: Complexes with π-Donor Ligands

The chemistry of π-arene complexes have attracted enormous attention over the years following the discovery of ferrocene,[1,2] and the effect of π-coordination of metal fragments to different types of ring systems has been extensively studied especially for rings containing no heteroatoms like cyclopentadienyl and benzene. These systems have been employed in the synthesis of sandwich and half-sandwich complexes.[3] Well known examples of this kind are the arene-chromium-tricarbonyls which in particular have attracted attention[4], Figure 3.1.

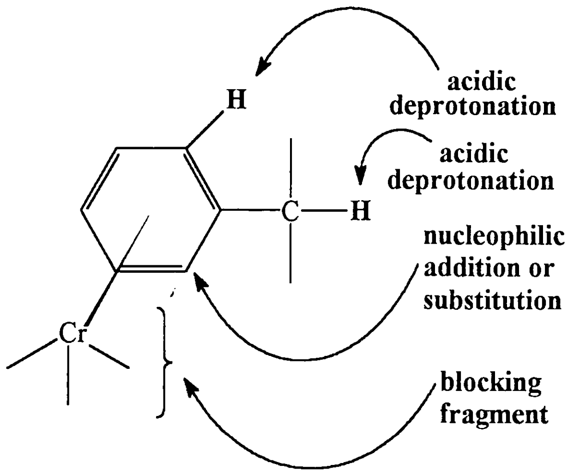

Figure 3.1 Ring Activation by $Cr(CO)_3$

Since the activating substituent, $Cr(CO)_3$, is symmetrically bonded to the arene ring carbons and shows no directing effect, apart from steric crowding on one face of the arene ring, the substituents attached by σ-bonds to the arene ligand will have the primary influence on site selectivity, eg. in (π-toluene)$Cr(CO)_3$ proton abstraction occurs predominantly at the *meta* position, whereas deprotonation will occur solely at the *ortho* position in (π-fluorobenzene)$Cr(CO)_3$.[5] This illustrates the regio-control of reaction sites by ring substituents owing to the presence of the π-bonded metal moiety. The substituents also determine the orientation of

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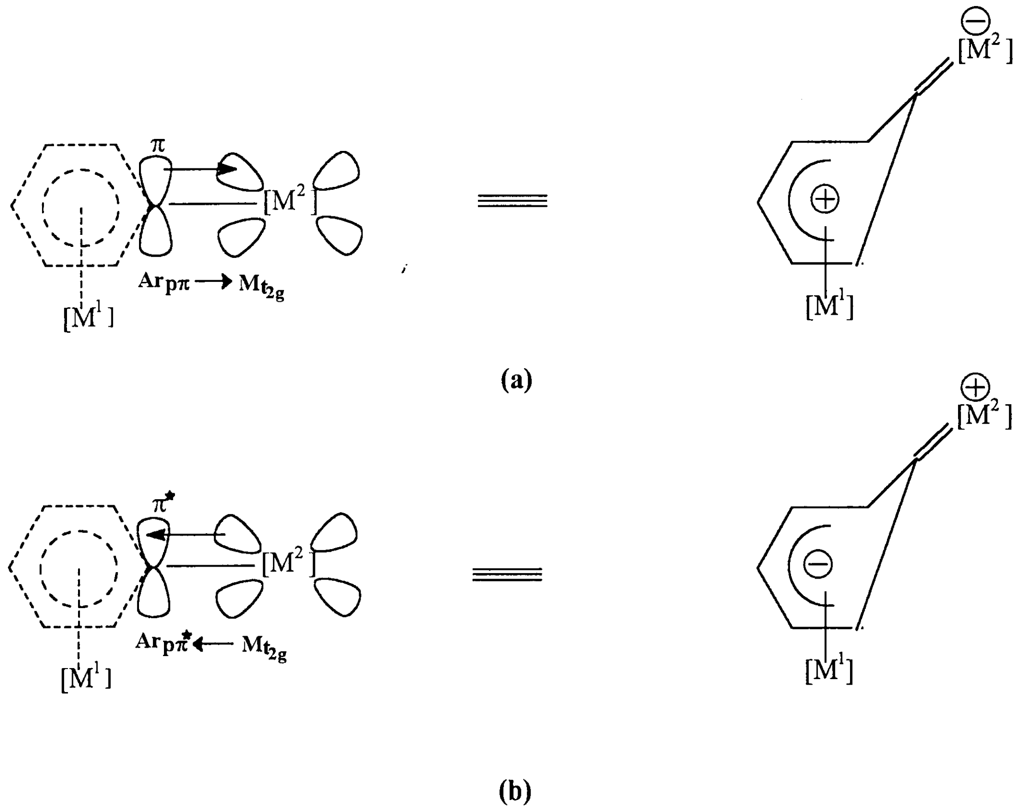
ents owing to the presence of the π-bonded metal moiety. The substituents also determine the orientation of the carbonyls of the $Cr(CO)_3$. Nucleophilic and electrophilic substitution reactions of these complexes have received considerable interest in the past two decades.[6, 7, 8]

3.2 σ,π-Bimetallic Complexes

3.2.1 σ,π-Complexes of Cyclopentadienyl and Benzene

In bimetallic compounds linked by bridging organic substrates *via* σ- and π bonding modes, ligand activation is achieved in both the σ, (through inductive effects) and π, (through π-resonance effects) modes of the bridging ligand.[9] Furthermore, when π-conjugated bridging ligands are utilized the metal centres are directly in contact *via* π-resonance effects.[10] Figure 3.2 shows how a σ-bonded transition metal can interact *via* π-resonance effects with the π-bonded metal when the bridging ligand is benzene; (a) electron density is withdrawn from the π-cloud of benzene ring to the vacant t_{2g} orbitals on the metal, (M^2 "stealing electron density from the M^1), (b) electron density is withdrawn from the filled t_{2g} orbitals on metal to the empty π* orbitals of the benzene ring.



(a)

(b)

Figure 3.2 Possible π-Contact between Metals in σ, π-Bimetallic Benzene Compounds

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by metal carbonyl anions analogous to reactions with carbanion nucleophiles studied by Semmelhack.[6, 14, 15] The treatment of (η^6-haloarene)Cr(CO)$_3$ with dianionic metal complexes, such as Na$_2$[Fe(CO)$_4$] [11, 13] and K$_2$[M(CO)$_5$], M = Cr, W[13] provides an established route to the synthesis of anionic heterobimetallic compounds with σ,π-coordinated bridging ligands. By contrast, complexes such as Na[Co(CO)$_4$] [16, 17], Na[Mn(CO)$_5$] and Na[MoCp(CO)$_3$] failed to react with haloarenes and it is perceived that the anionic metal substrate is too weak a nucleophile[18] possibly due to diffusion of the negative charge over the whole complex, to make this a general method of synthesis of σ,π-bimetallic complexes. The investigation into the formation of metal to phenyl carbon σ-bonds reveals that the reaction between arryllithium reagents and metal carbonyl halides are not general synthetic routes.[12] An important complication is the direct attack on the coordinated carbonyl ligand leading to the formation of acylates. The σ-bonded metal-arene derivatives are instead obtained indirectly by treating the metal carbonyl anion with benzol halides and subsequent decarbonylation of the metal benzoyl intermediates.[19, 3a] On the other hand two routes are employed for the formation of σ,π-bridged cyclopentadienyl derivatives of bimetallic complexes, firstly the salt elimination reaction between lithiated (η^5-C$_5$H$_5$)Mn(CO)$_3$[20, 21] and halide complexes of various metals, or alternatively the reaction of the halide substituted arene compound (η^5-C$_5$H$_4$X)Cr(CO)$_2$L[22, 23], chloroacetylferrocene[24, 25], and (η^6-C$_6$H$_5$X)Cr(CO)$_3$[11, 12, 17] with the metallated transition metal complexes. An altenative route to the synthesis of neutral heterobimetallic compounds with σ,π-(η^1:η^6)-bridging arene ligands, is the prospect of applying (η^6-lithioarene)Cr(CO)$_3$ in the reverse type reaction, in which the arene-chromium substrate is employed as the nucleophile in reactions with transition metal electrophiles. This reaction type was employed in the synthesis of (aryllithium)tricarbonylchromium precursors.[5, 26]

Complexes in which the metal atom is directly coordinated to a phenyl ring carbon or *via* a carbon atom bonded to the ring were synthesised in our laboratories.[27] Examples of complexes in which the metal atom is directly bonded to the ring *via* a σ-bond include (η^6-C$_6$H$_5$Mn(CO)$_4$L)Cr(CO)$_3$, L = PPh$_3$[27b], P(OMe)$_3$[27d]. The reaction under similar conditions with bidentate ligands ($\overline{L\ L}$) yields the product (η^6-C$_6$H$_5$C(O)Mn($\overline{L\ L}$)Cr(CO)$_3$, in which CO has been inserted into the Mn-C(*ipso*) bond, where $\overline{L\ L}$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$, Me$_2$NCH$_2$CH$_2$NMe$_2$. Other examples were obtained by reacting (η^6-C$_6$H$_4$RLi)Cr(CO)$_3$ with titanocene dichloride. This reaction yielded compounds in which the second transition metal is directly bonded to the ring with a sigma bond or *via* a carbon atom eg. the compound Cr(η^6-C$_6$H$_5$)Ti(η^5-C$_5$H$_5$)$_2$Cl(CO)$_3$. The lithiated benzene derivative reacts similarly and affords the unstable (η^6-C$_6$Me$_5$)CH$_2$Ti(η^5-C$_5$H$_5$)$_2$Cl(CO)$_3$Cr.[27]

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3.2.2 Complexes of Thiophene

Although π-complexes of various transition metals with heteroatom rings displaying pseudo-aromatic character have long been known, the properties and chemical reactions of these have as yet remained unexplored.[28] Of late, however, the emphasis has shifted and rings containing heteroatoms eg. thiophene, pyrrole and pyridine have been employed with ever increasing frequency.[29, 30] Especially the coordination chemistry of thiophene is vigorously being explored and some fascinating results have emerged. The coordinating properties of thiophenes are closer to those of arenes than to thioethers. On comparing the various systems it has been found that thiophene is somewhat more nucleophilic than benzene as suggested by the ionization potential of 8.9 versus 9.3 eV for benzene. Evaluation of the interaction of thiophene with transition metals requires knowledge of the electronic stucture of the heterocycle. There are six valence orbitals, all of which primarily have *p*-orbital character. The five *p* orbitals orthogonal to the ring give rise to five nondegenerate π states. Three of the π-molecular orbitals are occupied. The symmetries of the π levels of thiophene resemble those for cyclopentadienyl, however, the presence of the heteroatom lifts any degeneracies. The major difference in the coordinating properties of thiophene and cyclopentadienyl anion is the significantly higher basicity of the latter. For this reason benzene represents a superior model for thiophene coordination, at least as it applies to η^2, η^4 and η^5-thiophene complexes.[29] These considerations thus present an explanation for the weaker π-coordination of the metal fragment to a ring like thiophene, compared to the coordination to a benzene ring and hence the fact that the $Cr(CO)_3$-fragment is lost more easily in reactions to yield by-products which do not contain the π-fragment, as will become evident from the use of thiophene and benzothiophene in the synthesis of σ,π-bimetallic carbene complexes.

The most likely coordination sites in thiophene are the C(2)=C(3) and C(4)=C(5) bonds, where ring π-electron density is presumably concentrated, as well as, at the sulphur atom. Coordination at all these sites is known[30, 49, 51], as summarized by the known structural types in Figure 3.3.

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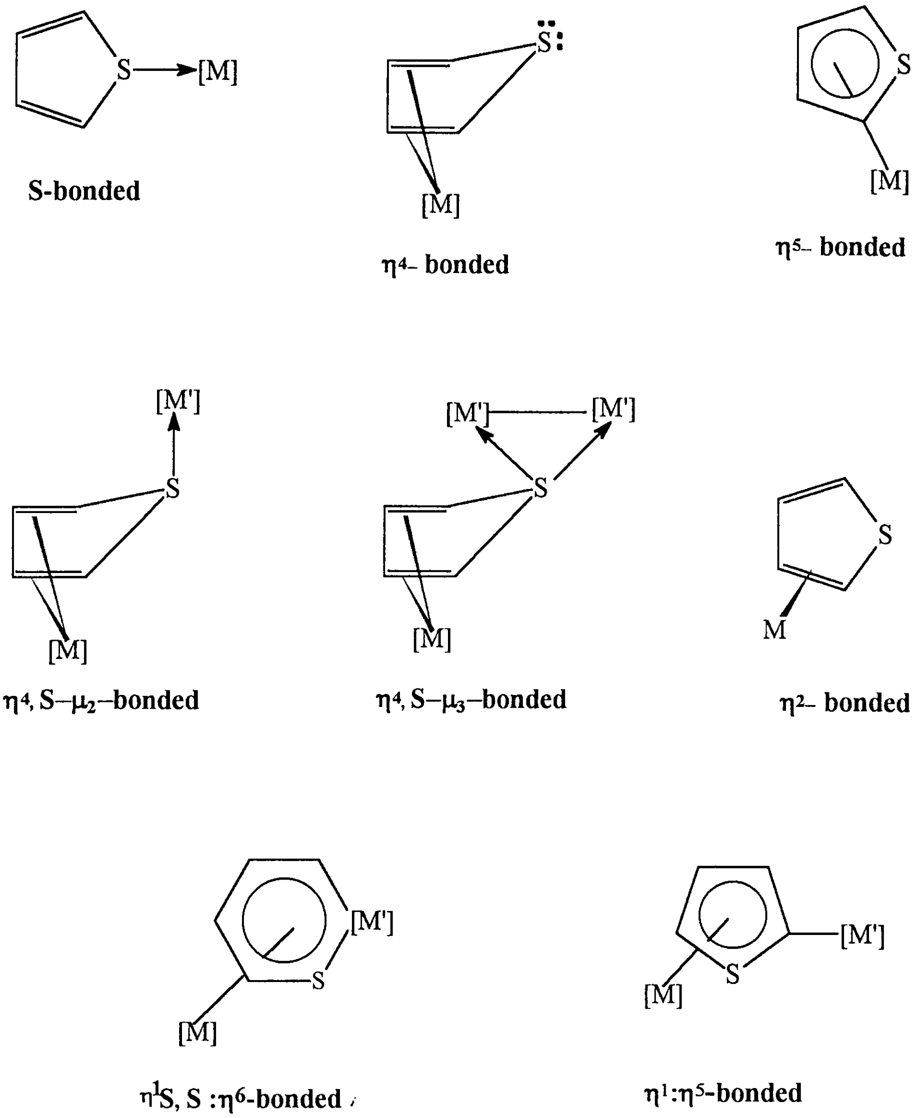

Figure 3.3 Coordination Modes of Thiophene

Examples of these types have been characterized by X-ray diffraction studies except that of the η^2-bonded thiophene, which is proposed to occur in $[(2,3\text{-}\eta^2\text{-thiophene})Os(NH_3)_5]^{2+}$, which is based on ^1H NMR studies. Further proof of this mode of coordination has recently been observed in the structure of (η^6:η^2-benzo[b]-thiopheneReCp$(CO)_2$)Cr$(CO)_3$.[31] Each stuctural type in Figure 3.3 will be referred to in this section, however, the emphasis will be placed on the η^5-type which dominates and is of relevance in this study.[29, 30]

In five and six membered monoheterocycles, in which the heteroatom forms part of the π-conjugation, the ring has a planar structure. An important feature of these compounds is the degree of aromaticity in the ring. Heterocycles are often classified as being π-excessive or π-deficient[32] or stated differently as having hard or

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Heterocycles are often classified as being π-excessive or π-deficient[32] or stated differently as having hard or soft donor atoms according to the hard and soft acids and bases concept (HSAB).[33] It is these properties that determine the coordinating properties of heterocycles, be it σ and / or π.

Compared to dialkyl or aryl-alkyl sulphides (R_2S) or tetrahydrothiophene ($(CH_2)_4S$), thiophene (Th) is a very weak sulphur-donor ligand and few S-bonded thiophene complexes are known.[34-39]

Until recently only two stuctures of complexes with η^4-thiophene ligands had been reported. The first of these being IrCp*(η^4-2,5-Me_2Th)[40] and [RhCp*(η^4-Me_4Th)].[41] In these complexes the η^4-thiophene ligand is no longer planar, the sulphur atom is bent out of the plane of the four carbons. In comparison with the weak S-donor ability of free thiophene, the sulphur in η^4-thiophene complexes is an excellent donor and therefore coordinates to various Lewis acids including transition metals, resulting in η^4,S-μ_2- and η^4,S-μ_3-thiophene complexes. Compounds exhibiting the η^4,S-μ_2-mode of bonding contain a bridging thiophene ligand which is η^4-bonded to one metal and S-bonded to a second metal (or Lewis acid). The simplest examples are the BH_3 adducts Ir(Cp)(η^4-Th·BH_3) which are formed by the reaction of a IrCp(η^4 -Th) complex with THF·BH_3 or $Me_2S{\cdot}BH_3$.[42, 43] The stuctures of some of these complexes were found to be very similar to one another, with the sulphur atom folded up out of the four-carbon plane.[42 - 45]

In complexes, which exhibit η^4,S-μ_3-modes of bonding, the bridging thiophene is η^4-coordinated through the diene to one metal and the sulphur atom using both available lone pairs to be S-coordinated to two other metals. Known examples of this type are the complexes, [CpIr(2,5-Me_2Th)][$Mo_2(CO)_4Cp_2$][46] and [CpIr(2,5-Me_2Th)][$Fe_2(CO)_7$].[44] Both these complexes contain metal-metal bonds which are bridged by the sulphur of the η^4-2,5-Me_2Thiophene. The M-M-S plane is essentially perpendicular to the C(2)-C(3)-C(4)-C(5) plane. These structures reinforce the observation that the η^4-thiophene structure remains unperturbed by the nature and the number of metal fragments coordinated to the sulphur.

The first reported structure of an η^5-thiophene complex was that of Cr(η^5-Th)$(CO)_3$.[47] Since then similar compounds have been isolated and characterized. One of these being the compound [Rh(η^5-Th)$(PPh_3)_2]^+$,[47] which was characterized with X-ray crystallography. The bond distances and angles were found to be similar to those in free thiophene, however, the ring is not exactly planar with the sulphur slightly out of the plane of the four carbons. More recently Rauchfuss and co-workers[48] published three structures containing the η^5-tetramethylthiophene ligand, [Ru(η^5-Me_4Th)$_2]^{2+}$, [Ru(η^5-Me_4Th)Cl]$_3S^+$ and [Ru(η^5-Me_4Th)$(OH_2)_3]^{2+}$, wherein the thiophene C-S distances are longer than in free thiophene but the C(2)-S-C(5) angles being essentially the same as in free thiophene.

Until recently not many examples of π-bonded pseudoaromatic heterocycles, which are σ-bonded to a second transition metal fragment through a ring carbon atom without a metal-metal bond have been reported. Thiophene, however, is an exception although some difficulties are experienced in the synthesis of these complexes. Various new bimetallic compounds of (η^5-thiophene)$Cr(CO)_3$ have been synthesized and characterized in our laboratories. Examples of these include the compounds (η^5-$C_4H_3SMn(CO)_5$)$Cr(CO)_3$, (η^1:η^5-$C_4H_3SPt(C_4H_3SL_2)$)$Cr(CO)_3$, (η^5-$C_4H_2S(TiCp_2Cl)$)$Cr(CO)_3$, etc.[49a] As yet only one example of bimetallic complexes in which the second transition metal atom is bonded to the ring *via* a carbene carbon atom is known, *i e* (η^5-$C_4H_3SC(OEt)Re$)$Cr(CO)_3$[49b]

The insertion of Cp*Ir into a thiophene ring to give a six membered metallaheterocycle has been accomplished by UV photolysis and base catalysis.[50] It was shown that the iridathiabenzene ring can be considered to have a delocalized π-system which was demonstrated by coordinating it in a η^6-fashion to ML_n fragments to afford complexes of the type (η^6-SC(Me)CHCHC(Me)Ir(Cp))ML_3, (M = W, Cr, Mo; L = CO, Fc^+, L = Cp).[51]

The σ-coordination of substituents, especially heteroatom substituents or metal fragments cause polarization and activation in the bonds. Metal fragments can be attached *via* carbon atom or heteroatom substituents, or directly to the ring. Heteroatoms on the other hand form part of the ring, eg. in thiophene, pyridine, pyrrole, etc. and an electron polarization factor is introduced into the π-bonding.

3.3 σ,π-Bimetallic Monocarbene Complexes

Five and six membered rings without a heteroatom, to which a metal fragment is π-bonded have been successfully employed in the synthesis of bimetallic σ,π- monocarbene complexes. Examples and the synthesis of some of these complexes will be discussed in this section.

3.3.1 Synthesis from Metallated Precursors

(η^6-Benzene) tricarbonylchromium was used as a precursor by Fischer and co-workers[52] in the synthesis of carbene- and carbyne complexes of the Group 6 transition metals. The reaction of (η^6-phenyllithium) tricarbonylchromium with the metal hexacarbonyls of Group 6 in diethyl ether and subsequent alkylation with triethyloxonium tetrafluoroborate yielded the η^6-phenyl carbene complexes of chromium, molybdenum and tungsten, see Figure 3.4. On reacting the chromium and tungsten analogues with boron trihalides (BX_3; X = Cl, Br) the corresponding carbyne complexes were afforded.

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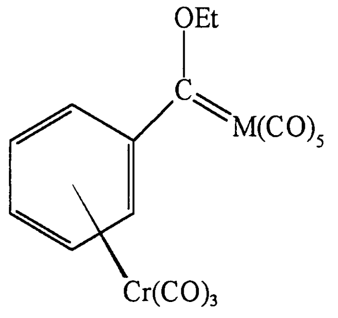

M = Cr, Mo, W

Figure 3.4 σ,π-Bimetallic Carbene Complexes

With this Fischer and co-workers[52] have demonstrated that contrary to the belief that the negative charge resulting from the metallation of the ring will be diffused over the entire complex, it is very much localized on the metallated carbon and is still strong enough to act as a nucleophile and attack a carbonyl of a metal carbonyl complex.

Fischer-type carbene complexes with bridging ligands which have π-cyclopentadienyl and σ-carbene bonding functionalities have been synthesized and studied.[53] A series of ferrocenyl carbene complexes of chromium, tungsten and manganese, $L_nMCXR(Fc)$, with $ML_n = Cr(CO)_5$, $W(CO)_5$ or $Mn(MeCp)(CO)_2$; $XR = O^-NMe_4^+$, OMe, OEt, NH_2, NMe_2, NC_4H_8 was prepared to study the electronic effects of the ferrocenyl substituent in the carbene ligand. The ferrocenyl substituent acts as an electron donor by means of resonance interaction with the carbene carbon atom.

The lithiated metallocenes ruthenocene and 1,1'-dimethylferrocene react with the metal hexacarbonyls of Group 6 to yield bimetallic acylates, from which, by subsequent alkylation with triethyloxonium tetrafluoroborate the corresponding carbene complexes of chromium, molybdenum and tungsten are obtained[54], see Scheme 3.1. The solid state structure of the tungsten complex displays a ruthenocenyl substituent with coplanar cyclopentadienyl rings which are in a staggered conformation relative to one another and located between two *cis*-carbonyls of the $W(CO)_5$-fragment.

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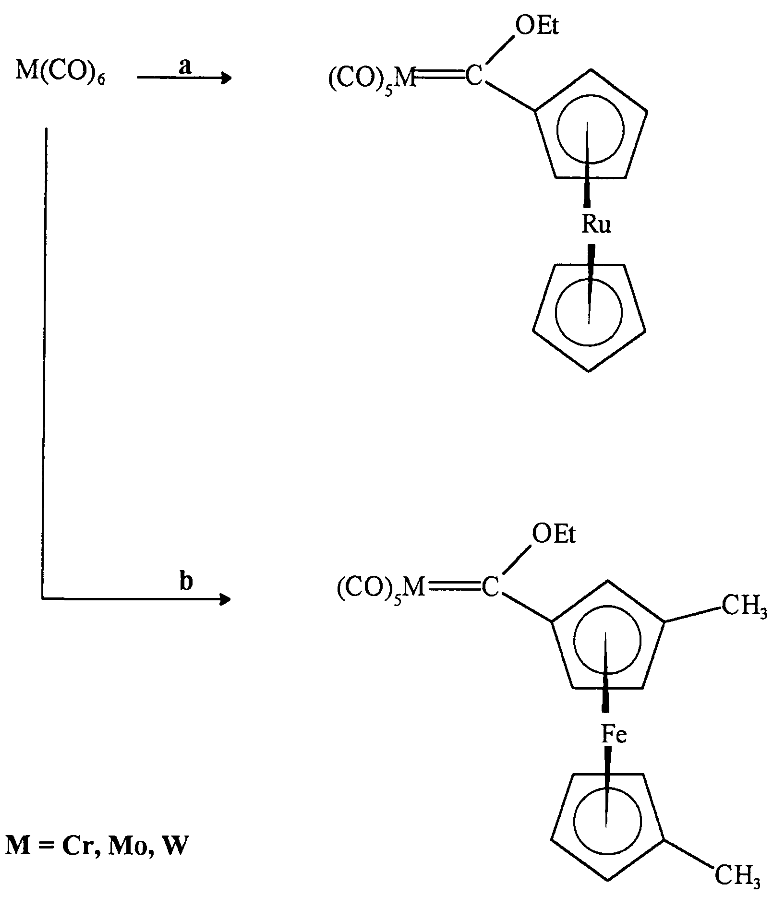

Reagents: (a) 1. Li[Ru(η^5-C_5H_4)(η^5-C_5H_5], Et_2O; 2. [Et_3O][BF_4], CH_2Cl_2

(b) 1. Li[Fe(η^5-$C_5H_3CH_3$)(η^5-$C_5H_4CH_3$)], Et_2O; 2. [Et_3O][BF_4], CH_2Cl_2

Scheme 3.1

The synthesis of pentacarbonyl tungsten carbene complexes of (η^5-C_5H_4)Mn$(CO)_3$ and ferrocenyl ligands, led to the synthesis being extended to the preparation of the analogous cationic manganese carbene complexes.[55]

The ruthenocenyl and ferrocenyl act as an electron donor by means of resonance interaction with the carbene carbon atom in these complexes.

Chiral binuclear carbene complexes of the Fischer type were synthesized utilizing (*R,R*)-1-(1-dimethylaminoethyl)-2-lithioferrocene. The lithiated precursor reacts with the tungsten hexacarbonyl to give a bimetallic acylate, CpFe{η^5-2-C_5H_3{C(Me)HNMe$_2$}C(OLi)W(CO$_5$)}, which can be converted to the achiral

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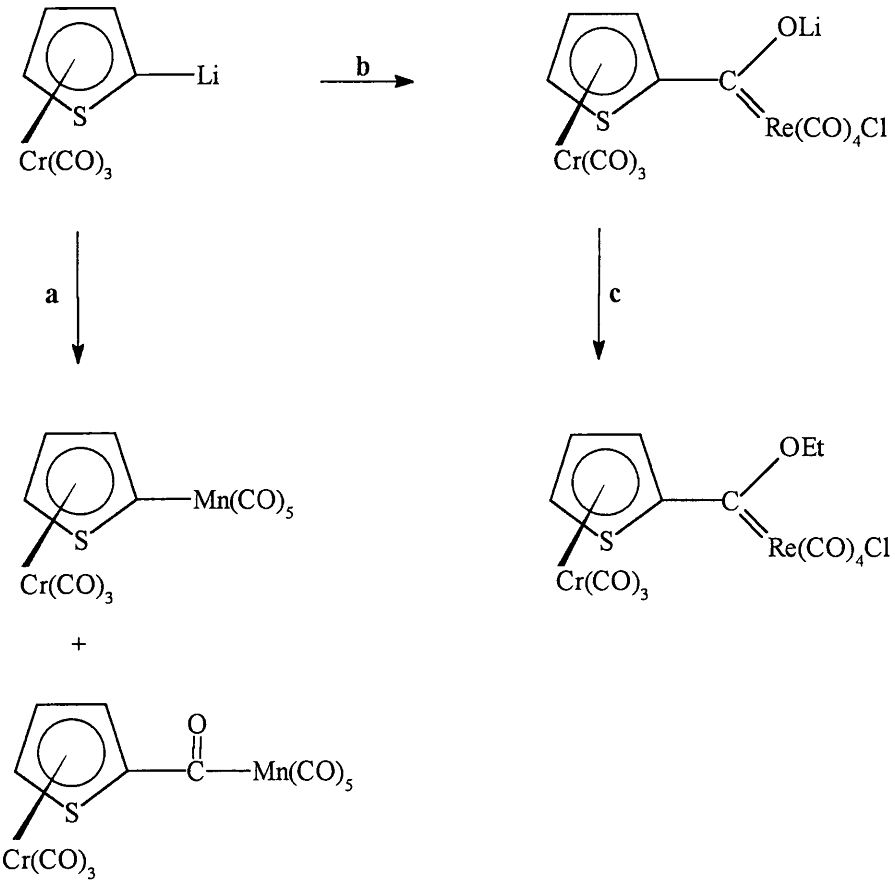
amino-carbene complex, CpFe{η^5-2-C_5H_3{C(Me)(OH)H}C(NMe_2)W$(CO)_5$} in the presence of a proton donor like *tert*-BuCl.[56] Unlike $Mn(CO)_5Br$, $Re(CO)_5Br$ reacts with the lithiated thiophene complex Cr(η^5-C_4H_3SLi)$(CO)_3$ to give after subsequent alkylation the σ,π-bimetallic carbene complex[49c], Scheme 3.2.

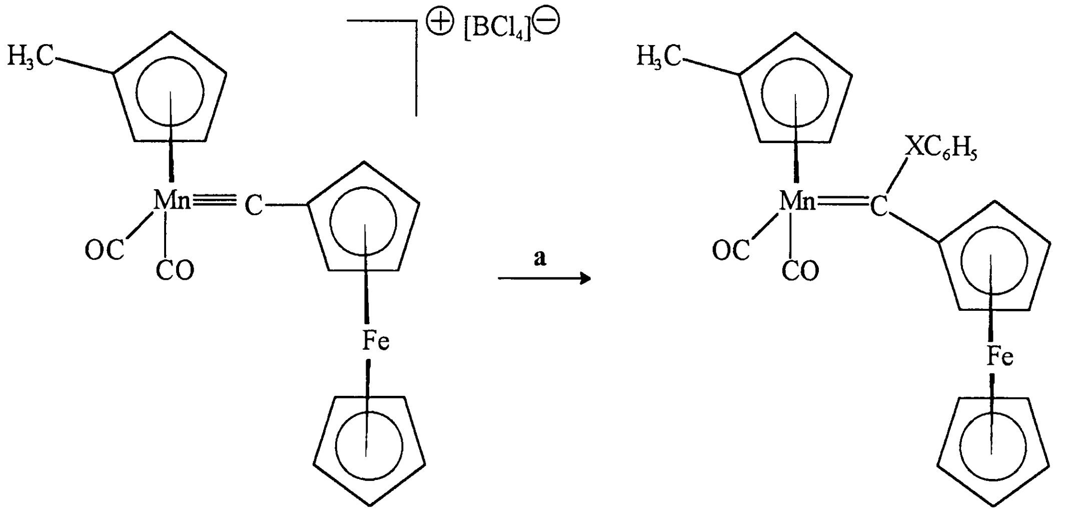


Reagents: (a) $Mn(CO)_5Br$, (b) $Re(CO)_5Cl$, (c) $[Et_3O][BF_4]$

Scheme 3.2

3.3.2 From Carbynes to Carbenes

Fischer and Wanner[57] synthesized some novel carbene complexes by reacting the thermally relatively stable cationic ferrocenyl carbyne complexes of manganese with lithium benzenethiolate, -selenolate and -telurolate, see Scheme 3.3. The reaction proceeds by the attack on the carbyne carbon atom to afford the neutral carbene complexes. The corresponding reaction with Na[Co$(CO)_4$] yields the carbene complex, $(CO)_2$ MeCpMn-{C(Fc)Co$(CO)_4$}.



X = S, Se, Te

+ $Li[BCl_4]$

Reagent: (a) $Li[XC_6H_5]$

Scheme 3.3

The reaction of the cationic methylcarbyne complex, $[(\eta^5\text{-}C_5H_5)(CO)_2MnCMe]BCl_4$, with dimethyl cyanimide, $Me_2NC{\equiv}N$, yielded a binuclear bis(*ansa*-dimethylaminocarbene) complex containing chelating cyclopentadienyl-carbene ligands. Figure 3.5 clearly shows how the two *ansa*-carbene ligands are connected *via* a CH group.[58]

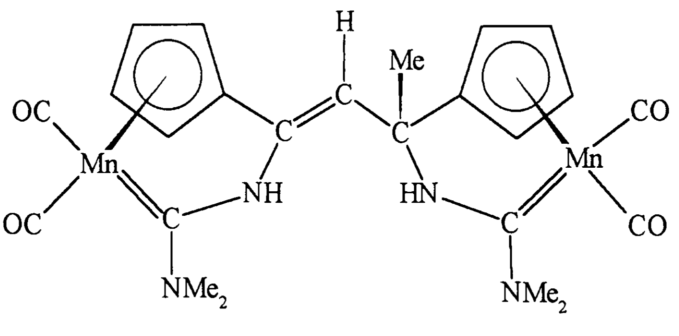


Figure 3.5 Structure of the Binuclear Bis(*ansa*-dimethylaminocarbene) Complex

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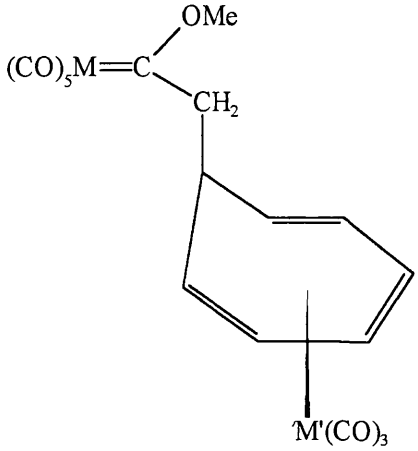
3.3.3 Reaction of β-Metallated Carbenes with Cationic π-Complexes

The addition of the anionic Fischer carbene complex, $[(CO)_5MC(OMe)CH_2]^-$ to cationic complexes with unsaturated hydrocarbons eg. the ethene rhenium complex $[(CO)_5Re(C_2H_4)]^+$ and the tropylium complexes $[(CO)_3M'(\eta^7\text{-}C_7H_7)]^+$, (M = Cr, Mo) affords the bimetallic hydrocarbon-bridged σ,π-complexes $(CO)_5M\{C(OMe)CH_2CH_2CH_2\}Re(CO)_5$ and $(CO)_5M\{C(OMe)CH_2C_7H_7\text{-}\eta^6\}M'(CO_3)$[59], see Figure 3.6.

An interesting series of mixed bimetallic chromium-iron complexes were prepared by Geoffroy *et al*[60] by the addition of the anion of the biscarbene complex μ-bis(alkoxycarbene)dichromium, synthesized according to the method described by Macomber and co-workers[61], to the coordinated olefin in a series of $[Cp(CO)_2Fe(\eta^2\text{-olefin})]^+$ (olefin = *cis*-2-butene, *trans*-2-butene, styrene) complexes and to the cyclohexadienyl ligand in $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$.



M	M'
Cr	Cr
Cr	Mo
W	Cr
W	Mo

Figure 3.6 π-Bridged Bimetallic Complexes

Macomber and co-workers[62] synthesized the σ,π-carbene complex (*E*)-$(CO)_5W[C(NMe_2)CH{=}CH\text{-}(\eta^5\text{-}C_5H_4)\text{-}Fe(\eta\text{-}C_5H_5)]$. The synthesis was afforded by first preparing the [(α-(trimethylsilyl)aminocarbene] complex in the reaction of $\{(CO)_5W{=}C(NME_2)CH_3\}$ with *n*-butyllitium followed by Me_3SiCl. The subsequent treatment of the trimethylsilyl carbene complex with butyllithium followed by the reaction with the appropriate aldehyde or ketone afforded the target complex, of which only the *E* isomer was formed, Scheme 3.4.

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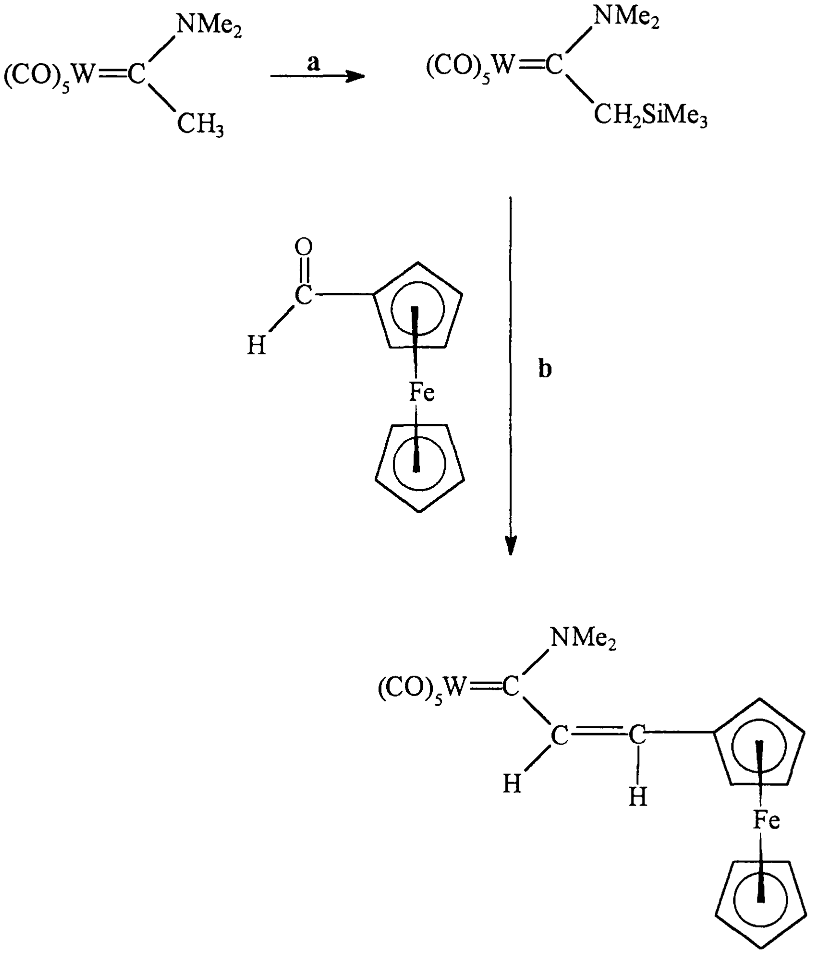
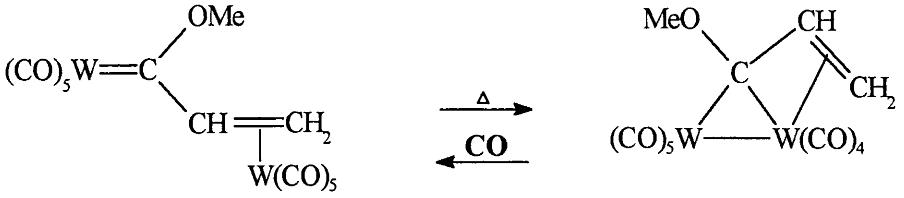


Reagents: (a) 1. *n*-BuLi, THF, – 78 °C ; 2. Me_3SiCl, – 78 °C; (b) *n*-BuLi, THF, – 78 °C.

Scheme 3.4

3.3.4 Carbonyl Substitution

On the other hand the treatment of $W(CO)_6$ with vinyllithium followed by $[Me_3O][BF_4]$ in the presence of H_2O afforded two products, one of which has a π-bonded moiety, $(CO)_5W\{C(OMe)CHCH_2\text{-}\eta^2\}W(CO)_5$. Heating of the π-bonded alkene complex in toluene produced the complex, $W_2(CO)_9[\mu\text{-}\eta^1,\eta^3\text{-}C(OCH_3)\text{-}CH{=}CH_2]$, which upon the treatment with CO converted back to the η^2-bonded complex[63], Scheme 3.5.



Scheme 3.5

3.4 Aim of the Study

As previously mentioned thiophene is considered to be an excellent distributor of electron density in molecules through π-conjugation, as was shown in Chapter 2, and stabilizes the carbene carbon atom in biscarbene complexes. The coordination of a $Cr(CO)_3$-fragment in a π-fashion to an aromatic ring has a marked influence on the stability, characteristics, (eg. shielding or deshielding of atoms in the ring) and activation through either the donation or withdrawal of electron density to or from the ring. Furthermore the presence of a heteroatom as a part of the aromatic system of the ring has an influence on the formation of a π-bond with the metal fragment, as seen in § 3.2.2. These considerations prompted the investigation into the synthesis of σ,π-bimetallic thiophene monocarbene complexes and to study the features and properties of the newly formed compounds.

A π-bonded pseudoaromatic heterocycle which can thus be used advantageously in the synthesis of σ-π-bimetallic complexes is the complex (η^5-thiophene)$Cr(CO)_3$. This complex was prepared for the first time in a low yield by Fischer and Öfele in the thermal reaction of $Cr(CO)_6$ and thiophene.[64] The slight basicity of S in thiophene led Öfele to develop an improved synthesis for $Cr(CO)_3$ adducts of various heterocycles including thiophene.[65] This procedure comprises a two-step synthesis, in which the $Cr(CO)_6$ is converted to $Cr(CO)_3(NH_3)_3$ after which the thiophene complex (η^5-thiophene)$Cr(CO)_3$ is prepared at room temperature from the displacement reaction of the Lewis acid BF_3 with the harder base NH_3 and the simultaneous coordination of the softer base thiophene, in diethylether as solvent.

Another π-bonded pseudoheterocycle which could be utilized with success and has the advantage of being related to the thiophene system is the complex (η^6-benzothiophene)tricarbonylchromium, which was prepared in a direct procedure by heating benzo[b]thiophene and chromium hexacarbonyl in *n*-dibutyl ether and hexane.[66] By employing this complex the role of the heteroatom on the stability of complexes in which the

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ane.[66] By employing this complex the role of the heteroatom on the stability of complexes in which the heteroatom forms a part of the π-system of the ring to which the $Cr(CO)_3$-fragment is π-coordinated can be compared to that in a system in which the heteroatom is not part of the π-system to which the metal fragment is π-coordinated, but is still present within the fused heteroaromatic ring system.

This study will examine the electronic and steric effects of a π-coordinated metal fragment being a substituent of a carbene ligand. The synthesis, features and properties of the new σ,π-bimetallic monocarbene complexes will be investigated by focusing on the bridging thienyl carbene and benzothienyl carbene ligands. Furthermore this investigation will focus on competition for electron density from the π-bonded electron withdrawing metal fragment and the attached electrophilic carbene ligands; compare steric implications of the compact bimetallic compound with a connecting thienyl-carbene instead of the less constrained benzothienyl-carbene unit and search for spectroscopic evidence of metal-metal communication.

3.5 Synthesis of the σ,π-Bimetallic Thienyl Monocarbene Complexes

3.5.1 Thienyl Carbene Complexes

The reaction of chromium- and tungsten hexacarbonyl complexes with lithiated $Cr(CO)_3(\eta^5$-thiophene) after subsequent alkylation afforded in addition to the desired σ,π-monocarbene complexes, $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)\text{-}M(CO)_5)Cr(CO)_3$, M = Cr **(8)** and M = W **(9)**, three additional products, Scheme 3.6. In both cases the first orange coloured product to be isolated with column chromatography was identified as the σ-monocarbene complex, $MC(OEt)(C_4H_3S)(CO)_5$, where M = Cr, **(A)**, and M= W, **(B)**, which is related to the purple σ,π-monocarbene complex, **8** and **9**, but to which the π-moiety is no longer bonded. These products are known[67] and were also obtained as by-products in the synthesis of the thiophene biscarbene complexes **1** and **2** described in Chapter 2.

The third and fourth products, respectively orange and purple, were isolated after the desired σ,π-carbene complexes **8** or **9** and were found to be related to each other. These products were identified as the mononuclear σ-carbene complexes, $M\{C(O(CH_2)_4OCH_2CH_3)C_4H_3S\}(CO)_5$, where M = Cr **(10)** and M = W **(11)**, and the bimetallic σ,π- monocarbene complexes, $(\eta^1{:}\eta^5C_4H_3SC\{O(CH_2)_4OCH_2CH_3\}M(CO)_5)Cr(CO)_3$, where M = Cr **(12)** and M = W **(13)**, with the only difference being the absence of the π-coordinated $Cr(CO)_3$-fragment in **10** and **11**.

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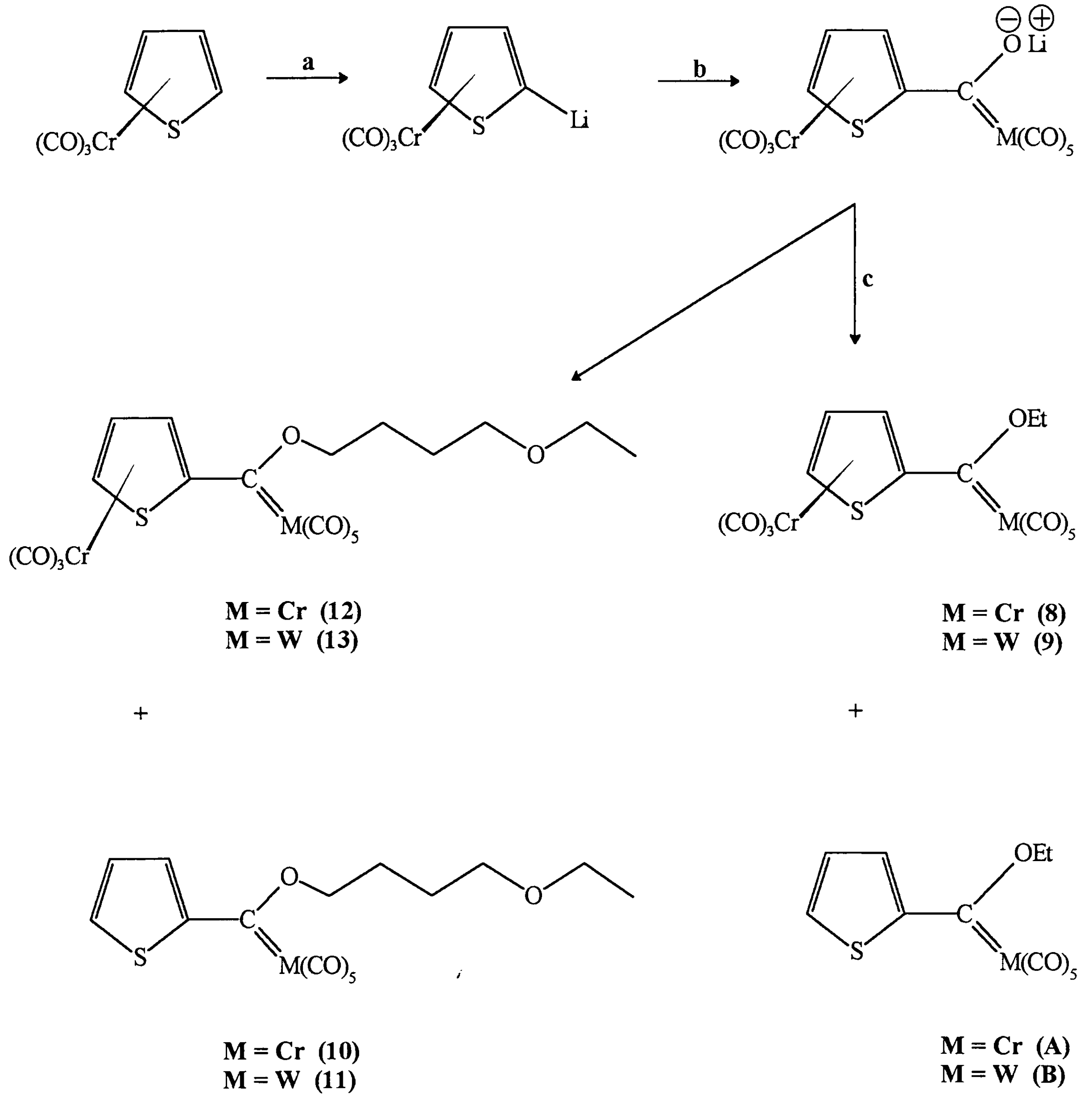

Reagents: (a) BuLi, THF, - 50 °C; (b) $M(CO)_6$, (c) $[Et_3O][BF_4]$, CH_2Cl_2

Scheme 3.6

The removal of one proton of thiophene is best achieved at temperatures of - 10 °C and lower, - 50 °C was, however, found to be an ambient temperature for the mono-deprotonation of (η^5-thiophene)-tricarbonylchromium with a slight excess (≈ 10 %) of butyllithium in THF as solvent to afford the lithium salt of the mono-anion. The formation of complexes **8** and **9** can be rationalized in terms of the classic Fischer procedure in which one of the six equivalent CO groups of the metal hexacarbonyl complex undergoes attack to produce the, lithium acylate intermediate, which upon the treatment with a hard alkylating agent like tri-

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ethyloxonium tetrafluoroborate in dichloromethane as solvent results in alkylation at the oxygen, producing the target ethoxycarbene complexes. The formation of products **10 - 13** was unexpected and a result of the π-coordinated $Cr(CO)_3$-fragment. Furthermore this type of product was not formed when the 2-lithium thienyl was reacted with $M(CO)_6$ substrates under similar reaction conditions[67] or during the synthesis of the biscarbene complexes reported in Chapter 2. Another possible explanation for the formation of these complexes, which are related, is presented in Scheme 3.7. The mono-anionic lithium acyl species can also in favour of a solvent molecule lose a carbonyl ligand in solution. Due to the lability of the thienyl ligand slow decomplexation affords "$Cr(CO)_3$" which causes a demand for carbonyl ligands in solution. The coordination of the oxygen of THF, (a group with which π-backbonding of electron density from the metal is not possible), activates the THF by increasing the polarity of the O-CH_2 bond, (through an electron "impoverishment" on the oxygen atom and subsequent flow of bonding electrons in the O-CH_2 bond), and hence the electrophilic character of the carbon atom. Due to CO substitution by THF the electron density is increased on the tetracarbonyl metal fragment resulting in greater backbonding to the acylate carbon and increased nucleophilic character on the adjacent oxygen atom. The negative oxygen of the acyl complex attacks the α carbon atom, (of which the electrophilic character has been increased), of the THF which leads to the opening of the THF ring. The coordination of THF instead of CO also increases the negative charge on the metal centre and hence the nucleophilic character of the oxygen atom. This type of product is not formed if thiophene is not π-coordinated to $Cr(CO)_3$. The oxygen can remain either coordinated, upon which the alkylation of the negative metal centre affords the unstable metal-ethyl intermediate which gives the final product **12** or **13** through a reductive elimination and addition of a carbonyl ligand. The oxygen can, however, also be localized and displaced from the metal due to the instability of the 8-membered ring to yield an intermediate which contains a free distal anionic terminal oxygen and upon alkylation affords the final product **12** or **13**. The π-coordination of the thiophene group to the $Cr(CO)_3$ plays an important role to localize the double bonds and the sulphur atom and hence causes weak delocalization of the negative charge on the oxygen atom. Eventhough we favour an intermediate with the tungsten centre accomodating the excessive negative charge from the oxygen other formulations involving the carbene carbon (ylide) may also be possible, see Figure 3.7. Alkylation, be it on either the metal or the oxygen leads to the formation of **12** or **13**. Recently Dötz and co-workers[68] ascribed the formation of a carbene with a ring-opened THF as being part of the alkoxy substituent, as resulting from an alkylated THF employed as alkylating agent. Due to the fact that all the THF had been removed prior to alkylation, we cannot in this case accept $[THF{\cdot}Et]^+$ to be the active alkylating agent. In fact, the metal acylate was washed with hexane before it was dissolved in dichloromethane. Either the proposed mechanism of Dötz is in error or we have a different mechanism operative in this case. This result will therefore be treated as resulting directly from the action of a bimetallic acylate intermediate.

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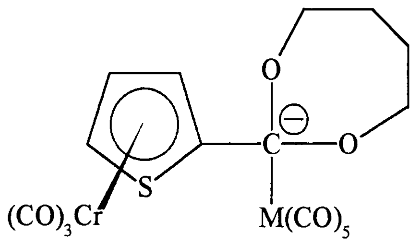

Figure 3.7 Ylide-intermediate (7-membered ring)

The proposed reaction route is without precedent in literature and differs from that suggested by Dötz only in the manner in which the THF is activated. The solvent THF, was not only coordinated at an appropriate position close to the oxygen atom of the acylate, but is attacked, opened and ultimately incorporated into the carbene unit. The reductive cleavage of free THF has, however, previously been reported at - 78 °C, where it is easily achieved by using Li powder or even lithium 4,4'-di-*tert*-butylbiphenyl and $BF_3 \cdot OEt_2$ in the presence of a catalytic amount of an arene, eg. naphthalene, biphenyl 4,4'-di-*tert*-butylbiphenyl or anthracene.[69]

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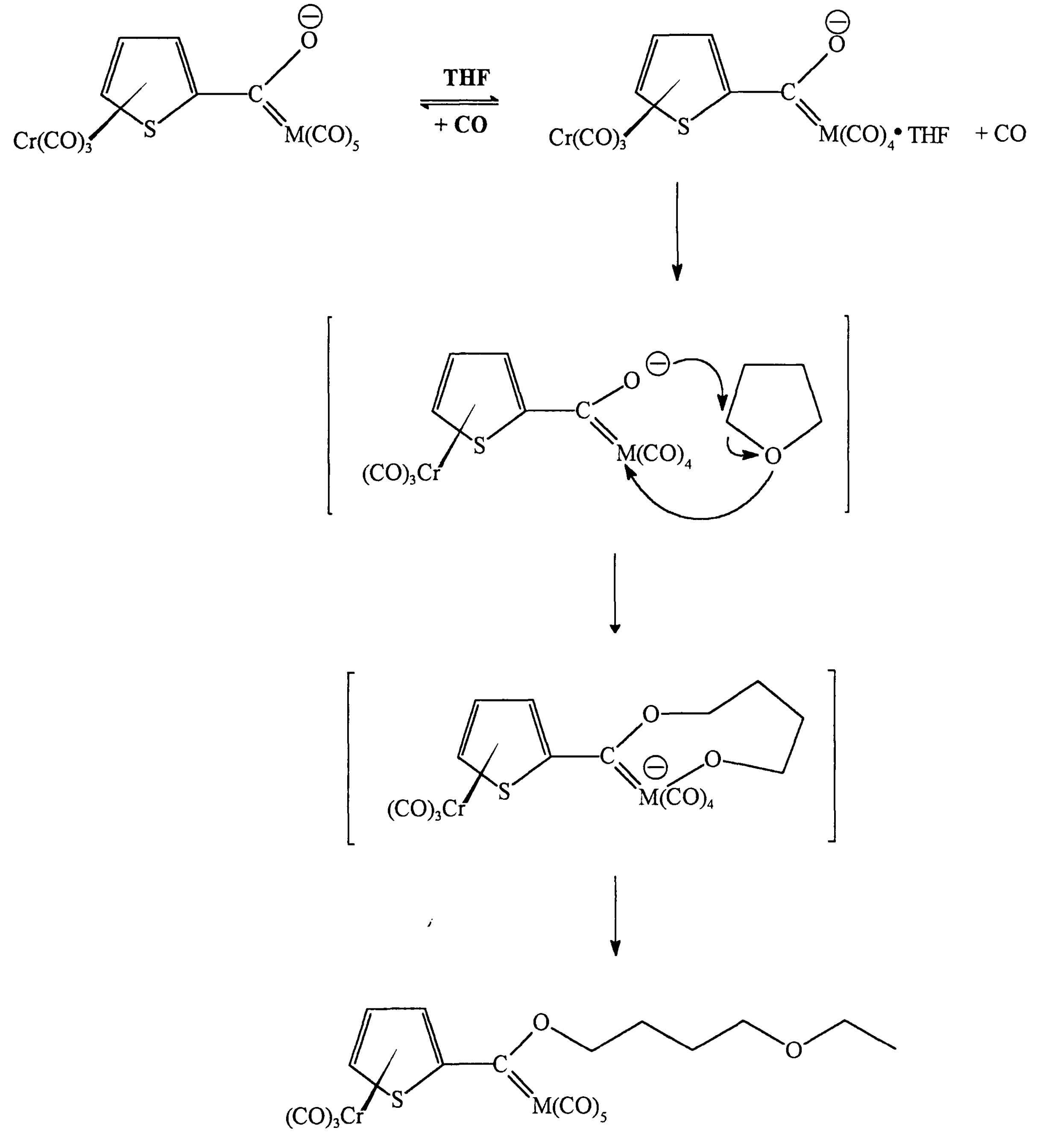

12; 13

Scheme 3.7

The formation of the monocarbene complexes, **A** and **B**, can be accounted for in exactly the same manner as **8** and **9**, with the only difference being the breaking of the π-bond between the thiophene ring and $Cr(CO)_3$-fragment at some stage during the reaction. Likewise, the same procedure as for the formation of **12** and **13**, can be offered for the formation of complexes **10** and **11**, with the additional step, the loss of the π-bonded

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$Cr(CO)_3$ at some time after the formation of the THF-incorporated species, *i e* before or after alkylation.

The synthesis of the analogous (cyclopentadienyl)dicarbonylmanganese and (methylcyclopentadienyl)dicarbonylmanganese monocarbene σ,π-bimetallic complexes was attempted, but without any success. A possible explanation for this could be that the cyclopentadienyl ring, which is an electron donating group, causes the carbonyl ligands, which should exhibit some positive character in order to undergo attack by the lithium thienyl complex, to be insufficiently electrophilic. The π-coordination of the thiophene on the other hand can also lead to a weaker thienyl nucleophile. Another consideration could be that attack by the nucleophile takes place on the activated cyclopentadienyl ring, however this can be ruled out, as it did not takes place during the synthesis of the biscarbene complexes, **3** and **4**. Due to excessive decomposition no definite conclusions could be drawn and further experiments were abandoned.

The products **8** and **9** were found to be moderately stable in the solid state, as well as, in solution. The tungsten complex 9 could be successfully crystallized from a mixture of hexane and dichloromethane, (ratio 3 : 1), to afford crystals from which a stucture analysis was possible. Complex **8**, however, afforded small asymmetrical crystals from a 3:1 mixture of hexane and dichloromethane, of which the standard was to poor for a structure analysis. During the prolonged storage, even in an inert atmosphere at low temperatures and in the solid state complex **8** converted to complex **A**, through the loss of the π-metal fragment, in a similar manner complex **9** converted to complex **B**. Complexes **12** and **13** were found to be less stable in the solid state and even more so in solution compared to complexes **8** and **9**. Neither **12** nor **13** could be successfully crystallized to afford crystals for a crystal structure analysis, after a prolonged attempt **13** eventually afforded thin hair-like crystals, which could not be used for diffraction studies. Even in an inert atmosphere at low temperatures complexes **12** and **13** converted, through the loss of the π-bonded $Cr(CO)_3$, to **10** and **11**, which were more stable in the solid state and in solution.

3.5.2 Benzothienyl Carbene Complexes

The reaction of benzo[b]thiophene under thermal conditions leads to the formation of the π-complex, (η^6-BT)$Cr(CO)_3$, however, in comparison to thiophene, it is the benzene ring to which the $Cr(CO)_3$-fragment is π-coordinated in this complex .[66] Despite this the thiophene ring is also, (due to the aromatic properties of the fused rings), activated by the coordination, to the extent that metallation preferably takes place on the 2-position of the thiophene ring rather than on the 4- or 7 positions of the benzene ring, see Figure 3.8.

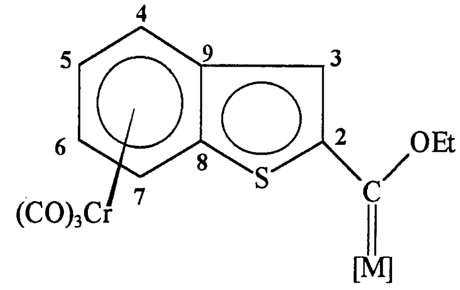

Figure 3.8 Atom Numbering in Benzothienyl Carbene Complex

In order to afford the π-coordinated benzothiophene tricarbonylchromium complex a mixture of benzothiophene and chromium hexacarbonyl was refluxed in *n*-dibutyl ether overnight. The yields obtained were poor, but the filtration of the reaction mixture through silica gel with hexane led to unreacted benzothiophene being recovered for further use. Higher yields are possible by using greater excesses of benzo[b]thiophene, but with the disadvantage that the isolation of the π-complex from the ligand became accordingly more difficult. Optimum yields were obtained by using 2.5 - 3 equivalents of benzo[b]thiophene. The deprotonation of (η^6-BT)Cr(CO)$_3$ to yield the metallated complex, was readily achieved in a similar manner as for the thiophene analogue by reacting one equivalent of the complex with 1.1 equivalents of *n*-butyllithium in THF at - 50 °C.

The rest of the reaction was performed in a similar manner as the reaction of the thiophene analogue, for the synthesis of Fischer carbene complexes, with the addition of the metal hexacarbonyl and quenching with triethyloxonium tetrafluoroborate to afforded the dark purple-blue ethoxycarbene complex, (η^1:η^6-$C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$, **(14)** in an excellent yield of about 90 %. The product was purified by crystallization from hexane and dichloromethane and found to be very stable, even in air and in acetone for short periods of time. The π-coordinated Cr(CO)$_3$-fragment was, however, lost, very slowly, in solution to give the monocarbene complex, $Cr\{C(OEt)C_8H_5S\}(CO)_5$, **(15)**. Scheme 3.8 presents a schematic outline for the synthesis.

This reaction yielded the σ,π monocarbene complex **14** in an almost qualitative yield as virtually the only product, with small quantities (less than 5%) of a second minor orange product which was later identified as the σ-monocarbene complex $Cr\{C(OEt)C_8H_5S\}(CO)_5$, **(15)**. In fact is was possible to purify **14** by a simple recrystallization of the reaction mixture after filtration through silica gel. This observation can only confirm the fact that the π-complex of benzothiophene, in which the Cr(CO)$_3$ is π-coordinated to the

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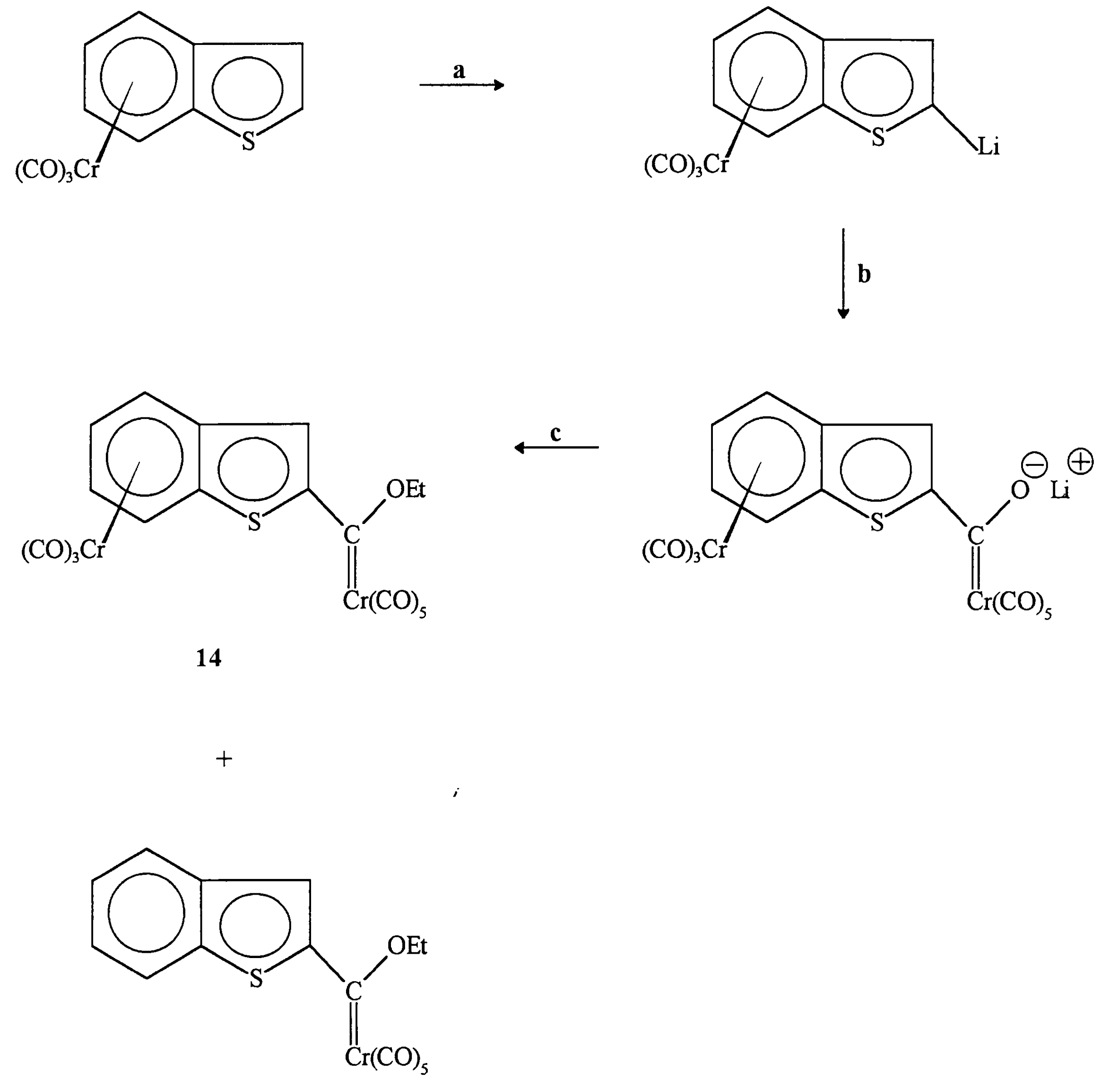
benzene ring, is much more stable than the analogous thiophene complex. Furthermore the importance of π-coordination to thiophene in order to yield products **12** and **13**, is emphasized as this does not happen in the case of benzothiophene. The compound **14** is also more stable and the yield much higher than the thiophene analogue **8**.



14

15

Reagents: (a) BuLi, THF; (b) $Cr(CO)_6$; (c) $[Et_3O][BF_4]$, CH_2Cl_2
Scheme 3.8

Quite interestingly, it was found that the reaction of benzothiophene with two equivalents of *n*-BuLi (in the monomeric BuLi·TMEDA complex, which was used in the synthesis of the biscarbene complex **1**,

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Chapter 2) did not yield the biscarbene complex, but the monocarbene complex **15**.

3.6 Spectroscopic Characterization of Bimetallic σ,π-Thienyl Monocarbene Complexes

The σ,π-bimetallic monocarbene complexes **8** and **9**, as well as the related complexes **12** and **13** were characterized with ^1H NMR-, ^{13}C NMR-, infrared- and mass spectroscopy and structural formulations, based on these spectroscopic data, were made. The monocarbene complexes **10** and **11** were characterized with ^1H NMR-, infrared- and mass spectroscopy. The benzothiophene monocarbene complexes **14** and **15** were characterized with ^1H NMR-, ^{13}C NMR-, infrared- and mass spectroscopy. All NMR spectra were recorded in $CDCl_3$ as deuterated solvent. The numbering of the carbon atoms of the thiophene ring are shown in Figure 3.9.

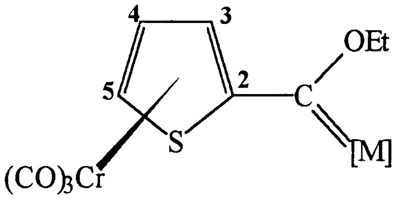

Figure 3.9 Atom Numbering in Thienyl Carbene Complexes

3.6.1 ^1H NMR Spectroscopy

^1H NMR data for the bimetallic σ,π-thienyl monocarbene- and σ,π-benzothienyl monocarbene complexes are summarized in Tables 3.1 - 3.3 respectively. First the ^1H NMR spectra of **8** and **9** will be discussed, followed by the ^1H NMR spectra of complexes **10** - **13**. Lastly the spectra of complexes **14** and **15** will be compared to the above.

(a) ^1H NMR Data of $(\eta^1:\eta^5\text{-}C_4H_3SC(OEt)M(CO)_5)Cr(CO)_3$, M= Cr, (8) and M = W (9)

The ^1H NMR data of complexes **8** and **9** are summarized in Table 3.1. Figure 3.10 represents the ^1H NMR spectrum of **9**. All spectra were recorded in $CDCl_3$ as solvent.

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Table 3.1 ^{1}H NMR Data of the Bimetallic σ,π-Thienyl Monocarbene Complexes

Assignment	**Complexes**			
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)			
	8		**9**	
Proton	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$
H3	5.81 (d)	3.7	5.95 (d)	3.8
H4	5.79 (t)	3.7	5.79 (t)	3.8
H5	6.54 (d)	3.7	6.49 (d)	3.7
$OCHHCH_3$[a]	4.99 (q) 5.02 (q)	7.2	4.83 (q) 4.89 (q)	7.1
$OCHHCH_3$[a]	4.88 (q) 4.82(q)	7.2	4.77 (q) 4.72(q)	7.2
OCH_2CH_3	1.53 (t)	7.1	1.51 (t)	7.1

[a] a second set of quartets of lower intensity, (0.33), was observed and δ-values are given below those of the first set.

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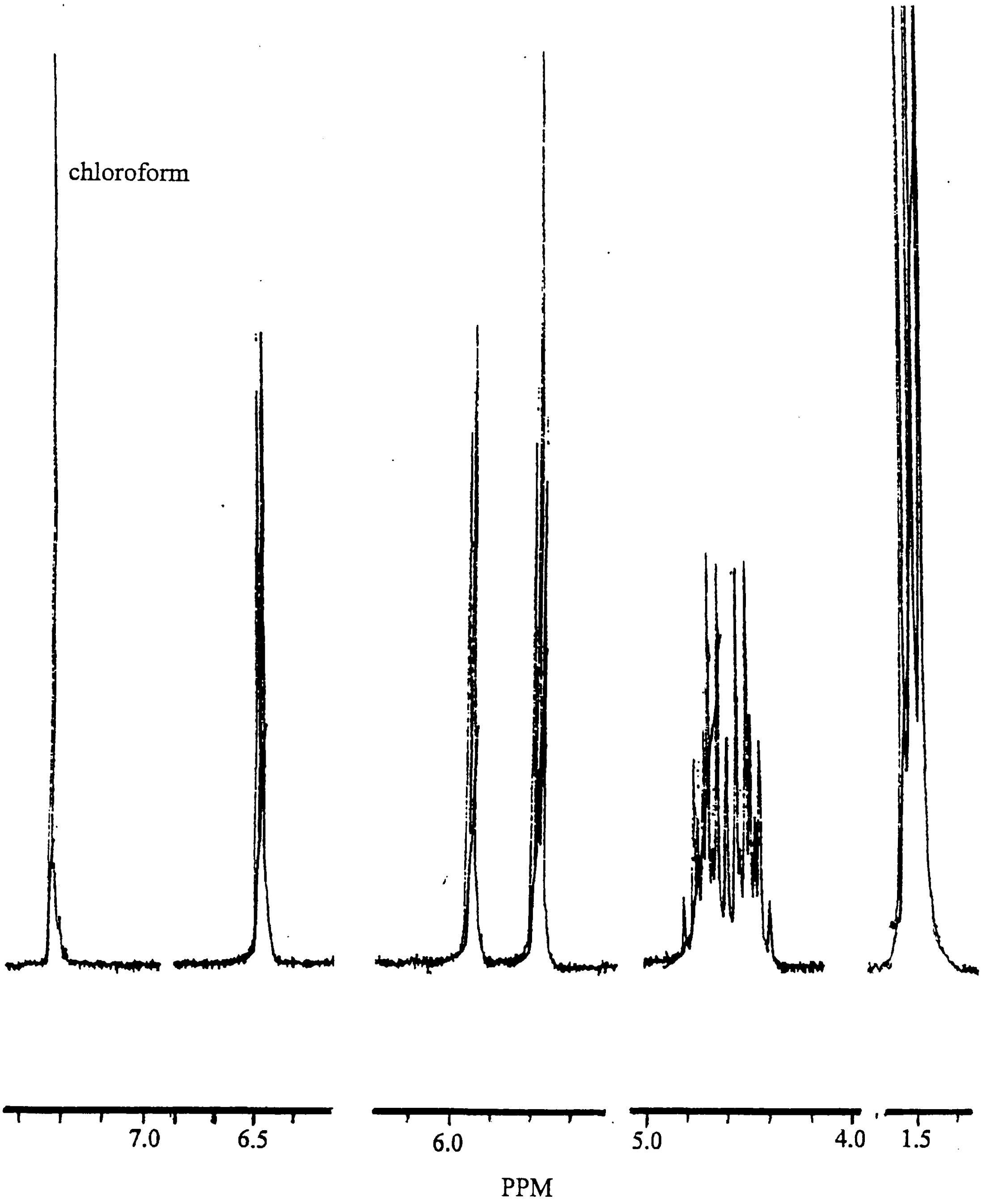

Figure 3.10 ^{1}H NMR Spectrum of (η^1:η^5-$C_4H_3SC(OEt)W(CO)_5)Cr(CO)_3$

Characteristic features of the σ,π-bimetallic monocarbene complexes are evident from inspection of the chemical shifts of the protons in the ^{1}H NMR spectrum of 9. Two features dominate, (a) the upfield shifts of the thienyl resonances by more than 1 ppm from those of free thiophene and (b) the duplication

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of the methylene resonances of the ethoxy substituent of the carbene ligand. The π-coordination of benzene and thiophene rings to $Cr(CO)_3$ leads to the localization of the double bonds and to the disruption of the aromaticity and ring current of the arene ligand, resulting in upfield chemical shifts for the ring protons. Other factors which may affect the free thiophene are related to π-coordination and are:[70]

(i) Changes in charge density on the ligand atoms,
(ii) Changes in the hybridization states of metal-bonded carbon atoms,
(iii) Various anisotropic effects.

Closer examination of the multiplet between 4.7 and 5.1 ppm of the ^1H NMR spectra of **8** and **9** indicate two sets of independent signals observed for the resonances of the methylene protons of the carbene ligand. The spectrum clearly shows two separate quartets of equal intensity resulting from two chemically non-equivalent protons of the methylene group of the carbene. The molecule lacks a plane of symmetry due to the π-coordination of the $Cr(CO)_3$ fragment on one side of the thiophene ring which makes the two methylene protons prochiral and duplicates the chemical shifts (planar chirality).[71] Other resonances are hardly affected, at most a little broadened. In addition, a second set of resonances appear on the sides of the stronger signals, roughly of about 30 % of the intensity of the stronger signals. These indicate the existence of a second isomer in solution, also subjected to chiral planarity and therefore duplicated. The two components, diastereoisomers, in solution are related by different orientations and restricted rotations around one of the three bonds associated with the carbene carbon atom, see Figure 3.11.

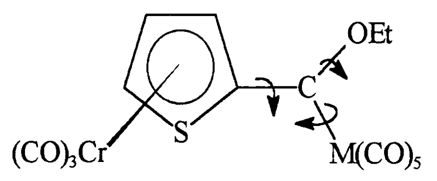
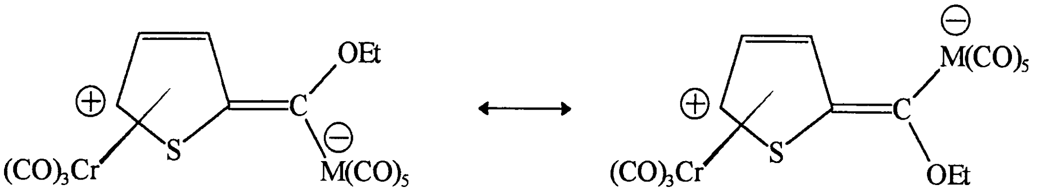
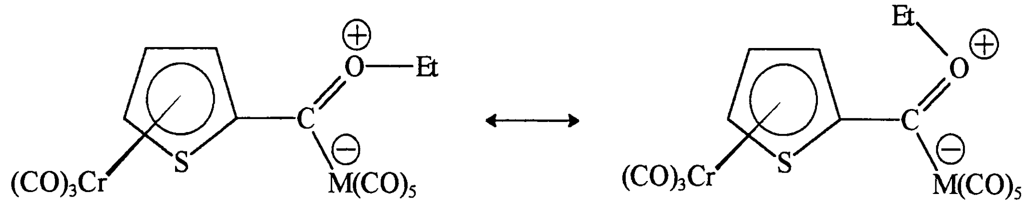


Figure 3.11 Possible Resticted Rotations around the C(Thienyl)-C(Carbene)-, C(Carbene)-O- or C(Carbene)-Metal Bonds

(i) Possible restricted rotation around the C(thienyl)-C(carbene) bond is found in electronic reasoning when the following two structures are considered placing the ethoxy group in two different chemical environments:

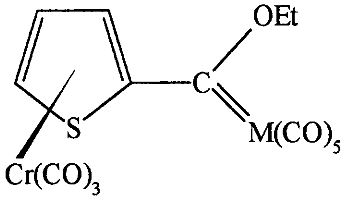


(ii) Restricted rotation around the C(carbene)-O bond will also result in different chemical environments for the ethoxy and thiophene groups. However, little effect is displayed in the resonances of the thienyl protons.



This phenomenon is well known for amino carbene complexes and at low temperatures for alkoxy carbene complexes.[72] This implies the greater participation of the oxygen lone pair of electrons in stabilizing the carbocationic carbene carbon atom which may be the result of the removal of electron density from the carbene carbon atom onto the thiophene ring and onto the electron withdrawing $Cr(CO)_3$-fragment. No evidence of non-equivalence is found in the chemical shifts and coupling constants of the thienyl protons or methyl protons of the ethoxy group.

(iii) Resticted rotation around the metal-C(carbene) bond will only be of some significance if different ligands were coordinated to the metal fragment.



The ethoxy protons appear at lower δ-values (upfield) in the spectrum of **9** compared to the corresponding δ-values in the spectrum of **8**. The same result was found comparing the resonances in **1** and **2** and is the result of higher electron density from the softer tungsten centre distribution to the car-

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bene carbon compared to chromium.

If the monocarbene complexes **A** and **B** are considered this splitting pattern for the methylene protons is not observed in the spectrum of either complex, these protons are observed as quartets in these spectra.[67] The fact that the non-equivalence is observed for the methylene protons of the ethoxy group only and that this observation disappears when the π-coordinated group disappears shows that this observation must be brought into context with the presence of the latter and could rather be due to steric instead of electronic causes. Therefore, it is concluded that at the temperature at which the reaction is executed the acylate intermediate which forms is locked in one of two orientations with respect to the thienyl-carbene bond due to the bulkiness of the π-coordinated $Cr(CO)_3$-fragment. Support for this is found in the structure determination of **9** (vide infra) which displays a very compact arrangement of $M(CO)_5$ and (π-thienyl)$Cr(CO)_3$ units, as illustrated by Figure 3.12.

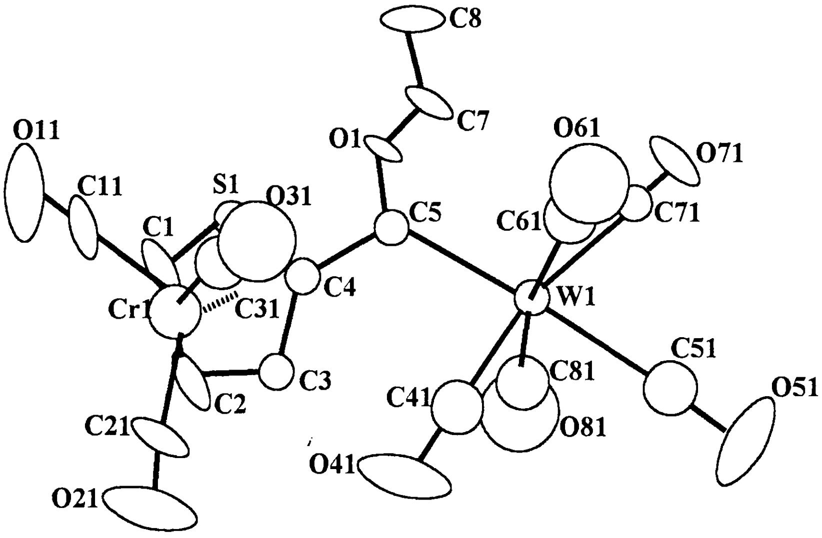

Figure 3.12 Bulkiness of Metal Carbonyl Fragments

The chemical shifts in the spectrum of the π-coordinated thiophene complex $Cr(CO)_3(\eta^5\text{-thiophene})$ appear as singlets with H2, H5 at 5.37 ppm and H3, H4 at 5.61 ppm.[73] On comparing these values it is evident that the protons of coordinated thiophene have upfield chemical shifts when a π-moiety is coordinated compared to those of uncoordinated thiophene. The chemical shifts of these protons appear further downfield in the spectra of the σ,π-carbene complexes **8** and **9**. Three chemical shifts with different mutiplicities are observed for protons in the spectra of the σ,π-thiophene carbene complexes; H3 a doublet, H4 a triplet and H5 a doublet. By comparison the thienyl protons appear downfield in the spectrum of **9** compared to the spectum of **8**. This is possibly an indication that the thienyl is either

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bonded more strongly to the $Cr(CO)_3$ or that it channels more electron density to the carbene carbon in **9** than in **8**. However, this effect illustrated by Figure 3.13 is of less importance than the corresponding donation of electron density from a cyclopentadienyl ring of a ferrocenyl substituent in the complexes $M(CO)_5\{C(OEt)Fc\}$.[53]

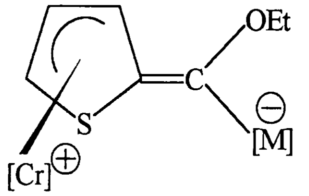

Figure 3.13 Donation of Electron Density from the π-coordinated Thiophene to the Carbene Carbon Atom

The chemical shift for H3 or H4, is 8.06 ppm for the chromium biscarbene complex **1** and 7.95 ppm for the tungsten σ,σ-biscarbene complexes **2**, see § 2.5.1. These are upfield for **8** and **9**, illustrating the influence of the π-fragment.

For the complex $((\eta^6\text{-}C_6H_5)C(OEt)M(CO)_5)Cr(CO)_3$, where M = Cr, Fischer *et al*[52] found the chemical shifts for $OC\mathit{H_2}CH_3$ and $OCH_2\mathit{CH_3}$ as 5.09 ppm and 1.75 ppm,for M = Cr and for M = W at 5.23 ppm and 1.77 ppm, respectively. These values are a little downfield from those obtained for **8** and **9**, the differences can be attributed to a different deuterated solvent being used, in this case acetone, or that the π-system being a phenyl ring, compared to the thiophene ring in **8** and **9**, is less electron donating to the carbene carbon due to its greater ring aromaticity.

(b) ^{1}H NMR Data of $M\{C(O(CH_2)_4OEt)C_4H_3S\}(CO)_5$, M = Cr, (10), M = W, (11) and $(\eta^1\!:\!\eta^5\text{-}C_4H_3SC\{O(CH_2)_4OEt\}M(CO)_5)Cr(CO)_3$, M = Cr, (12) and M = W, (13)

The above mentioned effect caused by π-coordination is clearly demonstrated by **10** and **11**, (without a π-moiety) and **12** and **13**, (with a π-moiety), see Table 3.2. For complexes without a π-moiety the chemical shifts appear further downfield than for the corresponding protons in the spectra of the complexes with the π-coordination. Figures 3.14 and 3.15 represent the ^{1}H NMR spectra of **11** and **13**, respectively. The numbering of the carbon atoms of the thiophene ring is the same as for **8** and **9**, presented by Figure 3.9.

The formation of **12** and **13** was unexpected and spectra could only be assigned by taking into consideration the information available from the data of different spectroscopic measurements. Each constituted to the final unravelling of the structure of 12 and 13.

Table 3.2 ^{1}H NMR Data for Thienyl Carbene Complexes

Assignment	**Complexes**							
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)							
	12		**13**		**10**		**11**	
Proton	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$
H3	5.81(d)	3.8	5.89(d)	3.9	7.67(d)	4.8	7.79(d)	4.9
H4	5.75(t)	3.7	5.75(t)	3.7	7.21(t)	4.3	7.20(t)	4.6
H5	6.54(d)	3.8	6.48(d)	3.7	8.24(d)	4.6	8.14(d)	4.1
$\mathrm{OC\mathbf{H}HCH_2}^a$	4.97(t) 5.02(t)	6.3	4.80(t) 4.83(t)	6.5	5.13(t)	6.5	4.95(t)	6.4
$\mathrm{OCH\mathbf{H}CH_2}^a$	4.96(t) 4.89(t)	6.3	4.77(t) 4.74(t)	6.5				
$\mathbf{CH_2}\mathrm{OCH_2CH_3}$	3.47(t)	6.2	3.46(t)	6.0	3.51(t)	6.3	3.51(t)	6.2
$\mathrm{CH_2O}\mathbf{CH_2}\mathrm{CH_3}$	3.49(q)	7.0	3.47(q)	6.9	3.48(q)	7.0	3.47(q)	7.0
$\mathrm{OCH_2}\mathbf{CH_2}\mathrm{CH_2}$	2.02 - 1.93 (m)		2.00 - 1.91 (m)		2.11 (q)		2.09 (q)	6.5
$\mathrm{OCH_2CH_2}\mathbf{CH_2}$	1.78 - 1.69 (m)		1.87 - 1.72 (m)		1.83 (q)		1.84 (q)	6.2
$\mathrm{OCH_2}\mathbf{CH_3}$	1.21 (t)	7.0	1.20 (t)	7.0	1.20 (t)	6.9	1.20 (t)	7.0

[a] a second set of triplets of lower intensity, (0.33), was observed and the δ-values are given below those of the first set.

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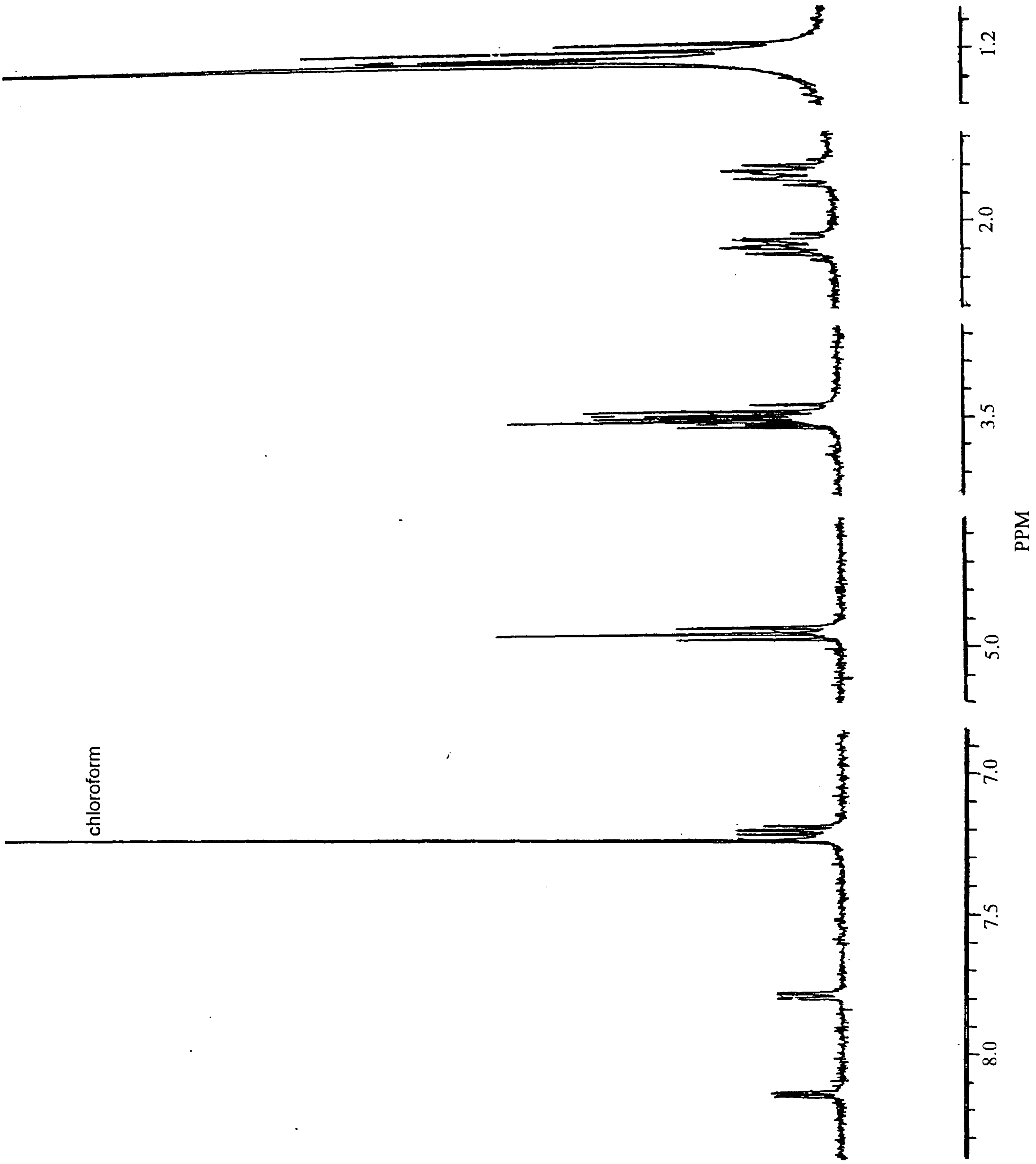

Figure 3.14 ^{1}H NMR Spectrum of $W\{C(O(CH_2)_4OEt)C_4H_3S\}(CO)_5$

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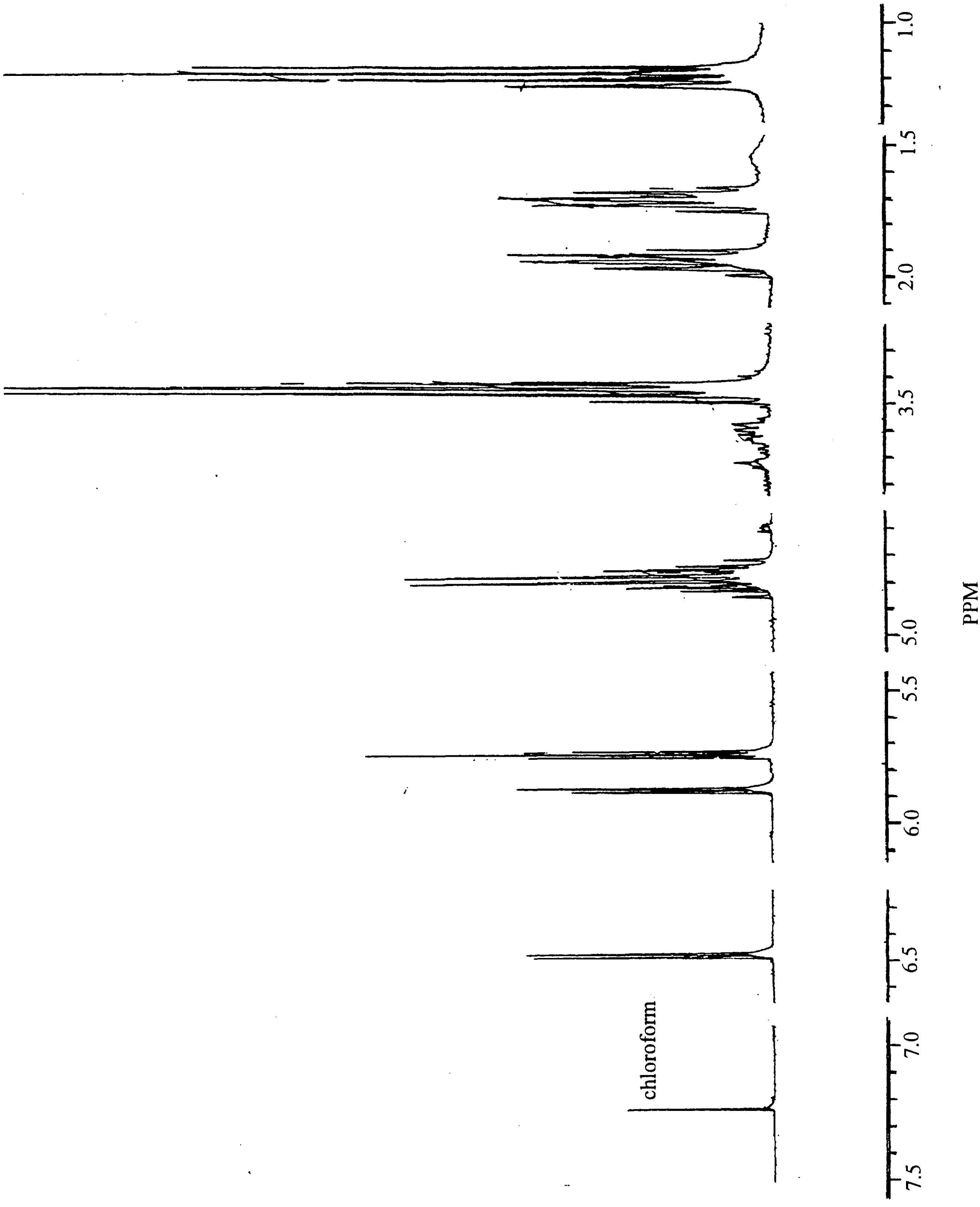

Figure 3.15 ^{1}H NMR Spectrum of (η^1:η^5-$C_4H_3SC\{O(CH_2)_4OEt\}W(CO)_5$)$Cr(CO)_3$

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Complexes **12** and **13** gave mass spectra with molecular ion peaks and chemical analysis values, that are exactly the same as those for **8** and **9**, except for an additional C_4H_8O (THF) group included in the formulae. Various different structures were considered for **12** and **13** and tested with the prevailing spectroscopic data, see Figure 3.16.

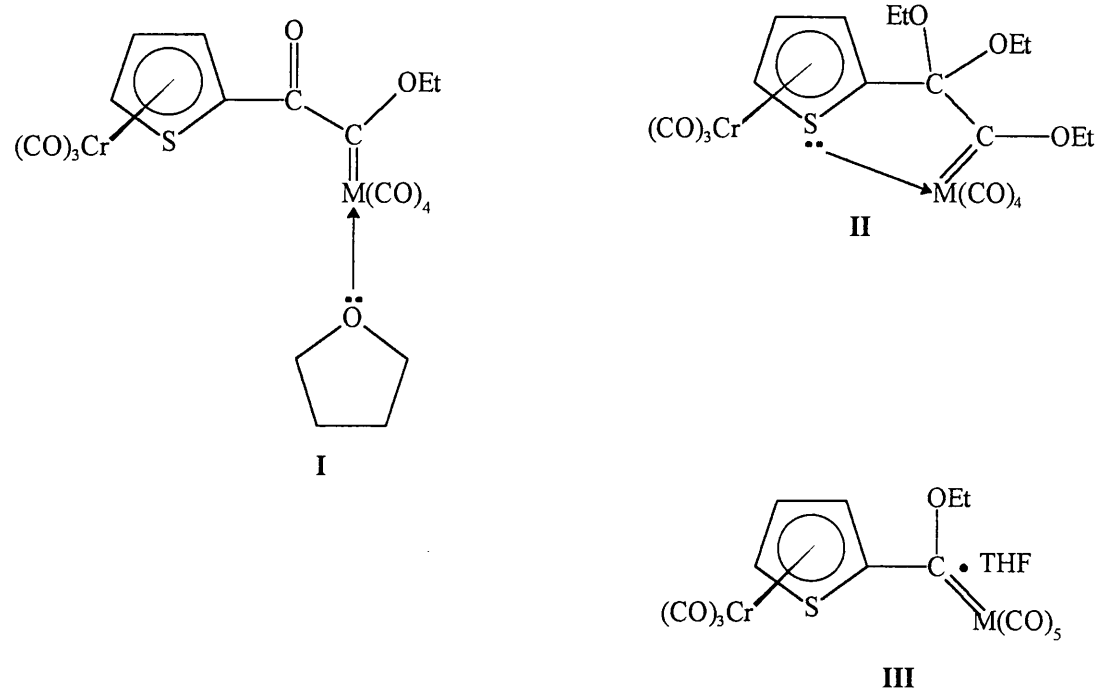

Figure 3.16 Possible Structures for Complexes 12 and 13

The structures **I** and **II** were eliminated as the infrared spectra of **12** and **13** clearly show the presence of only a $M(CO)_5$ and $M(CO)_3$ fragment and the absence of an acyl carbonyl. Furthermore the ^1H and ^{13}C NMR data could be identified with neither **I** nor **II**. The structure **III** was a possibility with THF, as a solvent in the crystal, this was, however, consider odd as it occurred in both compounds, as well as, the fact that the chemical shifts of the β and γ methylene protons of the THF unit are distinctly different. This led to the consideration of possible structures in which THF had been incorporated into the bridging ligand and two significant stuctures could be written, namely **IV** and **V**:

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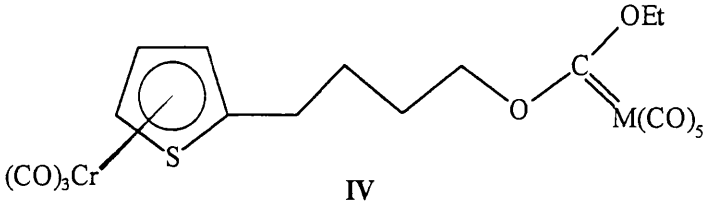
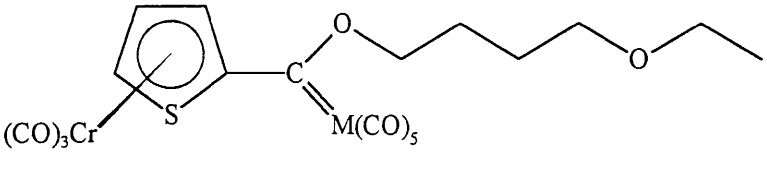


IV



V

IV represents the attack by the anionic carbon in the 2 position of thiophene on a THF molecule which leads to the splitting of the C-O bond. Attack by the negative oxygen on a carbonyl affords **IV** after alkylation. Both structures appear to fit the picture for the analytical data, (mass-, ^{1}H- and ^{13}C- NMR and infrared spectra). The methylene protons of the carbene unit again show two or more non-equivalent structures and a complex splitting pattern is observed. The splitting pattern shows a multiplet which can be described as a quartet of high intensity and two triplets of low intensity or four triplets of which two have a higher intensity and overlap and two which have a lower intensity, Figure 3.17.

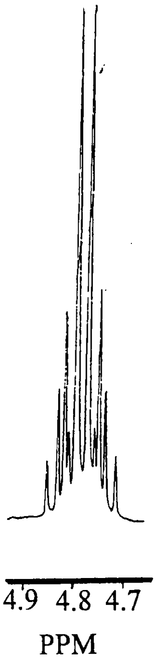


Figure 3.17 Splitting Pattern of the Methylene Protons of the Carbene Unit

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These protons appear as quintets, see Figure 3.18, however, coupling constants of no significance can be obtained and either **IV** or **V** remains a possibility.

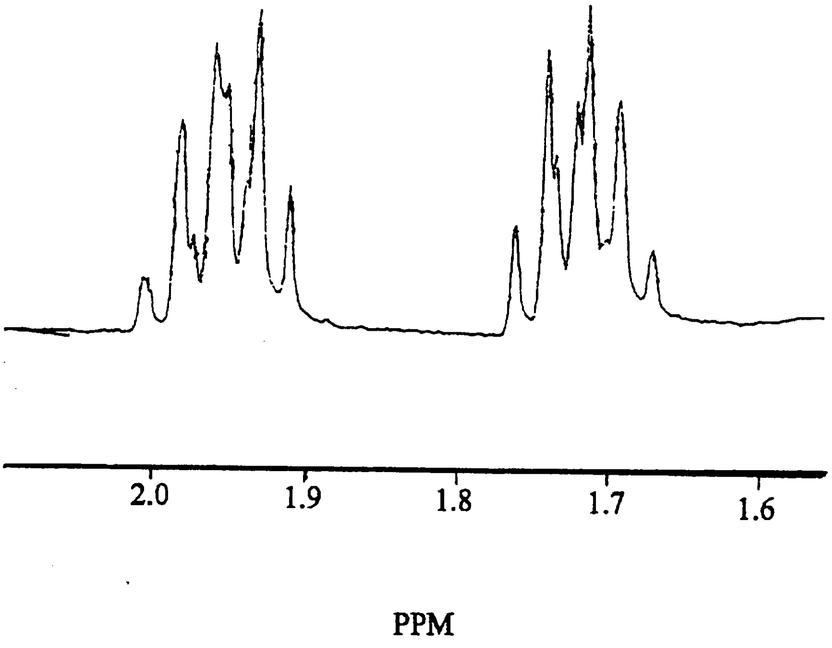

Figure 3.18 Splitting Pattern of β and γ Methylene Protons

The chemical shifts at 3.50 ppm are an indication of methylene protons that overlap and are adjacent to an oxygen atom, these are decisive in the assigning of **V** as the structure for **12** and **13**. The splitting pattern of a triplet and quartet that overlap and the respective magnitude of the coupling constants which agree for the methyl triplet and the quartet of the methylene protons are in agreement with the structure **V** but not with **IV**. Furthermore carbene methyl protons appear at chemical shifts of ± 1.5 ppm which is downfield from the 1.20 ppm observed and indicates the presence of an ethoxy substituent. Structure **IV** gives no reason for limited rotation owing to steric reasons, as the carbene carbon is far removed from the *ipso*-carbon atom of the π-coordinated thiophene, but nevertheless a similar complicated pattern as those observed for **8** or **9** are found for **12** and **13**, respectively, again supporting structure **V**.

Final confirmation for the structure **V** is obtained when the ^{1}H NMR spectra of the decomposition products **10** and **11** are studied. Controlled decompositions starting from pure samples of **12** and **13** were excecuted in polar solvents, Scheme 3.9. Products **10** and **11** were isolated purified and compared with samples obtained from the initial reaction mixture.

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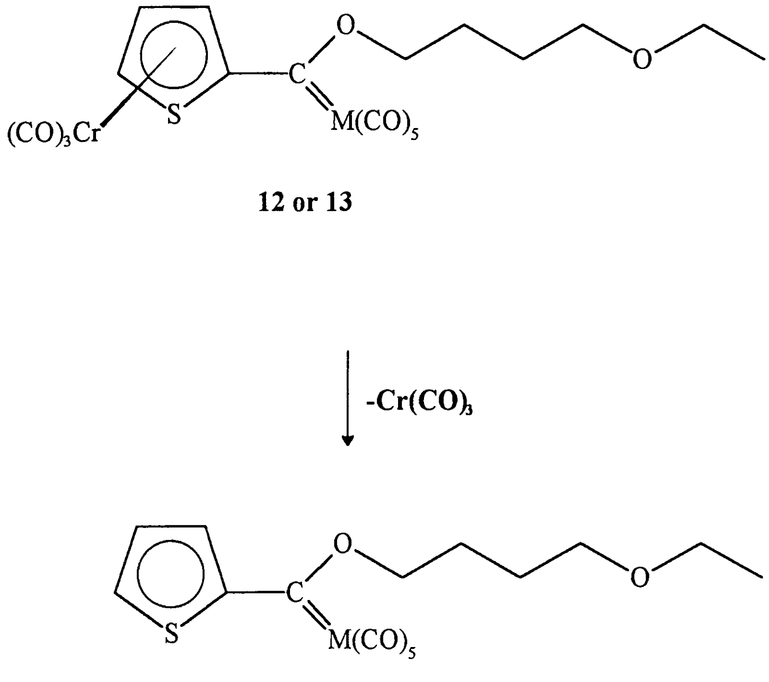

Scheme 3.9

The restricted rotation of the carbene carbon is lifted by the loss of the $Cr(CO)_3$-fragment and the carbene methylene now appears as a perfect triplet, as can be expected for **V** and not as a quartet as would have been the case had **IV** been the correct structure.

After this unambiguous determination of the stuctures of **12** and **13** mainly with NMR spectra the assignment of splitting patterns and calculation of coupling constants could be executed more thoroughly and hence confirmed the assignment of structure **V** to **12** and **13** to be correct.

The spectra with respect to the chemical shifts for the thienyl and methylene protons on the oxygen adjacent to the carbene carbon in the spectra of the thienyl monocarbene mononuclear complexes **A** and **10**, as well as, **B** and **11** are as is anticipated practically the same.

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(c) ^{1}H NMR Data of $(\eta^1{:}\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$, (14) and $Cr\{C(OEt)C_8H_5S\}(CO)_5$, (15)

The ^{1}H NMR data for σ,π-benzothienyl- and σ-benzothienyl monocarbene complexes, **14** and **15** are summarized in Table 3.3. Figure 3.19 represents the ^{1}H NMR spectrum of complex **14**. The proton chemical shifts for free benzothiophene are H2 7.40 ppm, H3 7.18 ppm, H4, H7 7.67 - 7.92 ppm and H5, H6 7.30 ppm,[74] the numbering system for the protons and carbon atoms is shown in Figure 3.8.

Table 3.3 ^{1}H NMR Data of the Benzothienyl Monocarbene Complexes

Assignment	Complexes					
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)					
	14			15		
Proton	δ	$^3J_{H\text{-}H}$	$^4J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	$^4J_{H\text{-}H}$
H3	8.14 (s)			8.47 (s)		
H4	6.07 (d)	6.7		7.78 (d)	7.8	
H5	5.62 (dt)	6.7	1.0	7.39 (dt)	6.9	1.2
H6	5.24 (dt)	6.7	1.0	7.47 (dt)	7.1	1.3
H7	6.29 (d)	6.8		7.97 (d)	8.0	
OCH_2CH_3 (**CH_2**)	5.20 (q)	7.0		5.24 (q)	7.1	
OCH_2CH_3 (**CH_3**)	1.68 (t)	7.0		1.71 (t)	7.1	

Owing to the magnetic anisotropy or electronic effects of the sulphur atom H7 is shifted downfield compared to H4, with H5 and H6 displaying similar upfield resonances in π-bonded benzo[b]thiophene.[75] On comparing the data of **14** with **15** it is once again evident that the chemical shifts for protons on rings which contain a π-bonded $Cr(CO)_3$-fragment are at significantly lower ppm values (more upfield) than the corresponding protons in the spectrum of a complex from which the π-moiety is removed. The chemical shift of H3 in the spectra of both **14** and **15** is at a higher δ-value (further downfield) compared to that in the spectrum of free benzothiophene, due to deshielding by the σ-coordinated carbene unit. As expected the chemical shift of H3 in the spectrum of uncoordinated thiophene is at a lower ppm value compared to that in the spectrum of **14**, however it appears further downfield in the spectrum of **15**. This shows that the aromaticity of the benzothiophene is severely disrupted by the π-coordination of the benzene ring which affects the thiophene ring and is reflected in the chemical shifts of H3 as seen in the

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upfield shift in the spectrum of **14** compared to the chemical shift in the spectrum of **15**.

A feature in the ^{1}H NMR spectra of **14** and **15** is the two independent signals observed for the resonances of the benzene protons H5 and H6, in the spectra of **14** and **15**. The splitting pattern of each signal is a doublet of triplets for both H5 and H6.

An interesting observation made in the spectrum of **14** is the one single resonance, a quartet, observed for the methylene protons of the carbene moiety compared to the two sets of signals of different intensities observed for these protons in the spectra of **8** and **12**. The same steric factors discussed for **8** and **12** are thus not present in **14** as no non-equivalence is found in the chemical shifts of either the methylene or methyl protons of the ethoxy group. As expected these factors are also not present in **15** as is evident from the chemical shifts of these protons and as was the case for **10** and **11**. The π-coordination of benzothiophene to the $Cr(CO)_3$-fragment sufficiently seperates the carbene metal fragment from the π-coordinated fragment to alow free rotation around the C(thienyl)-C(carbene) bond.

The chemical shifts of the ethoxy protons of the carbene with the benzothienyl substituent in **15** are shifted downfield compared to those recorded for the thienyl carbene complex, **A**, indicating poorer donation by the benzothienyl substituent compared to the thienyl substituent. It appears as if the phenyl ring withholds electron density from the thienyl ring causing H3 to be less shielded in **15** than in **A** eventhough less charge is donated to the carbene in **15** than in **A**.

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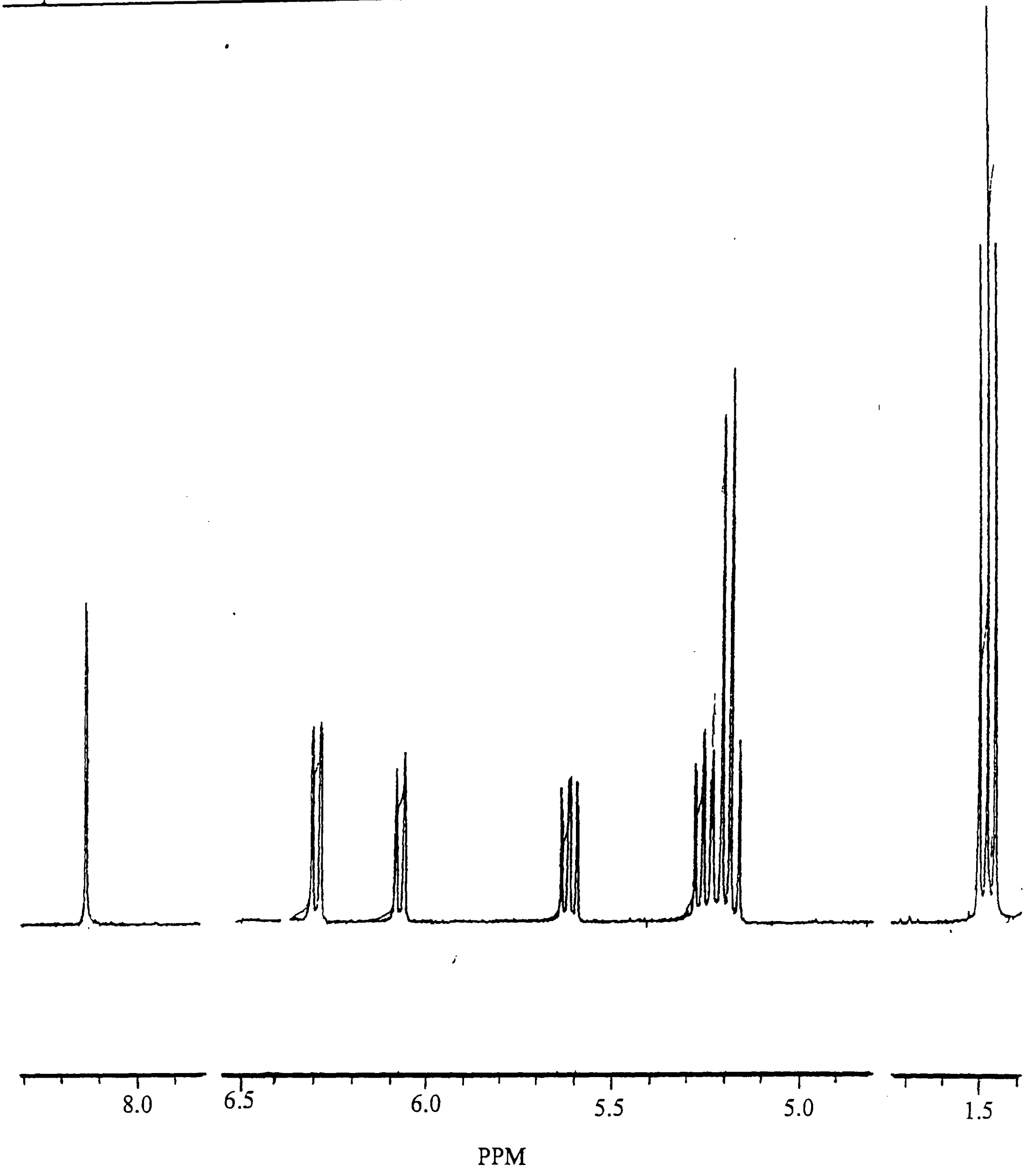

Figure 3.19 ^{1}H NMR Spectrum of $(\eta^1{:}\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$

3.6.2 ^{13}C NMR Spectroscopy

^{13}C NMR data for complexes **8**, **9**, **12**, **13**, **14** and **15** are summarized in Tables 3.4 and 3.5. Significant spectra could not be obtained for **10** and **11**, due to insufficient material.

(a) ^{13}C NMR Data of (η^1:η^5-$C_4H_3SC(OEt)M(CO)_5)Cr(CO)_3$, M= Cr, (8) and M = W (9), and (η^1:η^5-$C_4H_3SC\{O(CH_2)_4OEt\}M(CO)_5)Cr(CO)_3$, M = Cr, (12) and M = W, (13)

The ^{13}C NMR data of complexes **8**, 9, **12** and **13** are summarized in Table 3.4

Table 3.4 ^{13}C NMR Data of the Bimetallic σ,π-Thienyl Monocarbene Complexes

Assignment	**Complexes**			
	Chemical Shifts, (δ, ppm)			
Carbon Atom	**8**	**9**	**12**	**13**
C (carbene)	312.3 268.8	311.2 285.7	312.8 303.5	312.0 n.o
$Cr(CO)_3$	232.6	232.6	232.4	232.5
$M(CO)_5$, (*trans*)	222.2	201.6	222.1	201.7
$M(CO)_5$, (*cis)*	215.8	196.4	216.9	196.6
C2 (*ipso*)	108.8	111.8	123.5	113
C3	93.5	93.1	93	92.8
C4	88.1	88.4	83.3	88.1
C5	96.8	97.8	96.5	97.4
O**CH₂**CH₂CH₂			83.2	82.1
OCH₂**CH₂**CH₂			29.4	26.2
CH₂**CH₂**CH₂O			29.4	26.2
CH₂CH₂**CH₂**O			69.9	69.6
O**CH₂**CH₃	76.6	78.2	66.3	66.2
OCH₂**CH₃**	15.1	14.9	15.4	15.1

The $Cr(CO)_3$, $Cr(CO)_5$ and $W(CO)_5$ chemical shifts are insensitive to changes in substituents in the complexes and are practically the same in all the spectra. These characteristic values were very helpful in:

(i) comparing bimetallic complexes; (ii) discriminating between possible structures for **12** and **13** by

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excluding $M(CO)_4$ fragments and indicating π-coordination to the thienyl ring. Therefore, although not very informative on electronic properties in those complexes, nevertheless very helpful in supporting infrared observations.

The most striking feature of the carbene chemical shifts for the complexes are the fact that two resonances are observed for **8**, **9** and **12**. The second signal was not found for **13**. This is consistent with the ^1H NMR data, indicating restricted rotation around the C(thienyl)-C(carbene) bond resulting in two isomers being present in solution, with the $M(CO)_5$ fragment on the same side as the sulphur atom in one of these and on the opposite side in the other.

If the $-CH_2CH_3$ group is replaced by the $-(CH_2)_4OCH_2CH_3$ group the chemical shift for methylene carbon is observed further downfield when in $-O(CH_2)_4OCH_2CH_3$ from the chemical shift of CH_2 in OCH_2CH_3. The chemical shift of the methyl carbon atom on the other hand is not much affected.

As is the case for the ^1H NMR chemical shifts, the ^{13}C NMR chemical shifts of the thienyl carbons are more upfield for thiophene containing a π-coordinated $Cr(CO)_3$-fragment by *ca* 40 ppm compared to the monocarbene thienyl complexes **A** and **B**, Chapter 2.

(b) ^{13}C NMR Data of $(\eta^1:\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$, (14) and $Cr\{C(OEt)C_8H_5S\}(CO)_5$, (15)

^{13}C NMR data for the bimetallic σ,π benzo[b]thiophene monocarbene complex **14** and the mononuclear benzo[b]thiophene carbene complex **15** are summarized in Table 3.5. The ^{13}C chemical shifts for uncoordinated benzothiophene are C2 126.4 ppm, C3 124.0 ppm, C4 123.8 ppm, C5 124.3 ppm, C6 124.4 ppm, C7 122.6 ppm, C8 139.9 ppm and C9' 139.8 ppm[75]. When coordinated in the σ,π benzo[b]thiophene monocarbene complex, **14**, the chemical shifts are as expected found to be downfield, compared those in the spectrum of the uncoordinated benzothiophene, owing to the presence of the metal carbene moiety.

The most striking feature in the spectrum of **14** when compared with **15** is that the chemical shifts of the thiophene are at lower field values, whereas the chemical shifts of the benzene carbons are more upfield. A possible explanation for upfield resonances for C2 and C3 in **14** compared to **15** is that in **14** two opposing electron withdrawing functions operate with the thiophene unit caught in between. This may result in less polarization and relatively more shielding in **14** compared to the stronger electron withdraw-

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ing properties and polarized effect of the carbene unit only, in **15**. The second phenomenon is well known for π-coordination and has been stated before. By contrast the chemical shifts for the carbene carbons in **14** and **15** give practically the same δ-value.

Whereas the carbene carbon atom in **8** and **12** is bonded to a carbon atom which forms part of the π-system to which the $Cr(CO)_3$ fragment is coordinated, this is not the case for **14**, which displays a slightly downfield carbene resonance. The π-system to which the $Cr(CO)_3$ fragment is coordinated in **14** is that of the benzene ring which is more distant from the carbene carbon. The obsevation of one chemical shift only, for the carbene carbon atom in the spectra of **14** and **15** is consistent with the observation made in the ^1H NMR spectra. This confirms the earlier findings made from the ^1H NMR spectra that there is no restricted rotation around the C(thienyl)-C(carbene) bond present in either complex **14** or **15**.

Table 3.5 ^{13}C NMR data of the Benzothienyl Monocarbene Complexes

Assignment	**Complexes**	
	Chemical Shifts, (δ, ppm)	
Carbon Atom	**14**	**15**
C (carbene)	318.1	320.1
$Cr(CO)_3$	231.4	—
$M(CO)_5$, (*trans*)	223.3	222.0
$M(CO)_5$, (*cis*)	216.5	216.9
C2 (*ipso*)	167.0	176.0
C3	138.0	155.1
C4	92.3	126.7
C5	84.3	122.8
C6	88.9	123.5
C7	89.8	125.0
C8	124.0	139.0
C9	106.0	128.9
$O\mathbf{CH_2}CH_3$	76.6	76.6
$OCH_2\mathbf{CH_3}$	15.1	15.1

The chemical shifts for the methylene- and methyl carbon atoms of the ethoxy group of the carbene unit appear at 76.6 ppm and 15.1 ppm in the spectra of both of the carbene complexes **14** and **15**. These δ-values are similar to those observed in the spectrum of **8**, however the chemical shift for the CH_2 group is as expected upfield from that observed in the spectrum of **12**, as it forms part of the $O(CH_2)_4OCH_2CH_3$ group in **12**, the same observation was made when the spectrum of **9** was compared to that of **13**.

3.6.3 Infrared Spectroscopy

The infrared data for **8** - **15** are summarized in Tables 3.6, 3.8 and 3.9. As far as possible the spectra were recorded in hexane and dichloromethane.

(a) Infrared Data of $(\eta^1:\eta^5\text{-}C_4H_3SC(OEt)M(CO)_5)Cr(CO)_3$, M= Cr, (8) and M = W (9)

The infrared data of **8** and **9** are summarized in Table 3.6. From the spectra of complexes **8** and **9** it is apparent that both of these complexes contain a $M(CO)_5$-, as well as a $M(CO)_3$-fragment. The spectrum of **9**, shown in Figure 3.20, is typical for all of the compounds which contain a $M(CO)_5$, as well as, a $M(CO)_3$ fragment. Fortunately the bands are resolved well and do not overlap as is often the case for bimetallic carbonyl species.

In this spectrum there can quite easily be distinguished between the $Cr(CO)_3$ and $M(CO)_5$ fragments and the respective A_1 and E, as well as, the $A_1^{(1)}$, B_1, E and $A_1^{(2)}$ bands can be identified with relative ease. An interesting observation is that the degeneracy of the E band (A', A") of the $Cr(CO)_3$ fragment is lifted and it appears as two separate bands in the spectrum. The presence of the heteroatom in the ring and the carbene substituent on the 2-position influences the backbonding to the carbonyls to such an extent that it leads to the splitting of the E band. In comparison to this the pattern for $Cr(CO)_3(\eta^6\text{-}C_6H_6)$ and $Cr(CO)_3(\eta^5\text{-}C_4H_4S)$ is that of the typical A_1 band and E band of higher intensity and at lower wavenumber.[76]

Two problems which are experienced during the recording of spectra are, firstly the low solubility of these compounds in hexane and secondly the shifting of the bands to lower wavenumbers and the overlapping of bands when spectra are recorded in dichloromethane. It is then impossible to unambiguously allocate a specific wavenumber to a specific band.

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Table 3.6 Infrared Data of the Bimetallic σ,π-Thienyl Monocarbene Complexes

Assignment	Complexes	
	Stretching Vibrational Frequency, (νCO, cm^{-1})	
	8	**9**
$Cr(CO)_3$		
A_1	1990	1989 1981
E (A', A")	1935, 1920	1947[a] 1895 (sh)
$M(CO)_5$		
$A_1^{(1)}$	2062	2069 2069
B_1	1978	— —
E	1952	1947 1941
$A_1^{(2)}$	1963	1952 1941

For 9 the first set of values was recorded in hexane and the second in dichloromethane

[a] Obscured by E-band of $M(CO)_5$

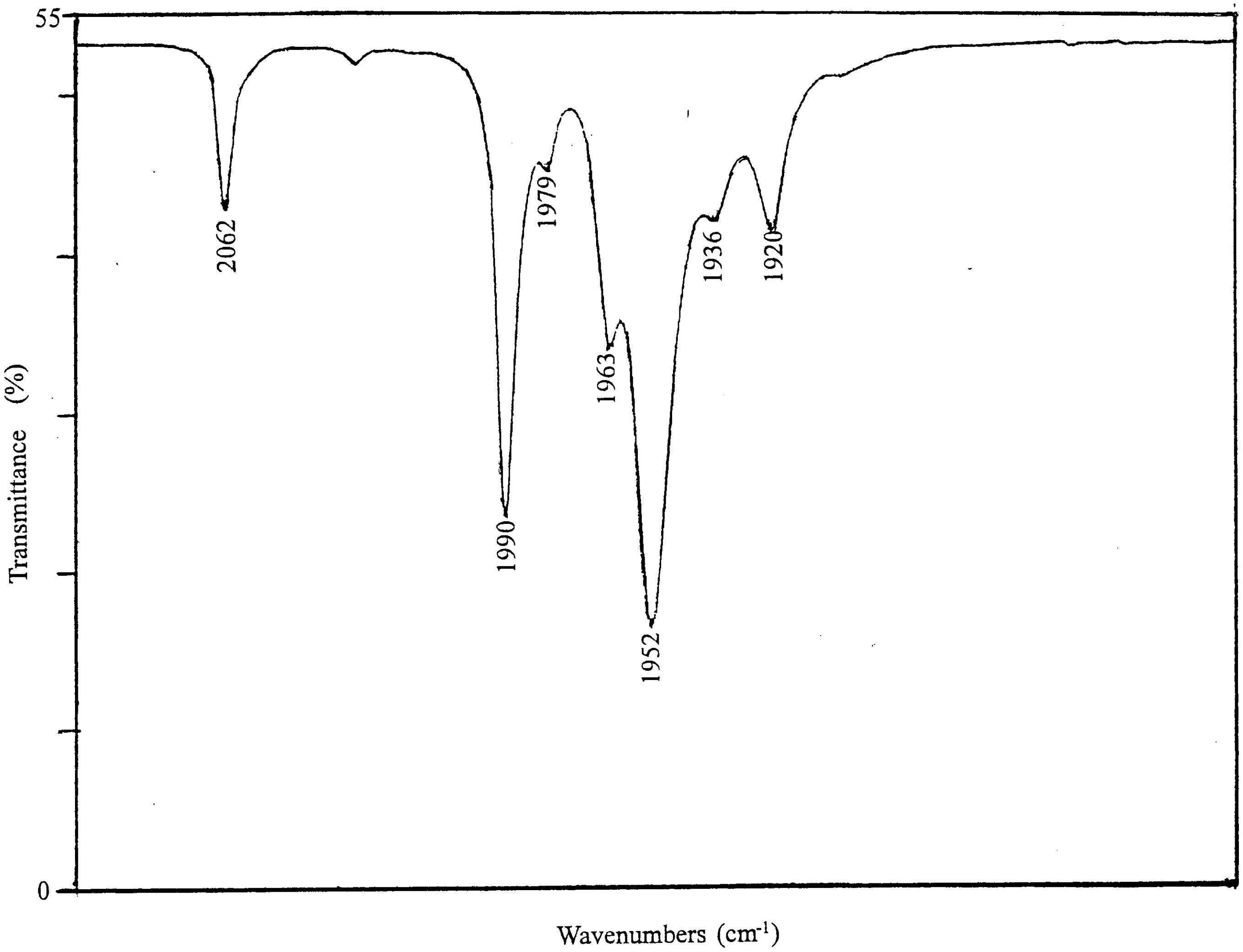

Figure 3.20 Infrared Spectrum of the Carbonyl Region of (η^1:η^5-$C_4H_3SC(OEt)Cr(CO)_5)Cr(CO)_3$

The infrared data of complexes **8** and **9** are compared in Table 3.7 to that of the complexes (η^1:η^6-$C_6H_5)C(OEt)M(CO)_5)Cr(CO)_3$, where M = Cr or W. The spectra were recorded in hexane as solvent.[52]

Table 3.7 Infrared Data of the Complexes $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)M(CO)_5)Cr(CO)_3$ and $(\eta^1{:}\eta^6\text{-}C_6H_5C(OEt)M(CO)_5)Cr(CO)_3$, where M = Cr or W

Assignment	**Complexes**			
	8	**9**	**Benzene Complex**	
	M = Cr	**M = W**	**M = Cr**	**M = W**
$Cr(CO)_3$	Stretching Vibrational Frequency, (νCO, cm^{-1})			
A_1	1990	1989	1982	1978
E (A', A")	1936, 1920	1947	1924	1918
$M(CO)_5$				
$A_1^{(1)}$	2062	2069	2060	2058
B_1	1978	—	—	—
E	1952	1947	1945	1934
$A_1^{(2)}$	1963	1952	1951	1942

The wavenumbers for the bands of the $M(CO)_5$-fragment in the spectra of **8** and **9** are higher than those in the spectra of the corresponding benzene complexes which on the assumption that the ethoxy substituent exhibits a constant contribution in both cases, is an indication of less electron density being placed on the carbene carbon atom by the thienyl fragment. The positions of the bands of the $Cr(CO)_3$-fragments indicate that less electron density is also donated by the thienyl ring compared to the benzene ring.

(b) Infrared Data of $M\{C(O(CH_2)_4OEtC_4H_3S)\}(CO)_5$, M = Cr, (10), M = W, (11) and $(\eta^1{:}\eta^5\text{-}C_4H_3SC\{O(CH_2)_4OEt\}M(CO)_5)Cr(CO)_3$, M = Cr, (12) and M = W, (13)

The infrared data for complexes **10** - **13** are summarized in Table 3.8.

Once again an interesting feature is the lifting of the degeneracy of the E band into A', A" of the $Cr(CO)_3$-fragment in the spectra of **12** and **13**. Even in the absence of the carbene substituent, a very bulky group, the nature of the thiophene ring causes this effect. The influence of the π-coordinated $Cr(CO)_3$-fragment on the wavenumbers of the bands in the spectra is clearly demonstrated by the wavenumbers for espe-

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cially the $A_1^{(1)}$ bands of the $M(CO)_5$ fragment which are lower in the spectra of **12** and **13**, which contain the π-coordinated $Cr(CO)_3$-fragment, than in the spectra of **10** and **11**, from which the π-coordinated fragment is absent.

Table 3.8 Infrared Data of the Bimetallic σ,π-Thienyl- and σ-Thienyl Monocarbene Complexes

Assignment	**Complexes**			
	Stretching Vibrational Frequencies (νCO, cm^{-1})			
	12	**13**	**10**	**11**
$M(CO)_3$				
A_1	1989 —	1984 1935		
E (A', A")	1947, 1919	1915, 1895		
	1945, 1901 (sh)	—		
$M(CO)_5$				
$A_1^{(1)}$	2062 2061	2080 2069	2069 2059	2082
B_1	— —	— 1980	1988 1972	—
E	1951 1945	1953 1941	1948 1940	1942
$A_1^{(2)}$	1964 (sh) 1945	1942 1941	1978 1940	1984

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

(c) Infrared Data of $(\eta^1{:}\eta^6\text{-}C_8H_5SC(OEt)Cr(CO)_5)Cr(CO)_3$, (14) and $Cr\{C(OEt)C_8H_5S\}(CO)_5$, (15)

The infrared data of complexes **14** and **15** are summarized in Table 3.9. Of all the infrared data, the spectra of complexes **14** and **15** illustrate the effect of π-coordination, (to an aromatic ring system), on the carbonyl stretching frequencies of an $M(CO)_5$-fragment the most clearly.

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Table 3.9 Infrared Data of the Benzothienyl Monocarbene Complexes

Assignment	**Complexes**	
	Stretching Vibrational Frequency, (νCO, cm^{-1})	
	14	**15**
$Cr(CO)_3$		
A_1	1980	
E	1893	
$Cr(CO)_5$		
$A_1^{(1)}$	2060	2069
B_1	n.o.	2009
E	1980	1987
$A_1^{(2)}$	1980 (sh)	1987 (sh)

Solvent: hexane

Table 3.9 indicates that the wavenumbers for the $Cr(CO)_5$ bands in the spectrum of complex **14** which contains the π-coordinated $Cr(CO)_3$-fragment are lower than in the spectrum of complex **15** from which this π-coordinated fragment is absent.

In brief it can thus be stated that the π-coordination of the $Cr(CO)_3$-fragment to the aromatic ring leads to the stretching vibrational frequencies of the $M(CO)_5$-fragment of the carbene unit being shifted to lower wavenumbers. This phenomenon is evident when the spectra of π-coordinated thiophene and benzothiophene carbene complexes are compared to the spectra of the corresponding carbene complexes from which the π-coordinated $Cr(CO)_3$-fragment is absent.

3.6.4 Mass Spectroscopy

A molecular ion peak was recorded for all of the carbene complexes **8** - **15**. Fragmentation patterns were evident for related molecules, these patterns are shown in Schemes 3.10 - 3.13. The relevant fragment ions and corresponding peaks for complexes **8** - **15** are summarized in Table 3.10.

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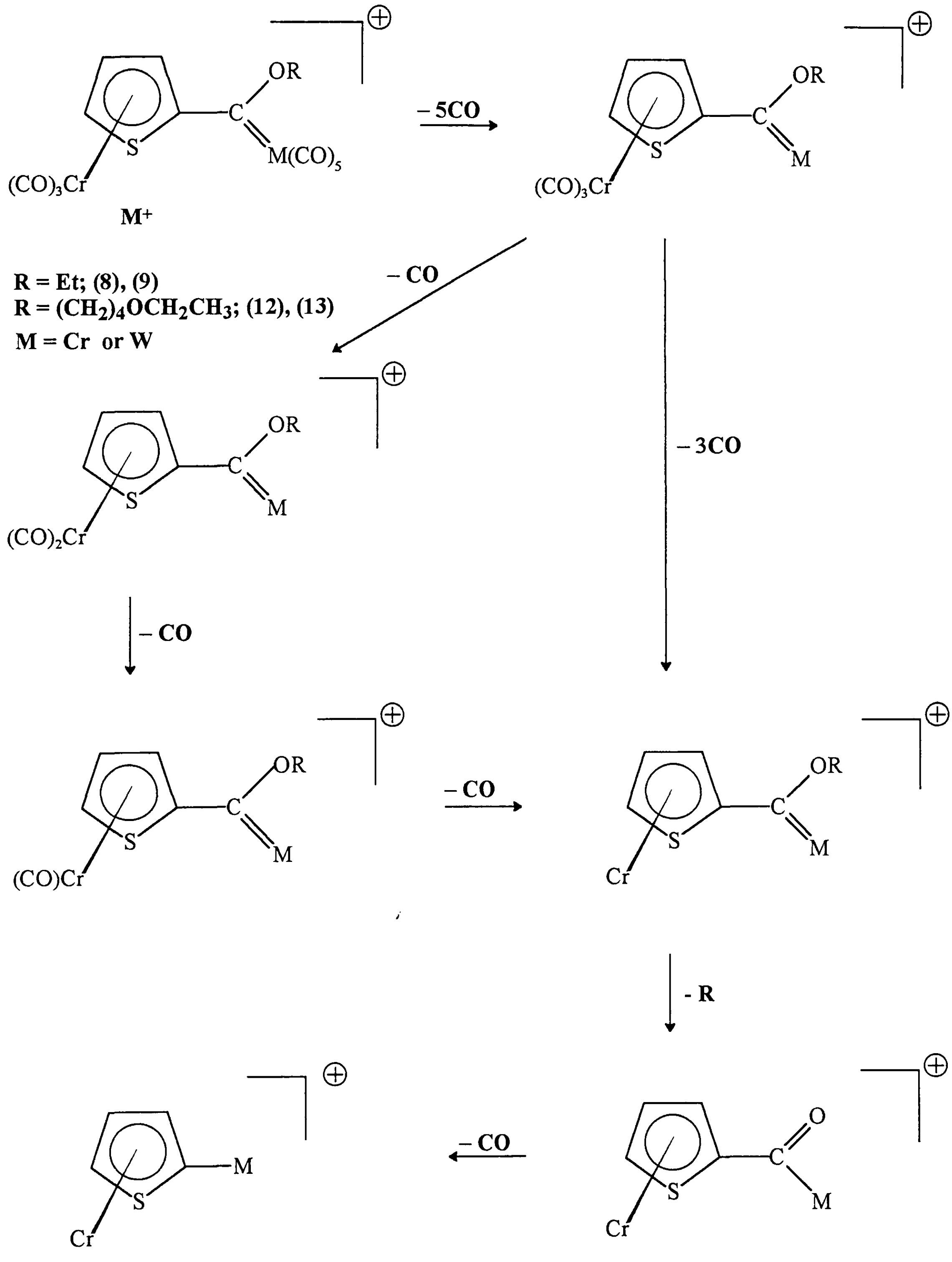

R = Et; (8), (9)
R = $(CH_2)_4OCH_2CH_3$; (12), (13)
M = Cr or W

Scheme 3.10

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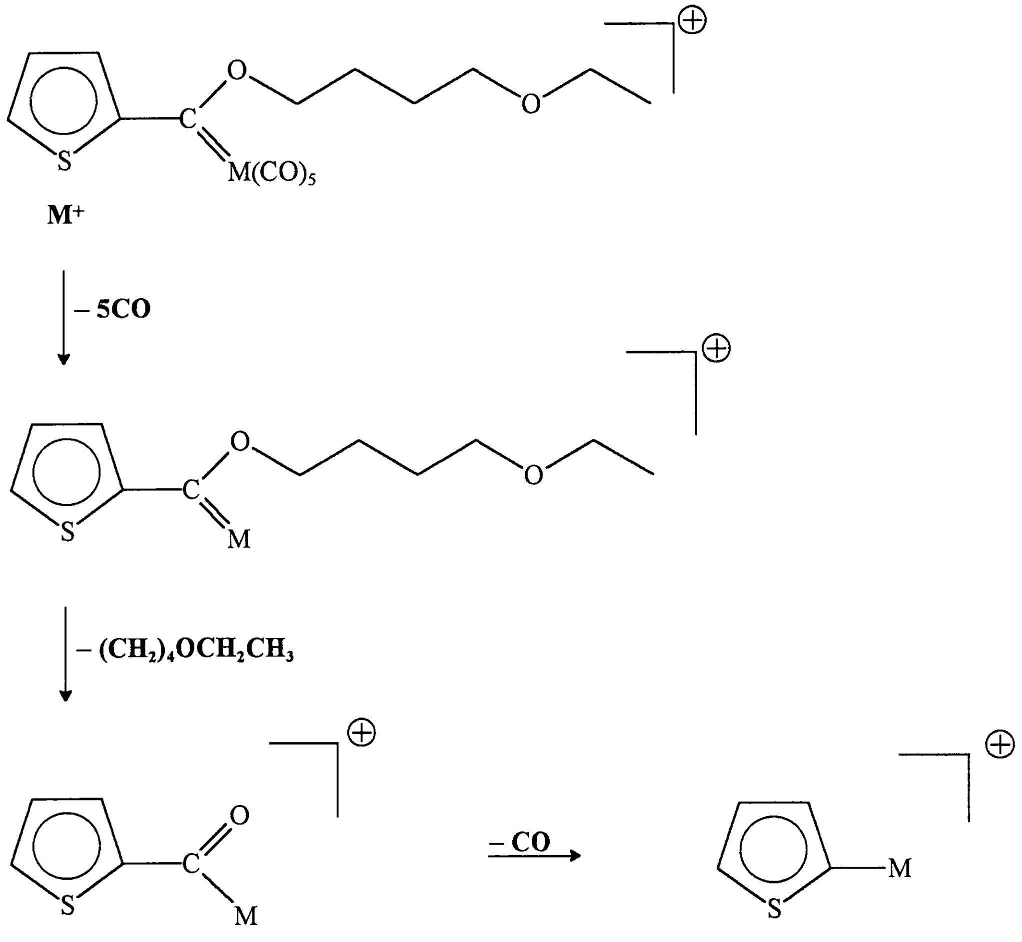
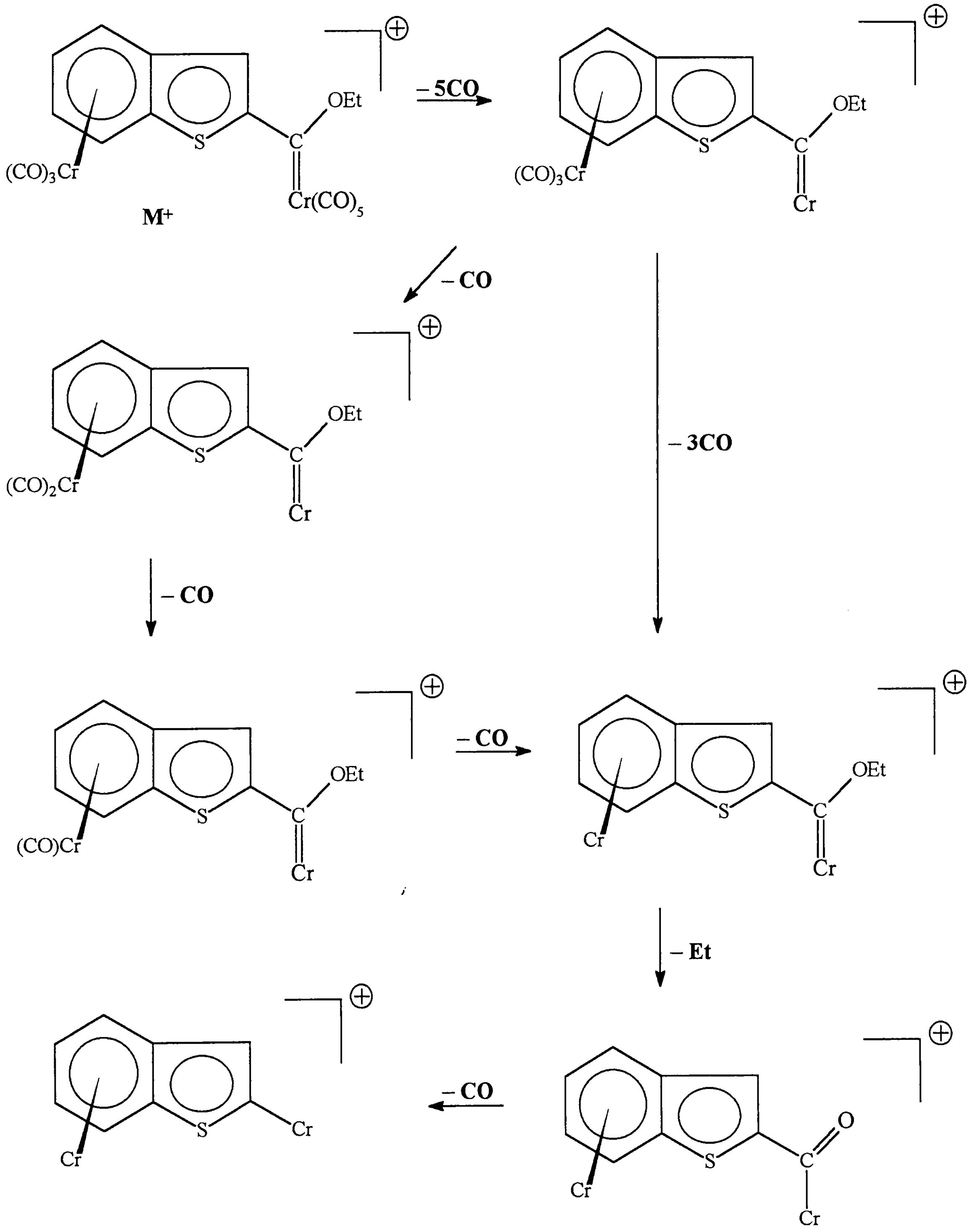
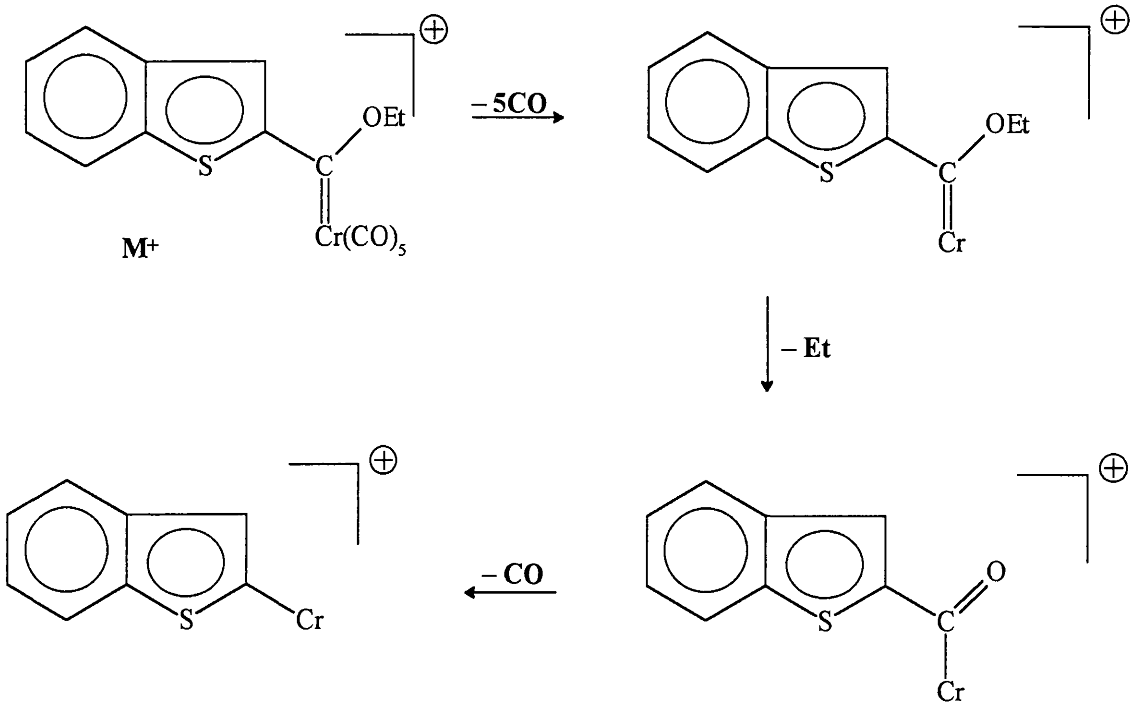


M = Cr (10)
or W (11)

Scheme 3.11


(CO)$_3$Cr
M$^+$
OEt
C
S
Cr(CO)$_5$
– 5CO
(CO)$_3$Cr
OEt
C
Cr
– CO
(CO)$_2$Cr
OEt
C
Cr
– 3CO
– CO
(CO)Cr
OEt
C
Cr
– CO
Cr
OEt
C
Cr
– Et
Cr
O
C
Cr
– CO
Cr
Cr

Scheme 3.12



Scheme 3.13

These fragmentation patterns, as well as, the fragment ions obtained afforded valuable information in elucidating the structures of the various compounds.

3.6.5 X-Ray Crystallography

Final confirmation of the structure of $(\eta^1\text{:}\eta^5\text{-}C_4H_3SC(OEt)W(CO)_5)Cr(CO)_3$, was obtained from a single crystal X-ray diffraction study. The crystallographic data for the complex are given in Table 1 of Appendix 3, whereas the atomic coordinates are listed in Table 2 of Appendix 3. Figure 3.21 shows down views along the b- and c-axes. The results of the X-ray crystallographic study are illustrated by an ORTEP plot in Figures 3.22, which shows the structure with the atom numbering. Important to note is that the numbering system for the thiophene ring has been adapted to facilitate the comparison of bond lengths and bond angles with those given for complex 9, (which is normally numbered C(2) is now C(1) etc.). Selected bond lengths and bond angles are listed in Table 3.11, with all the bond lengths and bond angles in Tables 3 and 4 of Appendix 3. The anisotropic displacement parameters, as well as the H-atom coordinates and isotropic displacement parameters are listed in Tables 5 and 6 respectively of Appendix 3.

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Complex 9 was isolated from a dichloromethane hexane solution and crystallized in the triclinic space group $P\bar{1}$, with a = 6.938(2), b = 10.855(4), c = 12.847(3)Å, Z = 2 with the two molecules in the asymmetric unit essentially different.

Table 3.11 Selected Bond Lengths (Å) and Bond Angles (°) for 9

Bond Lengths	9
W-C(Carbene)	2.173(9)
Cr-S	2.360(3)
Cr-C(1)	2.176(10)
Cr-C(2)	2.205(10)
Cr-C(3)	2.183(9)
Cr-C(4)	2.152(9)
C(1)-C(2)	1.420(15)
C(2)-C(3)	1.416(13)
C(3)-C(4)	1.404(13)
S-C(1)	1.726(11)
S-C(4)	1.780(9)
C(4)-C(5)	1.499(13)
Bond Angles	
C(1)-S-C(4)	90.6(5)
S-C(4)-C(3)	111.8(7)
S(1)-C(4)-C(5)	117.3(7)
C(1)-C(2)-C(3)	112.7(9)
C(2)-C(3)-C(4)	112.1(8)
W-C(5)-C(4)	124.6(6)
Cr-C(4)-S	73.1(3)
Cr-S-C(1)	62.1(4)
Cr-C(1)-C(2)	72.2(6)
Cr-C(2)-C(1)	70.0(6)
Cr-C(3)-C(4)	69.9(5)

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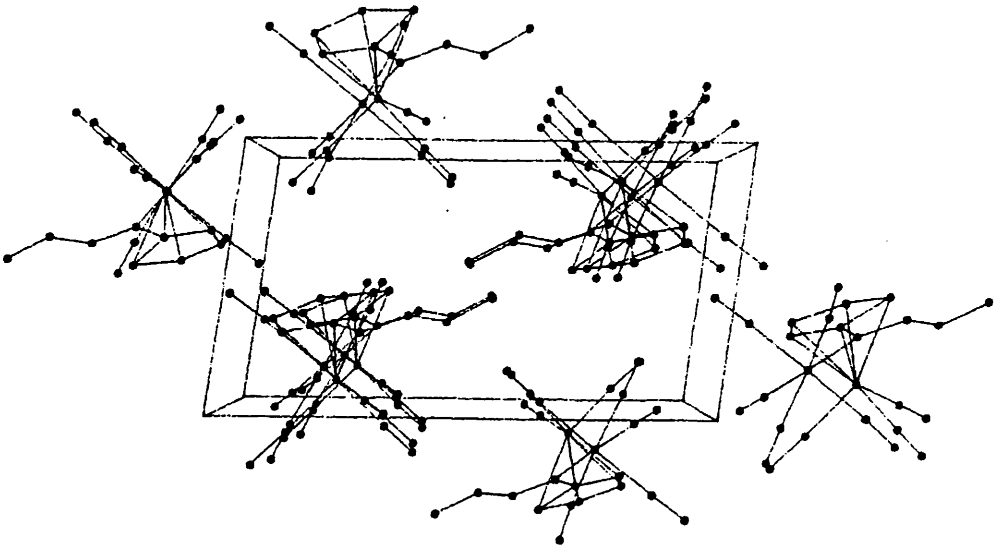
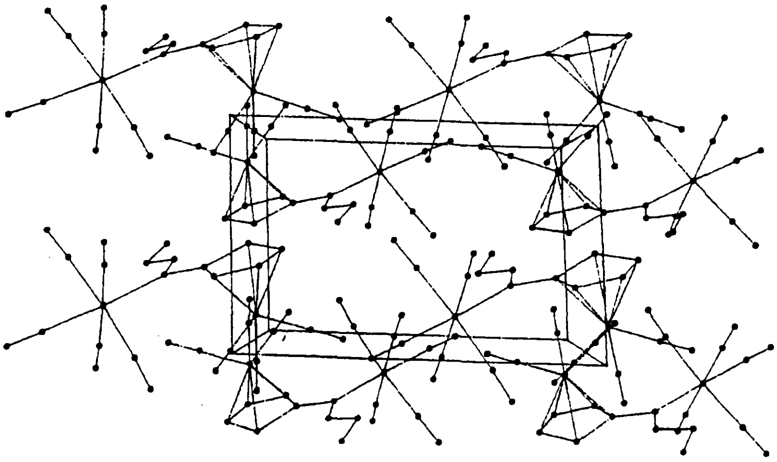


(i)



(ii)

Figure 3.21 Packing in the Molecule as seen along the (i) b-Axis and (ii) c-Axis

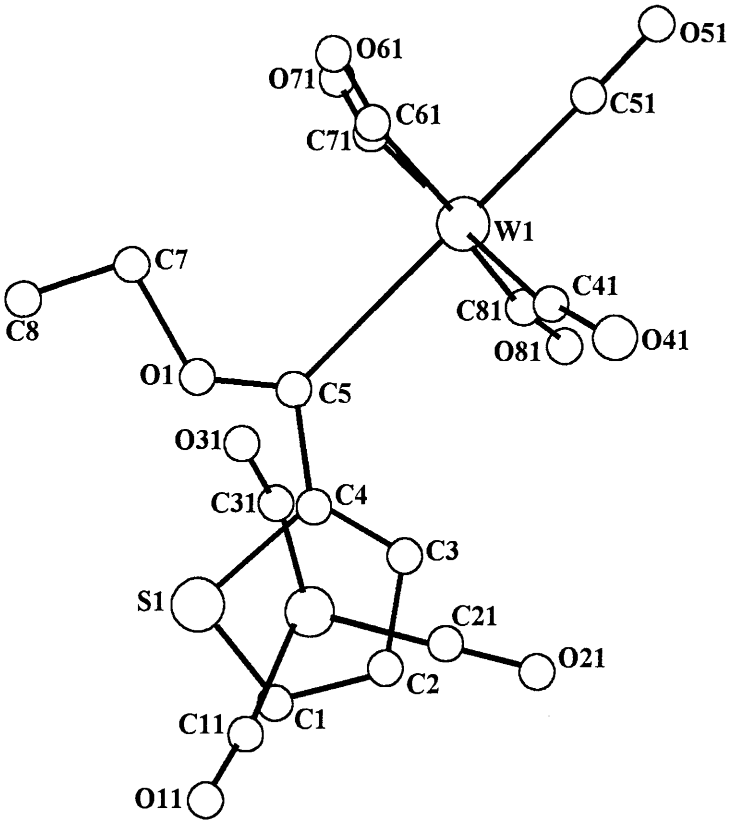


Figure 3.22 ORTEP plot of $(\eta^1\text{:}\eta^5\text{-}C_4H_3SC(OEt)W(CO)_5)Cr(CO)_3$ with Atom Numbering

The bond lengths and bond angles of free thiophene were determined as S-C(1) 1.714(1) Å, C(1)-C(2) 1.370(2) Å, C(2)-C(3) 1.424(2) Å, C(3)-C(4) 1.370(2) Å, C(4)-S 1.714 Å. The bond angles were determined as C(1)-S-C(4) 92.2(1) °, C(1)-C(2)-C(3) 111.5(3)° and C(2)-C(3)-C(4) 112.5(3)°.[30] The thiophene ring coordinated to chromium is planar and the ring carbons are at equal distances from the chromium with the *ipso*-carbon closest and the C2 the furthest away from the chromium. The three C-C distances in the ring are the same indicating delocalization of electron density in the ring. By contrast, free thiophene displays localized double (C2-C3, C4-C5) and single (C3-C4) bonds. Delocalization is also evident in the bonds around the carbene carbon atom, Figure 3.23.

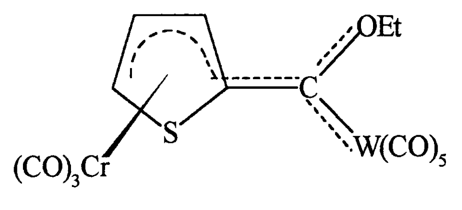


Figure 3.23 Delocalization in Bonds of the Thienyl Ligand

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The thienyl ring is coplanar with the plane through the tungsten, oxygen of the ethoxy and thienyl *ipso*-carbon. The angles C4-C5-O1, W1-C5-C4 and W1-C5-O1 of 102.2, 124.6 and 131.6 respectively are typical for Fischer carbene complexes[77] and the same as the corresponding angles in **2**, Figure 3.24.

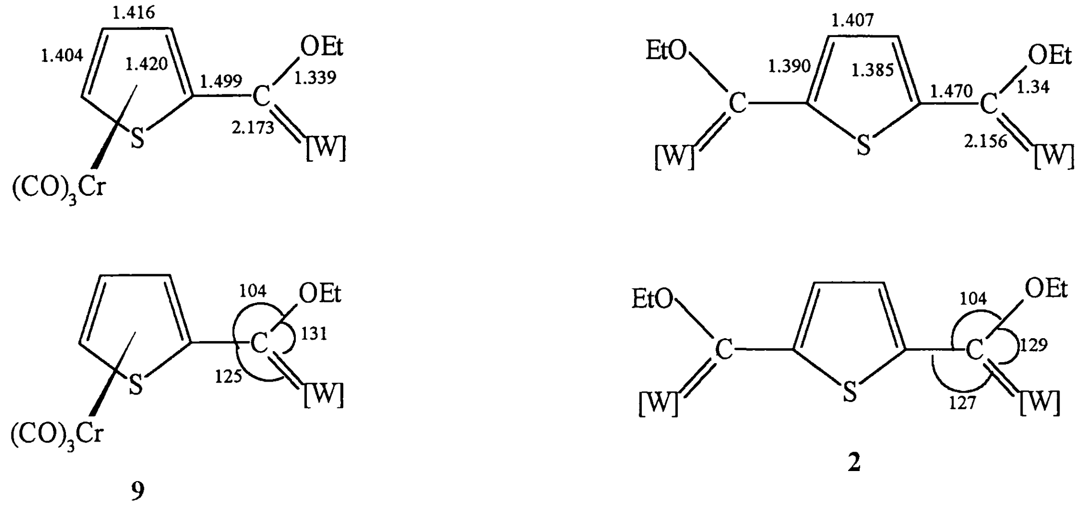

Figure 3.24 Comparison of Carbene Units in 2 and 9

The bridging unit in **9** displays bond distances which are all slightly longer than the corresponding distances in **2**. π-Coordination of the thienyl ring in **9** causes the ring distances to lengthen (1.413(6) Å) in **9** compared to 1.34(10) Å in **2**. The close proximity of the bulky metal moieties could be held responsible for the longer C(thienyl)-C(carbene) and W-C(carbene) distances in the small compact **9** to the open structure of **2**. The only comparable distance is the C(carbene)-O(oxygen) distance of 1.311(11) Å for **2**. In the crystal structure the thiophene sulphur atom is on the same side as the carbene ethoxy substituent and *trans* to one of the three carbonyl groups of the $Cr(CO)_3$ tripod.

The W-C(carbene) distance of 2.173(9) Å is significantly shorter in **9** compared to the corresponding distance of 2.23(2) Å in $CpRu(\eta^5\text{-}C_5H_4C(OEt)W(CO)_5$.[54] Also the C(carbene)-C(ring) distance of 1.499(13) Å in **9** is longer than the same distance of 1.43(3) Å in $CpRu(\eta^5\text{-}C_5H_4C(OEt)W(CO)_5$, which is an indication that the Cp-ring in the ruthanocene complex donates more electron density to the carbene than the thienyl in **9**. Eventhough the W-C(carbonyl) of the carbonyl *trans* to the carbene ligand (2.005(13) Å) is not the shortest of the five $W(CO)_5$ carbonyls it is shorter than the average distance of 2.041(15) Å for the four *cis* carbonyls.

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3.7 Summary

Interesting to note is that the spectroscopic data designate the carbene substituent in all the compounds, **8 - 15**, to be an electron withdrawing group in spite of competition exerted by the ring substituent with the π-coordinated $Cr(CO)_3$-fragment. This behaviour is in agreement with that observed for benzene and cyclopentadienyl to which a $Cr(CO)_3$ -fragment has been π-coordinated.

The π-coordination of the $Cr(CO)_3$-fragment to the thiophene ring plays an important roll in localizing the electron density of the double bonds, as well as, that of the sulphur and leads to the formation of the carbene complexes **12** and **13**, thus leading to unique reaction pathways, in which a THF ring is opened and incorporated into the carbene moiety. The NMR data, (^1H- and ^{13}C NMR) indicate that the presence of the π-coordinated $Cr(CO)_3$ -fragment in a complex leads to upfield chemical shifts of the ring protons in complexes **8**, **9**, **12**, **13** and **14**. The π-coordination of this fragment leads to the methylene protons of the ethoxy group of the carbene unit being subjected to non-equivalent orientations when coordinated to the thiophene ring in complexes **8**, **9**, **12** and **13**, whereas this is not the case when it is coordinated to the benzene ring of benzothiophene in complexes **14**. Steric factors for π-coordinated thienyl result in restricted rotation around the C(thienyl)-C(carbene) bond, which leads to the duplication of resonances associated with the methylene protons. The presence of two chemical shifts for the carbene carbon atom in the ^{13}C NMR spectra of σ,π-coordinated thiophene complexes is consistent with observations made in the ^1H NMR spectra. Consideration of the X-ray crystal structure shows that restricted rotation around the C(*ipso*)-C(carbene) bond is more than likely, considering the close proximity of the $Cr(CO)_3$-and $M(CO)_5$-fragments. Bond distances reveal some π-interaction in all three the bonds associated with the carbene carbon atom, but no single substituent dominates. Delocalization is disrupted evenly over all the bonds and the structure seems to represent the best picture of electron density over the entire complex with no or little localized effects.

3.8 References

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4 σ,σ-Biscarbene Decomposition Reactions

4.1 Introduction

For some time it was an open question whether carbene complexes might be regarded as sources of free carbenes. Several methods have been developed to cleave the carbene metal bond, however, none of these have been shown to involve free carbenes.[1] These methods include:

(a) ligands substitution
(b) thermal decomposition
(c) base-induced decomposition
(d) reductive cleavage
(e) oxidative cleavage
(f) cleavage by hydrogen halides

Although no systematic study has yet been reported on the thermal-, base-induced- or photochemical decomposition of carbenoid complexes, some observations have been recorded.

4.1.1 Thermal Decomposition

The influence of elevated temperatures on the stability of Fischer-type carbene complexes has been investigated and interesting results were obtained.

On heating, carbene complexes decompose to yield the parent carbonyls and alkenes, formed from the coupling of two carbene ligands, as the main products, as illustated by the reaction, in Scheme 4.1.[2, 3] The decomposition occurs more readily in the absence of stabilizing heteroatom carbene substituents.[4, 5, 6] In some cases the corresponding alkanes, instead of the olefins were obtained.[7, 8]

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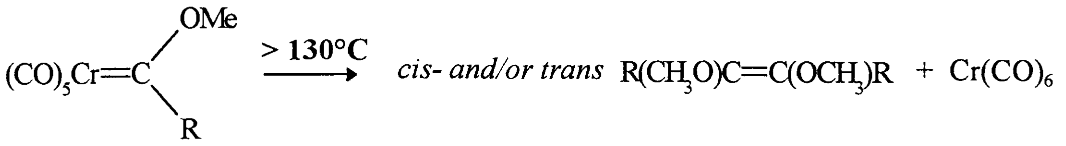
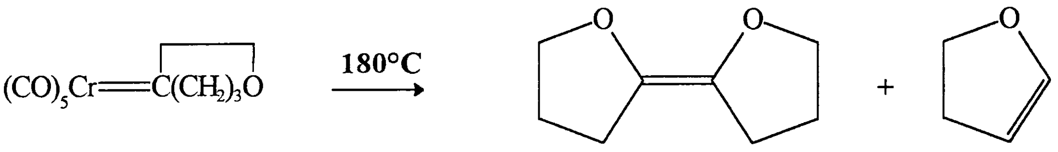


$$(CO)_5Cr{=}C(OMe)R \xrightarrow{> 130^\circ C} \textit{cis- and/or trans } R(CH_3O)C{=}C(OCH_3)R + Cr(CO)_6$$

Scheme 4.1

The thermolysis of pentacarbonyl(2-oxacyclopentylidene)chromium was studied to test for the intermediacy of free carbenes.[9] In addition to the dimeric main product, a small amount of dihydrofuran was obtained. The intervention of an uncoordinated carbene was ruled out by the absence of cyclobutanone, which is known to be formed in significant amounts on the pyrolysis of the sodium salt of butyrolactone tosylhydrazone. It was further found by a kinetic investigation of this decomposition that the reaction is second order in the carbene complex and is inhibited by carbon monoxide, Scheme 4.2. A mechanism was proposed involving a primary dissociation of a CO ligand, followed by the formation of a biscarbene complex to account for the formation of the olefin product.



Scheme 4.2

On the other hand a surprising observation was made, in that no dimerization of the carbene ligand occurs in the decomposition of an ethoxy(pentafluorophenyl)carbene complex of iron. Instead a novel metal facilitated alkyl migration to the carbene carbon led to the formation of an alkylarylketone.[10] Similarly the decomposition of a hydroxy(methyl)carbene complex of rhenium led to the formation of acetaldehyde along with the parent metal carbonyl.[11] Metal alkylation versus oxygen alkylation of acylate intermediates was studied by Semmelhack and Tamura[12] and where the latter afforded Fischer-carbenes the former, after reductive elimination gave among other products alkylaryl ketones.

4.1.2 Base-induced Decomposition

Pyridine and related basic nitrogen compounds have been found to induce the decomposition of alkoxy(alkyl)carbene and 2-oxacyclopentylidene complexes to give enol ethers.[2, 9, 13] Arylcarbene complexes are considerably more stable in the presence of pyridine. These complexes finally decompose to give

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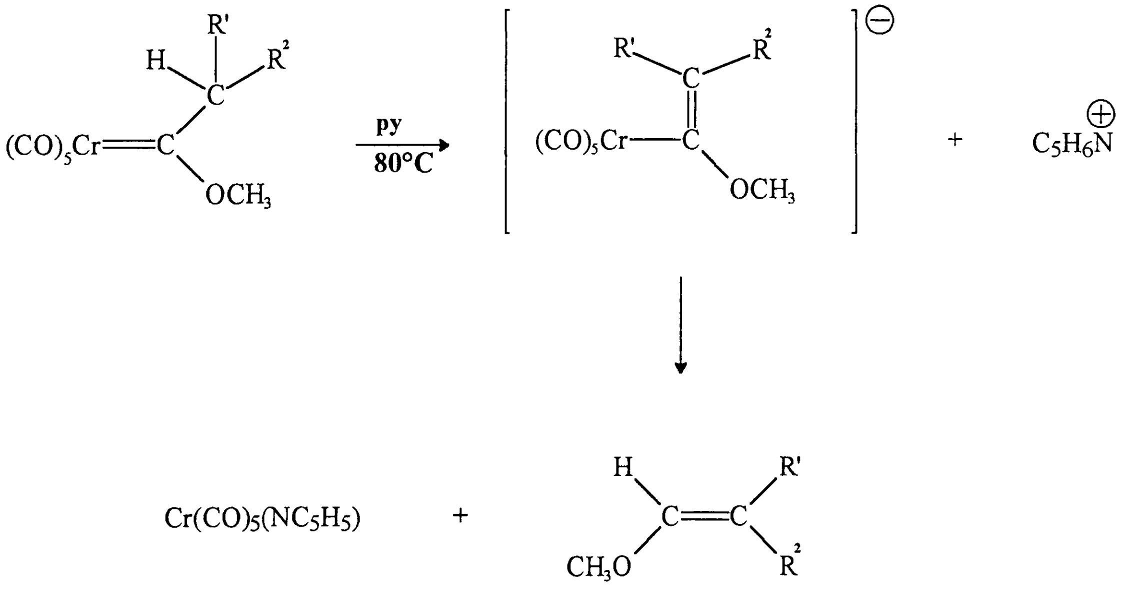
alkenes.[3] A reaction route involving carbene anions for this decomposition has been proposed, Scheme 4.3.[14] A similar hydrogen shift is observed in the reaction of pyridine with aminocarbene complexes derived from primary amines. Along with pyridine complexes, imines have been obtained as main products.



Scheme 4.3

In a closely related reaction a tetrahydroharman derivative was isolated, when starting with a tryptaminocarbene compound.[15] It should be noted that even in the absence of a base the thermolysis of aminocarbene complexes may also lead to imines.[16]

4.1.3 Photochemical Decomposition

Fischer *et al*[17] conducted a study on iron acylates and found that the isolable complex $[Me_4N][Fe(CO)_4C(O)Ph]$ decomposed to form benzaldehyde and $Fe_2(CO)_9$ upon prolonged standing in light, Scheme 4.4.

$$[Me_4N][Fe(CO)_4C(O)Ph] \xrightarrow[h\nu]{\text{light}} Fe_2(CO)_9 + PhC(O)H$$

Scheme 4.4

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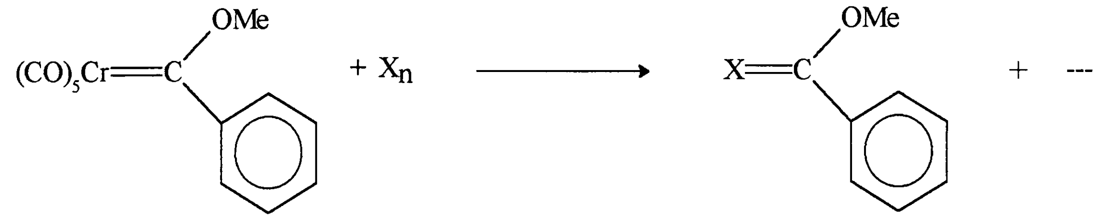
4.1.4. Oxidative Cleavage

The metal-carbene bond can be replaced by an oxygen-carbon double bond through oxidative cleavage. This procedure has proven useful in the characterization of carbene complexes. Early work indicated that oxygen could be employed directly as an oxidizing agent.[18], Scheme 4.5.[30]



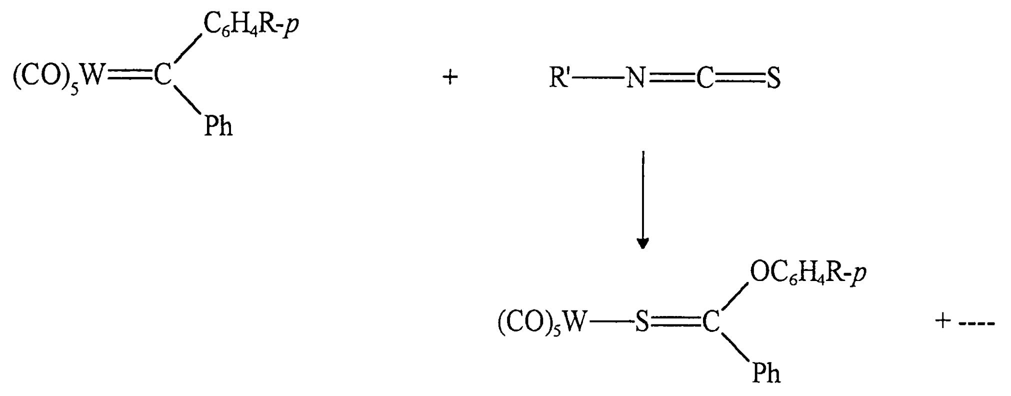
Xn = O_2, S_8, Se_n
Scheme 4.5

The metal-carbene cleavage occurs under mild conditions if dipolar reagents such as sulfoxides, amine-*N*-oxides or iodosobenzene are used.[5, 19, 20, 21] The latter is known to transform aminocarbene ligands into amides, although in low yields.

A versitile method is the use of ceric compounds. The oxidation of an enol ester substituted carbene complex of tungsten afforded the enediol diester in high yield, with the olefinic double bond being unaffected.[5, 22] Diaminocarbene complexes of palladium, on the other hand, are oxidized by silver(I)oxide to afford a variety of carbodiimide derivatives.[23]

Thioketone complexes are formed by the insertion of either organyl isothiocyanates or elemental sulphur and selenium into the metal-carbene carbon bond.[30]

Aryl(phenyl)carbene complexes of tungsten react with organyl isothiocyanates, R'-N=C=S, (R' = Me, Et, Ph), inserting sulphur from the organyl isothiocyanate into the metal-carbene bond to give the corresponding thioketone complexes[24], Scheme 4.6.



Scheme 4.6

{Aryl(phenyl)carbene}pentacarbonyltungsten complexes react similarly with elemental sulphur to insert one sulphur atom into the metal-carbene bond to yield the aryl(phenyl) thioketone pentacarbonyltungsten complexes.[25] The rate of the reaction is enhanced by the use of CS_2, instead of pentane as solvent, as elemental sulphur is more soluble in CS_2. It was found that the solvent CS_2 can also act a source of sulphur, although the reaction is much slower than with S_8.

Apart from oxidative cleavage metal-carbene complexes undergo reductive cleavage, as well as, cleavage by hydrogen halides. The reductive cleavage of the metal-carbene bond is best achieved by hydrogenolysis to yield the saturated hydrocarbons derived from the carbene ligand.[26] During cleavage of the metal-carbene bond, the nature of the carbene ligand determines the nature of the products which are formed.[27a - c] Hydrogen halides like hydrogen chloride[27 c - d], trifluoro-acetic acid[28], and trihalomethyl mercury[29] have been found to cleave the metal-carbene bond. Non-halogenated carboxylic acids were found to react with alkoxycarbene complexes to yield esters derived from the insertion of the carbene ligand into the O-H bond.[27c]

4.2 Aim of the Study

Biscarbene complexes containing a thiophenylene spacer between two carbene functionalities provide the interesting possibility that upon carbene-carbene carbon-carbon coupling the spacer may grow. The newly formed biscarbene complex will have an additional thiophenylene unit and still maintain π-conjugation between the two metal centres, Scheme 4.7.

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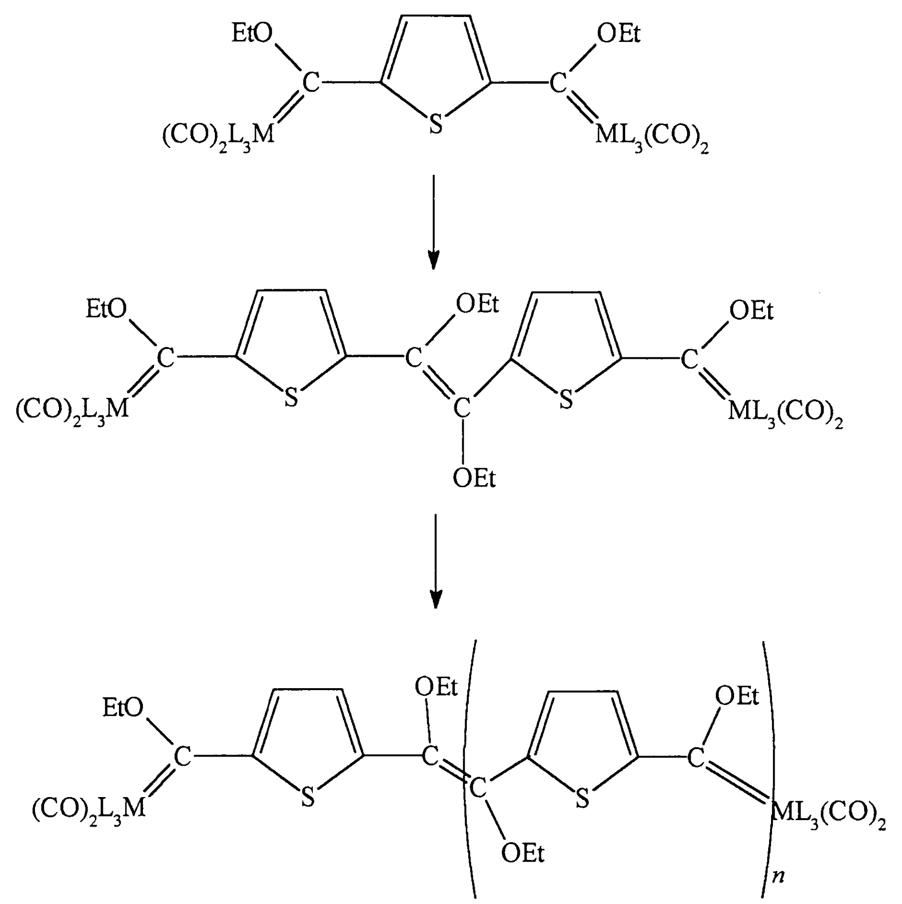

Scheme 4.7

If, by repeating the process the newly formed biscarbene is of higher stability than the precursor a conducting polymer may start to grow. On the other hand, if the newly formed biscarbene is less stable, as can be expected, the process should break down *via* an alternative decomposition pathway at one or both carbene ligands.

The properties displayed by the biscarbene complexes were those of enhanced activation and greater reactivity compared to the corresponding monocarbene complexes. It is anticipated that the biscarbene complexes will be more easily oxidized and it was decided to study the reactivity and/or stability of bimetallic biscarbene complexes of chromium, tungsten and manganese in solvents such as acetone, hexane and carbon disulphide, at room temperature, as well as, at elevated temperatures. Also the role played by thiophene (a conjugated bridging ligand) in these activation processes needed to be investigated.

4.3 Stability of the Thienylene σ,σ-Bimetallic Biscarbene Complexes in Acetone

The biscarbene complexes, **1** and **2**, were dissolved in an excess of acetone and left under magnetic stirring at room temperature in an inert atmosphere of nitrogen, a solution of the biscarbene complex **3**, had to be exposed to uv light rays whilst being stirred, to enable the reaction to proceed. After an average time of about 3.5 hours two products were formed. The main product from each reaction, was characterized as the monocarbene complex, $M\{C(OEt)C_4H_2SC(O)OEt\}L_3(CO)_2$, where M = Cr, L = CO **(16)**; M = W, L = CO **(17)**, M = Mn, L_3 = MeCp **(18)**. The second reaction product was of such low yield that characterization was impossible.

Considering a study done by Fischer and Riedmüller[30], in which the reactions of monocarbene complexes with oxygen, sulphur and selenium were investigated, it is evident that a related product is obtained for the reaction of the biscarbene complexes in acetone. On dissolving the biscarbene in acetone it immediately changes colour from purple to deep red. As oxygen free, dry solvent was used it was anticipated that an oxygen transfer had occurred from the acetone to the carbene. Several attempts to recover a second product from the reaction mixture failed and as some decomposition always occurred the formation of an unstable dimethylcarbene complex could not be proven or excluded, Scheme 4.8. The reaction was repeated with benzophenone, but no evidence for the formation of a second carbene species could be found. Because the ethyl carboxylate monocarbene complexes were obtained every time, irrespective of the nature of the oxygen containing solvent, it was concluded that the biscarbene complexes are extremely sensitive to oxygen and that the complexes **16** - **18** originate from rapid oxidation by oxygen, Scheme 4.9.

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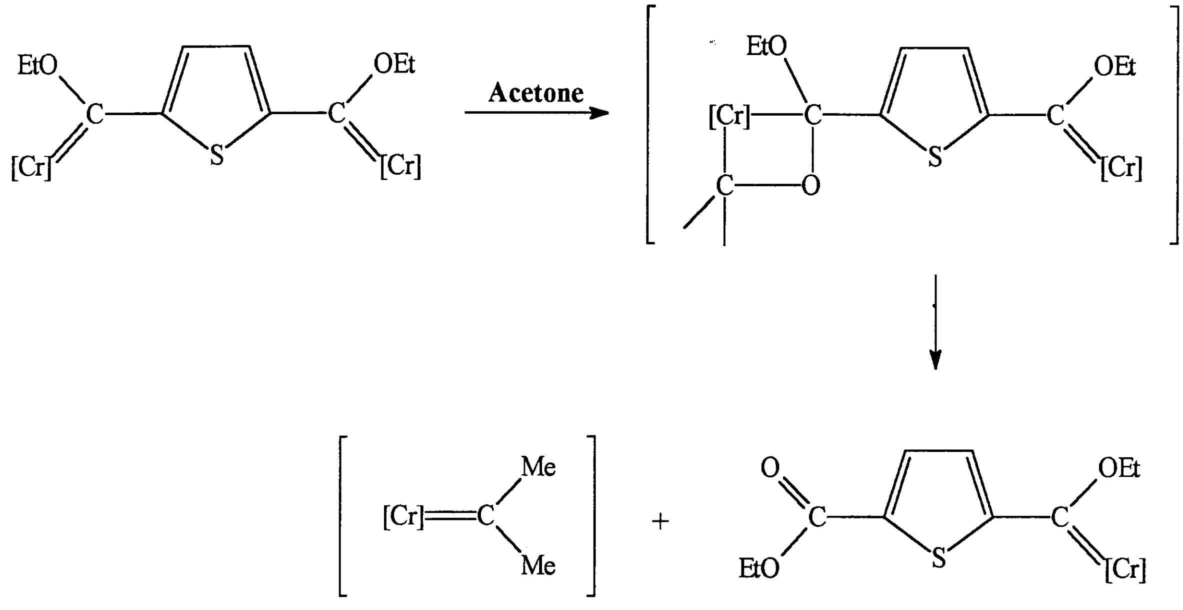

[Cr] = $Cr(CO)_3$

Scheme 4.8

The carbon atom in carbene complexes has a definitive electrophilic character,[1, 31] which leads to the belief that nucleophilic reagents, in this case oxygen, would preferably add to the carbene carbon atom. As a result a four membered dioxygen ring forms which results in the cleavage of the oxygen bond resulting in the formation of the ester and oxidized metal species. In the case of the oxygen addition product the reaction proceeds and leads to the formation of the *O*-ethyl thienyl carboxylate monocarbene complexes, **16** - **18**, with the loss of one carbene functionality. Scheme 4.9 presents a schematic illustration of the mechanism by which this reaction occurs.

These complexes were found to be relatively stable in the solid state, as well as in solution, in an inert atmosphere at low temperatures. Complex **18** was isolated as a yellow brown oil and complex **16**, was a red solid which could be crystallized from a mixture of dichloromethane and hexane, ratio 3 : 1, however these crystals were of poor quality. Complex **17** which was colourless has been prepared before by Aoki and co-workers[32] who in their strategy of protecting a thienyl carbene function by deprotonation in the 5-position, reacted this species with ClC(O)OEt to give **17** in high yields. The decomposition of **4** in acetone was not studied, however the related compound **24** was isolated from the reaction of **4** in carbon disulphide, § 4.4.

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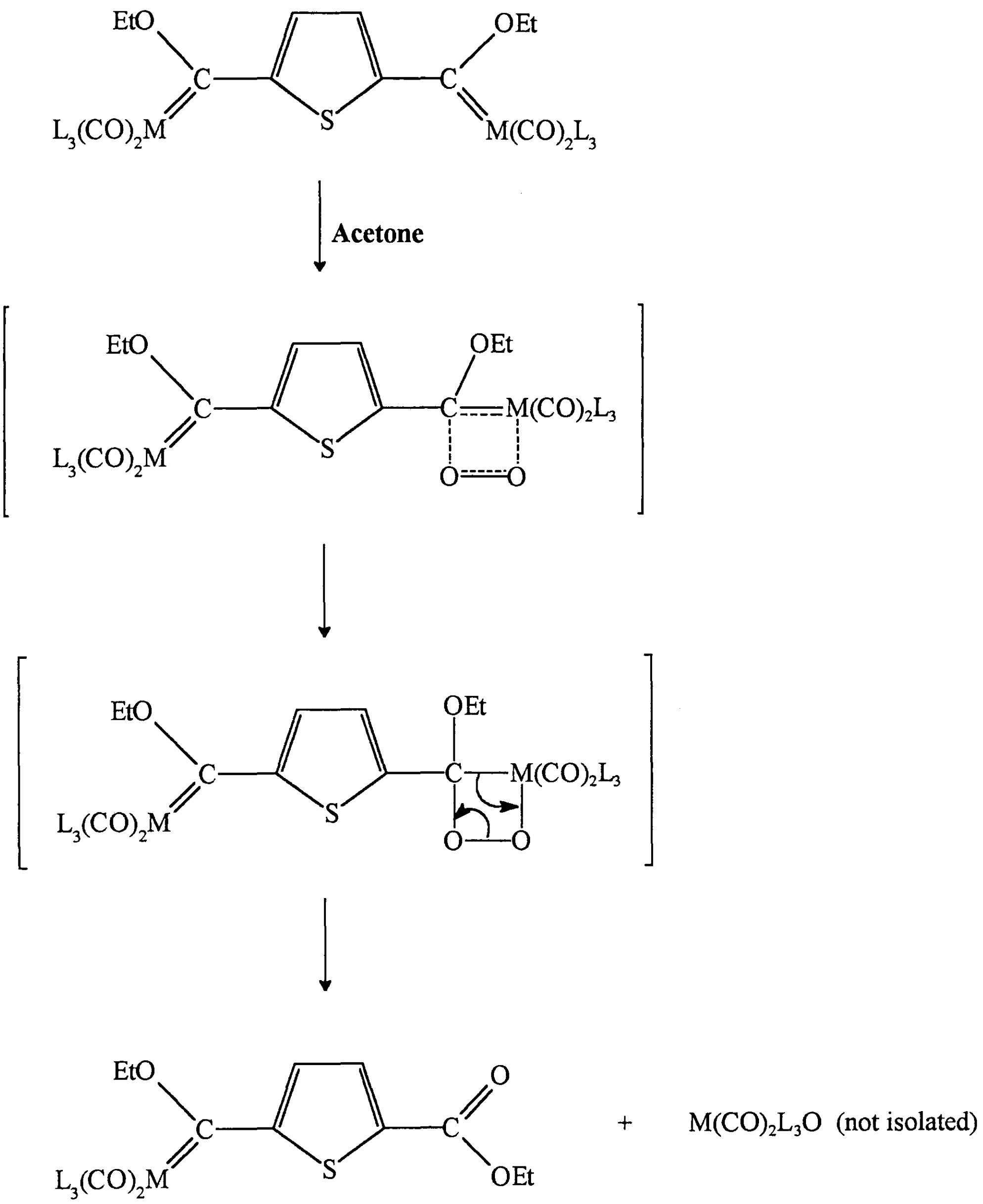

16 - 18, 24

Scheme 4.9

The same reaction under similar conditions with the exception of an argon atmosphere instead of a nitrogen atmosphere was repeated for the biscarbene complex **2**. A different product was isolated, which was identified as a monocarbene complex, $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2SC(O)OEt\}(CO)_5$, **(19)**, which contains three thiophene rings, linked by COEt units, as well as an ethyl carboxylate functionality furthest from the carbene, Figure 4.1.

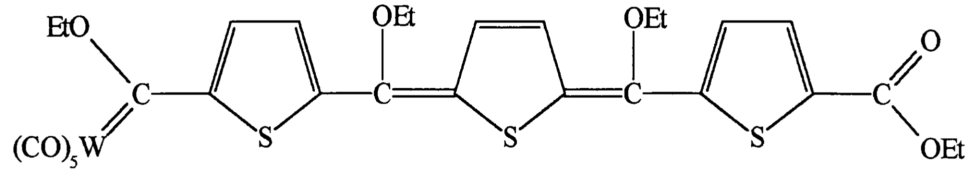

Figure 4.1 $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2SC(O)OEt\}(CO)_5$, (19)

It is not clear how this product could have formed. The combination of two carbene units and subsequent fragmentation resulting in a COEt link between R-substituents in carbene chemistry is without precedent in the literature. If one studies the connectivity displayed by the final product the following building blocks can be used to construct the final product, Figure 4.2. Variants whereby COEt's are moved from one thienylene to another are also possible.

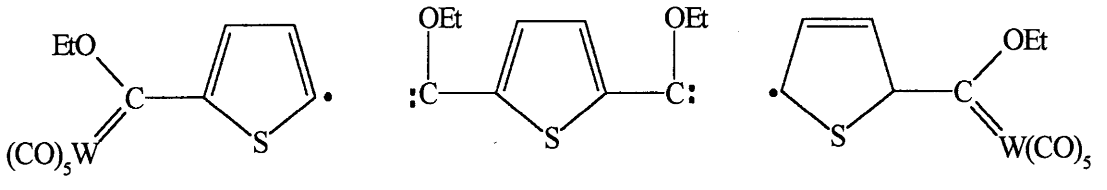

Figure 4.2 Connectivity of 19

The key step, the formation of a thienyl-carbon bond and the elimination of a carbene functionality can be accomplished by reversing the process of carbene formation. After the removal of an ethoxy substituent *via* ylide formation the carbon-carbon coupling is achieved by eliminating the parent metal carbonyl, Scheme 4.10.

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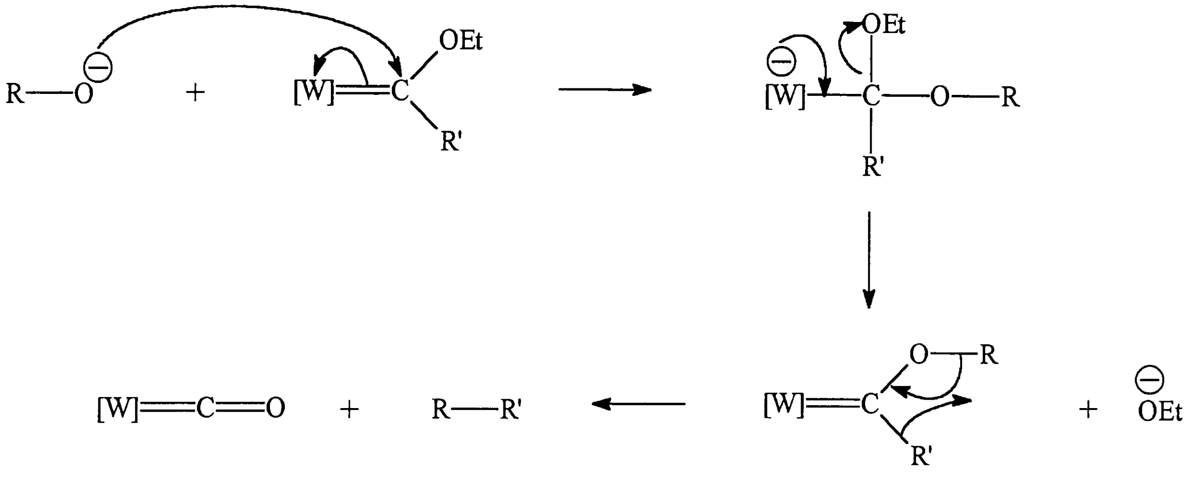
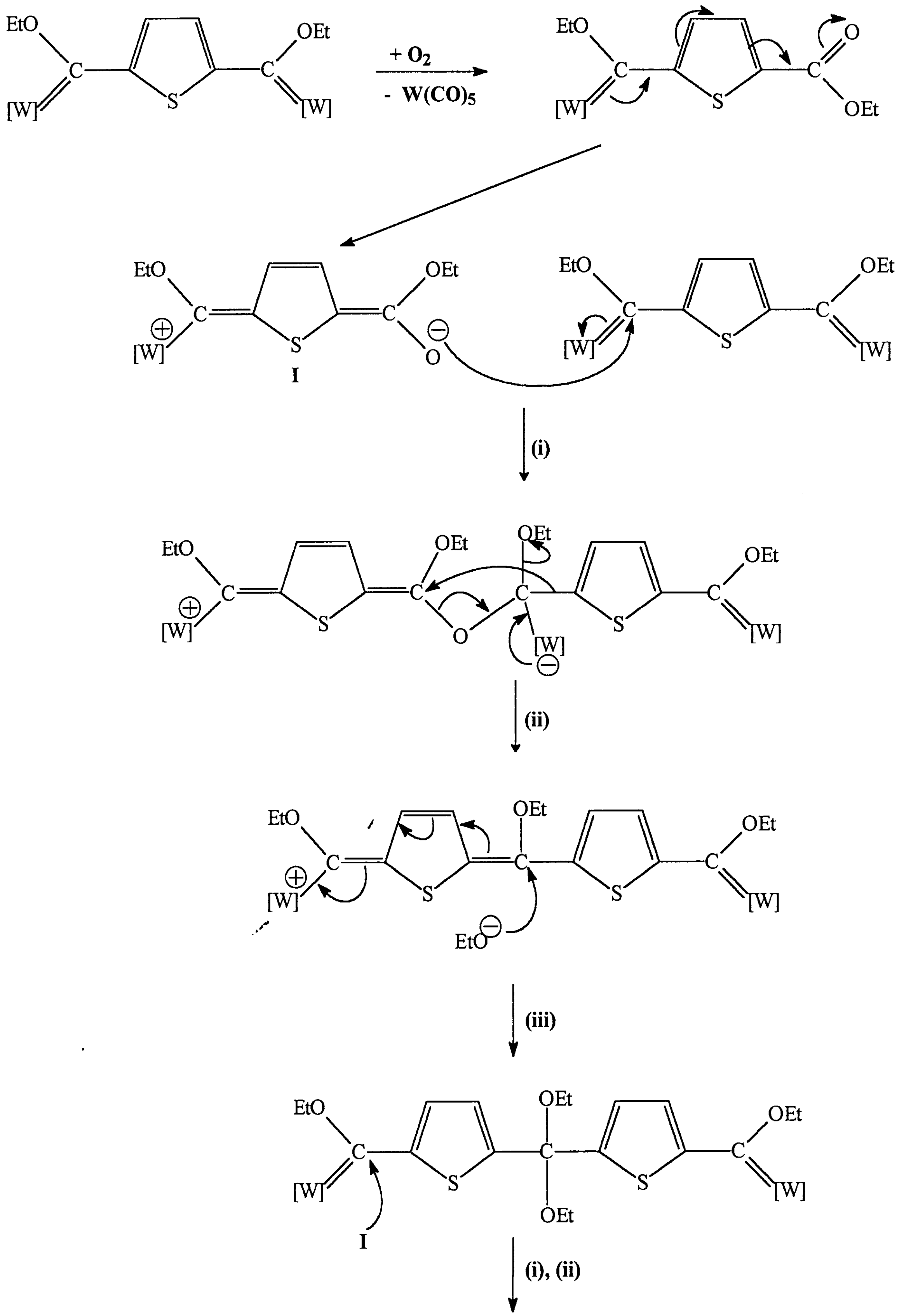
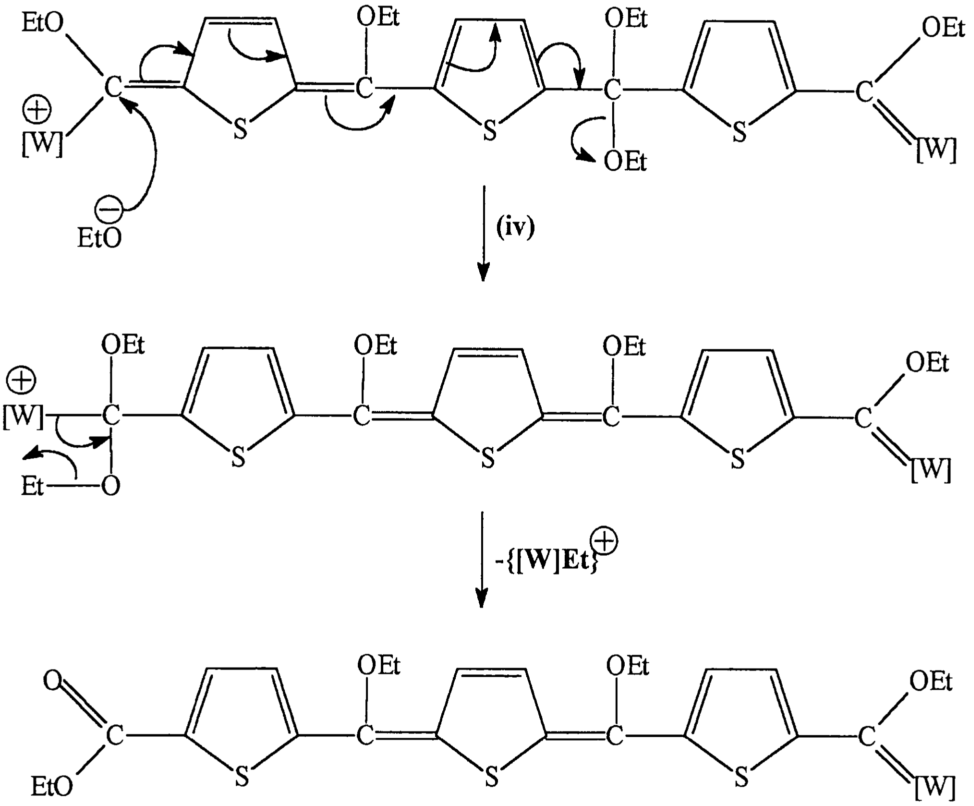


[W] = W(CO)$_5$

Scheme 4.10

A possible explanation for the formation of the different products could be attributed to the much slower availibility and lower concentration of oxygen when the much heavier noble gas, argon is used as inert atmosphere, as oxygen would not mix as easily with argon as it would with nitrogen which has more or less the same density as oxygen. Based on these results and assumption a reaction pathway is postulated to try and understand how **19** was formed, Scheme 4.11. Many other similar routes can be constructed. The ethylcarboxylate group in the 5-position of the thiophenylene carbene complex is electron withdrawing and owing to π-conjugation it is possible to draw a resonance structure **I** for **17** with a positive charge on the tungsten and a negative charge on the oxygen. Attack by the negative oxygen atom on the electrophilic carbene carbon atom of a biscarbene precursor, **2**, shown in **(i)**, results in the formation of an ylide. The elimination of firstly an ethanolate and thereafter a tungsten hexacarbonyl according to Scheme 4.11 is shown in step **(ii)**. The resulting intermediate, after attack by the ethanolate, affords, in step **(iii)** a new biscarbene complex. Steps **(i)** and **(ii)** are repeated by using **I** and the new biscarbene complex. Step **(iv)** represents the regeneration of π-conjugation through the briding ligand by moving the EtO$^-$ from the bisethoxy carbon to the carbon attached to the tungsten. The final product **19** is obtained by transfering an ethyl group to the tungsten and eliminating the pentacarbonyl tungsten fragment.


EtO
OEt
[W]
S
+ O2
- W(CO)5
O
I
(i)
(ii)
(iii)
EtO
(i), (ii)



19

Scheme 4.11

The complex **19** was isolated as a brown oil, which was stable for some time in air, but better stored in an inert atmosphere at low temperatures. Tungsten hexacarbonyl and an organic product were isolated as by-products from the reaction, however, no significant deductions could be made from the ^{1}H NMR spectroscopic data of the latter.

4.4 Reaction of the Thienylene Bimetallic Biscarbene Complexes with Carbon Disulphide

The stability of the biscarbene complexes **1** - **4** were tested in refluxing carbon disulphide. All of the complexes were dissolved in an excess of carbon disulphide and the solutions were refluxed at 46 °C, with the exception of the tungsten biscarbene complex **2**, which was unreactive at this temperature and had to be subjected to uv light rays in addition to being refluxed. After an average reaction time of about 3.5 hours the reactions were terminated and the various products isolated.

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The new products isolated from the reactions of the various biscarbene complexes were the following:

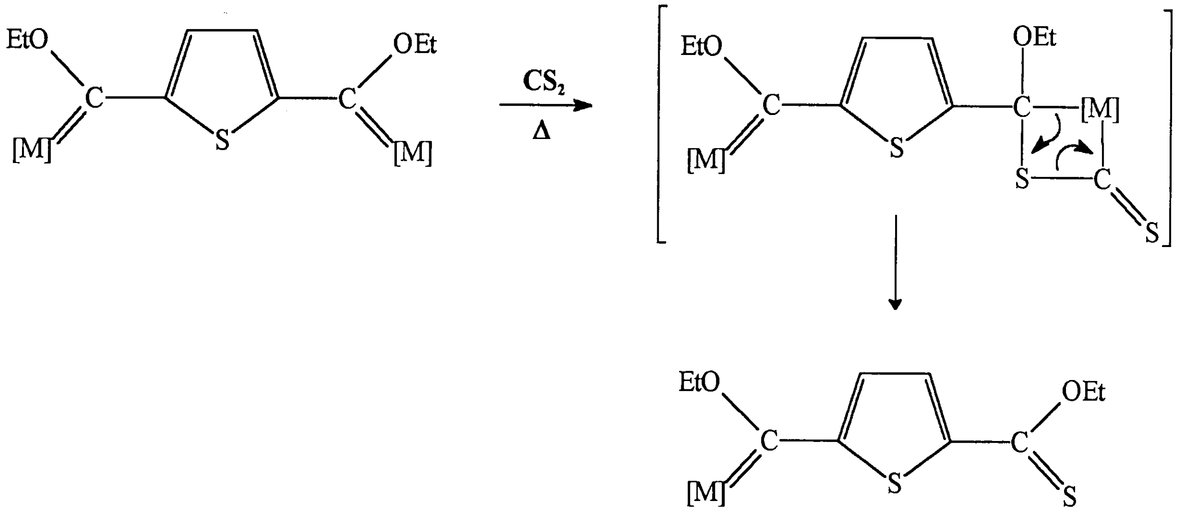
(a) Complex **1** afforded two products, a pink compound which was identified as a dithienylene carbene complex containing two thiocarboxylate substituents, $Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)(OEt)\}_2C_4HS]\}(CO)_5$, **(20)** and the *O*-ethyl thienylcarboxylate monocarbene complex, **16**.

(b) Complex **2** afforded two products, one of which the *O*-ethyl thienyl carboxylate monocarbene complex, **17** and the other the *O*-ethyl thienyl thiocarboxylate monocarbene complex, $W\{C(OEt)C_4H_2SC(S)\text{-}OEt\}(CO)_5$, **(21)**.

(c) Complex **3** afforded the *O*-ethyl thienyl thiocarboxylate monocarbene complex $Mn\{C(OEt)C_4H_2SC(S)OEt\}(\eta^5\text{-}C_5H_4CH_3)(CO)_2$, **(22)** and a dithienyl carbene complex containing a carboxylate and a thiocarboxylate substituent, $Mn\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)OEt\}\{C(O)OEt\}C_4HS\}(\eta^5\text{-}C_5H_4CH_3)(CO)_2$, **(23)**.

(d) Complex **4** afforded the *O*-ethyl thienyl carboxylate monocarbene complex, $Mn\{C(OEt)C_4H_2S\text{-}C(O)OEt\}(\eta^5\text{-}C_5H_5)(CO)_2$, **(24)** and the *O*-ethyl thienyl thiocarboxylate monocarbene complex, $Mn\{C(OEt)\text{-}C_4H_2SC(S)OEt\}(\eta^5\text{-}C_5H_5)(CO)_2$, **(25)**.

The formation of the *O*-ethyl thienyl thiocarboxylate monocarbene complexes, **21**, **22** and **25** can be accounted for similarly as the mechanism operational for the *O*-ethyl thienyl carboxylate monocarbene complexes **16**, **17**, and **18**, Scheme 4.12. The unsaturated C=S bond of CS_2 and the unsaturated metal-carbene bond cyclizises to form a 4 membered ring which opens in the opposite direction thereby cleaving the metal carbene bond forming a metal thiocarbonyl complex (compare well-known metathesis reactions)[33] with a thioketone moiety. The known thiocarbonyl complexes were identified spectroscopically.[34] The formation of complex **24** proceeds according to the mechanism discussed for complexes **16**, **17** and **18** in Scheme 4.9.



21, 22, 25

[M] = $ML_3(CO)_2$

Scheme 4.12

The monocarbene complexes **21** was stable in the solid state, as well as, in solution, however, after crystallization from a dichloromethane and hexane mixture, ratio 1 : 4, only very small crystals were obtained. The complexes **22** and **25**, were stable oils when stored in an inert atmosphere at low temperatures.

A working hypothesis for the formation of the dithienyl complexes containing either two thiocarboxylate substituents, **20**, or one carboxylate and one thiocarboxylate substituent, **23**, and the analogous chromium complex **26**, which contains two carboxylate substituents, the latter isolated as a product during the decomposition study of **1** in hexane, see § 4.5, is as follows: two biscarbene complexes react with each other in a thienyl-thienyl coupling reaction, Scheme 4.13. Electron density flows from M1 in one carbene complex to the C(thienyl)-C(carbene) bond, after which the double bond between C2 and C3 of the thiophene ring of this complex attacks C2 of a second complex with electron density being shifted to M4 in the second complex. The result is a positive charge on M1, (in complex 1) and a negative charge on M4, (complex 2). An unstable H-carbene species is lost at M3 which leads to the formation of a conjugated π-system through which the negative charge can be shifted from M4 through ring B and ring A to M1, resulting in the neutralizing of the charges. These complexes can then undergo oxidative cleavage by oxygen or carbon disulphide, as already described, (§ 4.3 and earlier in this section), to yield the products **20**, **23** and **26**, Scheme 4.14.

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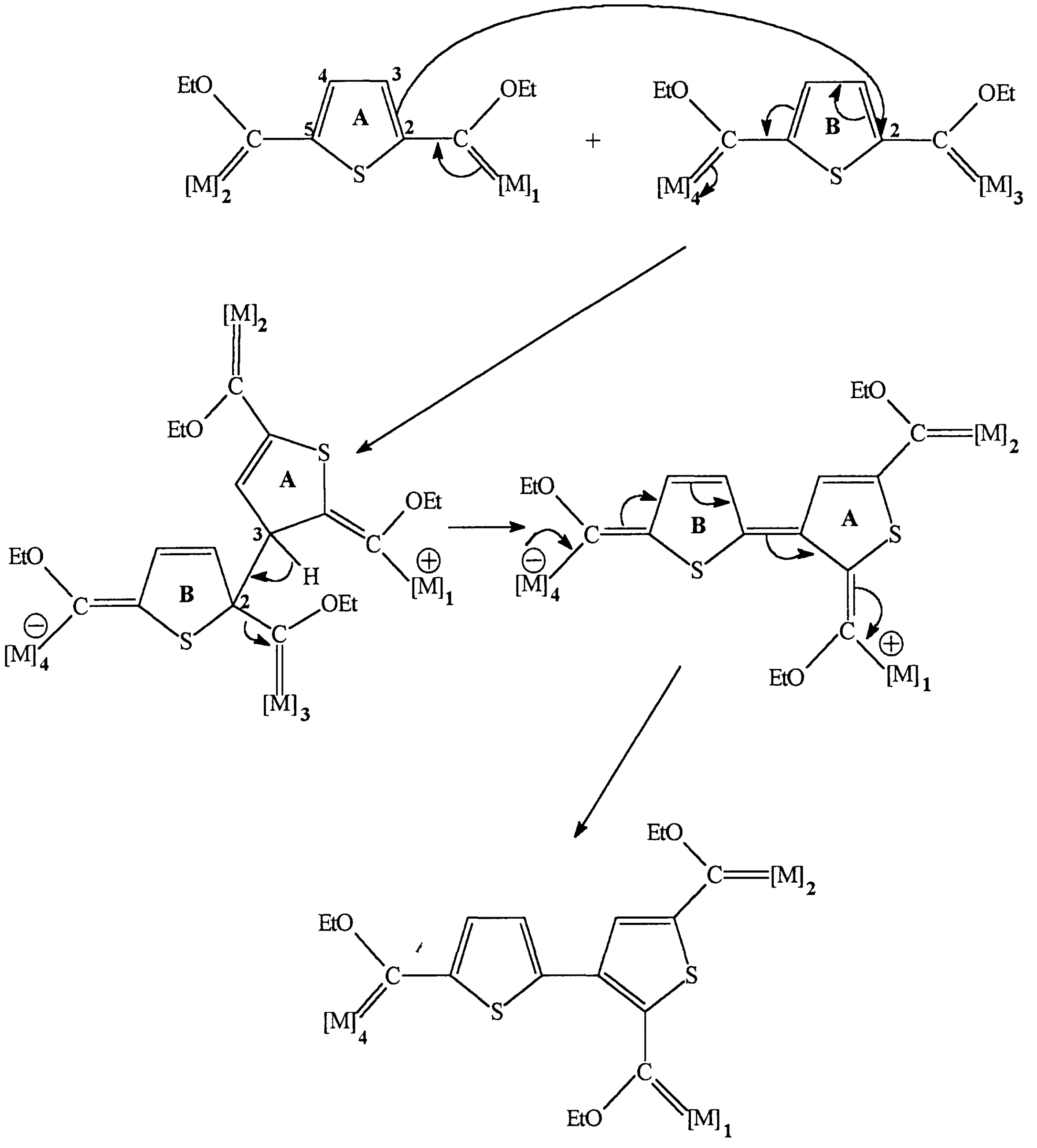
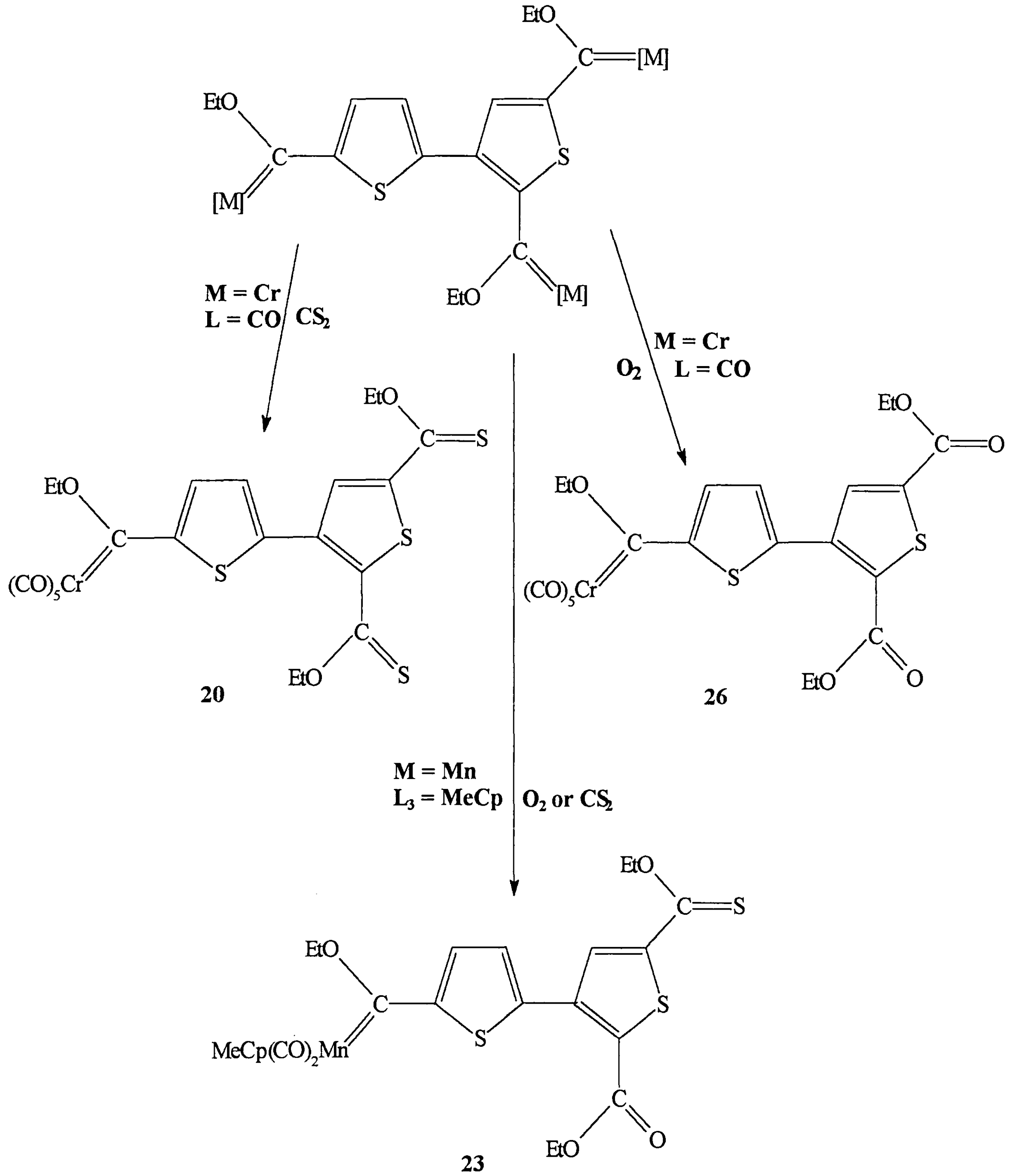


[M] = $ML_3(CO)_2$

Scheme 4.13



20

26

23

[M] = ML$_3$(CO)$_2$

Scheme 4.14

Complex **20** was isolated as a solid red product, which was stable in an inert atmosphere, as well as, in solution, this product after crystallization from a dichloromethane/hexane mixture afforded very small stable crystals. Complex **23** was isolated as a stable yellow brown oil.

It is interesting to note that the *O*-ethyl thienyl thiocarboxylate monocarbene complexes which are formed from the reaction between complexes **2** - **4** and CS_2 are similar to products isolated by Fischer and Riedmüller[30] from the reaction of the analogous methoxycarbene complex of chromium with oxygen and sulphur, as stated in § 4.1.4. The formation of the various other products confirms an increased reactivity of the bimetallic biscarbene complexes compared to that of the corresponding monocarbene complexes. Of further interest in this decomposition study is the formation of $Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(S)(OEt)\}_2C_4HS]\}(CO)_5$, **(20)**, in the reaction of **1** in CS_2,and that $Cr\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$ was not isolated, whereas **21** is formed in the reaction of **2** and a product related to **20** was not isolated. The reactions of the manganese carbene complexes afford the products **22** and **25**, which are related to **21**. It is not clear whether a η^2-coordinated CS_2 is a requirement for the formation of the corresponding thiocarboxylate decomposition products. The fact that product **21** is formed from the reaction of **2** can be due to the fact that the reaction mixture was subjected to photolysis. The more reactive chromium biscarbene leads to the formation of **16** and **20**. The formation of **20** might be a consequence of the longer reaction time, (4 h), to which the reaction mixture was subjected, and that a product analogous to **21**, **22** and **25** might indeed be formed.

4.5 Decomposition of the Chromium Thienylene Biscarbene Complex in Hexane

The biscarbene complex, **1**, was dissolved in an excess of hexane and refluxed for about 12 hours, after which time the colour of the solution turned from purple to very bright pink. Three products were isolated from the reaction mixture, the *O*-ethyl thienyl carboxylate monocarbene complex, **16**, the dithienyl carbene complex with two carboxylate substituents, $Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(O)OEt\}_2C_4HS\}(CO)_5$, **(26)** and lastly a complex in which a thienyl monocarbene complex containing two thienyl rings, which are connected by two carbonyl groups, this complex also contains a carboxylate moiety, $Cr\{C(OEt)C_4H_2SC(O)C(O)C_4H_2SC(O)OEt\}(CO)_5$, **(27)**. The formation of **16**, which is shown by Scheme 4.9 is, as already mentioned, due to the presence of oxygen in the system. The formation of **26**, is analogous to the formation of the dithienyl dithiocarboxylate monocarbene complexes, **20** and **23**, and described in § 4.4, see Schemes 4.13 and 4.14. An interesting observation is the formation of complex **27**, when the reaction is done at a higher temperature (69 °C). Scheme 4.15 presents a possible reaction route for the formation of this product. One molecule of the monocarbene **16**, which is formed by the oxidative cleavage of one of the metal carbene bonds, and complex **II**, react in a C-C coupling reaction, to yield **27** with the loss of a diethyl ether molecule (this is analogous to a C-C coupling by water elimination). The complex **II** can be formed by the transfer of an ethyl to the metal centre and the reductive elimination of the two organic ligands, Scheme 4.16. The intermediates

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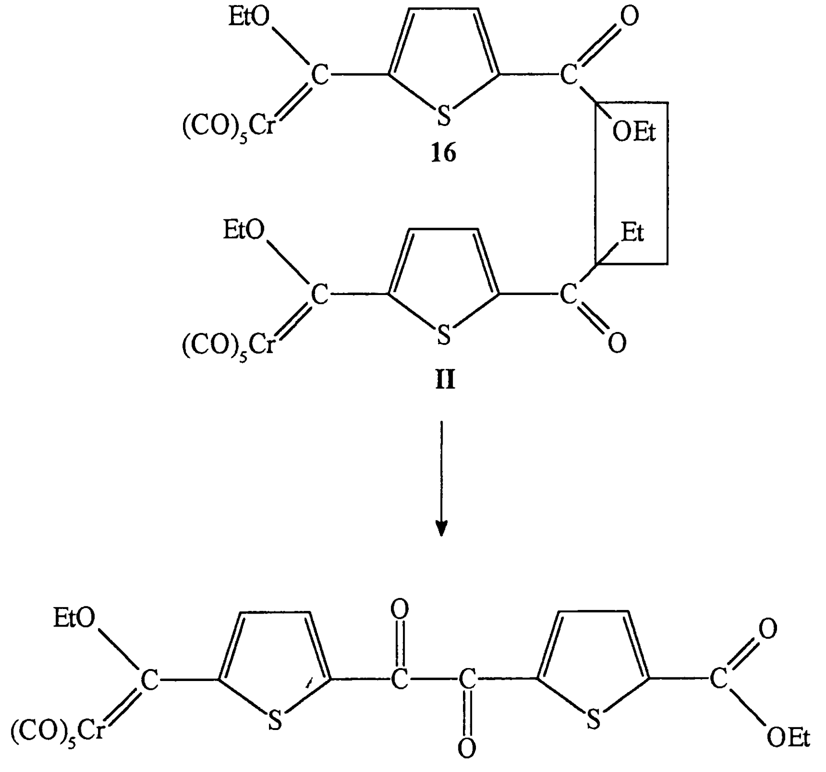
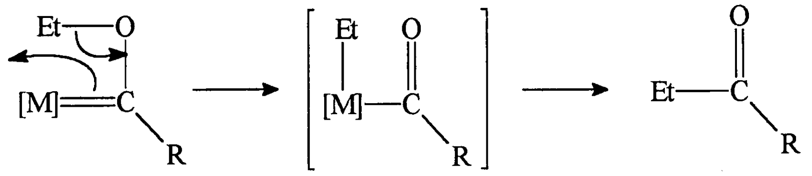
are often found when acylates are alkylated on the metal instead of the oxygen and the resulting unstable complex releases the two fragments by carbon-carbon bond formation and formally a reductive elimination at the metal centre. This represents another form of carbene destruction leading not to an ethylcarboxylate as before but an ethyl ketone.[12] Product **27** was the only example of such a decomposition pathway found in this study and is ascribed to the non-polar solvent and higher temperature of the reaction medium, a situation encountered more often by the less reactive monocarbene complexes.



Scheme 4.15



R = $(CO)_5Cr(OEt)C_4H_2S$

Scheme 4.16

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Complexes **26** and **27** were, respectively isolated as a red and a bright pink crystalline solid. These products were relatively stable in an inert atmosphere at low temperatures, however, if refluxing was maintained a mixture of organic decomposition products was obtained.

4.6 Spectroscopic Characterization of Compounds

All compounds obtained during the decomposition and activation studies were spectroscopically characterized. ^1H NMR spectra were obtained for all the complexes, however, ^{13}C NMR-, infrared- and mass spectra could not be obtained for all of the compounds, for reasons like insufficient material, especially in the case of ^{13}C NMR spectroscopy, as well as, the decomposition of compounds, when exposed to air.

4.6.1 Spectroscopic Data of the *O*-Ethyl Thienyl Carboxylate Monocarbene Complexes

Complexes **16**, **17**, **18** and **24** were characterized with ^1H NMR-, infrared- and mass spectroscopy, **16** was the only of these which afforded a significant ^{13}C NMR spectrum which could be interpreted. All NMR spectra were recorded in $CDCl_3$ as deuterated solvent. The spectroscopic data obtained are summarized in Tables 4.1 - 4.3. The numbering of the carbon atoms of the thiophene ring are the same as shown in Figure 3.9.

(a) ^1H NMR Spectroscopy

The ^1H NMR data obtained for complexes **16**, **17**, **18** and **24** are summarized in Table 4.1. Figure 4.4 shows the ^1H NMR spectrum of **16** and is representative of the spectra of all of these complexes. The data recorded[35] for **17** is in error with respect to the chemical shift assigned to the methylene protons of the non-carbenoid ethoxy group (a value of 4.93 was documented). Other values are within a 0.03 ppm range.

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Table 4.1 ^1H NMR Data of the *O*-Ethyl Thienyl Carboxylate Monocarbene Complexes

Assignment	**Complexes**						
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)						
	16		**17**		**18**	**24**	
Proton	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	δ	$^3J_{H\text{-}H}$
H3	8.09 (d)	4.3	7.99 (d)	4.2	7.70	7.65 (d)	4.3
H4	7.76 (d)	4.2	7.76 (d)	4.3	7.55	7.53 (d)	4.2
$O\mathbf{CH_2}CH_3$ (carbene)	5.20 (q)	7.1	4.98 (q)	7.1	4.97	4.96 (q)	7.1
$OCH_2\mathbf{CH_3}$ (carbene)	1.69 (t)	7.0	1.67 (t)	7.1	1.57	1.58 (t)	7.0
$O\mathbf{CH_2}CH_3$	4.37 (q)	7.2	4.36 (q)	7.1	4.49	4.34 (q)	7.1
$OCH_2\mathbf{CH_3}$	1.37 (t)	7.1	1.39 (t)	7.1	1.36	1.47 (t)	7.1
C_5H_4R (Cp)					4.34 n.o.	4.61 (s)	
CH_3 (Cp)					1.86		

The chemical shifts for the thiophene protons H3 and H4 in **16**, **17**, **18** and **24** are observed as doublets between 8.09 - 7.53 ppm owing to different substituents in the 2 and 5-positions. These chemical shifts are as expected downfield from the positions observed in the spectrum of free thiophene. When the chemical shifts of the corresponding protons in the spectra of the relevant biscarbene complexes **1** - **4** are taken into consideration not only do the positions in the spectra differ, but also the multiplicities. The chemical shifts for H3 appear a little downfield from those observed in the spectra of the biscarbene complexes, the opposite is, however, observed for the chemical shifts of H4. Figure 4.3(a) illustrates the competitive electron withdrawing effects in complexes **16**, **17**, **18** and **24**, as oxygen is more electronegative it will "pull" density from the thienyl ring, however the carbene functionality is electron poor and thus will also drain electron density from the ring.

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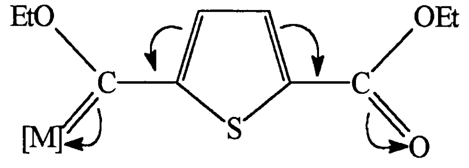

Figure 4.3(a) Competitive Electron Withdrawing Effects by Substituents in 16, 17, 18 and 24

Figure 4.3(b) shows individual electron withdrawing effects of substituents *via* π-resonance effects through the whole ligand as is represented by the resonance structures.

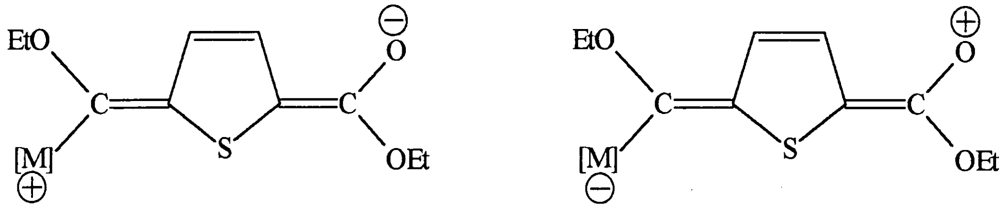

Figure 4.3(b) Resonances Structures for 16, 17, 18 and 24

The question which arises is whether more electron density will be drained towards the oxygen atom or towards the carbene functionality. Based on the chemical shifts of H3 and H4 one must conclude that the carbene metal combination would indeed drain more electron density than the oxygen atom.

The chemical shifts for the thiophene proton H3 in the spectra of the monocarbene thienyl complexes, **A** and **B** are observed downfield from those for H3 in **16** and **17**, possible due to a weaker withdrawing effect by the carbene-metal substituent owing to competition by the ethyl carboxylate group in **16** and **17**. The chemical shifts of H4 are, as expected, further upfield in the spectra of the monocarbene complexes **A** and **B**.

As expected the chemical shifts for the chromium complex **16** are downfield from those in the spectra of the corresponding tungsten complex **17**, see, § 2.5.1. The presence of a methyl group which is coordinated to the cyclopentadienyl ring in **18**, should lead to the chemical shifts of the Cp protons to appear as two doublets in the spectrum of **18**, however, only one chemical shift was observed at 4.49 ppm. On the other hand one singlet only should be observed in the spectrum of **24**, this singlet is much sharper and appears at 4.61 ppm. The reason for the difference in chemical shifts is due to the electron donating characteristics of

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the methyl group, § 2.5.1.

The chemical shifts for the protons of the methylene and methyl carbons of the ethoxy groups of **16**, **17**, **18** and **24** appear as quartets and triplets respectively. However the resonances for the corresponding protons of the ethyl carboxylate group appear further upfield. The difference in chemical shifts for the protons of the two different "types" of ethoxy groups can be attributed to the presence or absence of the metal nucleus.

The chemical shifts for the methylene and methyl protons of the ethoxy group of the carbene functionality of **A** and **B** differ only marginally from those observed in the spectra of complexes **16** and **17**, as do those observed in the spectra of the corresponding biscarbene complexes **1** and **2**.

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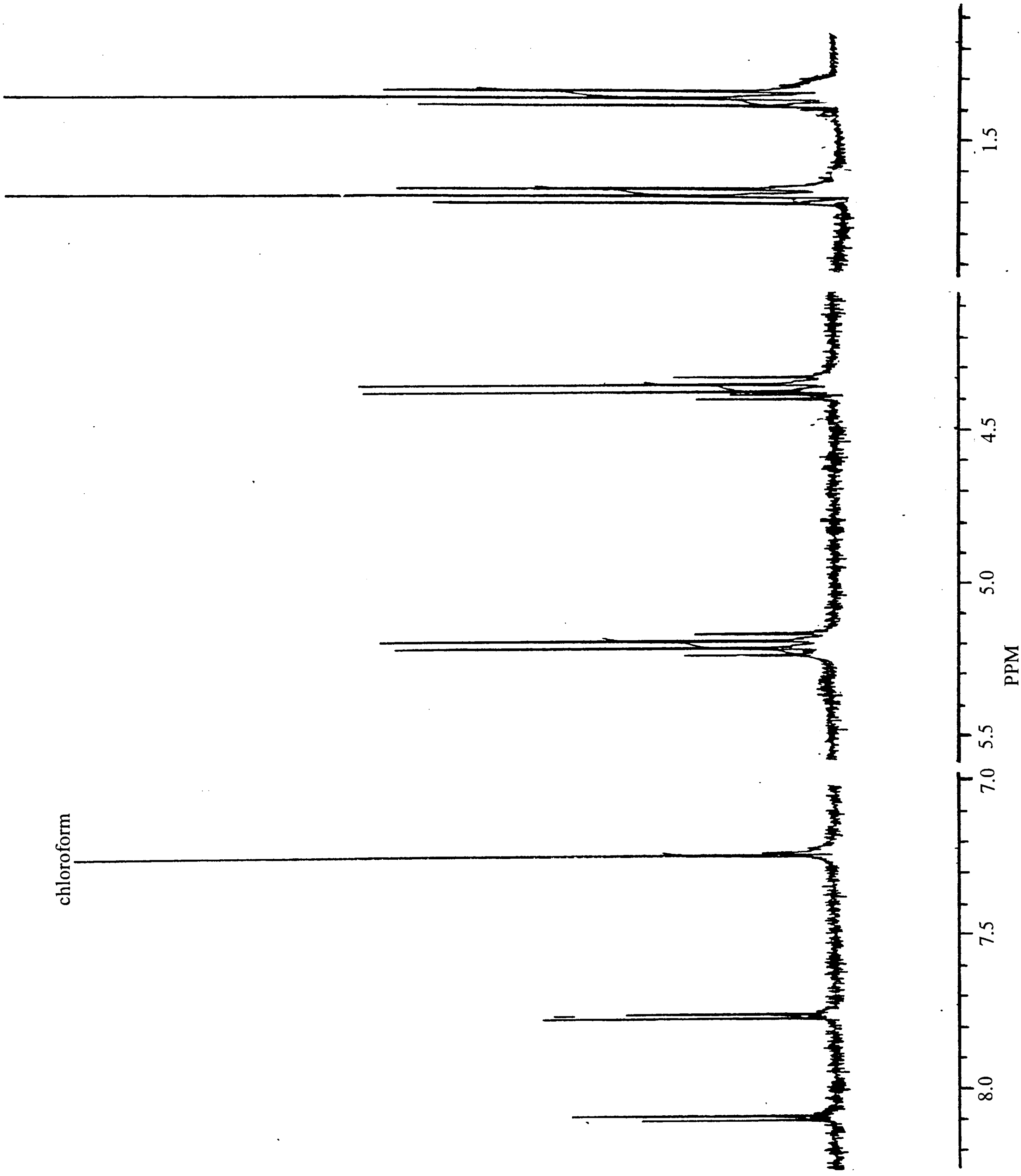

Figure 4.4 ^{1}H NMR Spectrum of Cr{C(OEt)(C$_4$H$_2$S)C(O)OEt}(CO)$_5$

(b) ^{13}C NMR Spectroscopy

The ^{13}C NMR spectrum of **16** was recorded and the assignment of all resonances was possible. The data (δ-values, ppm) are as follows: 320.2 (C(carbene)), 233.3 (C(*trans* carbonyl), 216.6 (C(*cis* carbonyls)).

The chemical shifts for the thiophene carbon atoms C2, C3, C4 and C5 appear as follows in the spectrum of complex **16**, C2: 162.3, C3: 138.8, C4: 133.0 and C5: 158.4 ppm. These chemical shifts are observed further downfield in the spectrum of **16** compared to the spectrum of free thiophene. As illustrated by Figure 4.3 electron flow from the ring is to the carbene functionality, as well as, the oxygen atom of the ester substituent in **16**. The further downfield chemical shift for C2 compared to C5 confirms the conclusion drawn from the ^{1}H NMR data, that more electron density is transferred from the ring to the carbene functionality than to the carboxylate substituent. The chemical shift for the carbon atom of the carboxylate group appears at 207.5 ppm.

The chemical shifts for the methylene- and methyl carbon atoms of the ethoxy group of the carbene moiety appear at 77.5 and 15.9 ppm respectively, whereas the chemical shifts for the corresponding carbon atoms of the ethoxy group of the ethyl carboxylate moiety appear further upfield, at respectively 61.9 and 14.2 ppm in the spectrum of **16**. The difference in chemical shifts is not unexpected as the presence of the metal nucleus in the carbene moiety would lead to more downfield chemical shifts. The chemical shifts for the methylene- and methyl carbon atoms of the carbene moiety are strikingly similar to those in the spectra of the corresponding biscarbene complex **1** and the monocarbene complex **A**, which once again shows that these chemical shifts are characteristic for a metal and are fairly insensitive to changes in the substituent. The chemical shifts of the thiophene carbon atoms on the other hand are more sensitive and are thus more affected by changes in substituents.

(c) Infrared Spectroscopy

The infrared data for **16**, **17**, **18** and **24** are summarized in Table 4.2. All the spectra were recorded in hexane as solvent, with the spectrum of **18** also recorded in dichloromethane as solvent. However, all the bands could not be observed with dichloromethane as solvent due to shifting of the bands which leads to overlapping.

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Table 4.2 Infrared Data of the *O*-Ethyl Thienyl Carboxylate Monocarbene Complexes

Assignment	Complexes			
	16	**17**	**18**	**24**
M(CO)$_5$	Carbonyl Stretching Vibrational Frequency, (νCO, cm^{-1})			
A$_1^{(1)}$	2060	2094 2081		
B$_1$	1980	1979		
E	1951	1948 1941		
A$_1^{(2)}$	1963	1962 1963		
-C(O)OEt	1726	1726	1725	1724
M(CO)$_2$				
A′			1940	1954
A″			1877	1898

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

In addition to the terminal carbonyl vibration frequencies a band is observed at more or less the same wavenumber, 1726 - 1724 cm^{-1}, in the spectra of all the complexes, the presence of this band is an indication of an additional carbonyl group, that of the carboxylate substituent.

(d) Mass Spectroscopy

In the mass spectra of **16**, **17**, **18** and **24** a molecular ion peak, M$^+$, was obtained for each complex. Fragment ions in the spectra of **16** and **17** indicate that the initial loss of the carbonyl ligands is stepwise, whereas a stepwise fragmentation could not be observed in the spectra of **18** and **24**. Two fragments of m/z-values of 29 could indicate the loss of the two ethyl groups, one from the carbene functionality and the other from the *O*-ethyl carboxylate group, which is stepwise in the spectra of **16** and **17**, however, this stepwise fragmentation could not be observed in the spectra of **18** and **24**. Interesting to note is that the cyclopentadienyl ring remains bonded to the Mn and that the principle ion in both **16** and **17** is the metal carbene fragment.

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Table 4.3 gives the most important peaks and fragment ions associated with these in the spectra of the *O*-ethyl thienyl carboxylate complexes. Scheme 4.17 presents a general fragmentation pattern for these complexes.

Table 4.3 Fragment Ions and Peaks of the *O*-Ethyl Thienyl Carboxylate Complexes

Complex	Fragment Ions; (%I)
16	404 (9) M^+; 376 (8) M^+ - CO; 348 (10) M^+ - 2 CO; 320 (9) M^+ - 3 CO; 292 (9) M^+ - 4 CO; 264 (100) M^+ - 5 CO; 235 (11) M^+ - 5 CO - CH_2CH_3; 206 (20) M^+ - 5 CO - 2 CH_2CH_3; 178 (9) M^+ - 6 CO - 2 CH_2CH_3; 150 (2) M^+ - 7 CO - 2 CH_2CH_3 - 2 CO
17[a]	535 (15) M^+; 507 (9) M^+ - CO; 479 (8) M^+ - 2 CO; 451 (2) M^+ - 3 CO; 423 (14) M^+ - 4 CO; 395 (79) M^+ - 5 CO; 366 (29) M^+ - 5 CO - CH_2CH_3; 337 (27) M^+ - 5 CO - 2 CH_2CH_3; 309 (12) M^+ - 6 CO - 2 CH_2CH_3; 281 (46) M^+ - 7 CO - 2 CH_2CH_3
18	402 (9) M^+; 346 (72) M^+ - 2 CO; 288 (100) M^+ - 2 CO - 2 CH_2CH_3; 232 (1) M^+ - 4 CO - 2 CH_2CH_3
24	388 (5) M^+; 332 (1) M^+ - 2 CO; 274 (3) M^+ - 2 CO - 2 CH_2CH_3; 218 (20) M^+ - 4 CO - 2 CH_2CH_3

[a] Based on ^{183}W

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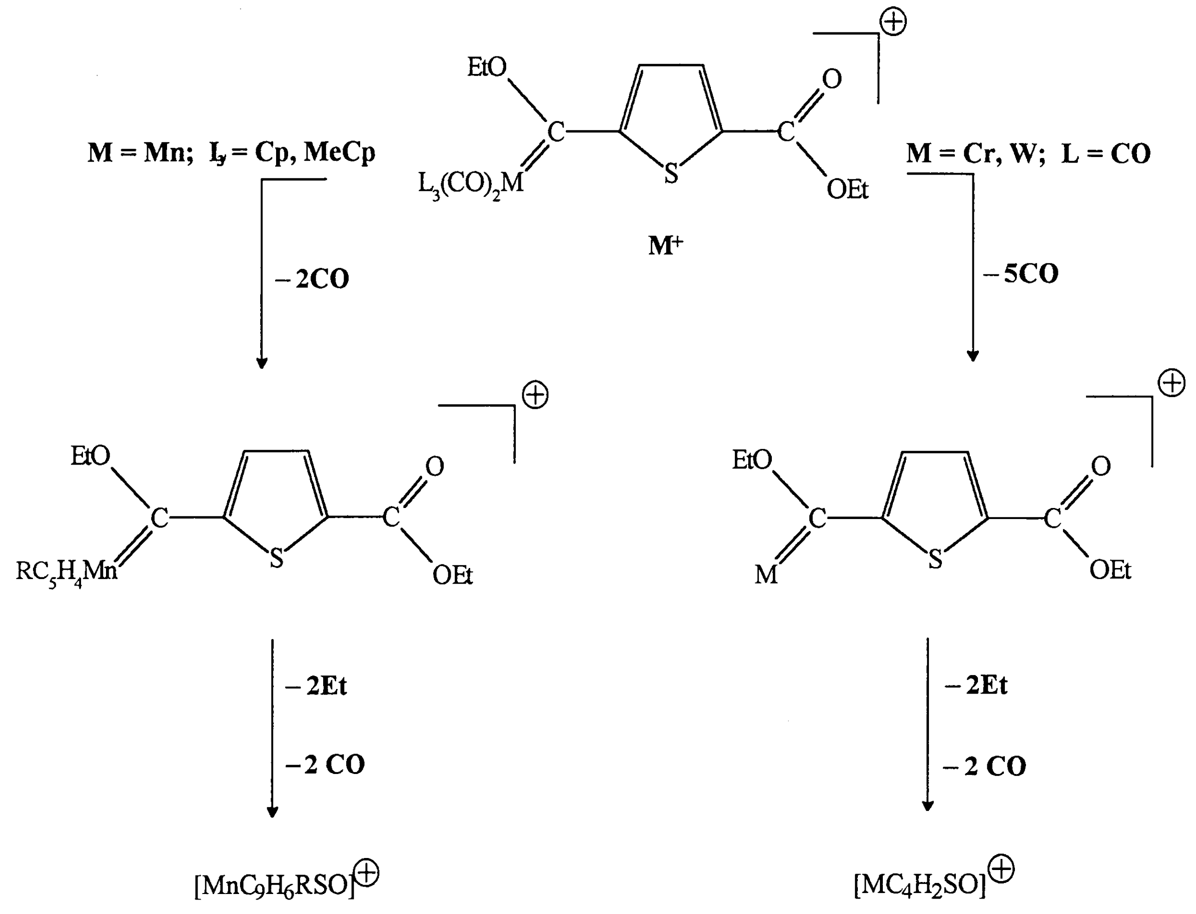

Scheme 4.17

4.6.2 Spectrosopic Data of $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2SC(O)\text{-}OEt\}(CO)_5$,(19)

Complex 19 was spectroscopically characterized by ^1H NMR-, ^{13}C NMR and infrared spectroscopy and identified as a monocarbene complex, containing three thiophenyl ligands. The numbering of the three thiophene rings, I, II and III, as well as that of the carbon atoms of the rings, is shown in Figure 4.5.

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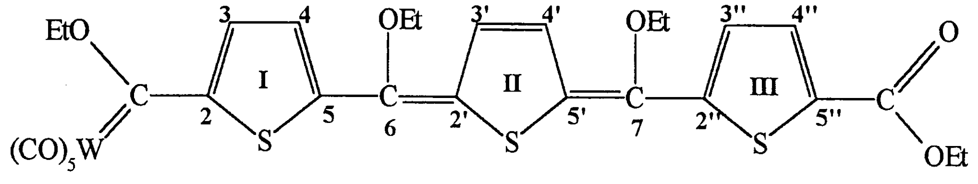

Figure 4.5 Numbering of Thiophene Rings and Carbon Atoms in W{C(OEt)C_4H_2SC(OEt)C_4H_2SC-(OEt)C_4H_2SC(O)OEt}$(CO)_5$, (19)

(a) ^{1}H NMR Spectroscopy

The ^{1}H NMR spectrum of **19** is shown by Figure 4.6 and the data given below. The chemical shifts, (δ-values, ppm) of these protons are as follows in the ^{1}H NMR spectrum:

Ring I: H3 a doublet, ($^3J_{H-H}$ = 4.2) at 8.00 and H4 a doublet, ($^3J_{H-H}$ = 4.3) at 7.76.

Ring II: H3′ H4′ a multiplet (two overlapping doublets, $^3J_{H-H}$ = 3.3) at 7.51.

Ring III: H3″, H4″ a multiplet (two overlapping doublets, $^3J_{H-H}$ = 3.3) at 7.69.

Methylene and methyl protons of the ethoxy groups:

Carbene moiety: CH_2 a quartet ($^3J_{H-H}$ = 7.1) at 4.99 and CH_3 a triplet ($^3J_{H-H}$ = 7.0) at 1.67.

O-ethyl carboxylate substituent: CH_2 a quartet ($^3J_{H-H}$ = 7.2) at 4.36 and CH_3 a triplet ($^3J_{H-H}$ = 7.1) at 1.38.

Two internal ethoxy groups: CH_2 a quartet (or two overlapping quartets, $^3J_{H-H}$ = 6.9) at 4.20 and CH_3 a multiplet (or two overlapping triplets, $^3J_{H-H}$ = 7.4), at 0.89.

The chemical shift of H3 appears more downfield than those of the rest of the thiophene protons due to the presence of a metal carbene functionality, which causes deshielding of the ring and hence of H3. The chemical shift of H4 is more upfield, but still downfield from the rest of the thiophene protons' resonances. It was anticipated that H4″ would be further downfield than H4, but it was possible to make assignments based on the coupling constants of H3 and H4. The chemical shifts observed for H3 in the specta of the corresponding biscarbene **2** and monocarbene **B**, appear further downfield. The chemical shifts of protons H3″ and H4″ are expected to be further upfield from H3 and H4 in the spectrum of **19**, owing to the *O*-ethyl carboxylate group bonded to ring III, but downfield from H3′ and H4′, hence the assignment. The coupling constants for H3′, H4′, H3″ and H4″ are smaller compared to those in ring I.

The chemical shifts of the methylene and methyl protons of the ethoxy groups of the carbene and *O*-ethyl carboxylate substituent appear as quartets and triplets respectively in the spectrum of **19**. The chemical shifts of the carbene ethoxy protons are remarkably similar to those in the spectra of complexes **17**, **2** and **B**, and it is clear that the incorporation of two more rings has little effect on the electronic environment around the carbene carbon. The chemical shifts of the methylene and methyl protons of the remaining two internal ethoxy groups, which are bonded to the carbon atoms connecting the thiophene rings, are observed even further upfield as multiplets or overlapping quartets and triplets.

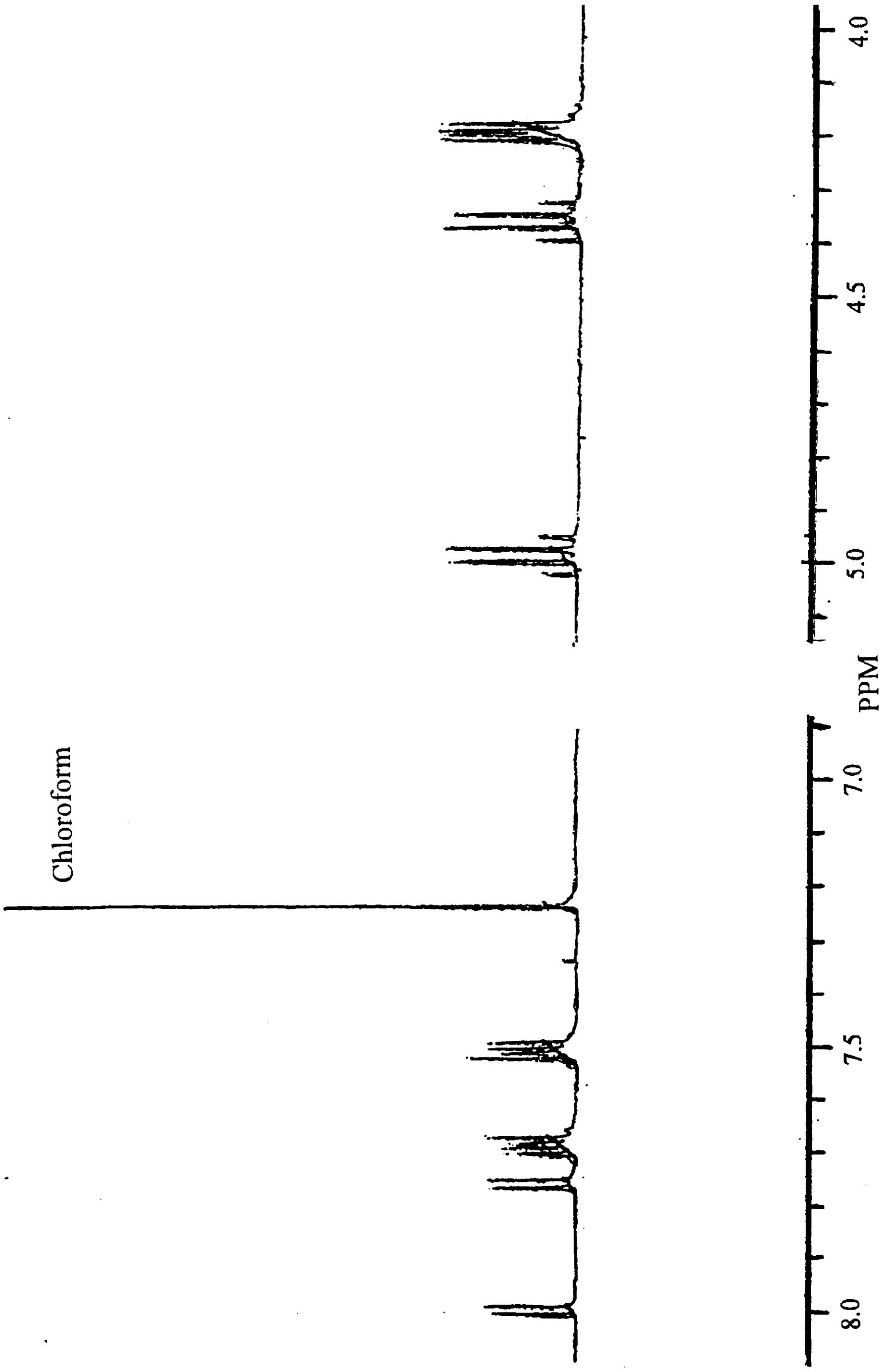

Figure 4.6 Thienyl and Methylene Regions in the ^{1}H NMR Spectrum of W{C(OEt)C_4H_2SC(OEt)-C_4H_2SC(OEt)C_4H_2SC(O)OEt}$(CO)_5$

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(b) ^{13}C NMR Spectroscopy

The data obtained from ^{13}C NMR spectroscopy for complex **19** are listed below.

C(carbene): 311.2, 239.6; C(*trans* carbonyl): 202.5, C(*cis* carbonyls): 197.1; C(ester, C(O)OEt): 207.7. Thiopene carbon atoms: C2: 162.3; Others: C3, C4, C5, C2′, C3′, C4′, C5′, C2″, C3″, C4″, C5″: 128.9, 130.9, 132.2, 132.4, 133.0, 139.5,162.0 ppm. (It seems reasonable to assume that the resonances will have the order (δ-values): C2 > C5″ > C5, C2′, C5′, C3, C4″ > C4, C3′, C4′, C3″).

Two internal **C**OEt: C6, C7:167.7

Methylene- and methyl carbon atoms of ethoxy groups:

Carbene ethoxy group: CH_2: 78.9; CH_3: 14.9.

O-ethyl carboxylate substituent: CH_2: 68.1; CH_3: 14.2.

Two internal ethoxy groups: CH_2: 61.9; CH_3: 10.9.

Two chemical shifts are observed for the carbene carbon atom in the spectrum of **19**. The presence of two chemical shifts is an indication that the complex can be present as one of two resonance structures. The electron flow and resonance structures are shown in Figure 4.7.

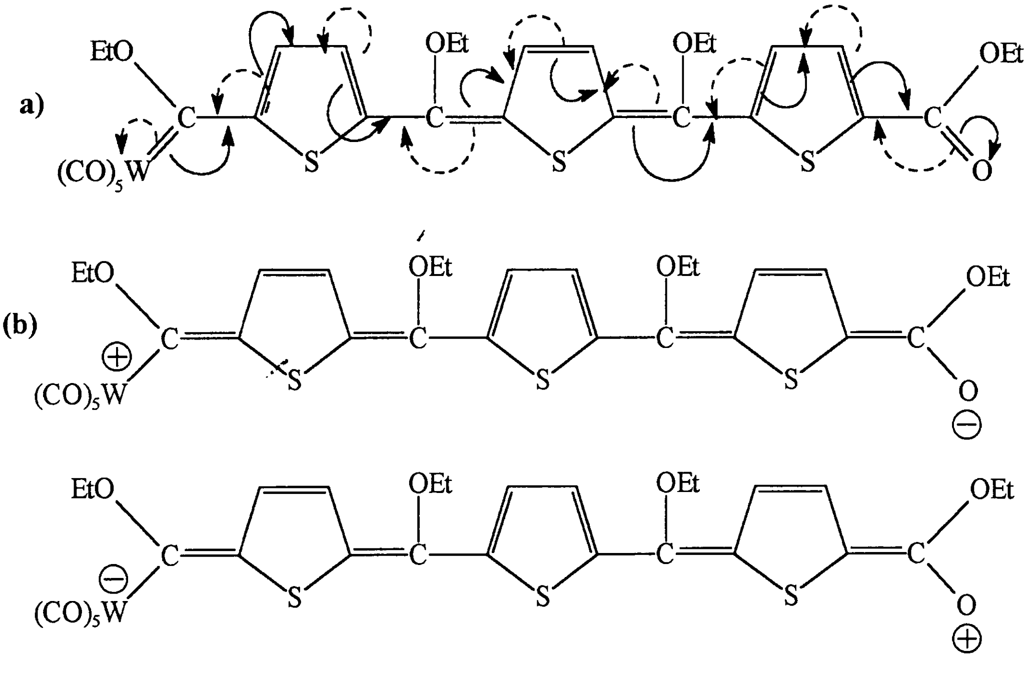

Figure 4.7 (a) Electron Flow or π-Resonance Effects and (b) Resonances Structures for 19

The downfield chemical shift of the carbene carbon atom is compared to the corresponding resonances for **2** and **B**, implies that less electron density is transferred from the thienyl ring to the carbene functionality in

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complex **19**.

The chemical shifts for the carbonyl ligands of W(CO)$_5$ appear at similar δ-values as observed in the spectra of **2** and **B**.

The chemical shifts of the thiophene carbon atoms appear from 128.9 to 162.3 ppm. The chemical shift for C2 appears at 162.3 ppm in the spectrum of **19**, which is very similar to the chemical shifts observed for this carbon atom in the spectra of **2** and **B**.

The chemical shifts of the methylene and methyl carbon atoms of the carbene ethoxy group are at 78.9 and 14.9 ppm respectively, whereas the chemical shifts for the ethoxy group of the *O*-ethyl carboxylate group appear at 68.1 and 14.2 ppm and the chemical shifts of the remaining two ethoxy groups of the carbon atoms connecting the thiophene rings at 61.9 and 10.9 ppm. These chemical shifts for the methylene and methyl carbon atoms of the ethoxy group of the carbene moiety are practically the same as in the spectra of complexes **2** and **B**, and once again shows that a change in substituents does not have a dramatic influence on these chemical shifts.

(c) Infrared Spectroscopy

The infrared spectrum of the monocarbene complex **19** was recorded in hexane as solvent and the data in the carbonyl region are (νCO, cm^{-1}): 2069 (A$_1^{(1)}$), 1984(B$_1$), 1955(A$_1^{(2)}$), 1947(E) for W(CO)$_5$ and the carbonyl band of the *O*-ethyl carbonyl substituent is at 1721 cm^{-1}.

The wavenumbers of the corresponding bands are of slightly lower wavenumbers compared with those of the biscarbene complex **2**.

The wavenumber of the band for the -C=O stretching frequency in -C(O)OEt appears at 1721 cm^{-1} in the spectrum of **19**, which is only a little lower from where it is seen in the spectrum of **17**.

4.6.3 Spectroscopic Characterization of the *O*-Ethyl Thienyl Thiocarboxylate Monocarbene Complexes

The spectroscopic data for **21**, **22** and **25** are summarized in Tables 4.4 - 4.6. ^{1}H NMR-, infrared and mass

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spectra were obtained for all three complexes, however, ^{13}C NMR spectra were obtained for complexes **21** and **25** only. The numbering of the carbon atoms of the thiophene ring is the same as shown in Figure 3.9.

(a) ^1H NMR Spectroscopy

The ^1H NMR data for these complexes are summarized in Table 4.4 and the spectrum of **25** is compared with that of **24** in Figure 4.9.

Table 4.4 ^1H NMR Data of the *O*-Ethyl Thienyl Thiocarboxylate Monocarbene Complexes

Assignment	**Complexes**					
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)					
	21		**22**		**25**	
Proton	δ	$^3J_{H-H}$	δ	$^3J_{H-H}$	δ	$^3J_{H-H}$
H3	7.97 (d)	4.4	7.70 (d)	4.0	7.69 (d)	4.0
H4	7.79 (d)	4.1	7.53 (d)	8.6	7.50 (d)	3.8
O$CH_2$$CH_3$ (carbene)	4.98 (q)	7.1	4.96 (q)	4.6	4.95 (q)	7.1
O$CH_2$$CH_3$ (carbene)	1.67 (t)	7.1	1.58 (t)	6.8	1.58 (t)	7.0
O$CH_2$$CH_3$	4.67 (q)	7.1	4.66 (q)	6.7	4.66 (q)	7.0
O$CH_2$$CH_3$	1.48 (t)	7.2	1.36 (t)	7.0	1.47 (t)	7.1
C_5H_4R (Cp)			4.50 (br) 4.39 (br)		4.61 (s)	
CH_3 (Cp)			1.79			

If the chemical shifts of H3 and H4 of **21**, **22** and **25** are compared with the corresponding resonances of the *O*-ethyl carboxylate monocarbenes **17**, **18** and **24** it is evident that the chemical shift are virtually the same. This implies that the chemical shifts of the thiophene protons are not dramatically influenced by exchanging a carbonyl for a thiocarbonyl in the 5-position substituent.

The question which once again arises is whether the metal carbene functionality or the *O*-ethyl thiocarboxylate group withdraws more electron density from the thienyl ligand, as shown in Figure 4.8. The answer to this lies in the positions of the chemical shifts of the thiophene protons H3 and H4, of which the

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chemical shift is more downfield for H3 in the spectra of these complexes than the chemical shift of H4. From this one can thus conclude that the metal carbene functionality extracts more electron density from the ring than the *O*-ethyl thiocarboxylate group. Further verification for this can be found in the comparison of the ^{13}C NMR chemical shifts of C2 and C5, see § 4.6.3 (b).

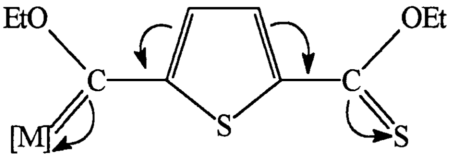

Figure 4.8 Competition between Substituents for Electron Density from the Thienyl Ligand

The chemical shifts of the protons of the Cp ring appear as two broad singlets due to poor resolution in the spectrum of **22** compared to one singlet in the spectrum of **25**. The chemical shifts of these protons appear at more or less the same positions in the spectra of complexes **3** and **4**.

The chemical shifts of the methylene and methyl protons of the carbene ethoxy group are virtually the same as the corresponding resonances observed in the spectra of **17**, **18** and **24**. The chemical shifts of these protons in the spectra of **2**, **3** and **4**, as well as, in the spectrum of **B** are also very similar to those observed in the corresponding spectra of **21**, **22** and **25**. The chemical shifts of the methylene and methyl protons of the ethoxy group of ethyl thiocarboxylate moiety appear as quartets and triplets respectively in the spectra of **21**, **22** and **25**. The δ-values of these chemical shifts are as expected upfield from those for the ethoxy group of the carbene functionality. An interesting observation is that these chemical shifts are in fact downfield from those of the ethoxy group of the *O*-ethyl carboxylate functionality in complexes **17**, **18** and **24**, see Figure 4.9.

In conclusion it can be stated that replacing a carbonyl (-C=O) with a thiocarbonyl (-C=S) in complexes does not have a marked influence on the chemical shifts of the thiophene protons, however the chemical shifts of the ethoxy group in the functionality, (either the *O*-ethyl carboxylate or *O*-ethyl thiocarboxylate) are more dramatically affected, as is evident from the ^{1}H NMR spectra.

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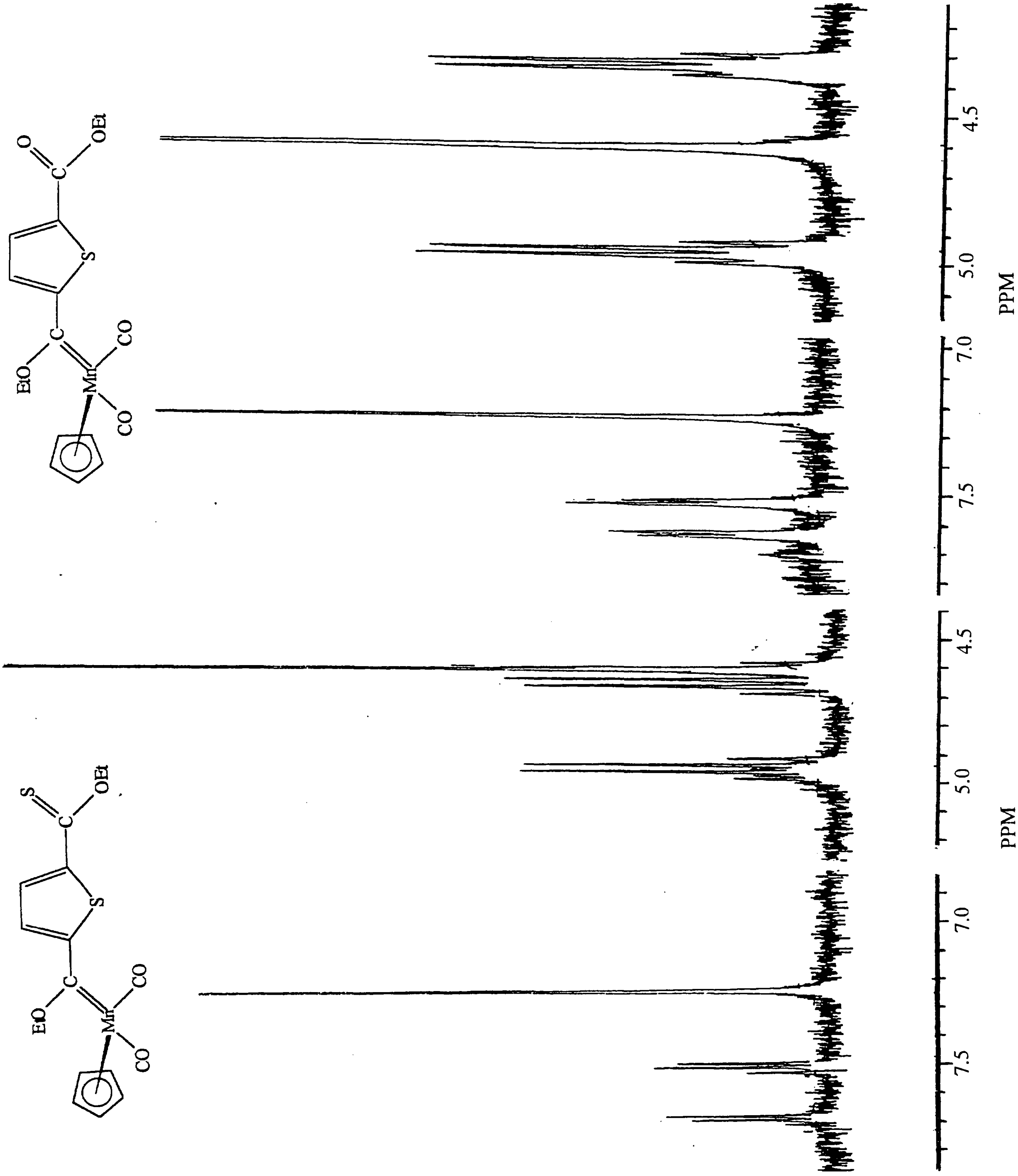

Figure 4.9 Thienyl and Methylene Regions in the ^{1}H NMR Spectra of Mn{C(OEt)C_4H_2SC(O)OEt}-$(CO)_2(\eta^5\text{-}C_5H_5)$ and Mn{C(OEt)C_4H_2SC(S)OEt}$(CO)_2(\eta^5\text{-}C_5H_5)$

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(b) ^{13}C NMR Spectroscopy

^{13}C NMR spectra could be obtained for complexes **21** and **25** only. The data are summarized in Table 4.5.

Table 4.5 ^{13}C NMR Data of the *O*-Ethyl Thienyl Thiocarboxylate Monocarbene Complexes

Assignment	**Complexes**	
	Chemical Shifts, (δ, ppm)	
Carbon Atom	**21**	**25**
C (Carbene)		312.2
	304.4	304.2
$M(CO)_5$, (*trans*)	202.9	—
$M(CO)_5$, (*cis*)	196.4	—
$M(CO)_2$	—	230.7
-C(S)OEt	182.1	182.1
C2	159.3	155.0
C3	141.9	139.0
C4	131.1	132.9
C5	152.0	150.0
C_5H_4R (Cp)	—	84.2
O**CH$_2$**CH$_3$ (carbene)	77.4	73.7
OCH$_2$**CH$_3$** (carbene)	15.3	15.2
O**CH$_2$**CH$_3$	51.3	53.4
OCH$_2$**CH$_3$**	14.0	14.1

The chemical shifts for the thiophene carbon atoms appear from 131.1 to 159.3 ppm in the spectra of **21** and **25**. The chemical shifts of C2 and C5 appear upfield in the spectra of **21** and **25** compared to those in the spectra of **2** and **4** which indicates that less electron density is donated from the thiophene ring to the metal carbene functionality and the *O*-ethyl thiocarboxylate moiety in complexes **21** and **25** compared to two carbene ligands. The chemical shifts of C2 are more downfield compared to the chemical shifts of C5 in the spectra of **21** and **25**, this is also evident for the chemical shifts of C3 compared to those of C4. This verifies deductions made from the ^{1}H NMR data that more electron density is transferred from the thienyl ligand to

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the carbene functionality than to the *O*-ethyl thiocarboxylate group. The chemical shifts of C4 are upfield from those in the spectra of **2** and **4**, which is not unexpected, as a carbene functionality would cause more deshielding than a thioester group and hence downfield chemical shifts. Interesting are the more downfield chemical shifts for C3 in the spectra of **21** and **25** compared to those in the spectra of **2** and **4**. This is in agreement with the more downfield chemical shift in the spectrum of the *O*-ethyl thienyl carboxylate complex, **16**, compared to that in the spectrum of the biscarbene complex, **1**.

The chemical shifts for the carbene carbon atoms in the spectra of **21** and **25** are somewhat upfield from those in the spectra of the corresponding biscarbene complexes **2** and **4**, which is in agreement with the assumption that more electron density is drained from the thienyl ligand towards the one carbene ligand in **21** and **25,** compared to that, that can possibly flow to two carbene ligands in **2** and **4**. The two chemical shifts for the carbene carbon atom in the spectrum of **25** may be an indication that two isomers are present in solution, presumably due to restricted rotation around the C(carbene)-manganese bond.

The chemical shifts for the C=S group appears in the spectra of both these compounds at 182.1 ppm. This chemical shift is as expected upfield from the -C=O chemical shift in complex **16**. The chemical shift of the Cp group in the spectrum of **25** appears at virtually the same position as observed in the spectrum of the biscarbene complex **4**.

(c) Infrared Spectroscopy

The infrared data for **21**, **22** and **25** are summarized in Table 4.6. The stretching frequencies for the complexes were recorded in hexane and dicloromethane as solvent but a well resolved spectrum for **21** could be obtained in hexane only.

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Table 4.6 Infrared Data of the *O*-Ethyl Thienyl Thiocarboxylate Monocarbene Complexes

Assignment	Complexes		
	Stretching Vibrational Frequency (νCO, cm^{-1})		
	21	**22**	**25**
$M(CO)_5$			
$A_1^{(1)}$	2068		
B_1	1957		
E	1923		
$A_1^{(2)}$	1934		
C=S	n.o.	1264	1247 1254
$M(CO)_2$			
A′		1937	1940 1938
A″		1892	1895 1876

The first set of data recorded in hexane and a second data set in dichloromethane

The bands in the infrared spectrum of **21** corresponding with those in the spectrum of the biscarbene **2** have higher wavenumbers, as do those in the spectrum of the *O*-ethyl thienylcarboxylate complex **17**. The following table presents a comparison of these wavenumbers in hexane as solvent.

Table 4.7 Infrared Stretching Frequencies of Tungsten Carbene Complexes

Assignment	Complexes		
	Stretching Vibrational Frequency (νCO, cm^{-1})		
$W(CO)_5$	**2**	**17**	**21**
$A_1^{(1)}$	2074	2094	2068
B_1	1985	1979	1957
E	1952	1948	1923
$A_1^{(2)}$	1960	1962	1937

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If the wavenumbers for these three complexes are considered the conclusion that can be made is that more electron density is left on the metal nucleus after π-backdonation to the carbene carbon in **21** which leads to an increase in the bonding order of M-C and the concomitant decrease in that of C=O, hence the lower wavenumbers.

The wavenumbers for the $M(CO)_2$-fragment in complexes **18**, **22**, **24**, **25**, **3** and **4** are compared Table 4.8.

Table 4.8 Infrared Stretching Frequencies of Manganese Carbene Complexes

Band	Stretching Vibrational Frequency, (νCO, cm^{-1})					
L_3	MeCp	Cp	MeCp	Cp	MeCp	Cp
Functio-nality	Carbene	Carbene	-C(O)OEt	-C(O)OEt	-C(S)OEt	-C(S)OEt
	3	**4**	**18**	**24**	**22**	**25**
$M(CO)_2$						
A′	1944	1948	1950	1953	1937	1940
A″	1893	1896	1893	1898	1892	1895

Solvent: Hexane

Table 4.8 shows that the wavenumbers of especially the A′ band are the lowest in the spectra of the thiocarboxylate complexes **22** and **25** and highest for **18** and **24**.

The C=S band could only be assigned in the spectra of complexes **22** and **25**, at 1264 cm^{-1} and 1247 cm^{-1} respectively, with hexane as solvent.

(d) Mass Spectroscopy

A molecular ion peak, M^+, was obtained for **21**, **22** and **25** and a general fragmentation pattern, shown by Scheme 4.18 was observed. After the intial loss of the carbonyl ligands from the carbene moiety, two fragments of m/z-value 29 (ethyl groups), are lost. This is followed by the loss of a CS-fragment and lastly by the loss of a carbonyl presumably an acyl carbonyl. Important to note is that the cyclopentadienyl ring remains bonded to complexes **22** and **25** and is part of initial fragment ions. The most important peaks and fragment ions associated with these are given in Table 4.9.

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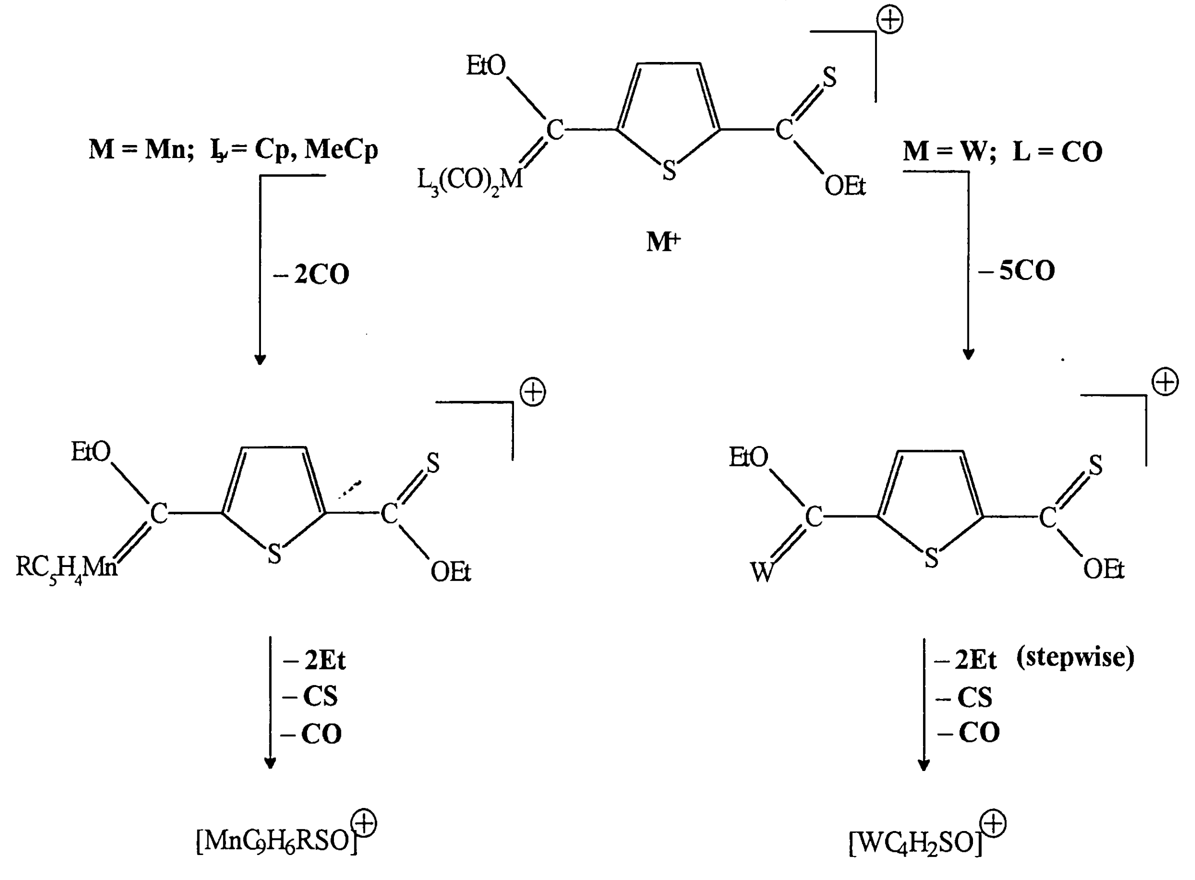
remains bonded to complexes **22** and **25** and is part of initial fragment ions. The most important peaks and fragment ions associated with these are given in Table 4.9.

Table 4.9 Fragmentation Ions and Peaks of the *O*-Ethyl Thienyl Thiocarboxylate Complexes

Complex	Fragment Ions; (%I)
21[a]	551 (1) M^+; 411 (40) M^+ - 5 CO; 382 (20) M^+ - 5 CO - CH_2CH_3; 353 (21) M^+ - 5 CO - 2 CH_2CH_3; 309 (17) M^+ - 5 CO - 2 CH_2CH_3 - CS; 281 (23) M^+ - 6 CO - 2 CH_2CH_3 - CS
22	418 (8) M^+; 362 (15) M^+ - 2 CO; 304 (14) M^+ - 2 CO - 2 CH_2CH_3; 260 (30) M^+ - 2 CO - 2 CH_2CH_3 - CS; 232 (10) M^+ - 3 CO - 2 CH_2CH_3 - CS
25	404 (1) M^+; 348 (33) M^+ - 2 CO; 290 (20) M^+ - 2 CO - 2 CH_2CH_3; 246 (30) M^+ - 2 CO - 2 CH_2CH_3 - CS; 218 (20) M^+ - 3 CO - 2 CH_2CH_3 - CS)

[a] Based on ^{183}W



Scheme 4.18

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4.6.4 Spectroscopic Characterization of the Dithienyl Carbene Complexes with Carboxylate or Thiocarboxylate Substituents

The monocarbene complexes **20** and **23** were obtained from the reactions of the biscarbene complexes **1** and **3** in carbon disulphide. The analogous complex **26** was obtained from the reaction of **1** in acetone. The complexes were characterized with ^{1}H NMR- and infrared spectroscopy. Complex **23** afforded the only significant ^{13}C NMR spectrum. Mass spectra were obtained for **20** and **23**. The numbering of the carbon atoms in these complexes is illustrated by Figure 4.10.

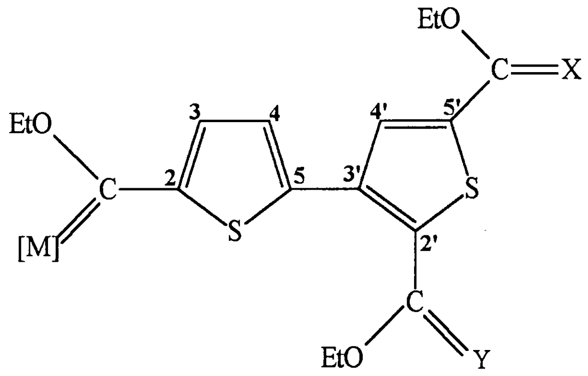

Figure 4.10 Numbering of Carbon Atoms in 20, 23 and 26

(a) ^{1}H NMR Spectroscopy

The ^{1}H NMR data for the dithienyl carbene complexes with carboxylate or thiocarboxylate substituents are summarized in Table 4.10. Figure 4.11 presents the ^{1}H NMR spectra of complexes **20** and **26**.

Table 4.10 ^{1}H NMR Data of the Dithienyl Carbene Complexes with Carboxylate or Thiocarboxylate Substituents

Assignment	Complexes					
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)					
	20 (Cr, S, S)		**23 (Mn, S, O)**		**26 (Cr, O, O)**	
Proton	δ	$J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$
H3	8.06 (d)	4.4	7.64 (d)	3.9	8.09 (d)	4.3
H4	7.79 (d)	4.4	7.55 (d)	3.9	7.76 (d)	4.3
H4'	7.71 (s)		7.71 (s)		7.71 (s)	
O**CH$_2$**CH$_3$ (carbene)	5.19 (q)	7.0	4.97 (q)	7.1	5.20 (q)	7.1
OCH$_2$**CH$_3$** (carbene)	1.69 (t)	7.1	1.57 (t)	7.1	1.69 (t)	7.0
2 x O**CH$_2$**CH$_3$	4.65 (m)	7.1	4.35 (m)	6.9	4.37 (m)	7.1
2 x OCH$_2$**CH$_3$**	1.49 (m)	7.1	1.37 (t)	7.0	1.37 (m)	7.1
C_5**H_4**R (Cp)				4.49 (br) 4.40 (br)		
CH$_3$ (Cp)				1.79 (s)		

The presence of a second trisubstituted thiophene ring in the spectra of **20**, **23** and **26** is confirmed by a sharp singlet in the thiophene region. The chemical shifts of the thienyl protons are virtually the same in the spectra of **20** and **26**, which confirms that the substition of CO by CS in the substituents does not have a marked influence on the chemical shifts of the thiophene protons. Surprisingly is the similar chemical shift for H4' in all three spectra, which is an indication of similar environments and influences. This proton is in all probability to far from the coordinated metal nucleus in the carbene functionality to experience any effects or influences from it in any of the complexes, hence the same chemical shift. The chemical shifts for H3 are the same as in the spectra of the corresponding biscarbene complexes **1** and **3**. The chemical shifts for H4 in complexes **20**, **23** and **26** appear upfield from those in the specta of **1** and **3**. The reason for this difference is as previously discussed the absence of the metal nucleus in the vicinity of H4 in complexes **20**, **23** and **26**. Another interesting observation is that the chemical shifts of the thiophene protons H3 and H4 are similar in the spectra of the chromium complexes **16**, **20** and **26**. This observation is also made when the spectra of the manganese complexes **18**, **22** and **23** are compared.

The chemical shifts of the methylene and methyl protons of the ethoxy group of the carbene moiety are

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similar in the spectra of **20** and **26** and in agreement with the chemical shifts observed in the spectra of complexes **1** and **A**, something which is not unexpected. These are also very similar in the spectra of **23** and **3**.

The chemical shifts for especially the methylene protons of the ethoxy group appear further downfield when the CS group is present compared to the chemical shifts when a CO group is present. This phenomenon was also observed for the *O*-ethyl carboxylate and *O*-ethyl thiocarboxylate complexes, § 4.6.1 and 4.6.3. The chemical shifts of these protons are also very similar in the spectra of the *O*-ethyl carboxylates **16** and **26**. These observations confirm earlier findings that for some reason the oxygen atom in the *O*-ethyl carboxylate group affords a more shielded ethoxy group compared with the *O*-ethyl thiocarboxylate on the substituent. However, none of this is evident in the resonances of the thiophene ring.

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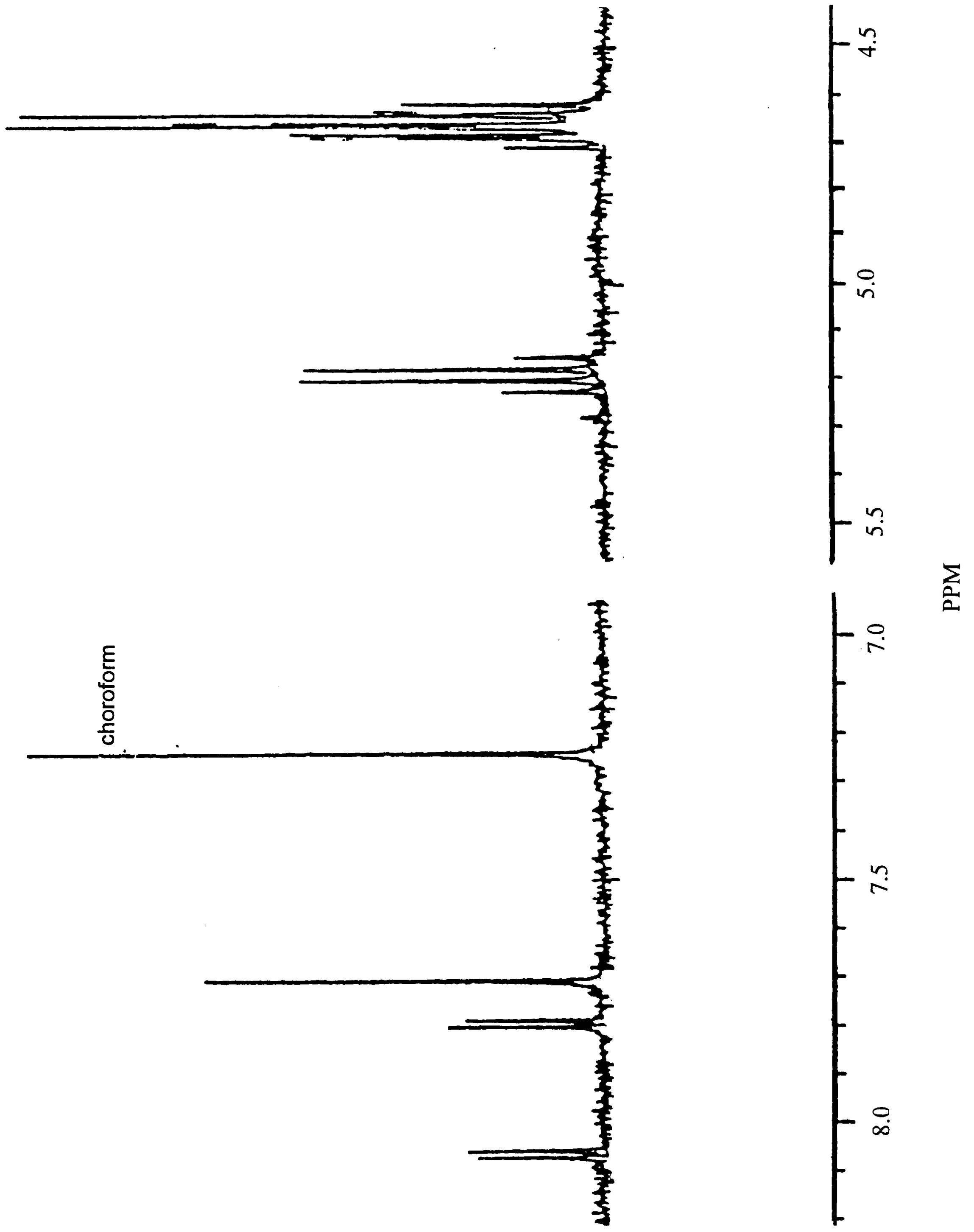
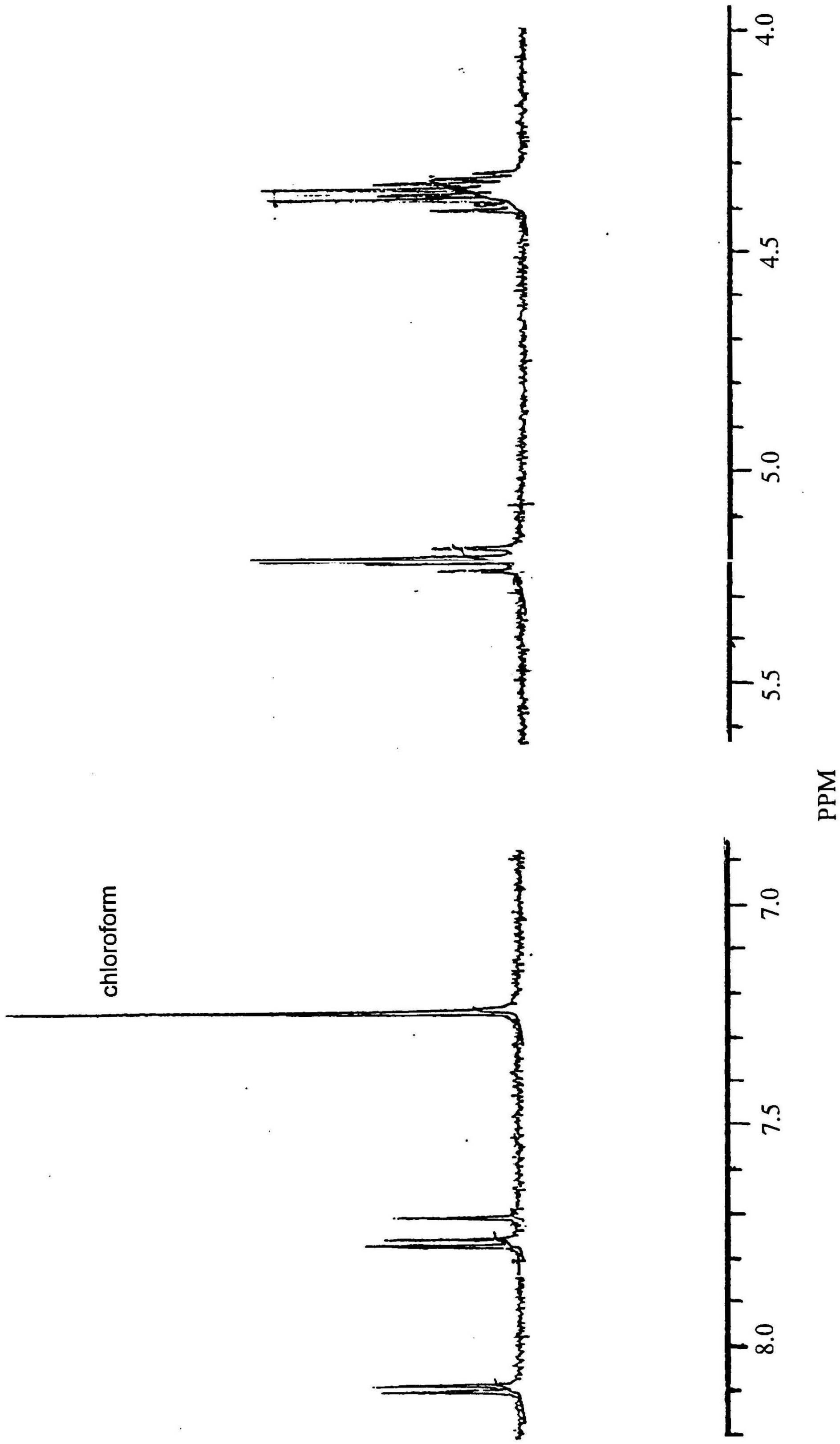


(a)



(b)

Figure 4.11 Thienyl and Methylene Regions in the ^{1}H NMR Spectra of (a) Cr{C(OEt)C_4H_2S-3-[2,5-{C(S)OEt}$_2$$C_4HS$}$_2$]}(CO)$_5$ and (b) Cr{C(OEt)C_4H_2S-3-[2,5-{C(O)OEt}$_2$$C_4HS$}$_2$]}(CO)$_5$

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(b) ^{13}C NMR Spectroscopy

A ^{13}C NMR spectrum of any significance could be obtained for complex **20** only. The data are as follows:
C(carbene): 319.9; C(*trans* carbonyl): 223.5; C(*cis* carbonyl): 216.6; C(thiocarbonyl): 182.0.
Thiophene carbon atoms: C2: 158.3; Others: C3, C4, C5, C2′, C3′, C4′, C5′: 130.9, 131.0, 131.2, 139.3, 149.4, 149.5.
Methylene and methyl carbon atoms:
Carbene ethoxy group: CH_2: 77.4; CH_3: 15.1.
2 x Thiocarboxylate group: CH_2: 67.9; CH_3: 13.7.

The chemical shift for the carbene carbon atom is similar in the spectra of **A** and **16**, either of which also contains one carbene functionality only.

The chemical shifts of the thiophene carbon atoms appear in the range of 130.9 to 158.3 ppm. The chemical shifts of C2 in the spectra of complexes **1** and **A** differ only slightly from that in the spectrum of **20**, in appearing only a little further upfield. The chemical shift of C5, (when 149.5 is assigned), is downfield from the corresponding resonance in the spectrum of **A**.

The chemical shifts for the methylene- and methyl carbon atoms in the ethoxy group of the carbene moiety are the same in the spectrum of **20**, compared to the corresponding chemical shifts in the spectra of **1**, **A** and **16**.

As expected the chemical shifts for the methylene- and methyl carbon atoms of the ethoxy group of the (ethoxythiocarboxylate) substituents appear upfield from those of the ethoxy group of the carbene moiety. These chemical shifts are downfield from those for the ethoxy carbon atoms of the *O*-ethyl carboxylate group in the spectrum of **16** and support the ^{1}H NMR data. This fact has already generally been established on comparing the spectra of complexes **17**, **18** and **24** to those of complexes **21**, **22** and **25**.

The chemical shift of the C=S group appears at 182.0 ppm in the spectrum of complex **20**, which is similar to the chemical shifts in the spectra of **21** and **25**.

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(c) Infrared Spectroscopy

The infrared data for complexes **20** and **23** are summarized in Table 4.11. A well resolved spectrum for **23** could be obtained in hexane only. These stretching frequencies are very similar to those observed in the spectrum of **1**.

Table 4.11 Infrared Data of the Dithienyl Carbene Complexes with Carboxylate or Thiocarboxylate Substituents

Assignment	**Complexes**	
	Stretching Vibrational Frequency, (νCO, cm^{-1})	
	20	**23**
$M(CO)_5$		
$A_1^{(1)}$	2059 2059	
B_1	1987 —	
E	1952 1945	
$A_1^{(2)}$	1952(sh) 1945(sh)	
C=O		n.o.
C=S	1278 1277	1263 1277
$M(CO)_2$		
A′		1906
A″		1859

First set of values recorded in hexane and a second set in dichloromethane

The wavenumbers of the carbonyl bands in the spectrum of **23** are much lower than for the corresponding biscarbene complex **3**, which is an indication that less electron density is removed by the single carbene ligand in complex **23**, compared to the two carbene-metal combinations in **3**.

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The wavenumber of the C=S band appears at 1278 cm^{-1} with hexane as solvent and at 1277 cm with dichloromethane as solvent in the spectrum of **20** and at 1263 cm^{-1} with hexane as solvent and at 1277 cm^{-1} with dichloromethane as solvent in the spectrum of **23**.

(d) Mass Spectroscopy

A molecular ion peak, M^+, was obtained from the spectra of **20** and **23**. The fragmentation patterns for the two complexes are similar. A similar route of fragmentation is observed for **20**and **23**. After the initial fragmentation of carbonyls three ethyl groups are lost in steps and lastly three carbonyl groups are lost from the compounds, (three steps in the spectrum of **20** and two steps in the spectrum of **23**. The most important peaks and fragment ions associated with these are summarized in Table 4.12.

Table 4.12 Fragment Ions and Peaks of the Dithienyl Carbene Complexes with Carboxylate or Thiocarboxylate Substituents

Complex	Fragment Ions; (%I)
20	590 (1) M^+; 450 (2) M^+ - 5 CO; 421 (2) M^+ - 5 CO - CH_2CH_3; 392 (3) M^+ - 5 CO - 2 CH_2CH_3; 363 (5) M^+ - 5 CO - 3 CH_2CH_3; 307 (9) M^+ - 7 CO - 3 CH_2CH_3; 279 (18) M^+ - 8 CO - 3 CH_2CH_3)
23	576 (10) M^+; 520 (1) M^+ - 2 CO; 491 (1) M^+ - 2 CO - CH_2CH_3; 433 (1) M^+ - 2 CO - 3 CH_2CH_3; 349 (2) M^+ - 5 CO - 3 CH_2CH_3

4.6.5 Spectroscopic Characterization of the Thienyl Carbene Complex containing a Carboxylate- and two Carbonyl Substituents

The numbering for the thiophene rings and carbon atoms are shown in Figure 4. 12.

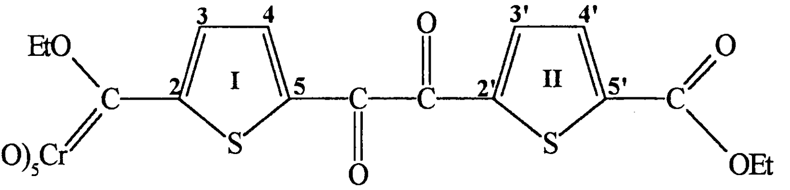

Figure 4.12 Ring- and Carbon Atom Numbering in 27

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(a) ^{1}H NMR Spectroscopy

The ^{1}H NMR spectrum of **27** is presented by Figure 4.14 and the chemical shifts (δ, ppm) with assignments are: H3 a doublet ($^3J_{H-H}$ = 4.4) at 8.16 ppm; H4 a doublet ($^3J_{H-H}$ = 4.4) at 7.36 ppm; H3' a doublet ($^3J_{H-H}$ = 3.9) at 7.32 ppm; H4' a doublet ($^3J_{H-H}$ = 4.0) at 7.71.
Methylene and methyl protons: Carbene ethoxy group: CH_2 a quartet ($^3J_{H-H}$ = 7.0) at 5.16; CH_3 a triplet ($^3J_{H-H}$ = 7.0) at 1.67.
O-ethyl carboxylate group: CH_2 a quartet ($^3J_{H-H}$ = 7.1) at 4.35; CH_3 a triplet ($^3J_{H-H}$ = 7.1) at 1.37.

The chemical shift of H3 of **27** appears downfield from where it is observed in the spectrum of **1**, but upfield from the position in the spectrum of **A**. The chemical shift of H4 on the other hand, also appears as a doublet at 7.36 ppm which is more upfield in the spectrum of **27** compared to where it is found in the spectrum of **1**, but downfield from the position in the spectrum of **A**. These results fall into the pattern now clearly established from the resonances of the thiophene protons. The biscarbene complexes cannot withdraw as much electron density per carbene unit from the thienyl substituent as a monocarbene thienyl complex. The combination of one carbene, (2-position), and one electron withdrawing substituent, (5-position), however, withdraws less charge than two carbene substituents, (2- and 5-positions) but more than one carbene unit without an electronwithdrawing substituent in the 5-position. The chemical shifts of H4' and H3' appear as doublets in the spectrum of **27**, the difference in chemical shifts can be attributed to the stronger withdrawing ability of the *O*-ethyl carboxylate group compared to a carbonyl bonded to C2'. The chemical shift for H4' compares favourably with the chemical shift of the corresponding proton, H4, in the spectrum of the *O*-ethyl carboxylate monocarbene complex **16**, which is an indication that these two protons are in similar environments and experience similar influences. Figure 4.13 shows two possible directions of electron flow in the ligand and the discontinuity of π-conjugation at the internal carbonyls. The more downfield chemical shift for H3 compared to H4', as well as for H4 compared to H3' clearly show that the metal carbene fuctionality withdraws more electron density from the ring and that the flow of electron density is better represented from the inside to the outside of the ligand (a) than from the outside to the centre of the ligand (b).

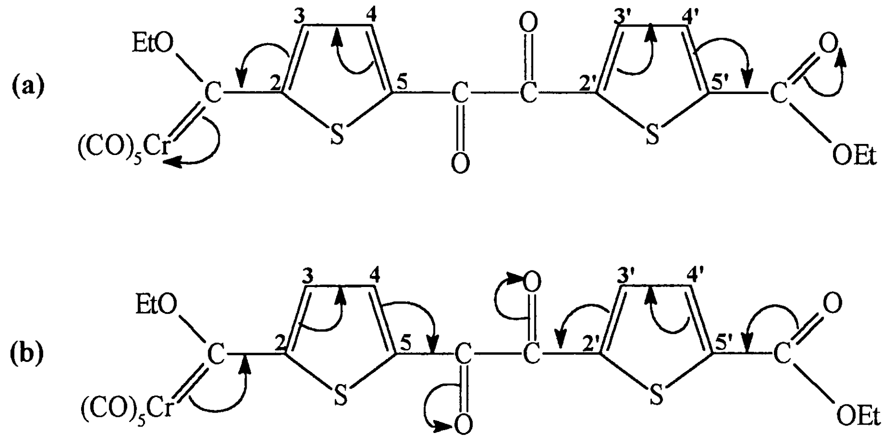

Figure 4.13 Possible Directions of Electron Flow in 27 by π-Resonance Effects

The methylene and methyl protons of the ethoxy group of the carbene moiety are practically the same as the corresponding chemical shifts in the spectra of **1** and **A**.

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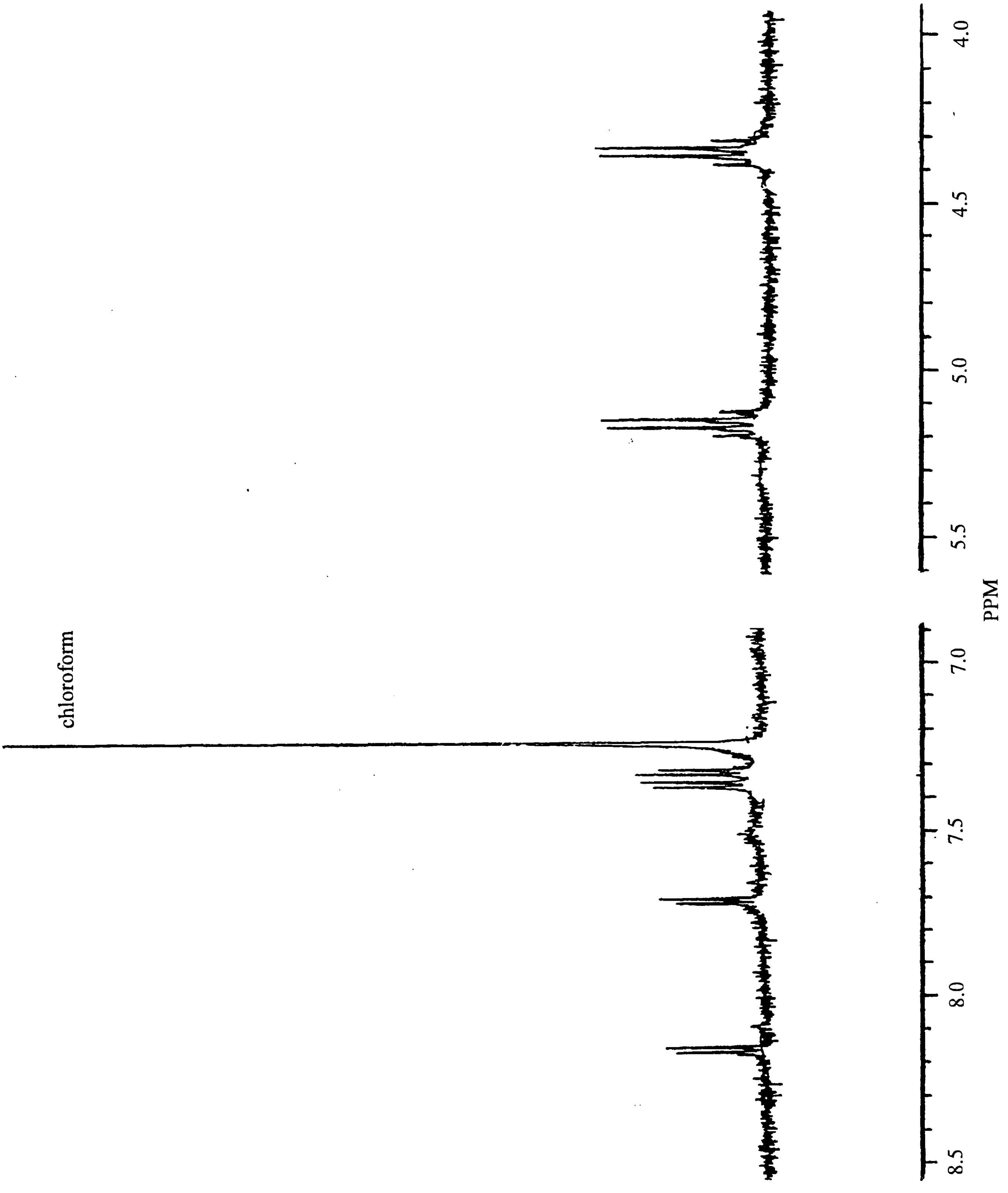

Figure 4.14 Thienyl and Methylene Regions in the ^{1}H NMR Spectrum of $Cr\{C(OEt)C_4H_2SC(O)C(O)C_4H_2SC(O)OEt\}(CO)_5$

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(b) ^{13}C NMR Spectroscopy

The ^{13}C NMR data (δ, ppm) of the monocarbene complex **27** are listed below:
C(carbene): 312.2; C(*trans* carbonyl) 223.0; C(*cis* carbonyl) 217.0; C(C(O)OEt) 207.1; 2 C=O: 184.0.
Thiophene carbon atoms: C2:153.0; Others: C3, C4, C5, C2′, C3′, C4′, C5′: 127.5, 128.5, 134.1, 145.0, 150.2.
Methylene- and Methyl carbon atoms:
Ethoxy group of carbene moiety: CH_2: 77.4;CH_3: 14.9.
Ethoxy group of *O*-ethyl carboxylate functionality: CH_2: 62.0; CH_3: 14.1.

The chemical shifts for the thiophene carbon atoms appear from 127.5 to 153.0 ppm. The resonances could, however, not be assigned unambiguously. The above assignments are based on previous related data that would lead to the following expected order of chemical shifts: C2 > C5' > C5 > C2'. The rest based on this are likely to have the following pattern: C3 > C4' > C4 > C3'. The assignment of resonances would thus be as follows: C2 > C5' > C5 > C2' > C3 > C4' > C4 > C3', with the greatest uncertainty lying in assigning the chemical shift values for the last four in the range.

The chemical shift for the carbene carbon atom appears upfield, in the spectrum of **27**, from the position in the spectrum of the biscarbene **1** and the monocarbene complex **A**. The chemical shifts of the carbonyl groups appear at virtually the same δ-values as in the spectrum of **1**. The chemical shifts for the C(O)OEt group in the spectrum of **27**, compares very favourable with the position in the spectrum of **16** which is indication that these groups are in similar environments experiencing similar influences.

The chemical shifts for the methylene- and methyl carbon atoms of the ethoxy groups are similar to the corresponding chemical shifts of these carbon atoms in the spectra of other thienyl carbene complexes.

(c) Mass Spectroscopy

A molecular ion peak, M^+, (542 (8 %), was obtained from the mass spectrum of **27**.

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4.7 Summary

An array of products, some of which expected and others not were isolated and characterized from this study. The enhanced activation associated with the two metal fragment biscarbene combination leads to new patterns of decomposition not observed in monocarbene chemistry.

One important observation made from the spectroscopic data of all of the products is the fact that the metal carbene functionality in these complexes drains more electron density from the thiophene ring than is withdrawn by the *O*-ethyl carboxylate or *O*-ethyl thiocarboxylate moieties. Another interesting observation is that the *O*-ethyl thiocarboxylate group in the thioester complexes in fact accommodates more electron density on the functional group compared to less electron density being present on the *O*-ethyl carboxylate substituent.

This study has also shown the high sensitivity encountred on altering the reaction conditions, eg. the temperature *i e* using different solvents with different boiling points and even a different atmosphere nitrogen compared to argon, leads to the formation of different products, specifically highlighted by **17** compared to **19**. Preventing the formation of **16**, **17**, **18** and **24** means working in an absolute oxygen free atmosphere, something not achievable on our systems. However the importance of the presence of these products in solution to initiate secondary reactions is clear.

The results have paved the way for further intensive studies under better controlled reaction conditions which would lead to the exploration of the potential of these and other σ, σ-bimetallic biscarbene complexes in the synthesis of new products, which could potentially act as building blocks in organic synthesis and as materials with exceptional conducting properties. The most important hurdle to overcome would be to get reactions reproduceable and to increase the yields of products.

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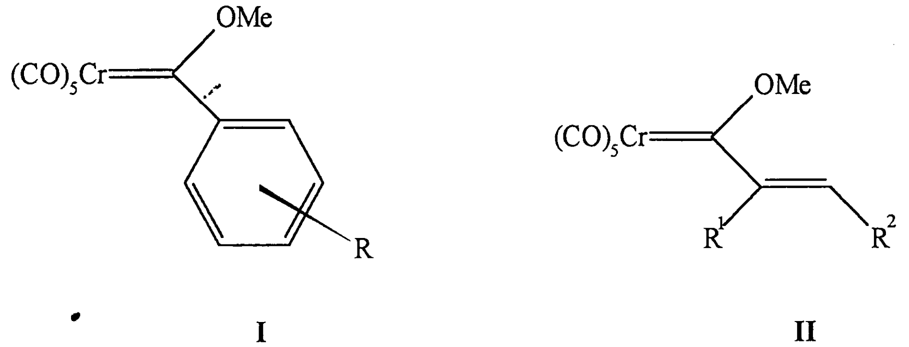
5 Reactions with Alkynes

5.1 Introduction

Fischer carbene complexes of the Group 6 metals are versatile reagents in organic synthesis and a dramatic increase in the interest in these reagents by synthetic organic chemists in recent years can be noted.[1, 2] One reaction of carbene complexes which has been most utilized in natural product synthesis to date is the benzannulation reaction. This reaction was first reported for an aryl complex[3] of the type **I**, (Figure 5.1) and depending on the reaction conditions can produce a number of different types of organic products, the most predominant of which is the naphthol species, which is accompanied in many cases by the indene as a by-product.[3, 4] The naphthol products have attracted the most attention to date in natural product synthesis[5] since they can be oxidatively converted to naphthoquinones, which are abundant molecular subunits of the bioscape. The annulations of alkenyl complexes of type **II**, (Figure 5.1), are more chemoselective, giving high selectivities for 4-methoxyphenol products, which have also been employed as key steps in natural product synthesis.[6]



I **II**

Figure 5.1 Transition Metal Carbene Complexes for Annulation Reactions

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5.2 Synthesis of π-Aromatic Systems

5.2.1 Formation of Naphthols by [3 + 2 + 1] Cycloaddition

Pentacarbonylchromium complexes with substituted phenyl-, naphthyl-, furyl-, thienyl- and cyclopentyl-carbene ligands react with various alkynes in a strongly stereoselective manner to give substituted naphthol, phenanthrene, benzofuran, benzothiophene and indene ligands π-coordinated to the tricarbonylchromium fragment.[3,7-9] Schematically these reactions could be reduced to a combination of the carbene ligand, a metal carbonyl ligand and the alkyne molecule used. The naphthol group and the alkoxy part (methoxy or ethoxy) originate from the carbene ligand. The alkyne is incorporated into the naphthol skeleton to yield the 2-alkyl compounds regiospecifically if unbranched 1-alkynes are used, Figure 5.2.

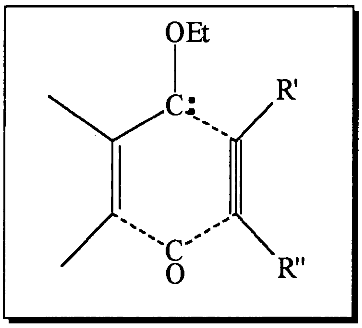
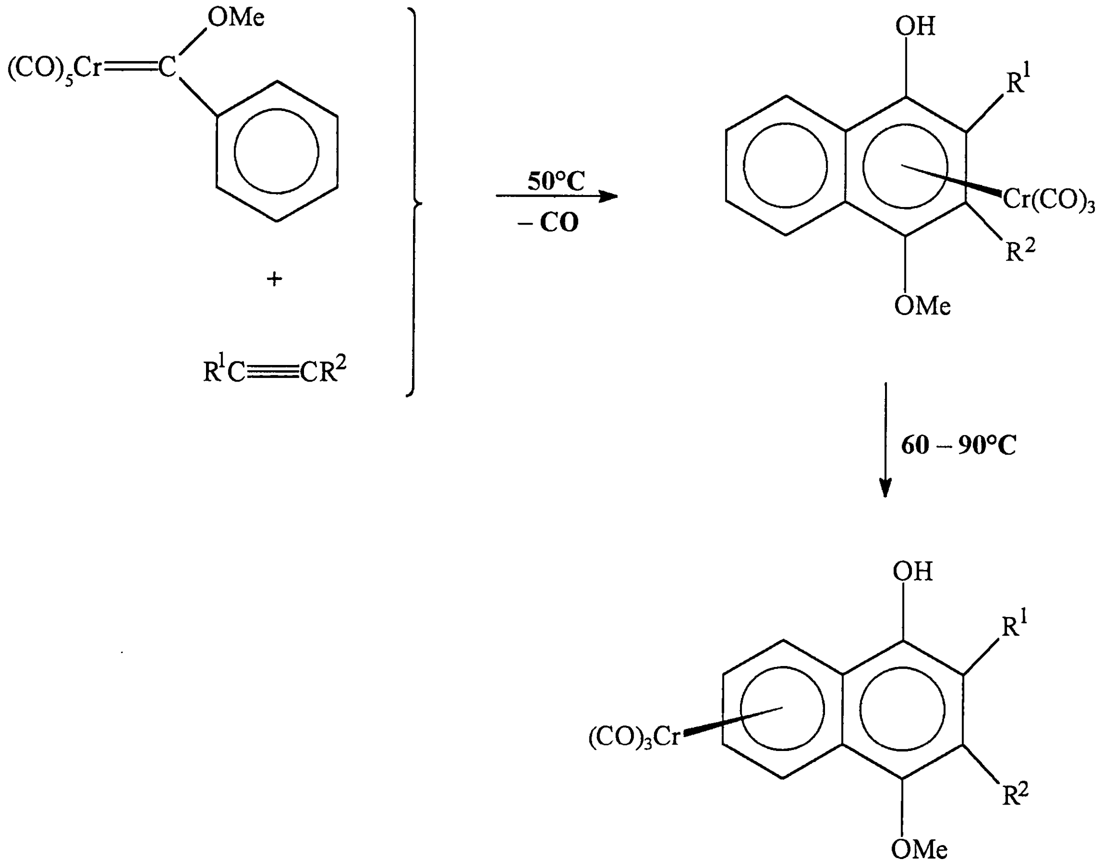


Figure 5.2 Components involved in Benzánnulation Connectivity

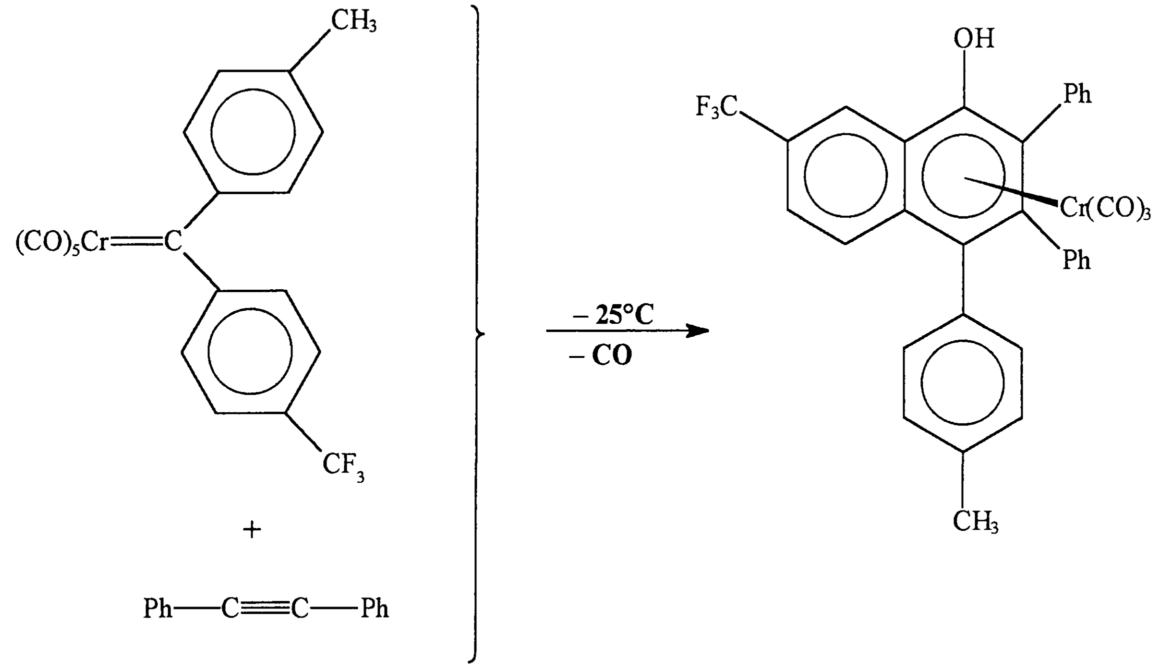
p-Substituted tolans, however, lead to the formation of both stereoisomers arising from a different orientation of the alkyne component.[9] If the reaction proceeds under kinetically controlled conditions the metal is π-coordinated exclusively to the substituted naphthol ring, on heating the chromium tricarbonyl fragment migrates to the unsubstituted naphthol ring to give the thermodynamically more stable isomers, Scheme 5.1. This reaction is generally known as the Dötz reaction because of his pionering studies in this area of carbene chemistry.



Scheme 5.1

Naphthol formation requires the presence of effective acceptor ligands in the carbene complex. If one carbonyl group is replaced with tri(*n*-butyl)phosphine the yields fall drastically even under more vigorous reaction conditions.[7]

The cyclization is favoured, if the electron deficiency at the carbene carbon atom is increased. Thus diaryl-carbene complexes are found to react at room temperature, even with acetylene and phenyl propynoic acid ester which fail to react with the carbene compound, $Cr\{C(OMe)C_6H_5\}(CO)_5$. Carbene complexes containing two different aromatic substituents have been used for competitive studies.[7] The annulation is favoured by electron accepting substitution of the aromatic group as shown for the *p*-tolyl(*p*-trifluoromethylphenyl)carbene complex, Scheme 5.2. Furthermore, phenyl rings are annulated in preference to furyl and naphthyl groups.



Scheme 5.2

It is known that carbene complexes can react with alkynes, by the insertion of the alkyne into the carbene bond.[2] This is the first step of the Dötz reaction which presumably proceeds *via* a four membered metallacycle. A neat example, Scheme 5.3, is found in the reaction of the methyl(methoxy)carbene complex with an excess of phenylacetylene.[10] This carbene precursor is not suited for a Dötz reaction and reacts in the first step to afford, after alkyne insertion, the new carbene complex which is suited for the Dötz reaction and, in fact, reacts with a second alkyne molecule in a Dötz reaction.

Based on the result of a kinetic study[11] and on activation parameters similar to those for dissociative ligand substitution reactions of carbene complexes, the suggested mechanism for the Dötz reaction involves: **(i)** the initial loss of a CO ligand, **(ii)** the coordination of the alkyne, **(iii)** formation of a four membered metallacycle, **(iv)** insertion of the alkyne and formation of a new less stable carbene complex, **(v)** carbonyl insertion and changing of the coordnation mode from σ to π, **(vi)** cyclization and **(vii)** keto-enol tautomerization to afford aromaticity in a six membered ring. The steps **(i)** - **(v)** presumably occur within the coordination sphere of the metal, which is believed to act as a template holding the reactants in a position favourable for cyclization. This idea is supported by the formation of the thermodinamically less stable product under kinetically controlled conditions and by the fact that chromium cannot be replaced by molybdenum or tungsten in these reactions.[12]

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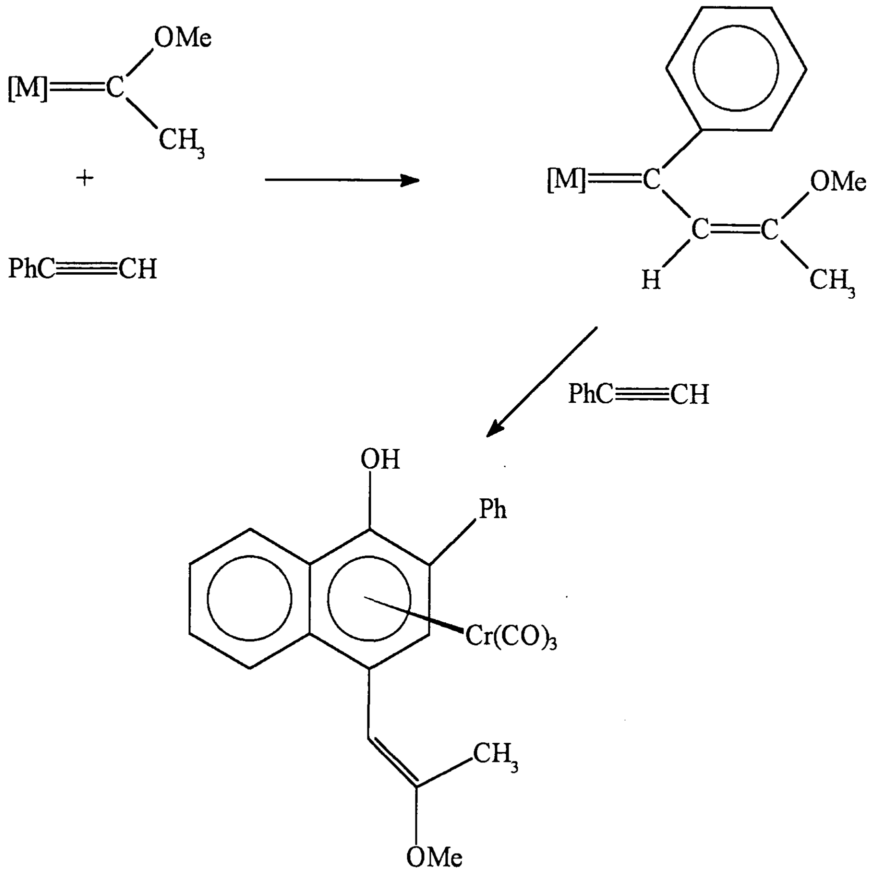

Scheme 5.3

5.2.2 Formation of Indenes by [2 + 3] Cycloaddition

In special cases phenylcarbene ligands can be annulated by alkynes to give indenes. The first example of this type of reaction was the reaction of the carbene complex, $(CO)_5CrC(OMe)Ph$, with tolane in a poorly coordinating solvent.[13] In addition to other products such as naphthohydroquinone derivatives and furan derivatives, the indene which is the formal [2 + 3] cycloadduct of the alkyne and the carbene ligand, is formed. This reaction is carried out selectively if the chromium compound is replaced by the analogous tungsten complex.[14] In this case the stronger metal-carbonyl bond (ΔHW-CO = 178 kJ mole^{-1} compared to ΔHCr-CO = 108 kJ mole^{-1})[15] inhibits the insertion of carbon monoxide into the reaction product, Figure 5.3.

The formation of the indene skeleton could take place *via* insertion of the alkyne into the metal-carbene bond. Such a reaction sequence has been demonstrated for nucleophilic alkynes. Ynamines and ynyl ethers add to the carbene carbon and are inserted into the metal-carbene bond, possibly *via* a four

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membered metallacycle.[16, 17, 18] The course of the reaction is better controlled if freedom of motion of the alkenyl chain is restricted by coordination to the metal. This is clearly demonstrated by the example of an ynediamine, which undergoes 1,3-addition to the phenylcarbene ligand, forming the diamino-indene complex *via* insoluble intermediates, the course of the reaction being temperature controlled.[19, 20]

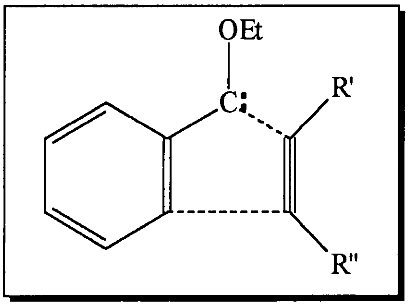
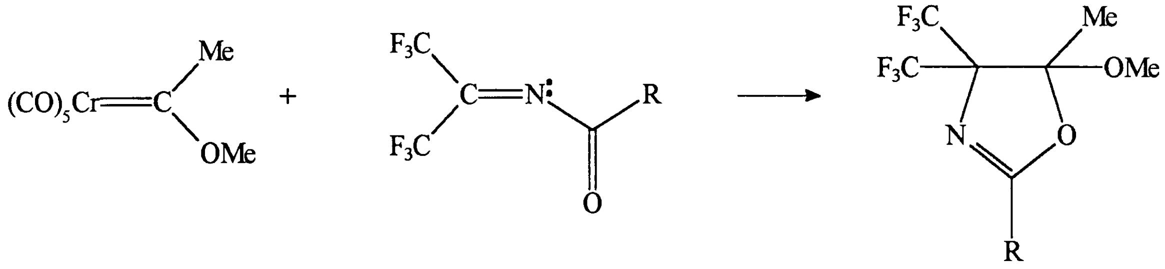


Figure 5.3 Components involved in Indene Connectivity

Heteroatom-substituted alkynes such as bis(diethylamino)acetylene or bis(trimethylsilyl)acetylene react with {phenyl(methoxy)carbene}pentacarbonylchromium to form either indene or naphthol π-complexes, (with a stable silyl-substituted vinylketene group on the naphthol frame).[14] The naphthol ligands can be released from the metal either by ligand substitution using carbon monoxide or by oxidation.[13]

5.2.3 Formation of Heterocycles by [4 + 1] Cycloaddition

N-Alkylideneamides react with alkoxy- and aminocarbene ligands, similarly as with carbenes of isocyanides to yield dihyrooxazoles[1c], as shown by Scheme 5.4.



Scheme 5.4

5.3 Synthesis of Natural Products

The simple preparation of alkoxycarbene carbonyl complexes, the easy manipulation and the possibility of functionalizing these, make these reagents of interest in natural product synthesis. The examples so far known are based on the electrophilicity of the carbene carbon atom, on the one hand and on the cycloaddition of alkyne, carbene and carbonyl ligands to form the hydroquinone skeleton on the other. These alkoxy-carbene carbonyl complexes are employed in the synthesis of peptides, vitamins like Vitamins K and E, as well as, that of antibiotics.[21]

5.3.1 Synthesis of Peptides

The smooth aminolysis of alkoxycarbene complexes was the impetus for the use of the "metalcarbenyl" function as a protecting group in the synthesis of peptides. Similarly to primary or secondary amines, amino acid esters react with methoxycarbene pentacarbonyl complexes of chromium and tungsten to give aminocarbene complexes.[22, 23] Owing to the nucleophilicity of carboxylate ions, the amino acids have to be protected by esterification. In order to form the peptide bond, the conventional method is used, namely saponification of the ester followed by coupling of the second amino acid ester component in the presence of dicylohexylcarbodiimide / *N*-hydroxysuccinimide.[24] The cleavage of the amino protecting group is accomplished under mild conditions at 20 °C with trifluoroacetic acid. This step proceeds most cleanly with phenylcarbene chromium complexes.

5.3.2 Synthesis of Vitamins K and E

The conventional synthesis of vitamins K 100 and E 101 is based on the condensation of isoprenoid alcohols with hydroquinones.[25] A carbene-complex route, on the other hand, to these compounds aims at the formation of the hydroquinone ring within the coordination sphere of chromium.[26] The synthesis of the K series starts with the phenylmethoxy carbene complex, $(CO)_5Cr\{C(OMe)C_6H_5\}$, and enynes. Under the reaction conditions used the cycloaddition takes place with retention of configuration, which is important insofar as only the *E* isomer of vitamin K1(120), the most important K vitamin, is biologically active.[27]

Vitamin E can also be synthesised according to a similar reaction sequence. A suitable starting material is the *E*-2-butenylcarbene complex $(CO)_5CrC(OMe)CH{=}CH_2$.[28]

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5.3.3 Synthesis of Antibiotics

The naphthoquinone skeleton appears as a part of the structure of a series of antibiotics. A carbene-complex route to this compound is based on two key reactions: the formation of the quinone ring by a cycloaddition reaction and the intramolecular alkoxy carbonylation of a hydroxy alkene to give the oxygen containing heterocycle.[3]

5.4 Aim of the study

The potential of bimetallic thiophene biscarbene complexes to yield new, novel organic compounds and complexes in their reaction with alkynes was investigated. The reaction of Ph-C≡C-Ph with monocarbene complexes, has already extensively been investigated, it was therefore deemed of interest to exploit and extend the reaction by using biscarbene complexes. Two objectives which came to mind were firstly to see whether different products would be formed due to the influence of the second carbene functionality, and secondly to test the influence of the sulphur in the heterocycle on product formation.

In a brief report the reactions of the thienyl monocarbene complex of chromium, $Cr\{C(OMe)C_4H_3S\}$-$(CO)_5$, with pentyne and diphenyl etyne have been recorded.[7] The products are shown in Figure 5.4 for R′ and R″, Ph, Ph and n-C_3H_7, H, respectively and are representative of the expected products *via* a [3 + 2+ 1] cycloaddition process according to the Dötz reaction. On heating no migration of the $Cr(CO)_3$-fragment to the thiophene ring was observed.

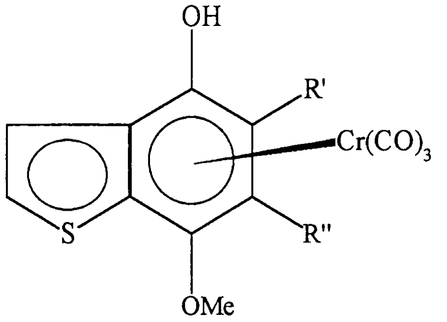

Figure 5.4 Products of Reaction of $(CO)_5Cr\{C(OMe)C_4H_3S\}$ with Alkynes

Also, if the reaction would proceed further than with one carbene functionality only, interesting synthetic possiblities would be provided, eg. the formation of condensed rings on either side of an unsaturated aromatic substituent. An interesting possibility would be the formation of the product **III**, Figure 5.5,

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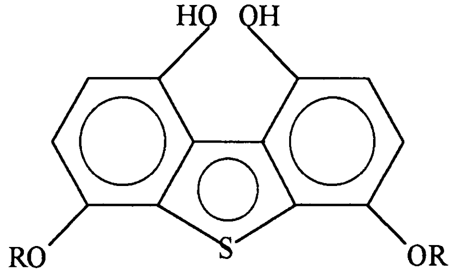
which has two hydroxy substituents in close proximity which may lead to water elimination and the formation of a back to back thiophene and furan ring as part of a condensed ring system.



III

Figure 5.5 Possible Product containing a Condensed Ring System

Further the possiblity of preparing σ,π-bimetallic complexes along this route was investigated, as well as, the preparation of π,π-bimetallic complexes. In Chapter 3 the synthesis of σ,π bimetallic monocarbene complexes was discussed and their scarcity was emphasized. Assuming that the Dötz reaction only occurs at one carbene unit and that the expected π-coordination of $Cr(CO)_3$ is found, it will be another synthetic method to σ,π-bimetallic monocarbene complexes, **IV**, Figure 5.6. On the other hand, if both carbene units are active and afford [3 + 2 + 1] cycloaddition reaction products, and the $Cr(CO)_3$ fragments stay π-coordinated, bimetallic complexes (**V**), Figure 5.6, with a novel π, π-bridging ligand could be isolated. With this background, a study of the reaction of the biscarbene complexes **1** and **2** was deemed worthwhile, promised novel reaction routes and as exciting results were anticipated, was thus undertaken.

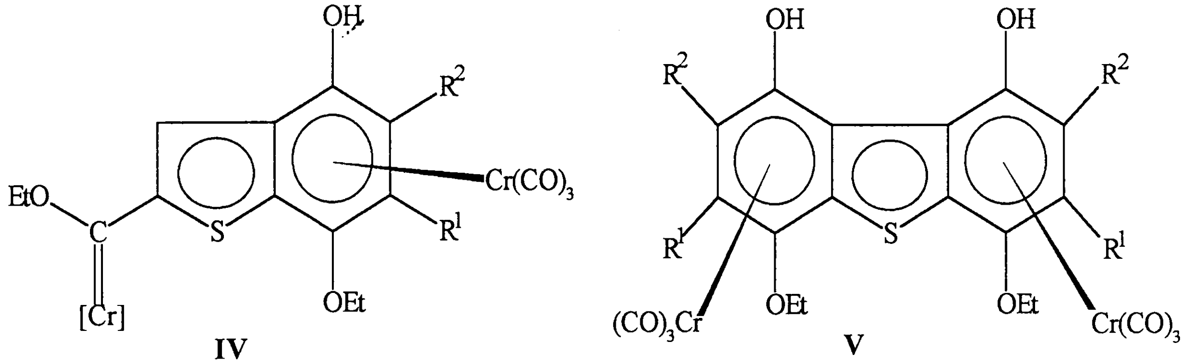


Figure 5.6 Possible σ,π- and π, π- Monocarbene Complexes

5.5 Reactions of Bimetallic Thienylene Biscarbene Complexes with Alkynes

The biscarbene complexes **1** and **2** were reacted with the two alkynes, hex-3-yne and biphenyl acetylene.

5.5.1 Reactions with Hex-3-yne

The chromuim thienylene biscarbene complex **1** was dissolved in THF and two equivalents of hex-3-yne was added. The reaction mixture was refluxed for a short time and only one reaction product **28** and one decomposition product, **16** were afforded. The analogous tungsten biscarbene complex **2** on the other hand had to be dissolved in toluene, which has a higher boiling point than THF, to afford the corresponding products **29** and **17**.

The formation of complexes **28** and **29** is attributed to the same reaction route, see Scheme 5.5. The mechanism, based on the mechanism proposed for the Dötz reaction, involves **(i)** a primary CO elimination process to afford a vacant coordination site on the metal to which the alkyne is bonded in a π-fashion, thereby leading to the formation of a *cis*-alkynecarbene complex. In step **(ii)** interligand carbon-carbon bond formation between the alkyne and the metal-carbene bond yields a metallacyclobutene, which is expected to be in equilibrium with its ring-opened product. The opening of the ring **(iii)** affords a new biscarbene complex of higher reactivity. Carbonylation **(iv)** of the alkenylcarbene carbon atom by an inserted CO ligand leads to a vinyl ketene system which is kept in *s-cis* conformation by a diene-like coordination to the metal, this should be regarded as the key intermediate in the reaction of carbonylcarbene complexes with alkynes. **(v)** Cyclization of the vinyl ketene species, involving one of the thiophene double bonds, affords a metal-coordinated bicyclic cyclohexadienone which after keto-to-enol tautomerization affords the benzothienyl products **28** and **29**, $\mathrm{M\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5}$, (M = Cr **(28)** ,M = W **(29)**).

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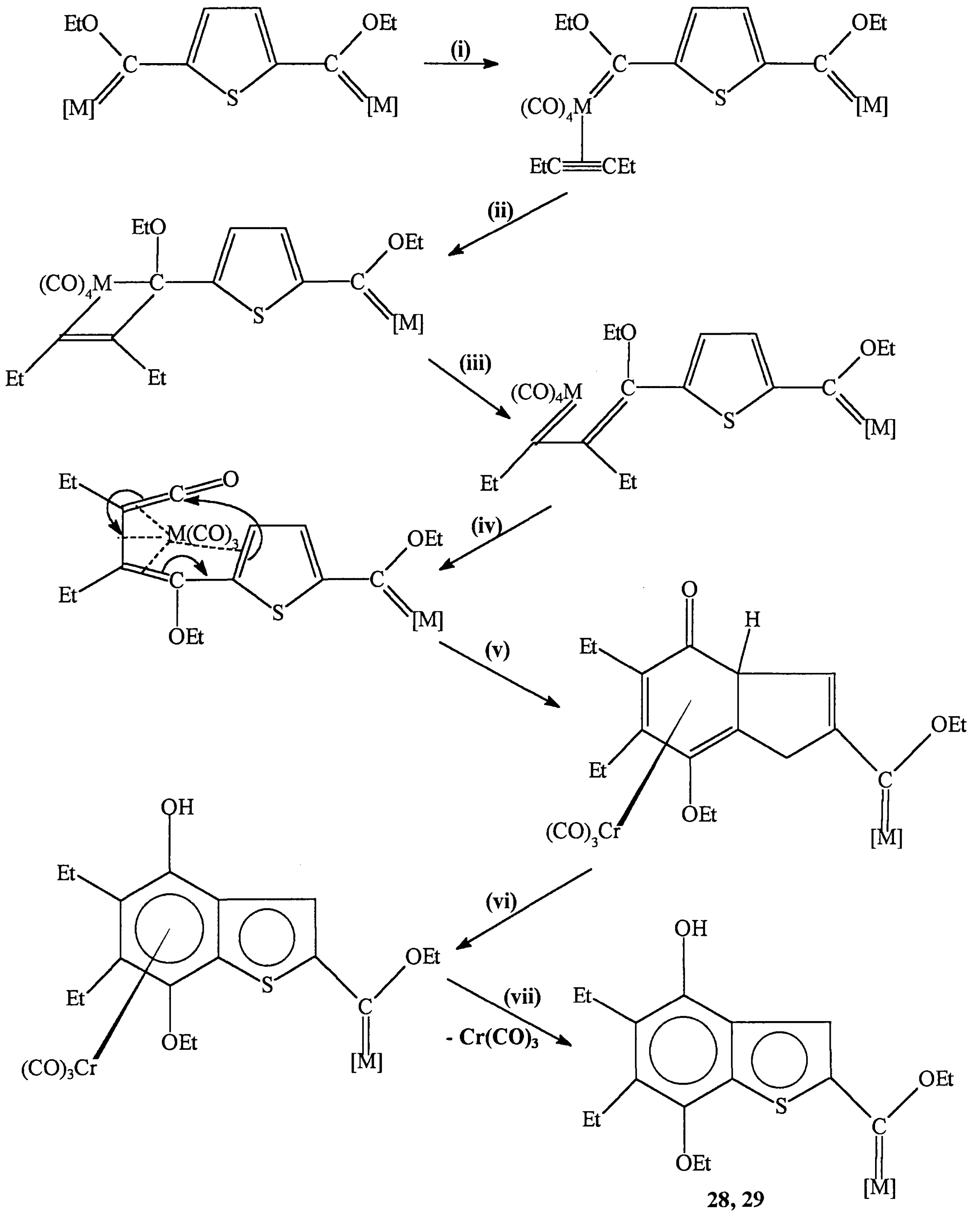

28, 29

[M] = $Cr(CO)_5$ or $W(CO)_5$

Scheme 5.5

Two aspects of great importance are the following, the first concerning the absence of a π-coordinated

$M(CO)_3$-fragment and the second the fact that similar products were obtained for $W(CO)_6$ and $Cr(CO)_6$. The instability of σ, π-bimetallic monocarbene complexes (see Chapter 3) is presumed to be the main reason why no π-bonded complexes containing a $M(CO)_3$-fragment bonded in a π-fashion to the phenyl- or thiophene ring could be isolated. In addition, it was shown that $Cr(CO)_3$ would migrate from the highly substituted naphthol ring, which is a poorer π-donor ligand, to the unsubstituted ring when heated.[9, 11] In this case, it will mean that the $Cr(CO)_3$-fragment will migrate to a thiophene ring which is known to be, compared to benzene, bonded much weaker in π-complexes to $Cr(CO)_3$. No complexes of the type (π-thiophene)$W(CO)_3$ are known to have been prepared. On the other hand σ, π bimetallic complexes of benzothiophene were synthesized and found to be of reasonable stability for chromium. More interesting is the fact that also for W a similar benzothiophene product was obtained which is uncommon for naphthol formation.[14, 15]

Of academic interest is a route whereby the metallacyclobutane intermediate inserts a carbonyl under thermal conditions to give a metallacyclopentanone species. This route places less emphasis on π-coordination of a metal fragment during conversions. Formally the five membered metallacycle affords an intermediate which is coordinatively unsaturated, see Scheme 5.6, and CH activation **(i)** of the thiophene C3-H3 bond may assist in the transfer of a proton to the ketone function **(ii)** forming a seven membered ring with an enol group attached to the tungsten. The final product **29** is formed directly on reductive elimination **(iii)** leading to cyclization. However carbonyl insertion under normal reaction conditions is inhibited for tungsten intermediates and pentene ring formation generally takes preference.

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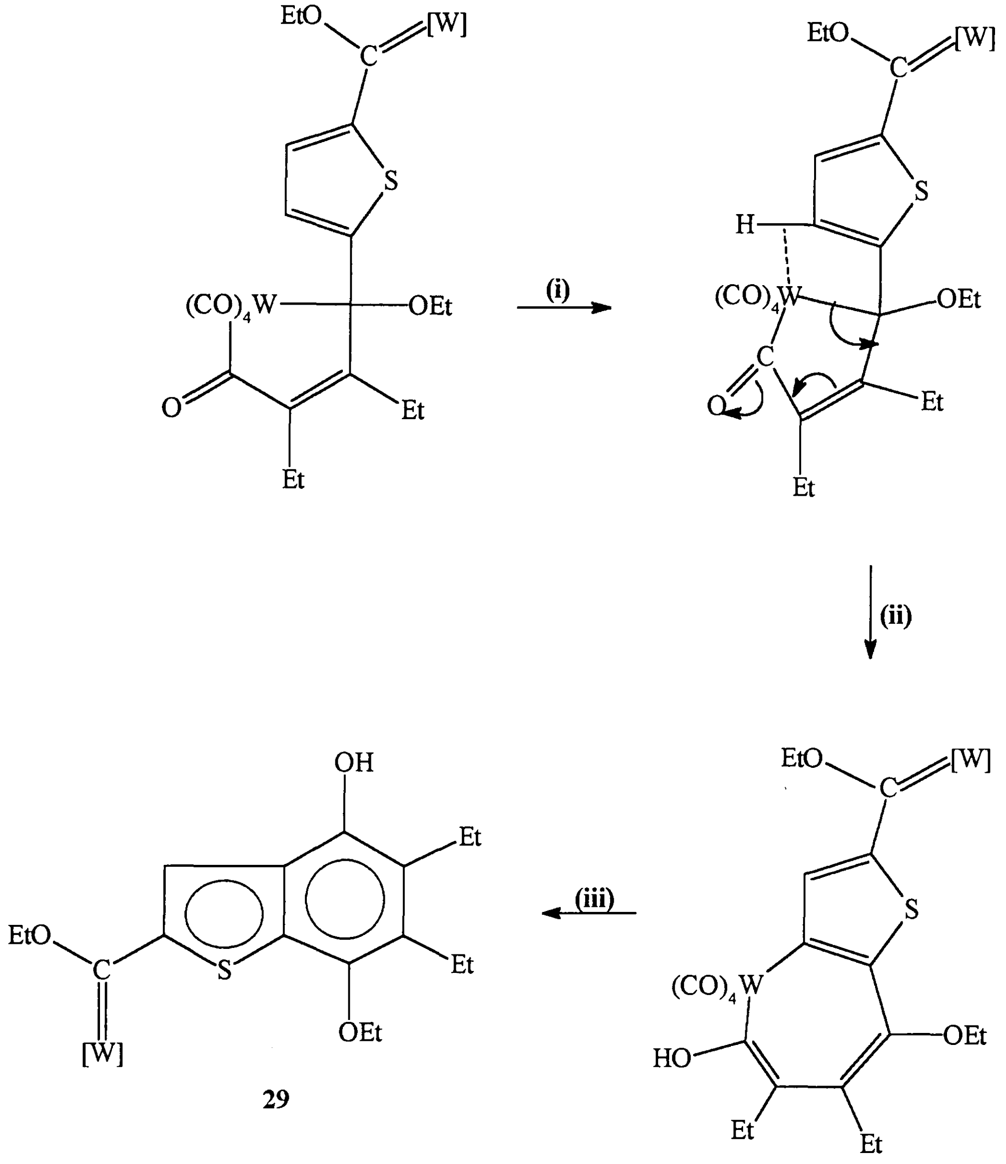

[W] = W(CO)$_5$

Scheme 5.6

A longer reaction time, as well as, higher temperature are required for the formation of complex **29** than for the formation of complex **28**. The reason for this being that more energy is required to labilize the stronger W-CO bonds.[15] Under these conditions decomposition to **17** is also favoured, thus leading to lower yields of **29** compared to **28**.

Complexes **28** and **29** were found to be stable in the solid state, as well as, in solution, in fact the pro-

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longed exposure of solutions to air proved these complexes to be extremely stable and not to be oxidized to yield the organic derivatives. The addition of two more equivalents of the alkyne, hex-3-yne to **28** and **29** afforded a mixture of decomposition products of which a sufficient amount of none could be isolated for full characterization. Therefore, eventhough the biscarbene complexes **1** and **2** are more reactive, the resulting monocarbene complexes **28** and **29** are less reactive towards hex-3-yne. This was a discouraging observation and shattered hopes of incorporating the heteroaromatic ring between two six membered rings. Crystallization of both complexes was attempted in mixtures of dichloromethane and hexane of various ratios, however, to no avail. Contrary to observations by Wulff and co-workers[5d] of the reaction between $(CO)_5Cr\{C(OMe)Ph\}$and $EtC\equiv CEt$ the analogous product with a butenone ring was not found in the analogous reaction of **1** and **2** with this alkyne, see Figure 5.7.

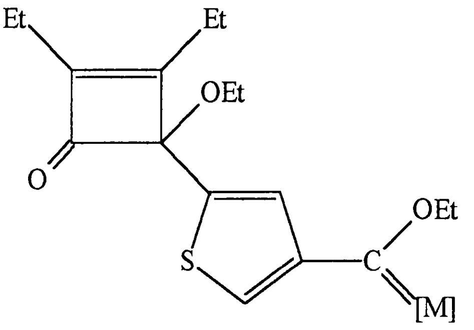

Figure 5.7 Butenone Monocarbene Complex

The formation and characterization of complexes **16** and **17** were reported in Chapter 4, § 4.3 and 4.6.1. These products do not promote alkyne insertion and no reactivity was observed. Also, oxidized products, Figure 5.8 were not screened for as no effort was made to positively oxidize metals and study organic fragments.

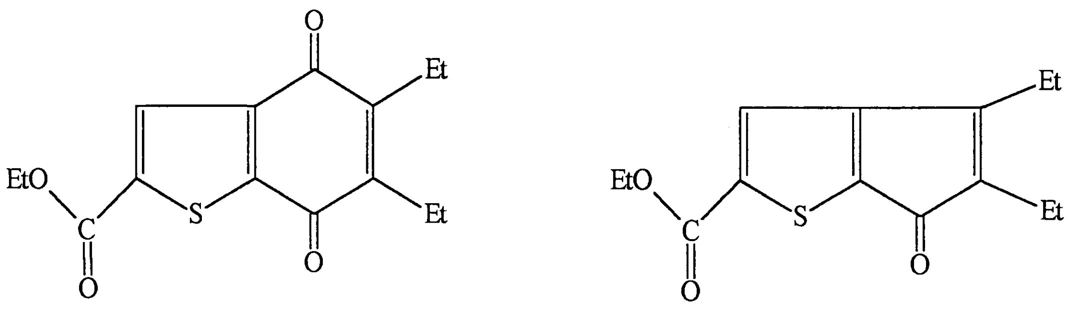

Figure 5.8 Oxidized Products

5.5.2 Reactions with Biphenyl Acetylene

The chromium thiophene biscarbene complex **1** was dissolved in THF, whereas the corresponding tungsten analogue **2** again had to be dissolved in toluene. The reaction of complex **2** with two equivalents of biphenyl acetylene afforded one significant product only, the cyclopentathienyl monocarbene complex, $W\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$, **(31)**, the formation of which took much longer than that of the analogous chromium complex, $Cr\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$, **(30)**. In solution an equilibrium exists between the isomeric forms **30a** and **30b**, as well as between **31a** and **31b**, Scheme 5.8.

The reaction of complex **1** afforded, in addition to the cyclopentathienyl monocarbene complex **30**, the intermediate, $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)C(Ph)C(Ph)\}Cr(CO)_5$, **(32)** into which the alkyne has been inserted, to give a new biscarbene complex, a benzothienyl complex $\{\eta^1:\eta^6$-$SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3$, **(33)** in which a π-bonded $Cr(CO)_3$-fragment is bonded alternatively to both unsaturated rings, when exposed to air this product converted to the monocarbene complex, $Cr\{C(OEt)CCHCC(OH)C(Ph)C(Ph)C(OEt)CS\}(CO)_5$, **(34)** from which the π-bonded fragment is absent, Scheme 5.9.

The formation of the complexes **30** and **31** proceeds according to the following postulated reaction pathway, shown in Scheme 5.7. The process begins with a primary CO elimination after which the alkyne enters the vacant coordination site leading to formation of the *cis*-alkynecarbene complex. The reaction route is thus the same as that suggested for the formation of the benzothienyl complexes **28** and **29**, up to the step where the four membered metallacycle is formed, as shown in Scheme 5.5. These complexes are the formal cycloaddition products of the alkyne and the carbene ligands. The formation of the skeleton thus also takes place by the insertion of the alkyne into the metal-carbene bond *via* a four-membered metallacycle. The newly formed carbene ligand is then cyclized into a cyclic metallahexadiene which after the subsequent reductive elimination affords the cyclopentathienyl skeleton. In these instances no carbonyl insertion is found and five membered ring formation is in competition with insertion and phenol formation. Complexes **30a** and **31a** can then undergo either a 1,3-hydrogen shift to afford **30b** and **31b**, or a 1,2-hydrogen shift to give **30c** and **31c**. Complexes **30a-c** and **31a-c** are diffirent isomeric forms of which two co-exist in solution, Scheme 5.8.

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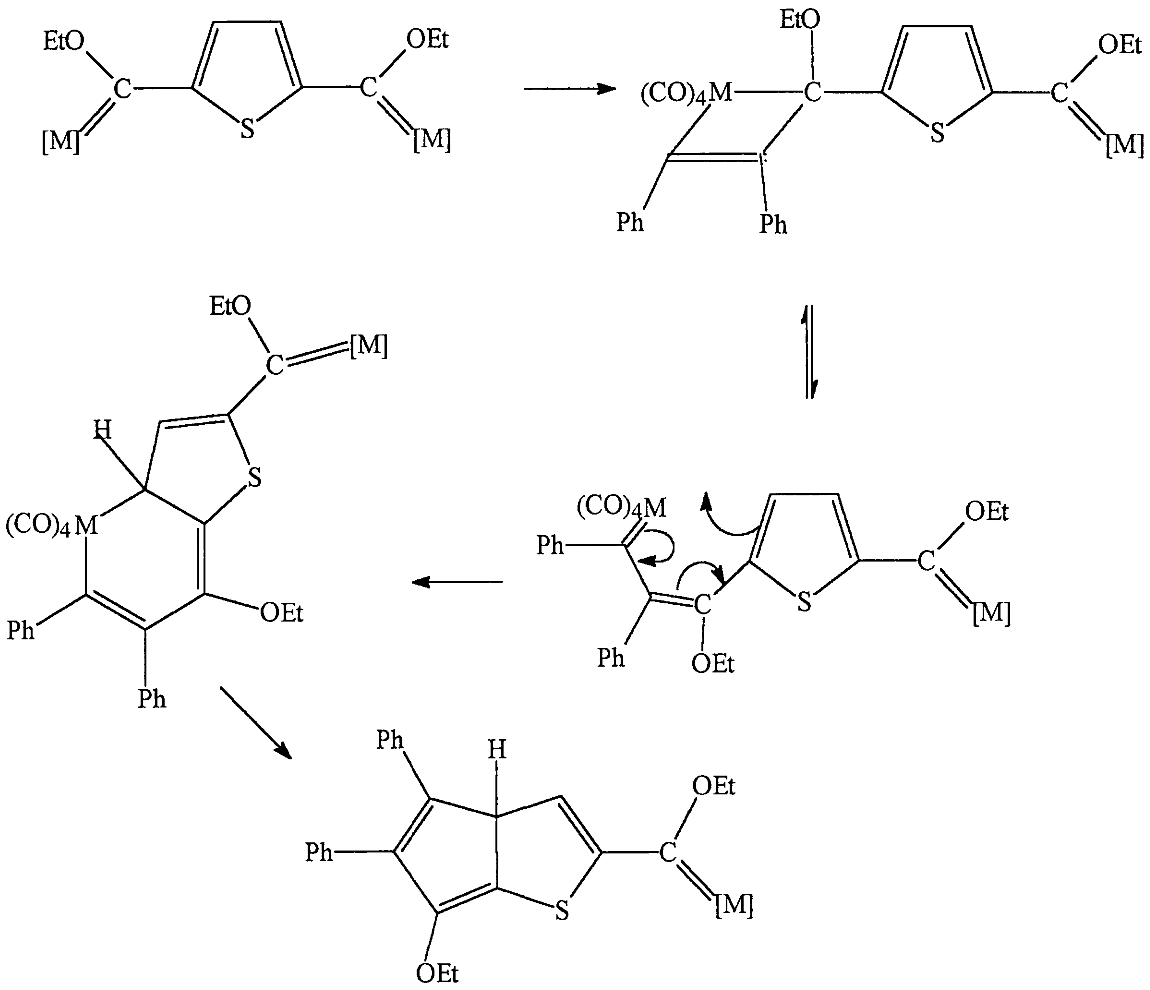
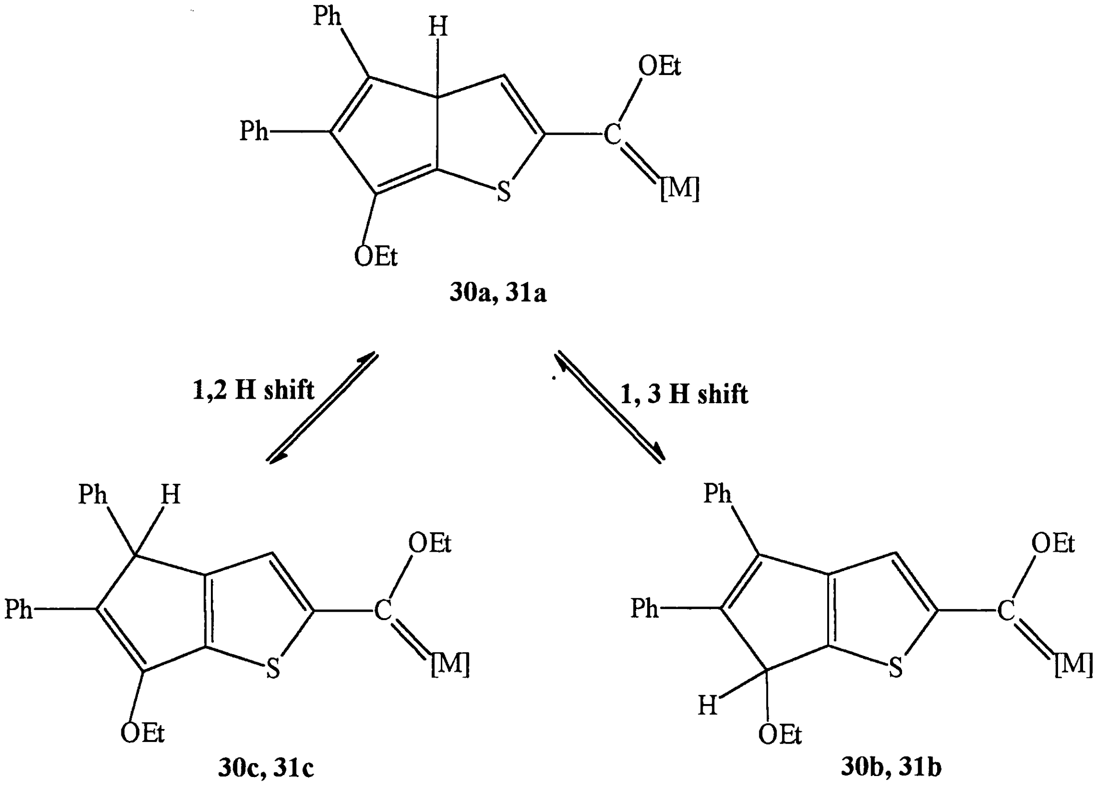


30a, 31a

[M] = $Cr(CO)_5$ or $W(CO)_5$

Scheme 5.7



[M] = $Cr(CO)_5$ or $W(CO)_5$

Scheme 5.8

The formation of **33**, also proceeds along the Dötz reaction pathway, described above, *via* the intermediate **32**, Scheme 5.9. It was possible to isolate and study a fraction from the column which could positively be identified by ^1H and ^{13}C NMR spectroscopy as containing the biscarbene, alkyne inserted, intermediate, **32**. This product converts to the σ,π-bimetallic complex **33a** which is the expected product from literature.[3, 7-9] In solution at room temperature migration to the thiophene ring to give **33b** was observed before fragmentation of the $Cr(CO)_3$ group from either **33b** or both to give the monocarbene **34**. Conversion occurs at room temperature and is indicative of the instability of the σ,π-bimetallic complexes which could only be identified in solution by NMR spectroscopy. By contrast, the corresponding σ,π-bimetallic complexes were not detected in the reaction with EtC≡CEt.

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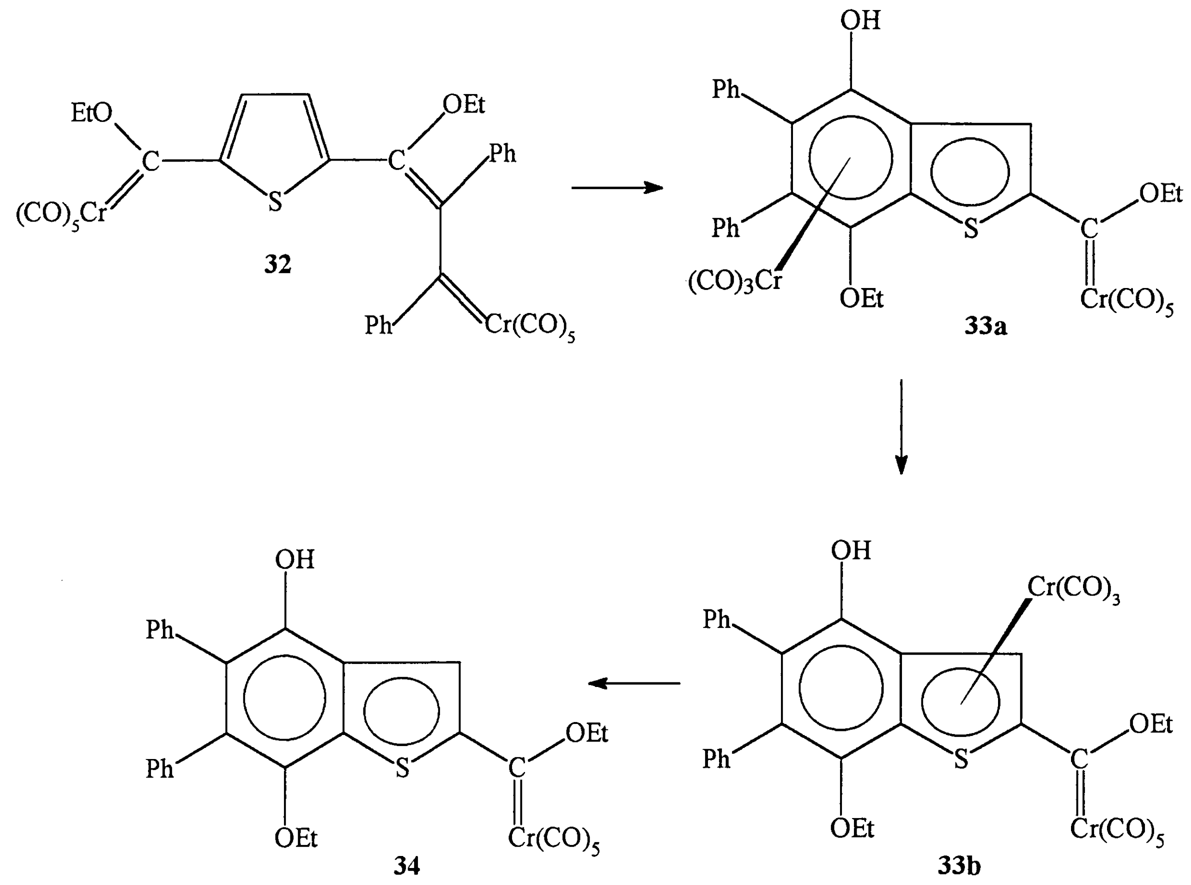

Scheme 5.9

The mechanistic scheme suggests the role of the metal as that of a template holding the building fragments together in a position favourable for carbon-carbon bond formation. Isolation of **32** indicates that this is an important intermediate. From here two possible routes exist, the cyclization, forming a metallacyclopentadiene to give **30a** or insertion of a carbonyl and π-coordination of $Cr(CO)_3$ to give **33**, Scheme 5.9. This idea is supported by the formation of the thermodinamically less stable product under kinetic control, as well as by the fact that chromium cannot be replaced by tungsten to give the same array of products in this reaction. Donor solvents such as THF are required to afford a clean reaction with overall yields of up to 90 %. The intermediacy of coordinatively unsaturated species may be held responsible for lowered product selectivity when a non-coordinating solvent is used. Although it is expected that the reaction in THF should afford virtually only **33**, the cyclopentathiophene derivative **30** was also isolated. This is the chromium analogue of the tungsten carbene complex, **31**, which was isolated as the only product from the reaction of **2** with the alkyne in toluene.

It is anticipated that the formation of the five membered frame for the W case leads to increased yields.

This is reflected by the 41 % yield of the tungsten complex **31** compared to a yield of 29 % for the chromium analogue **30**, due to the fact that more energy is required for the breaking of the stronger W-CO bond.

The π-bonded product **33a** and **33b** was stable in neither the solid nor liquid states and gradually converted to complex **34**. On exposing a solution of **33** in dichloromethane to air the same result was obtained, *i e* the formation of product **34**. Complex **34** remained stable in air even after the prolonged exposure (7 days and longer). The intermediate **32** was found to convert, in either the solid or liquid states, to the π-complex **33** and eventually **34**. Neither the intermediate, **32**, nor the π-coordinated complex **33a** or **33b** could be crystallized with success, as these complexes either interconverted or degraded to **34**.

5.6 Spectroscopic Characterization of the Products afforded by the Reactions with Alkynes

All of the products afforded by the reactions with the alkynes were spectroscopically characterized by ^{1}H NMR-, ^{13}C NMR-, and infrared spectroscopy. Significant mass spectra could be obtained for complexes **28** - **31**, only. The spectroscopic data led to the formulation of the various structures. All NMR spectra were recorded in $CDCl_3$ as deuterated solvent.

5.6.1 Characterization of the Benzothienyl Complexes, $M\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$, M = Cr, (28) and M = W, (29)

The data for the products isolated from the reaction of the biscarbene complexes **1** and **2** with hex-3-yne are summarized in Tables 5.1 - 5.3 and discussed in this section. Figure 5.9 shows the numbering of the carbon atoms of the rings in **28** and **29**, which corresponds with that of the benzothienyl monocarbene complexes in Chapter 3.

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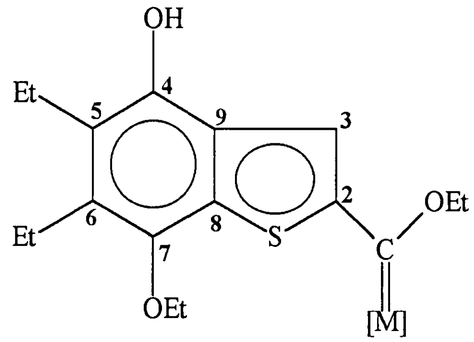

Figure 5.9 Numbering of Ring Carbon Atoms in 28 and 29

(a) ^{1}H NMR Spectroscopy

The ^{1}H NMR data of the monocarbene complexes **28** and **29** are summarized in Table 5.1. Figure 5.10 presents the thienyl and methylene regions in the ^{1}H NMR spectrum of **29**.

Table 5.1 ^{1}H NMR Data of the Benzothienyl Carbene Complexes

Assignment	**Complexes**			
	Chemical Shifts, (δ,ppm) and Coupling Constants, (J, Hz)			
	28		**29**	
Proton	δ	$^3J_{H-H}$	δ	$^3J_{H-H}$
H3	8.57 (s)		8.50 (s)	
OH	5.17 (s)		5.17 (s)	
O$\mathbf{CH_2}$$CH_3$ (carbene)	5.23 (q)	7.0	5.01 (q)	7.0
O$CH_2$$\mathbf{CH_3}$ (carbene)	1.70 (t)	7.0	1.68 (t)	7.1
O$\mathbf{CH_2}$$CH_3$	4.07 (q)	7.0	4.08 (q)	7.0
O$CH_2$$\mathbf{CH_3}$	1.46 (t)	7.0	1.46 (t)	7.0
2 x $\mathbf{CH_2}$$CH_3$	2.77 (q) 2.72 (q)	7.1 7.1	2.75 (q) 2.70 (q)	7.6 7.6
2 x $CH_2$$\mathbf{CH_3}$	1.22 (t) 1.18 (t)	7.2 7.2	1.20 (t) 1.16 (t)	7.5 7.5

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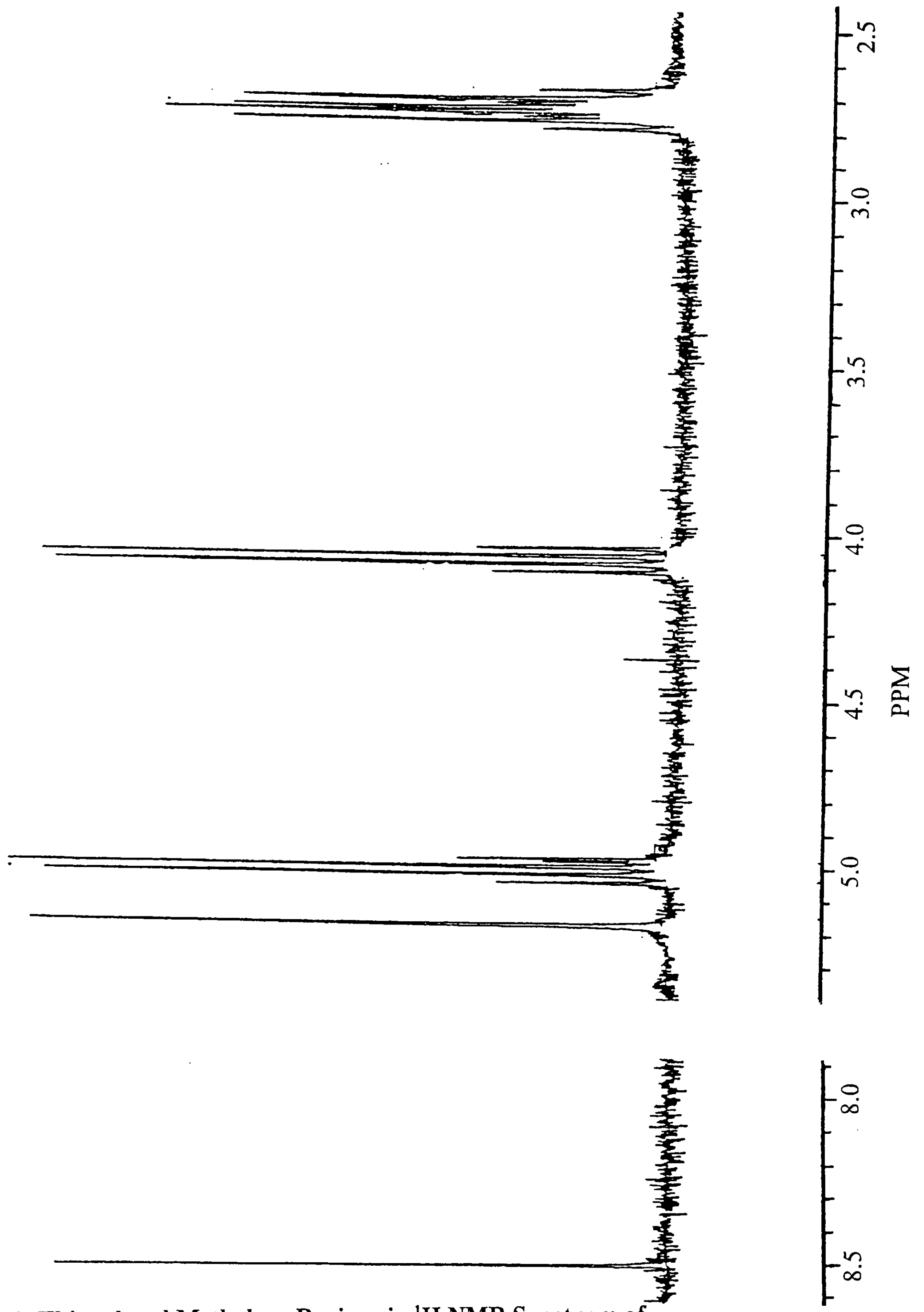

Figure 5.10 Thienyl and Methylene Regions in ^{1}H NMR Spectrum of $W\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$

As expected the chemical shift for the thiophene proton, H3, which appears as a singlet in the spectra of **28** and **29** are downfield from those in the spectrum of free thiophene, as well as, from those of the corresponding proton in the spectra of the monocarbenes **A** and **B** and biscarbenes **1** and **2**. This is an indication that more deshielding of this proton takes place in **28** and **29** than in the corresponding biscarbenes **1** and **2** and monocarbenes **A** and **B**. If the spectrum of the benzothiophene monocarbene complex, **14**, is considered, the chemical shift for H3 is downfield from that in the spectrum of **28**. This is an indication that the fused phenol ring system in **28** is able to delocalize electron density more effectively than the π-coordinated $Cr(CO)_3$-fragment in **14**. The chemical shift of H3 in the spectrum of **15**, on the other hand, has a δ-value closer to that in the spectrum of **28**.

Noteworthy is the chemical shift observed at 5.17 ppm as a singlet in the spectra of complexes **28** and **29**. These chemical shifts are assigned to the hydroxyl substituent of the six membered ring. Phenol protons have previously been observed to resonate in this region in the spectra of similar products.[7b] This chemical shift appears as a reasonably sharp signal in the spectra of **28** and **29**, which is an indication of the absence of a π-coordinated $Cr(CO)_3$-fragment, as the presence of this fragment would lead to a broader signal shifted further downfield (6.3 - 8.5 ppm).[7b]

The chemical shifts for the methylene and methyl protons of the ethoxy group of the carbene moiety of **28** and **29**, are virtually the same as those observed in the spectra of complexes **1** and **2**, respectively. A similar observation is made when these chemical shifts are compared to those in the spectra of the benzothienyl monocarbene complexes **14** and **15**. This confirms the observation made earlier that these chemical shifts are characteristic for a metal and ligand type and not markedly influenced by changes in substituents on ligands.

The chemical shifts for the methylene and methyl protons of the ethoxy substituent of the phenol ring also appear as quartets and triplets in the spectra of **28** and **29**, which are similar for the two compounds as these are subjected to similar environments with very little influence from the metal nucleus. These chemical shifts for the two ethyl substituents, on the other hand, appear further upfield, as two quartets and two triplets respectively, these different sets of quartets, as well as triplets which overlap, are the result of the slightly different environments experienced by the two ethyl groups. The ethyl group bonded to C5 experiences an influence from the adjacent hydroxyl group bonded to C4, whereas the one bonded to C6 experiences influences from the ethoxyl substituent. The absence of the electronegative oxygen atom which withdraws electron density from these protons leads to the increased shielding of the methylene protons and hence upfield chemical shifts of *ca* 1.3 ppm, compared to those observed for the ethoxy substituent.

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(b) ^{13}C NMR Spectroscopy

The ^{13}C NMR data of **28** and **29** are summarized in Table 5.2.

The chemical shifts of the carbene carbon atoms are observed at δ-values in the spectra of **28** and **29**, which, although that observed for **28** is somewhat upfield from that observed in the spectrum of **1**, compare rather favourably with those observed in the spectra of complexes **1** and **2**. This chemical shift in the spectrum of the benzothiophene monocarbene complex **15** is observed a little further downfield, an indication that more deshielding of the carbene carbon atom takes place in the latter compound. The chemical shifts of the *cis* and *trans* carbonyl carbons of the M(CO)$_5$-fragment in the spectrum of **28** and **29**, are also very similar to those observed in the spectra of the corresponding biscarbene complexes **1** and **2**, as well as in the spectrum of **15**.

Table 5.2 ^{13}C NMR Data of the Benzothienyl Carbene Complexes

Assignment	**Complexes**	
	Chemical Shifts, (δ, ppm)	
Carbon Atom	**28**	**29**
C (carbene)	317.5	312.2
M(CO)$_5$, (*trans*)	223.5	203.0
M(CO)$_5$,(*cis*)	217.1	197.7
C2 (*ipso*)	152.0	154.9
C3, C4, C5, C6, C7, C8, C9	124.0, 129.6, 136.4, 133.9, 138.0, 145.0, 147.0	124.0, 129.1, 135.0, 137.4, 138.4, 147.2
O**CH$_2$**CH$_3$ (carbene)	77.4	77.4
OCH$_2$**CH$_3$** (carbene)	15.9	16.0
O**CH$_2$**CH$_3$	60.7	60.5
OCH$_2$**CH$_3$**	15.4	15.3
2 x **CH$_2$**CH$_3$	53.4	53.4
2 x CH$_2$**CH$_3$**	15.2	15.0

The chemical shifts of the thiophene carbon atoms C2 in the spectra of **28** and **29** are further downfield compared to those in the spectra of the biscarbenes **1** and **2**, due to the number of carbene moieties.

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Although the unambiguous assignment of the thienyl and phenyl carbon atoms is not possible, it can be assumed that C8, C9 would display the chemical shifts 145.0, 147.2 ppm and 147.2, 147.2 ppm respectively in the spectra of **28** and **29**, as they are expected to resonate downfield from the phenyl carbons. The chemical shifts of C4 - C9 are observed downfield in the spectrum of **28** compared to that of **15**.

The chemical shifts of the methylene- and methyl carbon atoms of the ethoxy group of the carbene moiety are downfield from those of the ethoxy substituent which is again downfield from those of the ethyl substituents.

(c) Infrared Spectroscopy

The infrared spectroscopic data for complexes **28** and **29** are summarized in Table 5.3. Spectra were obtained in hexane, as well as, in dichloromethane.

Table 5.3 Infrared Spectroscopy of the Benzothienyl Carbene Complexes

Assignment	**Complexes**	
	Stretching Vibrational Frequency, (ν(CO),cm^{-1})	
	28	**29**
M(CO)$_5$		
A$_1^{(1)}$	2058 2057	2066 2066
B	1992 —	1977 —
E	1946 1941	1943 1937
A$_1^{(2)}$	1969 1941	1954 1937

First set recorded in hexane and second set in dichloromethane

The A$_1^{(2)}$ band was not observed in dichloromethane as overlapping of this band with the E band occurs in this polar solvent. The stretching frequencies in the spectra of **28** and **29** are observed at wavenumbers higher than those in the spectra of the corresponding biscarbene complexes **1** and **2**, which implies that

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more electron density is left on the metal nucleus, leading to an increase in the M-C bonding order and a concurrent decrease in the C≡O bond order, hence lower wavenumbers. The reverse is observed if the stretching frequencies observed in the spectrum of complex **15** are considered, with the wavenumbers being lower in the spectrum of **28**.

(d) Mass Spectroscopy

A molecular ion peak, M^+, could be obtained from the spectra of complexes **28** and **29**, it was also possible to obtain a general fragmentation pattern up to a certain point for both complexes. Table 5.4 presents a summary of the most important peaks and fragmentation ions which are associated with these.

The initial fragmentation comprises the stepwise loss of the carbonyl groups from the metal. This is followed by the loss of the ethyl groups, it is not obvious which ethyl groups are lost first.

Table 5.4 Fragment Ions and Peaks of the Benzothienyl Carbene Complexes

Complex	Fragment Ions; (%I)
28	498 (1) M^+; 470 (10) M^+ - CO; 442 (5) M^+ - 2 CO; 414 (5) M^+ - 3 CO; 386 (100) M^+ - 4 CO; 358 (50) M^+ - 5 CO; 300 (2) $^+$ - 5 CO - 2 CH_2CH_3; 242 (2) M^+ - 5 CO - 4 CH_2CH_3
29[a]	629 (3) M^+; 601 (10) M^+ - CO; 573 (20) M^+ - 2 CO; 545 (2) M^+ - 3 CO; 517 (1) M^+ - 4 CO; 489 (5) M^+ - 5 CO; 431 (10) M^+ - 5 CO - 2 CH_2CH_3; 373 (12) M^+ - 5 CO - 4 CH_2CH_3; 346 (10) M^+ - 6 CO - 4 CH_2CH_3

[a] Based on ^{183}W

5.6.2 Spectroscopic Characterization of the Cyclopentathienyl Complexes, M{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS}(CO)$_5$, M = Cr, (30) and M = W, (31)

The cyclopentathienyl complex, **31**, which was isolated as the main product from the reaction of the tungsten biscarbene complex with biphenyl acetylene and the analogous complex, **30**, isolated as one of the products from the reaction of the chromium biscarbene complex, with this alkyne, were spectroscopically characterized in order to make structural formulations possible. The numbering of the carbon atoms of the rings is shown by Figure 5.11.

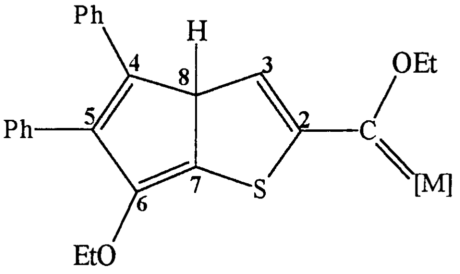
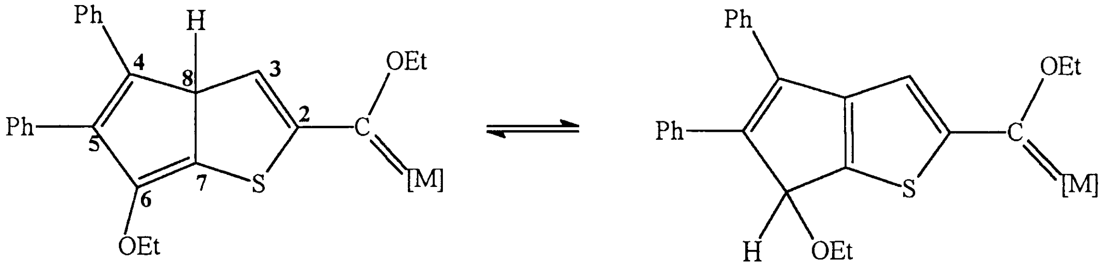


Figure 5.11 Numbering of Ring Carbon Atoms in 30 and 31

(a) ^{1}H NMR Spectroscopy

The ^{1}H NMR data of **30a,b** and **31a,b** are summarized in Table 5.5. The thienyl and methylene regions in the spectrum of **31** are shown in Figure 5.12.

The chemical shifts of the thiophene protons display interesting features and two unrelated resonances are observed. As expected H3 displays a single chemical shift in the spectra of **30a** and **31a**, however, additional resonances for H3 together with H8 also appear in the spectra of **30** and **31** as broad signals. From the ^{1}H NMR spectra it is evident that these compounds are present in two isomeric forms **VI** and **VII**. Based on signal intensities form **30a** is present as 35 % of the mixture while **30b** makes out 65 %. The same can be said for **31**, with the isomeric form **31a** present as 40 % and **31b** as 60 %. These two isomeric forms are present in an equilibrium as a 1,3 hydrogen shift and cannot be separated to afford the individual isomers. This equilibrium is shown by Scheme 5.10.



VI	**VII**
30a 35%	**30b 65%**
31a 40%	**31b 60%**

[M] = $Cr(CO)_5$ or $W(CO)_5$

Scheme 5.10

Table 5.5 ^{1}H NMR Data of the Cyclopentathienyl Carbene Complexes

Assignment		**Complexes**			
		Chemical Shifts (δ, ppm) and Coupling Constants, (J, Hz)			
		30		**31**	
Proton		δ	$^3J_{H-H}$	δ	$^3J_{H-H}$
H3	**VII**	7.83 (s)		7.75 (s)	
H3	**VI**	7.67 (br)		7.70 (d)	
H8		7.66 (br)		7.67 (d)	
2 x C_6H_5 (phenyl)	**VI, VII**	7.25 - 7.12 (m)	7.2	7.26 - 7.13 (m)	7.4
$\mathrm{O}\mathbf{CH_2}\mathrm{CH_3}$ (carbene)	**VI, VII**	5.04 (q)	7.0	4.88 (br)	7.1
$\mathrm{OCH_2}\mathbf{CH_3}$ (carbene)	**VI, VII**	1.61 (t)	7.0	1.58 (t)	7.0
$\mathrm{O}\mathbf{CH_2}\mathrm{CH_3}$	**VII**	4.52 (q)	7.0	4.52 (q)	7.0
	VI	4.48 (q)		4.48 (q)	
$\mathrm{OCH_2}\mathbf{CH_3}$	**VI, VII**	1.52 (t)	7.1	1.55 (t)	6.9
C(OEt)**H**	**VII**	4.96 (s)		4.96 (s)	

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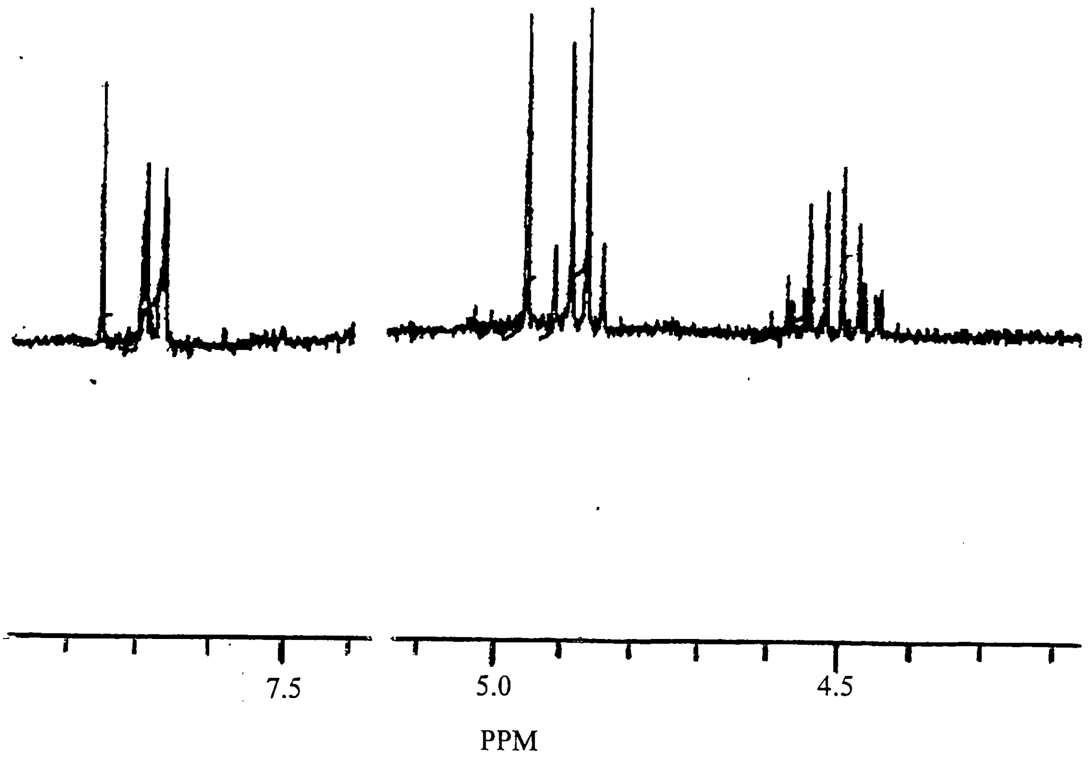

Figure 5.12 Thienyl and Methylene Region of the ^{1}H NMR Spectrum of $W\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$

The most striking feature in the spectra of **30** and **31** is the resonances associated with the methylene protons of the ethoxy group which appear as two independent, overlapping quartets emphasising the difference between the ethoxy environments in **a** and **b**. Isomeric forms **30c** and **31c**, which could result from a 1,2 hydrogen shift, were eliminated because of the similarity in the chemical environment of the ethoxy substituents.

Interesting also is the chemical shift of C(OEt)**H** in the spectra of **30b** and **31b** which appears at 4.96 ppm as a singlet. This proton has exactly the same chemical shift in the spectra of these compounds, which is an indication of a similar electronic environment. Again, a chemical shift upfield from this value is expected for isomeric form **c**.

The methylene and methyl protons of the ethoxy group of the carbene moiety appear as quartets and triplets in the spectra **30** and **31**. These chemical shifts are hardly affected by differences in the two condensed five membered rings.

The chemical shifts of the phenyl protons are observed in the range 7.26 -7.12 ppm and are complicated multiplicities in the spectra of complexes **30** and **31**. The similarity of the δ values signifies that these protons are subjected to similar influences and effects from the surrounding groups, and that these protons are to far from the carbene moiety to be significantly influenced by it.

(b) ^{13}C NMR Spectroscopy

The ^{13} C NMR data of complexes **30** and **31** are summarized in Table 5.6.

Table 5.6 ^{13}C NMR Data of the Cyclopentathienyl Carbene Complexes

Assignment	**Complexes**	
	Chemical Shifts, (δ, ppm)	
Carbon atom	**30**	**31**
C(carbene)	n.o. 307.3	311.2 282.3
$M(CO)_5$, (*trans*)	223.4	203.0
$M(CO)_5$, (*cis*)	217.3	197.8
C2	167.0	167.0
C3	156.0	152.0
C4, C5, C6	138.4, 135.0, 134.0, 131.0	138.3, 135.0, 133.0, 131.0
C7	152.0	150.5
C8	153.0, 149.0	153.0, 144.6
C_6H_5R (phenyl)	129.0 - 126.9	129.5 - 125.9
$\mathbf{OCH_2}CH_3$ (carbene)	77.4	77.6
$OCH_2\mathbf{CH_3}$ (carbene)	15.7	15.7
$\mathbf{OCH_2}CH_3$	67.4, 51.0	67.4, 51.0
$OCH_2\mathbf{CH_3}$	15.3	15.1

As opposed to one chemical shift which appears for the carbene carbon atom in the spectrum of **30**, two chemical shifts are observed in the spectrum of **31**. Owing to the sensitivity of the carbene resonances the presence of two chemical shifts is an indication of two isomeric forms of the compound, an observation already made from the ^{1}H NMR data.

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The chemical shifts of the carbonyl groups are again influenced only by the nature of the metal and are practically the same, as those recorded for **1**, **2**, **A**, **B** and **15**. Noteworthy was an additional resonance in the thiophene region of higher intensity (153 ppm) which was assigned to C8 of **30a** and **31a**. Two independent resonances were also observed for the methylene carbon of the ethoxy substituent on the five membered ring, supporting the ^{1}H NMR data and revealing very different electronic environments in the two isomeric forms.

The chemical shifts of the methylene- and methyl carbon atoms of the ethoxy group of the carbene moiety appear downfield from those of the ethoxy group bonded to the five membered ring.

The assignment of the protons and carbon atoms to the signals in the relevant spectra of these complexes led to the structures **30a,b** and **31a,b** being assigned to the chromium and tungsten complexes.

(c) Infrared Spectroscopy

The infrared data for **30** and **31** are summarized in Table 5.7. Whereas the spectrum of **30** was recorded in hexane and dichloromethane as solvent, the spectrum of **31** was recorded in hexane only.

Table 5.7 Infrared Data of the Cyclopentathienyl Carbene Complexes

Assignment	**Complexes**	
	Stretching Vibrational Frequency (v(CO), cm^{-1})	
	30	**31**
M(CO)$_5$		
A$_1$$^{(1)}$	2055 2054	2064
B	1989 1988	1980
E	1943 1938	1941 ^{c}
A$_1$$^{(2)}$	1954 1938^c	1941 ^{c}

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

^{c} : bands overlap

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The $A_1^{(2)}$ band is not observed in the spectrum of **30** with dichloromethane as solvent, as this band overlaps with the E band. No discrimination of **30** in **30a** and **30b** or of **31** in **31a** and **31b** is possible from the infrared data.

(d) Mass Spectroscopy

A general fragmentation pattern, which is not substantiated but serves as a working hypothesis, as well as, molecular ion peaks, M^+, were postulated from the spectra of **30** and **31**. The initial fragmentation of the carbonyl groups from the carbene functionality is followed by the loss of two ethyl groups, one from the carbene moiety and the other from the ethoxy group bonded to the five membered ring. Lastly a carbonyl group is lost from the molecule. This general pattern is presented by Scheme 5.11 and the most important fragment ions with the peaks associated with these are presented in Table 5.8.

Table 5.8 Fragment Ion Peaks of the Cyclopentathienyl Carbene Complexes

Complex	Fragment Ions ; (%I)
30	566 (20) M^+; 426 (100) M^+ - 5 CO; 397 (60) M^+ - 5 CO - CH_2CH_3; 367 (30) M^+ - 5 CO - 2 CH_2CH_3
31[a]	697 (5) M^+; 557 (50) M^+ - 5 CO; 500 (18) M^+ - 5 CO - 2 CH_2CH_3; 472 (8) M^+ - 6 CO - 2 CH_2CH_3

[a]: Based on ^{183}W

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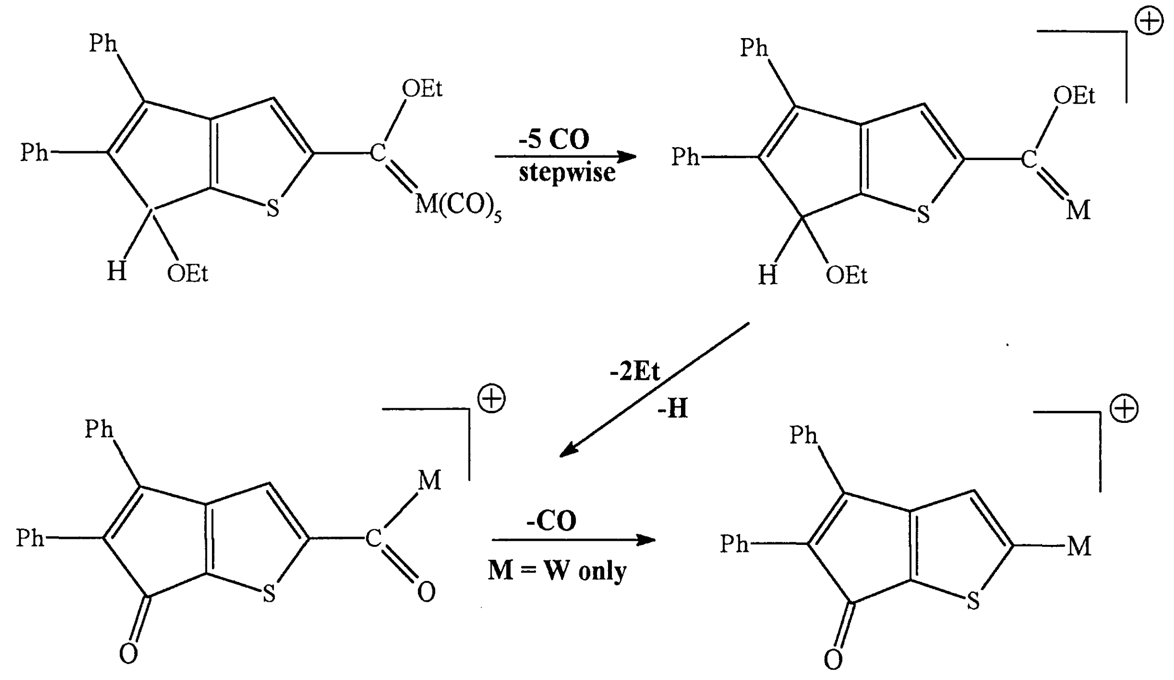

M = Cr, W

Scheme 5.11

5.6.3 Spectroscopic Characterization of the Intermediate, $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)C(Ph)C(Ph)\}Cr(CO)_5$, (32), and the Benzothienyl Carbene Complexes, $\{\eta^1:\eta^6$-$SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3$, (33) and $Cr\{C(OEt)CCHCC(OH)C(Ph)C(Ph)C(OEt)CS\}(CO)_5$, (34)

Three complexes were isolated from the reaction of **1** with biphenyl acetylene. These were spectroscopically characterized by ^{1}H-, ^{13}C NMR- and infrared spectroscopy and identified as an intermediate, **32**, a complex containing a benzothiophene skeleton in which a $Cr(CO)_3$-fragment is π-coordinated to the benzene ring , **33a** which converts to **33b** with the $Cr(CO)_3$ π-coordinated to the thiophene ring, and a decomposition product of **33**, to which the $Cr(CO)_3$-fragment is no longer π-coordinated, **34**. In order to determine whether an equilibrium exists between **33a** and **33b** with either decomposing to **34** or whether a definite route from **32** to **34** was followed, a reaction was set up to monitor changes in a $CDCl_3$ solution of **32** by ^{1}H NMR spectroscopy. It was found that **32** converted to

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33a without the immediate formation of **33b** and therefore it was concluded that the sequence **32** to **33a** to **33b** to **34** was followed. Small amounts of the cyclopentathienyl carbene complex, **30** could also be detected. The numbering of the carbon atoms of the ring and inserted alkyne in **32** is shown in Figure 5.13 and that in **33** and **34** corresponds with the numbering presented by Figure 5.9.

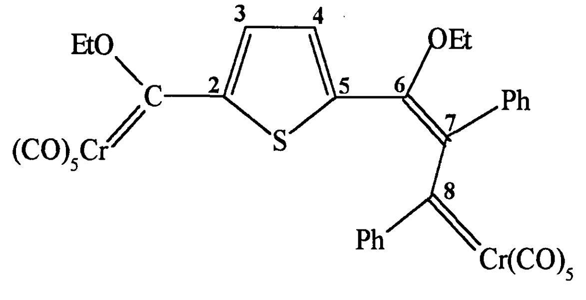

Figure 5.13 Numbering of Carbon Atoms in 32

(a) ^{1}H NMR Spectroscopy

The ^{1}H NMR data of complexes **32, 33a, b** and **34** are summarized in Table 5.9. Figure 5.15 represents the ^{1}H NMR spectrum of studies relating to **32** in solution and Figure 5.16 the ^{1}H NMR spectrum of complex **33**.

On considering the chemical shifts of protons in the spectra of **32, 33** and **34**, it is evident that there are similarities, as well as, differences, which confirms that these complexes are related but have distinct differences. It is interesting to note the chemical shifts of the thiophene protons and the methylene protons of the ethoxy substituent as they form the basis of structural assignments. In Figure 5.15 a spectrum consisting of mainly **32** but with some decomposition to essentially **33a** and in low yield **30**, is shown. The structural assignment was mainly based on the two doublets observed at 8.10 and 7.76 ppm, which are representative of an uncoordinated thiophene with protons H3 and H4 present. This implies a product before cyclization or a cyclopentathienyl complex such as **30a**. The presence of **30a** in low concentrations excludes the presence of a product prior to cyclization. Also significant is the broad quartet displayed by the methylene protons of the ethoxy group at 4.37 ppm which may be in a *cis* or *trans* conformation with respect to the carbene ligand, Figure 5.14. Also present are resonances assigned to **33a** which represent the cyclisized product with $Cr(CO)_3$ π-bonded to the benzene ring and the next significant product. The chemical shifts of H3 and H4 are shifted upfield relative to H3 in **33a** and δ-values are comparable to those observed in 2,5-disubstituted thiophenes with one carbene substituent only.

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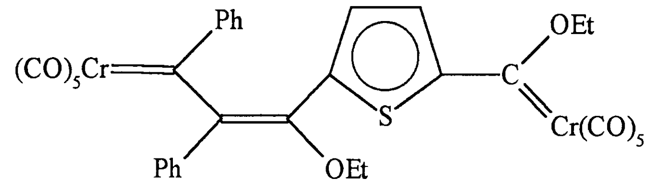
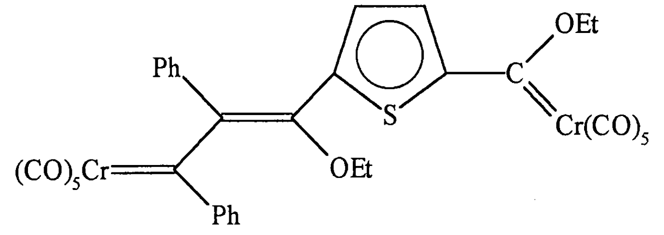


cis



trans

Figure 5.14 *Cis* or *Trans* Conformations

Figure 5.15 displays chemical shifts obtained for **33** and evidence for π-coordination to both the benzene, as well as, thiophene rings is found. It is known that the thermodinamically less stable π-coordination of $Cr(CO)_3$ to the phenol ring is a consequence of the reaction mechanism proposed by Dötz which converts to the more stable product at elevated temperatures by migration of the $Cr(CO)_3$-fragment to the unsubstituted benzene ring. Scheme 5.12 shows the migration of $Cr(CO)_3$ from benzene (**33a**) to thiophene (**33b**). A sharp singlet at 8.49 for H3 is contrasted by a singlet at 5.45 for H3, marking the effect of π-coordination to the thiophene ring. The features and chemical shift of 5.45 ppm are consistent with similar resonances for π-coordinated thiophene complexes which display ^{1}H NMR resonances in the range 4.9 - 5.6 ppm, e.g. (η^1:η^5-SC(Me)CHCHCMn$(CO)_5$, two doublets at 5.8 -5.9 ppm and Pt{(η^5-CCHCHCHS)Cr$(CO)_3$}(C_4H_3S)(PMe_3)CO, 4.90 - 5.58 ppm.[29] A stronger broad signal at 7.56 ppm was assigned to the phenol proton of a π-coordinated benzene ring and the chemical shift at 4.69 ppm to OH of the free ring. Also significant are the two independent sets of doublets of quartets for the methylene protons of the ethoxy substituent. The resonances at higher field strength were assigned to **33b** and those downfield at 3.65 ppm to **33a**.

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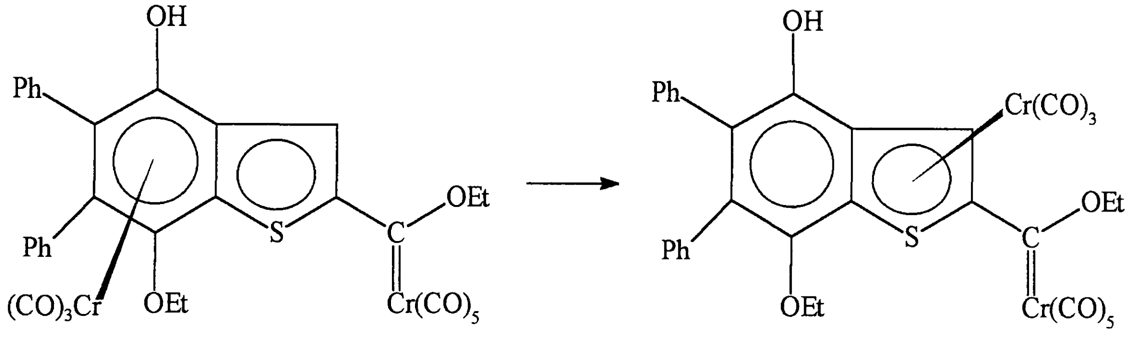

33a **33b**

Scheme 5.12 Conversion of 33a to 33b

Table 5.9 ^{1}H NMR Data of the Intermediate and Benzothienyl Carbene Complexes

Assignments	**Complexes**							
	Chemical Shifts, (δ, ppm) and Coupling Constants, (J, Hz)							
Proton	**32**		**33a**		**33b**		**34**	
	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$	δ	$^3J_{H\text{-}H}$
H3			8.49 (s)		5.45(s)		8.71 (s)	
H3	8.10 (d)	4.2						
H4	7.76 (d)	3.9						
OH			7.56 (br)		4.96 (br)		5.46 (s)	
C_6H_5R (phenyls)	7.45 - 7.10(m)		7.42 - 7.00(m)		7.42 - 7.00 (m)		7.27 - 7.08(m)	
$O\mathbf{CH_2}CH_3$ (carbene)	5.20 (m)	7.0	5.24 (m)		5.24 (m)		5.25 (q)	7.0
$OCH_2\mathbf{CH_3}$ (carbene)	1.67 (t)	7.1	1.74 (t)	7.1	1.73 (t)	7.1	1.73 (t)	7.1
$O\mathbf{CH_2}CH_3$	4.37 (br, q)	7.2	3.65 (dq)	7.1	3.52 (dq)	6.9	3.64 (t)	7.1
$OCH_2\mathbf{CH_3}$	1.37 (t)	7.1	1.11 (t)	6.9	1.08 (t)	7.1	1.05 (t)	7.0

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The chemical shifts for the methylene and methyl protons of the carbene functionality vary little and are practically the same for **32** - **34**. The duplication of these chemical shifts occur in the spectrum of **33**, indicating the effect of the significantly different electronic environment of **33a** compared to **33b**.

The chemical shifts of the phenyl protons appear in ranges from between 7.59 ppm - 6.95 ppm in the spectra of **32** - **34** and are broad multiplets which do not reveal any structural information.

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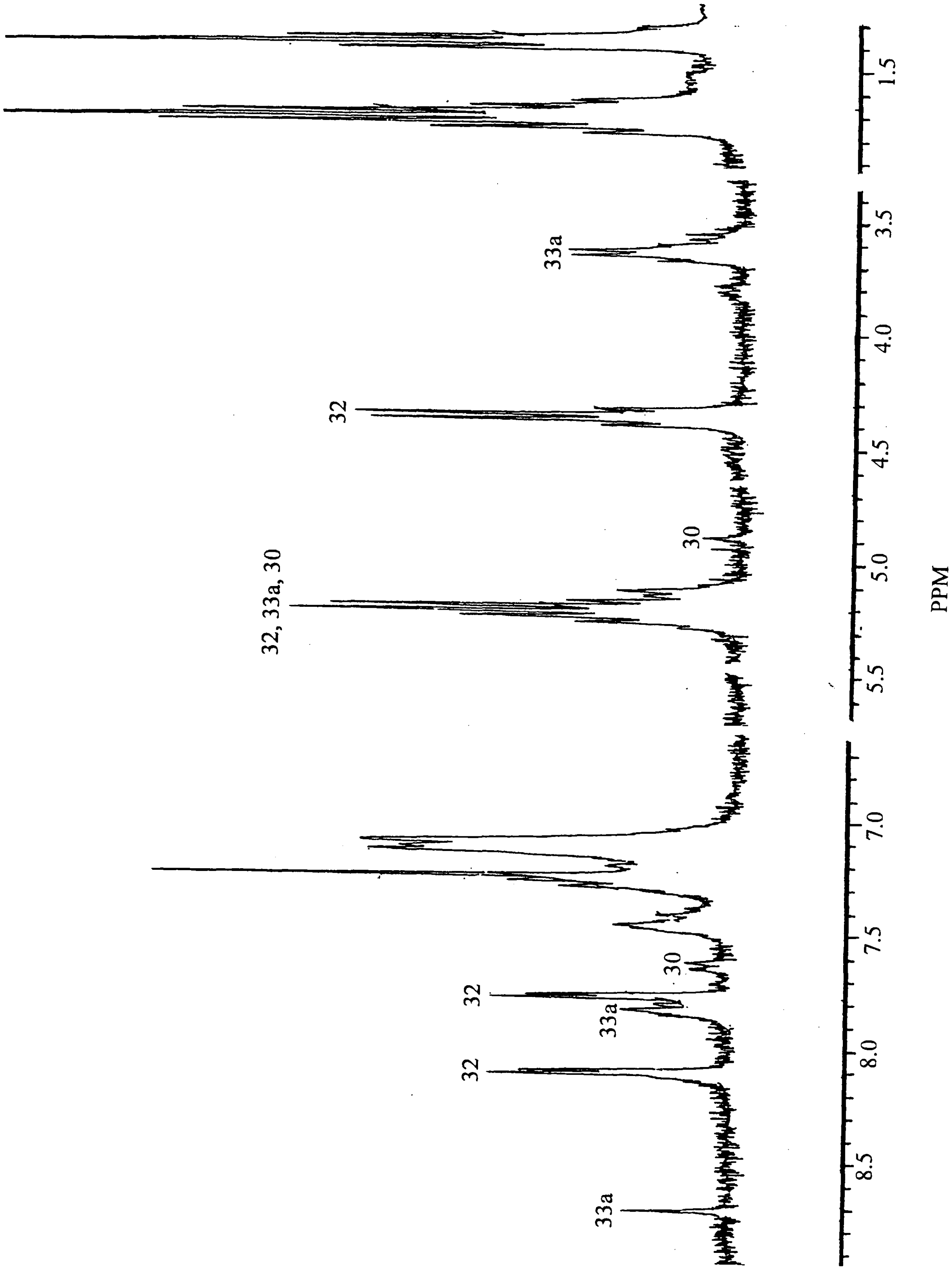

Figure 5.15 Decomposition of (CO)$_5$Cr{C(OEt)C$_4$H$_2$SC(OEt)C(Ph)C(Ph)}Cr(CO)$_5$, (32), to{η^1:η^6-SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)$_5$}Cr(CO)$_3$, (33a) and Cr{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS}(CO)$_5$, (30)

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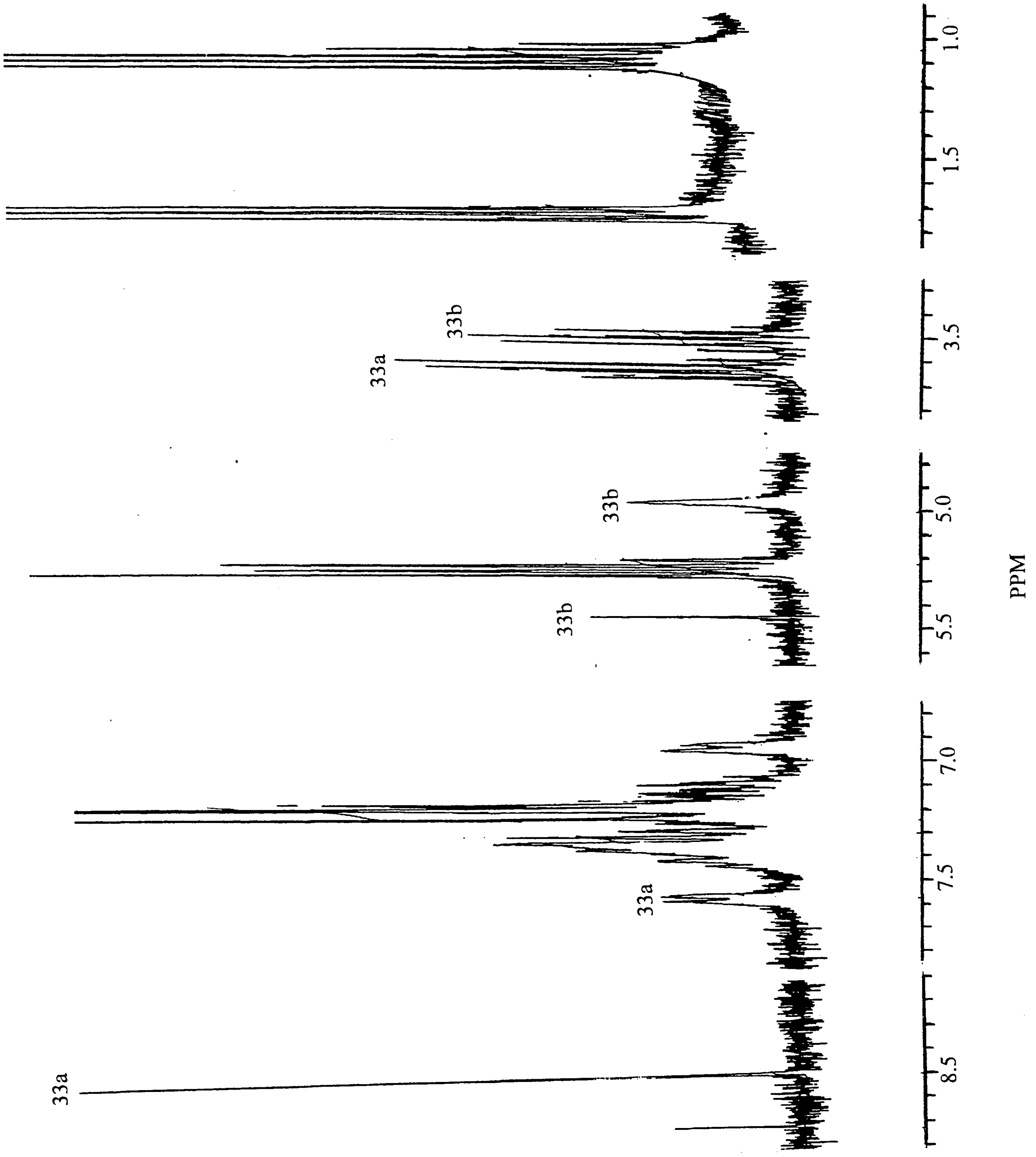

Figure 5.16 ^{1}H NMR Spectrum of $\{\eta^1:\eta^6\text{-SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)}_5\}\text{-Cr(CO)}_3$

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(b) ^{13}C NMR Spectroscopy

Selected ^{13}C NMR data of complexes **32**, **33** and **34** are summarized in Table 5.10.

Table 5.10 Selected ^{13}C NMR Data of the Intermediate and Benzothienyl Carbene Complexes

Assignment	**Complexes**		
	Chemical Shifts, (δ, ppm)		
Carbon Atom	**32**	**33a, b**	**34**
C(carbene)	320.3 311.2	n.o. 312.2	318.5 311.2
$Cr(CO)_3$		232.8	
$M(CO)_5$, (*trans*)	223.6 223.3	223.6	223.6
$M(CO)_5$, (*cis*)	217.1 216.6	217.1 216.5	217.1
C2	167.7	168.0	153.1
C3, C4, C5, C6, C7, C8, C9	138.9, 139.6, 144.5, 146.5, 153.2, 158.4, 162.3	136.3, 137.1, 144.5, 146.3, 149.9, 153.5, 155.3	135.6, 136.2, 137.2, 144.3, 147.3, 152.5,
2 x $\mathbf{C_6}H_5R$ (phenyls)	132.5 - 126.9	133.6 - 126.9	131.1 - 126.9
$\mathbf{OCH_2}CH_3$ (carbene)	75.9	74.1	76.6
$OCH_2\mathbf{CH_3}$ (carbene)	15.8	15.6	15.6
$\mathbf{OCH_2}CH_3$	68.8	68.8	66.8
$OCH_2\mathbf{CH_3}$	15.4	15.2	15.2

The carbene and carbonyl regions in the spectrum of **32** are displayed in Figure 5.17 and the carbonyl region in the spectrum of **33** in Figure 5.18. Unique features which are helpful in assigning or testing structures of complexes are the chemical shifts of the carbene and carbonyl carbon atoms and the distinct regions in which the different ring carbons resonate. The following regions were displayed in spectra **32** - **34**, see Figure 5.19 as an example which presents these regions in the spectrum of **33**. Uncoordinated, unsubstituted phenyl carbons gave strong signals over a narrow range 123 - 135 ppm, (Bz), whereas phenyls with electronegative or electron withdrawing substituents also gave relatively sharp signals further downfield but over a wider range 130 - 145 ppm, (BzX_n). When π-coordinated to $Cr(CO)_3$ the chemical shifts are upfield in the range 85 - 100 ppm, π-Bz. By contrast, thiophene resonances are found over a wider range 165 - 145 ppm, (Th), and when π-coordinated to $Cr(CO)_3$, 120 - 105 ppm, (π-Th).

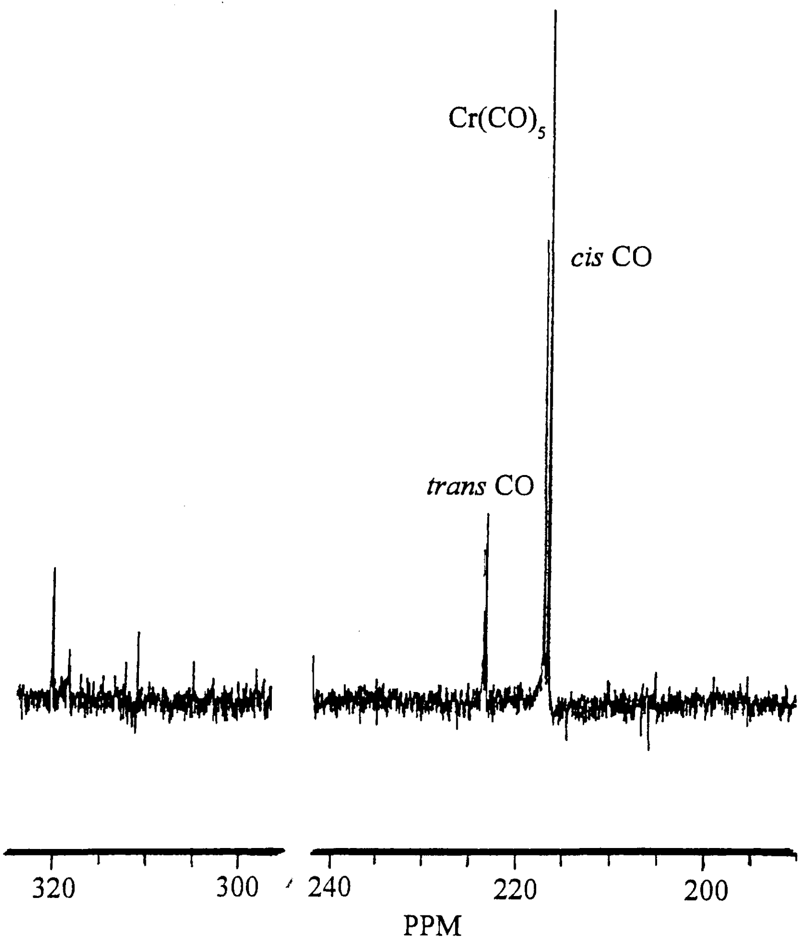

Figure 5.17 Carbene and Carbonyl Regions in the ^{13}C NMR Spectrum of $(CO)_5Cr\{C(OEt)C_4H_2S$-$C(OEt)C(Ph)C(Ph)\}Cr(CO)_5$

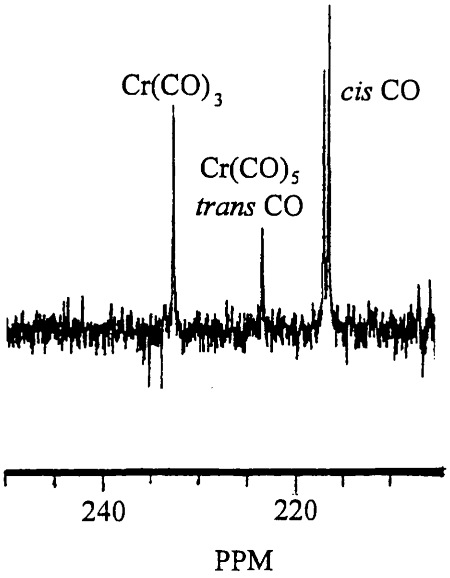

Figure 5.18 Carbonyl Region in the ^{13}C NMR Spectrum of $\{\eta^1:\eta^6$-$SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3$

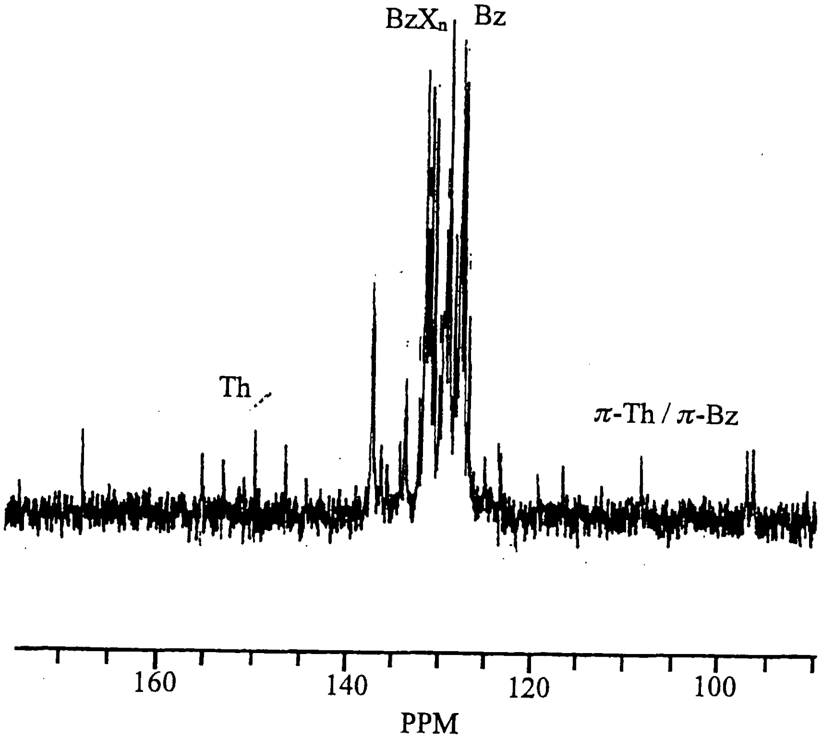

Figure 5.19 Thiophene Resonances in the ^{13}C NMR Spectrum of $\{\eta^1:\eta^5$-$SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3$

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An important feature of these spectra especially that of **32** is the duplicating of signals of the carbene carbon atom and of the carbonyl groups of the $Cr(CO)_5$ fragment, which is shown in Figure 5.17. This duplicating of chemical shifts indicate two different carbene ligands and support structural assignments for **32** based on the ^1H NMR data. Also $M(CO)_5$ resonances are displayed with a duplication of the $Cr(CO)_5$ signal.

The spectrum of **33** displays only one chemical shift at 312.2 ppm for the carbene carbon which is a little disturbing. It is assumed that a second resonance further downfield was not observed. The carbonyl region is more revealing clearly displaying a strong $Cr(CO)_3$ resonance. Owing to the insensitivity of $Cr(CO)_3$ resonances[30] and the high intensity of the signal it is assigned to $Cr(CO)_3$, when π-coordinated to either of the benzene (**33a**) and the thiophene rings (**33b**). Duplication of the $Cr(CO)_5$ signal is also consistent with different $Cr(CO)_5$-fragments as is found in **33a** and **33b**. The signals displayed in the spectrum of **33** are representative of all the regions described for thiophene and phenyl rings. The data support the ^1H NMR data and can be ascribed to a mixture of complexes where the $Cr(CO)_3$ migrates from the benzene, **33a**, to the thiophene, **33b**, ring.

Finally the spectrum of the monocarbene complex **34** is shown in Figure 5.20 . Significant is the absence of the $Cr(CO)_3$-fragment and only one set of resonances *cis* and *trans* for $Cr(CO)_5$, no signals in the range 80 - 120 ppm and easily assignable resonances for the thiophene, phenol and phenyl rings.

The chemical shifts for the phenyl carbon atoms appear from 133.6 ppm to 126.9 ppm in the spectra of the complexes **32** - **34**. These are downfield from where the chemical shifts appear in the spectrum of the cyclopentathienyl complex **30**.

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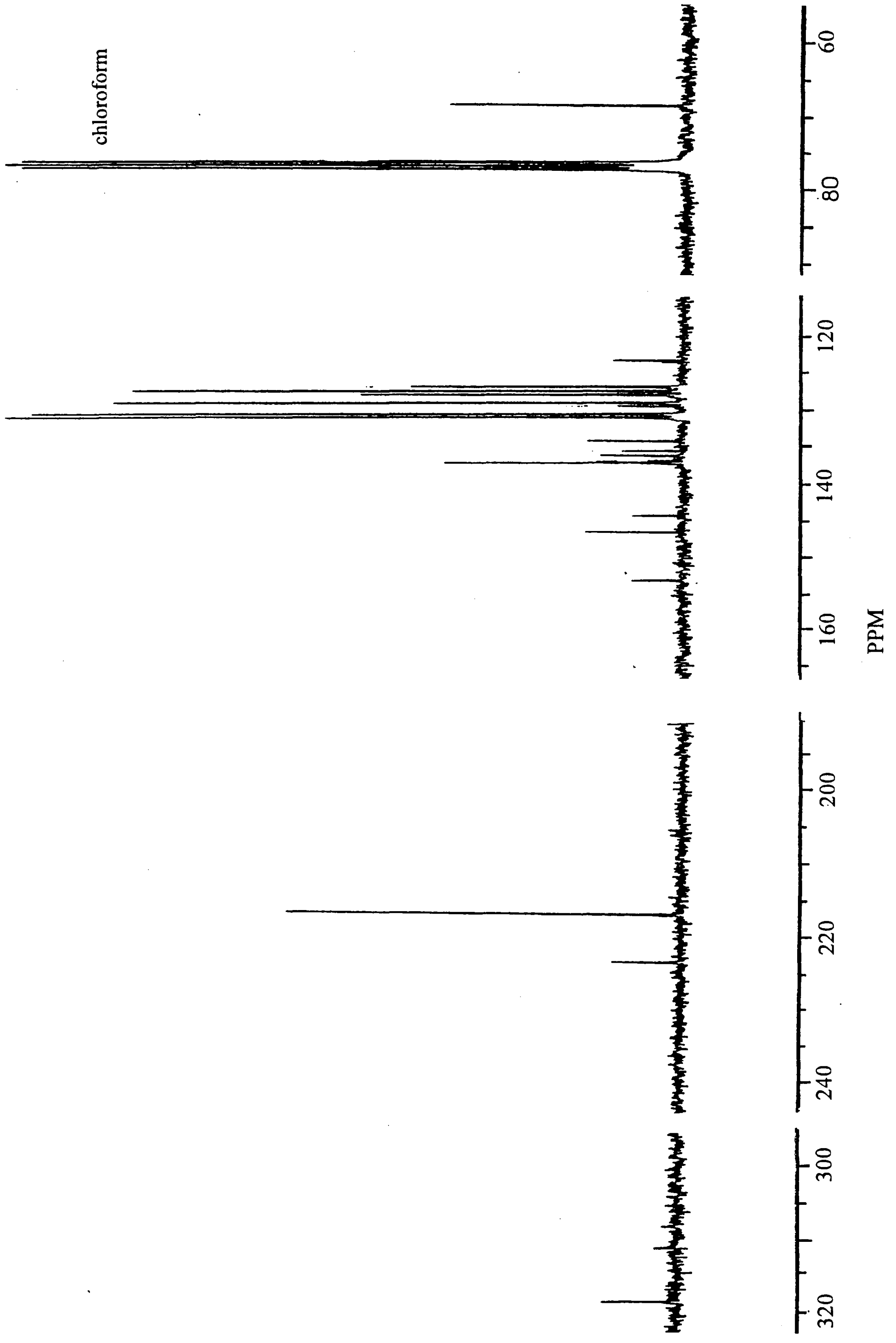

Figure 5.20 ^{13}C NMR Spectrum of Cr{C(OEt)CCHCC(OH)C(Ph)C(Ph)C(OEt)CS}(CO)$_5$

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(c) Infrared Spectroscopy

The infrared data for complexes **32, 33** and **34** are summarized in Table 5.11. The spectra of complexes **32** and **33** were recorded in hexane and dichloromethane as solvent, however, in hexane only, for complex **34**. The pattern and position of the bands in the spectrum of **33** indicate the presence of a $Cr(CO)_3$, as well as, a $Cr(CO)_5$-fragment. The spectra of **32** and **34** show a $Cr(CO)_5$-fragment only. The wavenumbers of the bands for the $Cr(CO)_5$-fragment are virtually the same.

Table 5.11 Infrared Data of the Intermediate and Benzothienyl Carbene Complexes

Assignment	**Complexes**		
	32	**33**	**34**
$M(CO)_5$	Stretching Vibrational Frequency, (νCO, cm^{-1})		
$A_1^{(1)}$	2060 2059	2060 2059	2060
B	1984 —	1984 —	1987
E	1950 1944	1950 1948	1950
$A_1^{(2)}$	1963 1944	1955 1948	1963
$M(CO)_3$			
A'		1955 1956	
A''		1912 1895	
A'''		1893 1895	

First values recorded in hexane and second in dichloromethane

The wavenumbers in the spectra of the six membered complexes are in general higher than those observed in the spectrum of the related five membered complex **31**. The degeneracy of the E band of the $Cr(CO)_3$ is lifted and three A bands are observed in the spectrum, of which the first overlaps with the

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$Cr(CO)_5$ bands in the spectrum of **33**.

5.7 Summary

The reaction of two different alkynes with the biscarbene complexes **1** and **2**, yielded different products and warrants a systematic investigation, including that of the oxidized organic products. The reaction of the carbene complexes with hex-3-yne yielded analogous complexes containing a benzothiophene skeleton, **28** and **29**. Quite surprising is the absence of a π-coordinated $Cr(CO)_3$-fragment from the benzothienyl in **28**. These reactions with hex-3-yne furthermore afforded the decomposition products **16** and **17**. This is a disturbing result as it is competitive to alkyne insertion and dramatically reduces the yields of the Dötz products. However, the reaction of these biscarbene complexes, especially the chromium complex with biphenyl acetylene yielded an interesting array of products and the stabilization of the intermediates by metal fragments affords an additional method of monitoring factors involved in product formation. From the reaction of the alkyne with **2**, one significant product only, containing a cyclopentathiophene skeleton, **31**, which was found in two preferred isomeric forms in solution, **31a, b**, could be isolated. However the more reactive chromium species gave exciting results, firstly the analogous cyclopentathienyl carbene complex **30**, isomers **30a, b** was isolated. This focuses attention on the fact that the stabilization of intermediates by coordination to more than one metal fragment may turn out to be a valuable tool in studying reaction mechanisms. Very suprising was the isolation of the very reactive newly formed biscarbene intermediate, **32**, which was a precursor during the synthesis of the benzothienyl carbene complex, **33**. It was established by studying a solution of **32** with ^1H NMR spectroscopy that **32** converts to the benzene π-bonded monocarbene complex **33a**. This product was found to convert spontaneously, even at reduced temperatures in an inert atmosphere, by the migration of the π-bonded $Cr(CO)_3$-fragment.

The exposure of the products **28**, **29** and **34** to air yielded suprising results, in that these products were found to be stable and that the metal carbene functionality was not substituted or the metal oxidized.

5.8 References

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6 Experimental

6.1 Standard Operational Procedure

The synthesis and characterization of all compounds, unless stated differently elsewhere, were performed in an inert atmosphere of either nitrogen or argon. All solvents were dried in an inert atmosphere according to conventional laboratory methods. Kieselgel 60 (particle size 0.0063-0.200 mm) was used as resin for chromatographic separations and purifications. Column chromatography , unless specified differently, was used for all separations, with the column cooled by circulating cold methanol (-30 °C) through the column jacket. The polarity of the eluting agent was proportionally increased, with increasing polarity of the compounds which were being separated (starting with 100% petroleum ether and finishing with 100% dichloromethane). All chemicals, with a few exceptions which will be stated, were directly used without prior purification.

6.2 Characterization of Compounds

6.2.1 Infrared Spectra

Infrared spectra were recorded on a Galaxy 3000 FT-Spectrophotometer (Mattson Instruments) . All spectra were recorded in solution with either or both of hexane and dichloromethane as solvents.

6.2.2 Nuclear Magnetic Resonance Spectra

NMR-spectra were recorded on a Bruker AC-300 nuclear magnetic resonance spectrometer. ^{1}H NMR spectra were recorded at 300.135 MHz and ^{13}C NMR spectra at 75.469 MHz. As reference the signal of the deuterated solvent was used, e.g. ^{1}H $CDCl_3$ 7.2400, ^{13}C $CDCl_3$ 77.000 ppm.

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6.2.3 Mass Spectra

Mass spectra were recorded on a Perkin-Elmer RMU-6H instrument (ionisation energy 70 eV).

6.2.4 X-ray Crystallography

The Röntgen stucture analysis was done with an Enraf-Nonius CAD 4 diffractometer (graphite monochromator, Mo-Kα radiation). Structures were solved and refined with the aid of the Patterson method employing the SHELX 76 and SHELX 86 programmes.

6.3 Preparation of Starting Compounds

The following compounds were prepared according to known literature methods: Trisammine(tricarbonyl)chromium[1], Triethyloxonium tetrafluoroborate[2], Tricarbonyl(η^5 -thiophene)chromium[3] and 2,2'-methylene dithiophene.[4]

6.4 Synthesis of Various Organometallic Compounds

6.4.1 Thienylene Bimetallic Biscarbene Complexes

The thiophene used in this reaction was purified prior to use as described by Spies and Angelici.[5]

These compounds were synthesized in part according to the method described by Brandsma and Verkruijsse.[6] An excess of 10 % of butyllithium was used in the syntheses.

(a) Chromium Thienylene Biscarbene Complex, $(CO)_5Cr\{C(OEt)C_4H_2S\text{-}C(OEt)\}Cr(CO)_5$, (1)

18.6 ml (27.3 mmole) of butyllithium was added to a solution of 3.7 ml (24.7 mmole) of TMEDA and 0.99 ml (12.4 mmole) of thiophene in 30 ml of hexane at room temperature. A white suspension gradually formed and the conversion was completed by refluxing the mixture for 30 min. The suspension was cooled to below 0 °C and 40 ml of THF was added. After further cooling to -40 °C, 5.00 g (22.7

mmole) of $Cr(CO)_6$ was gradually added to the vigorously stirred mixture. The temperature was allowed to rise to room temperature and stirring was maintained for a further 15 min during which time the colour changed to dark brown. After the reaction had been completed all solvents were removed under reduced pressure. 4.55 g (24.7 mmole) of triethyloxonium tetrafluoroborate dissolved in 30 ml of dichloromethane was carefully added to the stirred mixture at -30 °C, the temperature was allowed to rise to room temperature and the mixture turned a very dark purple. The mixture was washed through a filter containing Na_2SO_4 and kieselgel with dichloromethane and the solvent was removed under reduced pressure.

The mixture of carbene compounds was purified with column chromatography. The carbene mixture was dissolved in dichloromethane and adsorbed onto silica. Three bands were separated starting with pure petroleum ether as eluating agent and increasing the polarity by adding some dichloromethane (10 ml to 500 ml) to the eluting agent. The first yellow product was charaterized as the butyl carbene complex $Cr\{C(OEt)CH_2CH_2CH_2CH_3\}(CO)_5$, yield: 0.77g, 15.3 %. The second orange band was identified as the monocarbene complex $Cr\{C(OEt)C_4H_3S\}(CO)_5$, **(A)**, yield: 1.02 g, 20.4 %. The third product the biscarbene, $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$, **(1)**, had a deep purple colour and a yield of 3.04 g, 60.7 %.

(b) Tungsten Thienylene Biscarbene Complex, $(CO)_5W\{C(OEt)C_4H_2S\text{-}C(OEt)\}W(CO)_5$, (2)

10.7 ml (17.1 mmole) of butyllithium was added to a solution of 2.1 ml (14.2 mmole) of TMEDA and 0.58 ml (7.1 mmole) of thiophene in 30 ml of hexane at room temperatue. The same procedure was followed as for the chromium analogue with the addition of 5.00 g (14.2 mmole) of $W(CO)_6$. 2.61 g (14.2 mmole) of triethyloxonium tetrafluoroborate was used for alkylation. Three products were separated with column chromatography, in the same way as their chromium analogues. The butyl carbene complex, $W\{C(OEt)CH_2CH_2CH_2CH_3\}(CO)_5$ a yellow oil had a yield of 0.51g, 10.1 %, the orange monocarbene complex, $W\{C(OEt)C_4H_3S\}(CO)_5$, **(B)**, had a yield of 0.52 g, 10.3 %. The pure biscarbene, $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$, **(2)**, had a deep purple colour and yield of 3.03 g, 60,5 %.

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(c) Manganese Methylcyclopentadienyl Thienylene Biscarbene Complex, $(\eta^5\text{-}C_5H_4CH_3)(CO)_2Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_2$, (3)

17.2 ml (27.5 mmole) of butyllithium was added to a solution of 3.4 ml (23 mmole) of TMEDA and 0.92 ml (11.5 mmole) of thiophene in 40 ml of hexane at room temperature. The reaction was performed as described for the analogous chromium and tungsten reactions, however stirring had to be maintained for at least 30 min after the addition of 3.3 ml (22.9 mmole) of $Mn\{(\eta^5\text{-}C_5H_4Me)\}(CO)_3$. After the addition of 4.22 g (22.9 mmole) of triethyloxonium tetrafluoroborate as alkylating agent the colour became a very dark red purple. The product $(\eta^5\text{-}C_5H_4CH_3)(CO)_2Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_2$, **(3)**, had a red purple colour and was isolated with column chromatography in the same way as the chromium and tungsten analogues, yield: 4.1 g, 81,6 %.

(d) Manganese Cyclopentadienyl Thienylene Biscarbene Complex, $(\eta^5\text{-}C_5H_5)(CO)_2Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_5)(CO)_2$, (4)

7.4 ml (11.8 mmoles) of butyllithium was added to a solution of 1.5 ml (9.9 mmoles) of TMEDA and 0.40 ml (4.9 mmoles) of thiophene in 40 ml of hexane at room temperature upon which the reaction was proceeded according to the general method already described. As was the case with the $Mn\{(\eta^5\text{-}C_5H_4Me)\}(CO)_3$ analogue stirring had to be maintained for at least 30 min after the addition of 2.00 g (1.0 mmoles) of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$. Purification with column chromatography afforded the red purple product, $(CO)_2(\eta^5\text{-}C_5H_5)Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_5)(CO)_2$, **(4)**, with a yield of: 1.6 g, 80.2 %.

6.4.2 σ,σ-Bimetallic 2-2'-Methylene Dithienyl Biscarbene Complexes

The lithiation of MDT was done by one of two methods in the general synthesis of $L_3(CO)_2M\{C(OEt)\text{-}C_9H_6SC(OEt)\}M(CO)_2L_3$, (M = Cr, W, Mn; L = CO and $L_3 = \eta^5\text{-}C_5H_5$).

(a) Chromium 2,2'-Methylene Dithienyl Biscarbene Complex, $(CO)_5Cr\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}Cr(CO)_5$, (5)

(i) 0.82 g (4.5 mmole) of MDT was dissolved in THF at 5 - 10°C. An excess of butyllithium was added and stirring was maintained for 15 min at this temperature.[7] After the solution had changed from reddish brown to virtually black it was cooled to below -50 °C. 2g (9.1 mmole) of $Cr(CO)_6$ was added and the cooling bath was removed. As room temperature was reached the colour changed to dark green. The solvent was removed under reduced pressure and a solution of 0.85g (4.6 mmole) of triethyloxonium tetrafluoroborate in dichloromethane was added. The colour changed to reddish brown. The mixture was filtered through Na_2SO_4 and kieselgel. The solvent was removed under reduced pressure. The product was purified with column chromatography; starting with pure petroleum ether as eluting agent and gradually increasing the polarity by adding dichloromethane until the product could be isolated with a mixture of petroleum ether / dichloromethane 1/1. The product a red oil, yield: 1.2g, 60.2 %, was characterized as $(CO)_5Cr\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}Cr(CO)_5$, **(5)**, according to standard methods described.

(ii) As alternative to facilitate the lithiation of MDT, 0.41 ml (2.8 mmole) of TMEDA was added to a solution of 0.50 g (2.8 mmole) of MDT in THF after which 3.5 ml (5.6 mmole) of butyllithium (not an excess) was added and the mixture was refluxed for about 15 min during which time the colour became very dark. The mixture was cooled to below -50 °C and the reaction was further carried out as described above in (i) with the addition of 1.2 g (5.6 mmole) of $Cr(CO)_6$ and 0.51 g (2.8 mmole) of triethyloxonium tetrafluoroborate as alkylating reagent. The same product, $(CO)_5Cr\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}$-$Cr(CO)_5$, **(5)**, was isolated with column chromatography, yield: 0.85 g, 70.7 %.

(b) Tungsten 2,2'-Methylene Dithienyl Biscarbene Complex, $(CO)_5W\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}W(CO)_5$, (6)

The same procedures described for the chromium analogue in (i) and (ii) were employed but it was found that procedure (ii) was more effective with a 78.2 % yield compared to the 0.9g, 28.1 % yield obtained when using procedure (i). 0.50 g (2.7 mmole) of MDT was dissolved in THF to which 3.5 ml (5.6 mmole) of butyllithium and 0.4 ml (2.8 mmole) of TMEDA was added. The reaction was effected according to the general method already described with the addition of 3.31 g (9.4 mmole) of $W(CO)_6$. The alkylation was done with 1.02 g (5.5 mmole) of triethyloxonium tetrafluoroborate. The product was purified with column chromatography and the red oil was characterized as $(CO)_5W\{C(OEt)C_4H_2S$-$CH_2C_4H_2SC(OEt)\}W(CO)_5$, **(6)**, according to standard methods, yield: 2.6 g, 78.2 %.

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(c) Manganese Cyclopentadienyl 2,2'-Methylene Dithienyl Biscarbene Complex, $(CO)_2(\eta^5\text{-}C_5H_5)Mn\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_5)(CO)_2$, (7)

3.5 ml (5.6 mmole) of butyllithium and 0.4 ml (2.8 mmole) of TMEDA was added to 0.51 g (2.7 mmole) of MDT dissolved in THF. The reaction was performed according to the method already described in (ii). The addition of 1.13 g (5.5 mmole) of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ led to a colour change from very dark brown to a dark pink. 1.02 g (5.5 mmole) of triethyloxonium tetrafluoroborate was used for alkylation of the carbene complex. The product was purified with column chromatography and the product a brown red oil characterized as $(CO)_2(\eta^5\text{-}C_5H_5)Mn\{C(OEt)C_4H_2SCH_2C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_5)(CO)_2$, **(7)**, yield: 0.80 g, 70.4 %.

6.4.3 σ,π-Thienyl Bimetallic Monocarbene Complexes

General method for the synthesis of $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)M(CO)_5)Cr(CO)_3$ where (M = Cr, W)
An excess of 10 % of butyllithium was used in the syntheses.

(a) σ,π-Chromium Carbene Complexes, $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)Cr(CO)_5)\text{-}Cr(CO)_3$, (8) and $(\eta^1{:}\eta^5\text{-}C_4H_3SC\{O(CH_2)_4OEt\}Cr(CO)_5)Cr(CO)_3$, (12), and Related Complex, $Cr\{C(O(CH_2)_4OEt)C_4H_3S\}(CO)_5$, (10)

1.90 g (8.6 mmole) of (η^5-thiophene)tricarbonylchromium was dissolved in THF. The solution was cooled to -50 °C and 3.4 ml (5.5 mmole) of butyllithium was added to the stirred solution. Stirring was maintained for about 10 min until the mixture became very dark. 1.1 g (5.0 mmole) of $Cr(CO)_6$ was gradually (over a period of 10 min) added to the solution, after which stirring was maintained for a further 30 min. The solvent was removed under reduced pressure. The mixture was washed with hexane, dried and triethyloxonium tetrafluoroborate 0.91 g (5.0 mmole) dissolved in dichloromethane was carefully added at -30 °C upon which the colour changed to dark cerise pink. The mixture of carbenes was filtered through Na_2SO_4 and silica gel. The solvent was removed under reduced pressure.

Five bands were separated with column chromatography (eluting agent: petroleum ether / dichloromethane 1/1). The pure products were characterized using the standard methods already described. The first yellow product was characterized as the monocarbene complex, Cr{$C(OEt)C_4H_3S$}$(CO)_5$, **(A)**, yield: 0.1 g, 10.1 %. The second product had a blue pink colour, yield: 0.55 g, 50.2 % and was identified as the σ,π-carbene complex, $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)Cr(CO)_5)Cr(CO)_5$, **(8)**. The third orange band was characterized as the unreacted starting compound, yield: 0.06 g, 5.2 %. The fourth product, an orange compound was identified as the monocarbene complex, Cr{$C(O(CH_2)_4OEt)C_4H_3S$}$(CO)_5$, **(10)**, yield: 0.1g, 10.1 %. The last band had a blue pink colour and was characterized as the σ,π-carbene complex, $(\eta^1{:}\eta^5\text{-}C_4H_3SC\{O(CH_2)_4OEt\}Cr(CO)_5)Cr(CO)_3$, **(12)**, yield: 0.2 g, 20.5 %.

(b) σ,π-Tungsten Carbene Complexes, $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)W(CO)_5)\text{-}Cr(CO)_3$, (9) and $(\eta^1{:}\eta^5\text{-}C_4H_3SC\{O(CH_2)_4OEt\}W(CO)_5)Cr(CO)_3$, (13), and Related Complex, W{$C(O(CH_2)_4OEt)C_4H_3S$}$(CO)_5$, (11)

8.4 ml (13.5 mmole) of butyllithium was added to a solution of 2.70 g (12.3 mmole) of (η^5-thiophene)-tricarbonylchromium in THF. The reaction was effected in the same manner as for the chromium analogue with the addition of 4.32 g (12.4 mmole) of $W(CO)_6$ and alkylation done with 2.26 g (13.9 mmole) of triethyloxonium tetrafluoroborate.

Five products analogous to the chromium products above were purified with column chromatography. The first of these was the yellow monocarbene complex, W{$C(OEt)C_4H_3S$}$(CO)_5$, **(B)**, yield:0.46 g, 10.7 %. The second blue pink compound was the σ,π-carbene complex, $(\eta^1{:}\eta^5\text{-}C_4H_3SC(OEt)W(CO)_5\}\text{-}Cr(CO)_3$, **(9)**, yield: 2.16 g, 50.3 %. The third pure product had an orange colour and was identified as the unreacted starting compound, yield: 0.2 g, 5.1 %. The fourth and fifth compounds were respectively characterized as, the monocarbene complex, W{$C(O(CH_2)_4OEt)C_4H_3S$}$(CO)_5$, **(11)**, and σ,π-carbene complex $(\eta^1{:}\eta^5\text{-}C_4H_3SC\{O(CH_2)_4OEt\}W(CO)_5)Cr(CO)_3$, **(13)**, with respective yields of: 0.4 g, 10.2 % and 0.9 g, 20.6 %.

6.4.4 Benzothienyl Carbene Complexes

(a) σ, π-Chromium Benzothienyl Carbene Complex, $(\eta^1{:}\eta^6\text{-}C_8H_5SC(OEt)\text{-}Cr(CO)_5)Cr(CO)_3$, (14) and Related Complex Cr{$C(OEt)C_8H_5S$}$(CO)_5$, (15)

0.42 g (2.2 mmole) of benzothiophene was dissolved in THF. The solution was cooled to -50 °C and 1.4

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ml (2.2 mmole) of butyllithium was added to the stirred solution. The reaction was stirred for 30 min, after which it was further cooled down to -70 °C and stirred at this temperature for a further 2 h. The temperature was allowed to rise to - 50 °C and 0.48 g (2.2 mmole) of $Cr(CO)_6$ was added, upon which the colour of the solution changed to dark red. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane. The stirred solution was cooled to -30 °C and 0.40 g (2.2 mmole) of triethyloxonium tetrafluoroborate dissolved in dichloromethane was added. The solution was stirred at room temperature for 30 min during which time the colour changed to a dark purple blue. The solution was filtered through Na_2SO_4 and silica gel and the solvent was removed under reduced pressure.

A quantitative yield of 0.45 g, 95.2 % of the desired product was obtained. The main product was separated from unreacted starting compound and a minor orange product with column chromatography (eluting agent: petroleum ether / dichloromethane 1/1) and characterized as (η^1:η^6-$C_8H_5SC(OEt)$-$Cr(CO)_5)Cr(CO)_3$, **(14)**. The orange product was identified as the monocarbene complex, $Cr\{C(OEt)C_8H_5S\}(CO)_5$, **(15)**.

6.5 Decomposition Studies

The different bimetallic thiophene biscarbene complexes were subjected to temperature and solvents to yield new organometallic compounds.

6.5.1 Decomposition of the Chromium Thienylene Biscarbene Complex in Acetone, to yield $Cr\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$ (16)

0.50 g (0.9 mmole) of $Cr(CO)_5\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$ was dissolved in acetone (≈ 400 ml). The solution was stirred at room temperature. The reaction was continually monitored with thin layer chromatography. After 4 h three products were visible. The solvent was removed under reduced pressure and the products were purified with column chromatography, (eluting agent petroleum ether / dichloromethane 1/1.

The first band removed from the column was characterized as the purple starting compound, yield: 0.2g, 40.2 %. The second product was pale yellow compound of low yield and was not collected. The third red band was charaterized as $Cr\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$ **(16)**, yield: 0.2g, 45.1 %.

6.5.2 Decomposition of the Tungsten Thienylene Biscarbene Complex in Acetone, to yield, $W\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$, (17) and $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)O\}(CO)_5$, (19)

(a) Nitrogen Atmosphere

0.5 g (0.5924 mmole) of $W(CO)_5\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$ was dissolved in acetone. The solution was stirred at room temperature for 4.5 h. The solvent was removed under reduced pressure. Three bands were separated with column chromatography, (eluting agent: petroleum ether / dichloromethane 1/1). The first compound was identified as unreacted starting compound. The second band was a pale yellow band of very low yield and was not collected as no significant characterization would be possible. The third product, a pale yellow band was identified as $W\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$, **(17)**, yield: 0.3 g, 60.3 %.

(b) Argon Atmosphere

This reaction was repeated but in an argon atmosphere instead of a nitrogen atmosphere. The same procedure was followed but the solution was stirred for about 8 h. Three bands were separated on thin layer chromatography preparative plates. The first a purple product was identified as the starting compound. The second a brown band did not correspond with the product isolated from the same reaction done in a nitrogen atmosphere and was identified as, $W\{C(OEt)C_4H_2SC(OEt)C_4H_2SC(OEt)$-$C_4H_2SC(O)OEt\}(CO)_5$, **(19)** yield: 0.2 g, 45.2 %.

6.5.3 Decomposition of the Manganese Methylcyclopentadienyl Thienylene Biscarbene Complex in Acetone, to yield $Mn\{C(OEt)C_4H_2SC(O)OEt\}(\eta^5$-$C_5H_4CH_3)(CO)_2$, (18)

0.51 g (0.9 mmole) of $(\eta^5\text{-}C_5H_4CH_3)(CO)_2$ $Mn\{C(OEt)C_4H_2SC(OEt)\}Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_2$ was dissolved in acetone. The solution was exposed to ultra violet rays for 2 h during which time a colour change was detected. Thin layer chromatography showed that only one product had been formed. The product was filtered through kieselgel. The solvent was removed under reduced pressure and a brown red

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oil was isolated, yield: 0.46 g, 90.4 %. The compound was characterized as, Mn{C(OEt)C_4H_2SC(O)-OEt}(η^5-$C_5H_4CH_3$)$(CO)_2$, **(18)**.

6.5.4 Reaction of the Chromium Thienylene Biscarbene Complex in Carbon Disulphide, to yield Cr{C(OEt)C_4H_2S-3-[2,5-{C(S)OEt}$_2$$C_4$HS]}$(CO)_5$, (20).

0.51 g (0.9 mmole) of $Cr(CO)_5$\{C(OEt)C_4H_2SC(OEt)\}$Cr(CO)_5$ was dissolved in (about 300 ml) of carbon disulphide. The solution was refluxed at 46 °C. After about 4 h the colour of the reaction had changed from purple to reddish pink. Thin layer chromatography revealed that the starting compound had disappeared and that two products had been yielded. These products were isolated with column chromatography, (eluting agent petroleum ether / dichloromethane 1/1).

The first of these products, yield: 0.4 g, 70.5 %, had a bright pink colour and was charaterized as, a dithienyl carbene complex with two thiocarboxylate substituents, Cr{C(OEt)C_4H_2S-3-[2,5-{C(S)OEt}$_2$-C_4HS]}$(CO)_5$, **(20)** and the second red product as the *O*-ethyl thienylcarboxylate monocarbene complex, Cr{C(OEt)C_4H_2SC(O)OEt}$(CO)_5$, **(16)**, yield: 0.1 g, 20.5 %.

6.5.5 Reaction of the Tungsten Thienylene Biscarbene Complex in Carbon Disulphide, to yield W{C(OEt)C_4H_2SC(S)OEt}$(CO)_5$, (21)

0.50 g (0.6 mmole) of $W(CO)_5$\{C(OEt)C_4H_2SC(OEt)\}$W(CO)_5$ was dissolved in carbon disulphide. The reaction mixture was exposed to ultra violet rays at room temperature. After 2.5 h thin layer chromatography indicated the presence of three products. The reaction was stopped and the solvent removed under reduced pressure. The three bands were separated with column chromatography, (eluting agent petroleum ether / dichloromethane 1/1).

The first of the products was pale yellow and was identified as the *O*-ethyl thienyl carboxylate monocarbene complex, W{C(OEt)C_4H_2SC(O)OEt}$(CO)_5$, **(17)**, with a yield of 0.1 g, 33.6 %. The second a purple compound was identified as the unreacted starting compound, yield: 0.05 g, 9.5 %. The third was the *O*-ethyl thienyl thiocarboxylate monocarbene complex, W{C(OEt)C_4H_2SC(S)OEt}$(CO)_5$, **(21)**, with a yield of 0.2 g, 48.3 %.

6.5.6 Reaction of the Manganese Methylcyclopentadienyl Thienylene Biscarbene Complex in Carbon Disulphide, to yield Mn{C(OEt)C_4H_2SC(S)-OEt}(η^5-$C_5H_4CH_3$)$(CO)_2$], (22) and Mn{C(OEt)C_4H_2S-3-[2,5-{C(S)OEt}{C(O)OEt}C_4HS]}(η^5-$C_5H_4CH_3$)$(CO)_2$, (23)

0.52 g (0.9 mmole) of (η^5-$C_5H_4CH_3$)$(CO)_2$ Mn{C(OEt)C_4H_2SC(OEt)}Mn(η^5-$C_5H_4CH_3$)$(CO)_2$ was dissolved in carbon disulphide. The solution was refluxed at 46 °C for about 3 h, after which thin layer chromatography revealed that three products were present in the reaction mixture. The reaction was stopped and the solvent removed under reduced pressure. The three bands were separated with column chromatography, (eluting agent petroleum ether / dichloromethane 1/1). Both of the first and second products had a reddish pink colour and respective yields of 0.2 g, 33.4 and 0.2 g, 32.6 %. These products were identified as the *O*-ethyl thienyl thiocarboxylate monocarbene complex, Mn{C(OEt)-C_4H_2SC(S)OEt}(η^5-$C_5H_4CH_3$)$(CO)_2$, **(22)** and the dithienyl carbene complex with a carboxylate and thiocarboxylate substituent, Mn{C(OEt)C_4H_2S-3-[2,5-{C(S)OEt}{C(O)OEt}C_4HS]}(η^5-$C_5H_4CH_3$)$(CO)_2$, **(23)**. The third product was red purple, yield: 0.1g, 25.7 %, and was characterized as the starting compound.

6.5.7 Reaction of the Manganese Cyclopentadienyl Thienylene Biscarbene Complex in Carbon Disulphide, to yield Mn{C(OEt)C_4H_2SC(O)OEt}(η^5-C_5H_5)$(CO)_2$, (24) and Mn{C(OEt)C_4H_2SC(S)OEt}(η^5-C_5H_5)$(CO)_2$, (25)

The same procedure was followed as for the methylcyclopentadienyl analogue. The solution was refluxed for 4 h after which the solvent was removed under reduced pressure. Two products were separated with column chromatography. The first of these was identified as the *O*-ethyl thienyl carboxylate monocarbene complex Mn{C(OEt)C_4H_2SC(O)OEt}(η^5-C_5H_5)$(CO)_2$, **(24)** and the *O*-ethyl thienyl thiocarboxylate monocarbene complex, Mn{C(OEt)C_4H_2SC(S)OEt}(η^5-C_5H_5)$(CO)_2$, **(25)**. The respective yields of these products were 0.2 g, 42.3 %, **(24)** and 0.26 g, 50.1 %, **(25)**.

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6.5.8 Decomposition of the Chromium Thienylene Biscarbene Complex in Hexane, to yield, $Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(O)OEt\}_2C_4HS](CO)_5$, (26) and $Cr\{C(OEt)C_4H_2SC(O)C(O)C_4H_2SC(O)OEt\}(CO)_5$, (27)

0.5 g (0.9 mmole) of $Cr(CO_5)\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$ was dissolved in ± 300 ml of hexane. The stirred solution was refluxed at 69 °C. The reaction was continually monitored with thin layer chromatography. After 12 h the colour changed from purple to a bright pink. The solvent was removed under reduced pressure. Two products were separated with colomn chromatography (eluting agent petroleum ether / dichloromethane 1/1). The first of these was characterized as a dithienyl carbene complex containing two carboxylate substituents, $Cr\{C(OEt)C_4H_2S\text{-}3\text{-}[2,5\text{-}\{C(O)OEt\}_2C_4HS](CO)_5$, **(26)**, yield: 0.1 g, 26.5 %. The second a bright pink compound was identified as, $Cr\{C(OEt)C_4H_2SC(O)\text{-}C(O)C_4H_2SC(O)OEt\}(CO)_5$, **(27)**, yield:0.3 g, 63.3 %.

6.6 Reactions with Alkynes

The different thienylene bimetallic biscarbene complexes were reacted with alkynes to yield new products.

6.6.1 Reaction of the Chromium Thienylene Biscarbene Complex with Hex-3-yne, to form $Cr\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$, (28)

0.08 ml (0.7 mmole) of hex-3-yne was added to a stirred solution of 0.2 g (0.4 mmole) of $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$ in THF. Stirring was maintained while the reaction mixture was refluxed at 45 °C. After about 15 min a change in colour from purple to orange was visible. The reaction was stopped and the solvent was removed under reduced pressure.

Four bands were separated with column chromatography, (eluting agent petroleum ether / dichloromethane 1/1). The first product which was purple was characterized as the starting compound, yield: 0.02 g, 11.1 %. The second red compound was identified as the decomposition product $Cr\{C(OEt)C_4H_2SC(O)OEt\}(CO)_5$, **(16)**, yield: 0.03 g, 15.7 %. The third product which was orange was identified as $Cr\{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS\}(CO)_5$, **(28)**, yield: 0.1 g, 73.7 %.

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6.6.2 Reaction of the Tungsten Thienylene Biscarbene Complex with Hex-3-yne, to form W{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS}(CO)$_5$, (29)

0.06 ml (0.5 mmole) of hex-3-yne was added to a stirred solution of 0.21 g (0.2 mmole) of [(CO)$_5$W{C(OEt)C$_4$H$_2$SC(OEt)}W(CO)$_5$] in toluene. The reaction mixture was refluxed while magnetic stirring was maintained. The reaction was monitored with thin layer chromatography. After 8 h the reaction mixture had undergone a colour change from purple to orange. The reaction was stopped and the solvent was removed under reduced pressure.

Three bands were separated with column chromatography , (eluting agent: petroleum ether / dichloromethane 1/1. The first of these a purple band was identified as the starting compound, yield: 0.02 g, 10.2 %. The second and third products were respectively yellow and orange and were identified as the decomposition product, W{C(OEt)C$_4$H$_2$SC(O)OEt)}(CO)$_5$, **(17)**, yield: 0.05 g, 25.2 % and , W{C(OEt)CCHCC(OH)C(Et)C(Et)C(OEt)CS}(CO)$_5$, **(29)**, yield: 0.1g, 65.4 %.

6.6.3 Reaction of the Chromium Thienylene Biscarbene Complex with Biphenyl Acetylene to form Cr{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS}(CO)$_5$, (30), the Intermediate, (CO)$_5$Cr{C(OEt)C$_4$H$_2$SC(OEt)C(Ph)C(Ph)}Cr(CO)$_5$, (32), the σ,π-Complex, ({η^1:η^6-SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)$_5$}Cr(CO)$_3$, (33) and Cr{C(OEt)CCHCC(OH)C(Ph)C(Ph)C(OEt)CS}(CO)$_5$, (34)

0.19 g (1.1 mmole) of PhC≡CPh was added to a 0.31 g (0.5 mmole) solution of [(CO)$_5$Cr{C(OEt)C$_4$H$_2$SC(OEt)}Cr(CO)$_5$] in THF. The stirred reaction was refluxed at 45 - 50 °C. The reaction was monitored with thin layer chromatography. After 3.5 h the reaction was stopped and the solvent removed under reduced pressure. The mixture of compounds was dissolved in the minimum amount of eluting agent (petroleum ether / dichloromethane (1/1)) and separated with column chromatography.

Four products were separated. The first band a purple product was identified as the starting compound, yield: 0.03 g, 8.3 %. The second product had a bright pink colour and was identified as Cr{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS}(CO)$_5$, **(30)**, yield: 0.1 g, 30.8 %. The third orange product was characterized as an intermediate, $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)C(Ph)C(Ph)\}Cr(CO)_5$, **(32)**, yield: 0.1 g, 31.1 %. The last product could only be eluated from the column with pure dichloromethane as eluting agent. Charaterization revealed this product to be, $(\{\eta^1{:}\eta^6$-$SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3]$, **(33a)** yield: 0.1 g, 31.9 %.

Product **(33a)** on the exposure to air converted to, $\{\eta^1{:}\eta^5$-$SCC(OEt)C(Ph)C(Ph)C(OH)CCHCC(OEt)Cr(CO)_5\}Cr(CO)_3$, **(33b)** and ultimately to $Cr\{C(OEt)CCHCC(OH)C(Ph)C(Ph)C(OEt)CS\}(CO)_5$, **(34)**, an orange coloured product from which the π-coordinated $Cr(CO)_3$-fragment is absent, yield: 0.1g, 90.6 %.

6.6.4 Reaction of the Tungsten Thienylene Biscarbene Complex with Biphenyl Acetylene, to form, $W\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$, (31)

0.13 g (0.4 mmole) of $PhC{\equiv}CPh$ was added to a solution of 0.3 g (0.4 mmole) of $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$ in toluene. The stirred reaction mixture was refluxed at 70 °C. The reaction was monitored with thin layer chromatography and stopped after 10 h. The solvent was removed under reduced pressure.

Three bands were isolated with column chromatography. The first of these was a purple compound which was identified as the starting compound, yield: 0.02 g, 9.8 %. The second bright pink product was identified to be, $W\{C(OEt)CCHCHC(Ph)C(Ph)C(OEt)CS\}(CO)_5$, **(31)**, yield: 0.1 g, 40.2 %. Closer observation of the third orange band revealed that it was a mixture of various decomposition products of which the yields were too low to enable significant characterization, these compounds were therefore not isolated.

6.7 References

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Appendix 1

Crystallographic Data of $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$

Table 1 Crystallographic Data of $(CO)_5Cr\{C(OEt)C_4H_2SC(OEt)\}Cr(CO)_5$, (1)

	1
Empirical Formula	$C_{20}H_{12}Cr_2O_{12}S$
Molecular Weight	580
Crystal Dimensions, mm	0.14 x 0.17 x 0.24
Space Group	C2/c
Cell Dimensions a, Å b, Å c, Å β, °	 21.593(12) 10.235(3) 22.531(12) 92.06(4)
Z	8
Volume	4976(1)
D (calc), g.cm^{-3}	1.55
μ, cm^{-1}	9.47
Radiation (λ, Å)	Mo-K$_\alpha$,(0.7107)
T, °C	25
F(000)	2.336.90
Scan Type (ω:2θ)	1:1
Scan Range (θ°)	$3 \leq \theta \leq 30$
Max. scan speed (deg. min^{-1})	5.49
Scan angle (ω + 0.34 tan θ) °	0.45
Aperture size (mm)	1.3 x 4.0
Reflections collected	7771
Unique reflections used (> 3 σ (I))	3267
Parameters refined	325
Max. positional shift/esd	
R	0.0526

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Table 2 Fractional Atomic Coordinates (x 10^4) and Equivalent Thermal Factors (x 10^3 Å^2)

	x/a	y/b	z/c	U_{eq}
Cr(1)	2605(1)	3429(1)	1631(10)	37(1)
Cr(2)	589(1)	7032(1)	-1244(1)	40(1)
S(1)	1205(1)	7032(1)	-1244(1)	40(1)
C(1)	671(3)	6098(5)	-1969(2)	45(1)
C(2)	-282(3)	7060(6)	-1354(2)	54(2)
C(3)	572(3)	8628(6)	-1673(3)	59(2)
C(4)	478(3)	7974(6)	-525(3)	55(2)
C(5)	1455(3)	7188(6)	-1200(2)	48(1)
C(6)	3150(3)	4293(6)	1122(2)	50(2)
C(7)	2137(3)	3858(6)	2314(2)	54(2)
C(8)	3098(3)	3858(6)	2314(2)	54(2)
C(9)	2071(3)	2521(5)	2136(2)	43(1)
C(10)	3116(3)	1941(6)	1592(2)	48(1)
C(11)	1095(2)	5073(5)	-284(2)	36(1)
C(12)	1496(2)	5907(5)	25(2)	42(1)
C(13)	1876(3)	5306(5)	453(2)	41(1)
C(14)	1776(2)	3987(5)	487(2)	37(1)
C(15)	2072(2)	2991(5)	892(2)	38(1)
C(16)	2044(3)	615(5)	955(2)	62(2)
C(17)	1619(3)	-361(6)	718(3)	92(2)
C(18)	648(3)	5335(5)	-768(2)	42(1)
C(19)	-186(3)	4052(6)	-1263(3)	70(2)
C(20)	-209(4)	2684(7)	-1408(3)	126(3)
O(1)	727(2)	5578(4)	-2405(2)	75(1)
O(2)	-803(2)	7198(5)	-1443(2)	89(2)
O(3)	552(2)	9590(5)	-1920(2)	97(2)
O(4)	388(2)	8527(5)	-105(2)	92(2)
O(5)	1987(2)	7296(5)	-1188(2)	74(1)

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O(6)	3487(2)	4765(4)	810(2)	80(1)
O(7)	1862(2)	5878(4)	1892(2)	77(1)
O(8)	3405(2)	4040(4)	2732(2)	83(1)
O(9)	1755(2)	1992(4)	2452(2)	69(1)
O(10)	3456(2)	1089(5)	1606(2)	88(2)
O(11)	1890(2)	1851(3)	675(1)	50(1)
O(12)	306(2)	4259(4)	-823(2)	59(1)

$$\underline{U}_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j\underline{U}_{ij}\underline{a}_i{}^*\underline{a}_j{}^*(a_j \cdot a_j)$$

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Table 3 Bond Lengths (Å)

Cr(1)-C(6)	1.893(6)	Cr(1)-C(7)	1.906(6)
Cr(1)-C(8)	1.891(5)	Cr(1)-C(9)	1.893(5)
Cr(1)-C(10)	1.884(6)	Cr(1)-C(15)	2.040(5)
Cr(2)-C(1)	1.906(5)	Cr(2)-C(2)	1.889(6)
Cr(2)-C(3)	1.896(6)	Cr(2)-C(4)	1.909(6)
Cr(2)-C(5)	1.875(6)	Cr(2)-C(18)	2.043(5)
S(1)-C(11)	1.730(5)	S(1)-C(14)	1.732(5)
C(1)-O(1)	1.128(5)	C(2)-O(2)	1.145(6)
C(3)-O(3)	1.132(6)	C(4)-O(4)	1.126(6)
C(5)-O(5)	1.154(6)	C(6)-O(6)	1.137(6)
C(7)-O(7)	1.140(6)	C(8)-O(8)	1.147(6)
C(9)-O(9)	1.142(5)	C(10)-O(10)	1.139(6)
C(11)-C(12)	1.385(6)	C(11)-C(18)	1.456(8)
C(12)-C(13)	1.388(6)	C(13)-C(14)	1.371(6)
C(14)-C(15)	1.496(6)	C(15)-O(11)	1.319(5)
C(16)-C(17)	1.447(7)	C(16)-O(11)	1.447(6)
C(18)-O(12)	1.330(6)	C(19)-C(20)	1.438(8)
C(19)-O(12)	1.443(6)		

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Table 4 Valence Angles (°)

C(6)-Cr(1)-C(7)	93.6(3)	C(6)-Cr(1)-C(8)	92.3(2)
C(7)-Cr(1)-C(8)	87.5(2)	C(6)-Cr(1)-C(9)	178.4(2)
C(7)-Cr(1)-C(9)	88.0(2)	C(8)-Cr(1)-C(9)	87.8(2)
C(6)-Cr(1)-C(10)	88.4(2)	C(7)-Cr(1)-C(10)	172.3(2)
C(8)-Cr(1)-C(10)	85.0(2)	C(9)-Cr(1)-C(10)	90.1(2)
C(6)-Cr(1)-C(15)	87.3(2)	C(7)-Cr(1)-C(15)	91.9(2)
C(8)-Cr(1)-C(15)	179.3(2)	C(9)-Cr(1)-C(15)	92.6(2)
C(10)-Cr(1)-C(15)	95.7(2)	C(1)-Cr(2)-C(2)	91.1(2)
C(1)-Cr(2)-C(3)	89.9(2)	C(2)-Cr(2)-C(3)	85.4(3)
C(1)-Cr(2)-C(4)	178.1(2)	C(2)-Cr(2)-C(4)	87.0(2)
C(3)-Cr(2)-C(4)	89.8(3)	C(1)-Cr(2)-C(5)	88.0(2)
C(2)-Cr(2)-C(5)	172.8(3)	C(3)-Cr(2)-C(5)	87.4(3)
C(4)-Cr(2)-C(5)	93.8(2)	C(1)-Cr(2)-C(18)	91.0(2)
C(2)-Cr(2)-C(18)	97.1(2)	C(3)-Cr(2)-C(18)	177.4(2)
C(4)-Cr(2)-C(18)	89.5(2)	C(5)-Cr(2)-C(18)	90.1(2)
C(11)-S(1)-C(14)	92.3(2)	Cr(2)-C(1)-O(1)	177.9(5)
Cr(2)-C(2)-O(2)	173.3(6)	Cr(2)-C(3)-O(3)	178.4(6)
Cr(2)-C(4)-O(4)	177.2(6)	Cr(2)-C(5)-O(5)	178.1(5)
Cr(1)-C(6)-O(6)	177.3(6)	Cr(1)-C(7)-O(7)	176.4(5)
Cr(1)-C(8)-O(8)	175.9(6)	Cr(1)-C(9)-O(9)	178.3(5)
Cr(1)-C(10)-O(10)	174.2(5)	S(1)-C(11)-C(12)	109.3(4)
S(1)-C(11)-C(18)	120.3(4)	C(12)-C(11)-C(18)	130.4(5)
C(11)-C(12)-C(13)	114.8(5)	C(12)-C(13)-C(14)	112.6(5)
S(1)-C(14)-C(13)	111.0(4)	S(1)-C(14)-C(15)	119.1(4)
C(13)-C(14)-C(15)	129.8(5)	Cr(1)-C(15)-C(14)	124.3(4)
Cr(1)-C(15)-O(11)	130.4(4)	C(14)-C(15)-O(11)	105.2(4)
C(17)-C(16)-O(11)	108.1(5)	Cr(2)-C(18)-C(11)	125.3(4)
Cr(2)-C(18)-O(12)	129.2(3)	C(11)-C(18)-O(12)	105.5(4)
C(20)-C(19)-O(12)	108.4(6)	C(15)-O(11)-C(16)	123.5(4)

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C(18)-O(12)-C(19)	125.3(4)		

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Table 5 Anisotropic Temperature Factors (x 10^3 Å^2)

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Cr(1)	40(1)	42(1)	28(1)	0(1)	-4(1)	2(1)
Cr(2)	38(1)	48(1)	33(1)	6(1)	-4(1)	2(1)
S(1)	55(1)	44(1)	35(1)	5(1)	-13(1)	-10(1)
C(1)	47(4)	48(4)	40(3)	9(3)	0(3)	6(3)
C(2)	48(4)	79(5)	35(3)	-2(3)	5(3)	-2(4)
C(3)	62(4)	61(4)	52(4)	7(3)	-13(3)	2(4)
C(4)	60(4)	47(4)	56(4)	-1(3)	-12(3)	5(3)
C(5)	47(4)	56(4)	39(3)	14(3)	-7(3)	-1(3)
C(6)	54(4)	54(4)	40(3)	-1(3)	-5(3)	-9(3)
C(7)	59(4)	48(4)	41(3)	2(3)	-11(3)	2(3)
C(8)	60(4)	57(4)	43(3)	-2(3)	-8(3)	-7(3)
C(9)	44(3)	46(4)	40(3)	-2(3)	-2(3)	4(3)
C(10)	47(4)	62(4)	36(3)	-1(3)	-6(3)	3(3)
C(11)	36(3)	47(3)	26(2)	5(2)	-3(2)	-2(3)
C(12)	48(4)	40(3)	37(3)	6(3)	-10(3)	-4(3)
C(13)	52(4)	39(3)	32(3)	1(2)	-6(3)	-6(3)
C(14)	34(3)	51(4)	25(2)	0(2)	-1(2)	-3(3)
C(15)	39(3)	48(3)	28(3)	0(3)	7(2)	-4(3)
C(16)	93(6)	37(4)	56(4)	2(3)	-15(4)	-1(4)
C(17)	141(8)	53(5)	80(5)	11(4)	-39(5)	-37(5)
C(18)	47(4)	49(4)	30(3)	3(3)	-9(2)	-9(3)
C(19)	62(5)	92(5)	55(4)	11(4)	-29(3)	-26(4)
C(20)	172(9)	87(7)	114(7)	18(6)	-84(6)	-61(7)
O(1)	90(4)	93(4)	41(2)	-15(2)	-3(2)	16(3)
O(2)	41(3)	154(5)	70(3)	-3(3)	1(2)	10(3)
O(3)	117(5)	71(4)	100(4)	44(3)	-11(3)	4(3)
O(4)	106(4)	108(4)	63(3)	-41(3)	0(3)	8(3)
O(5)	44(3)	106(4)	72(3)	22(3)	-4(2)	-8(3)

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O(6)	84(4)	94(4)	63(3)	8(3)	15(3)	-32(3)
O(7)	104(4)	60(3)	68(3)	-9(2)	10(3)	29(3)
O(8)	106(4)	86(4)	53(3)	-3(3)	-38(3)	-11(3)
O(9)	78(3)	70(3)	59(3)	11(3)	23(2)	-3(3)
O(10)	98(4)	86(4)	80(1)	-7(3)	-5(3)	49(3)
O(11)	71(3)	37(2)	41(2)	1(2)	-18(2)	-2(2)
O(12)	69(3)	59(3)	46(2)	15(2)	-27(2)	-22(2)

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Table 6 Fractional Coordinates (x 10^4) of the Hydrogen Atoms with Isotropic Thermal Parameters (x 10^3 Å^2)

	x / a	y / b	z / c	U
H(12)	1511(2)	6944(5)	-61(2)	106(7)
H(13)	2214(3)	5822(5)	730(2)	106(7)
H(16A)	2514(3)	346(5)	861(2)	106(7)
H(16B)	1999(3)	695(5)	1430(2)	106(7)
H(17A)	1763(3)	-1302(6)	891(3)	106(7)
H(17B)	1506(3)	-447(6)	249(3)	106(7)
H(17C)	1216(3)	-32(6)	946(3)	106(7)
H(19A)	-97(3)	4611(6)	-1658(3)	106(7)
H(19B)	-623(3)	4353(6)	-1088(3)	106(7)
H(20A)	-619(4)	2627(7)	-1694(3)	106(7)
H(20B)	-183(4)	1833(7)	-1125(3)	106(7)
H(20C)	196(4)	2723(7)	-1675(3)	106(7)

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Table 7 Valence Angles Involving the Hydrogen Atoms (°)

C(11)-C(12)-H(12)	122.6(3)	H(12)-C(12)-C(13)	122.6(3)
C(12)-C(13)-H(13)	123.7(3)	H(13)-C(13)-C(14)	123.7(3)
H(16A)-C(16)-H(16B)	109.5(0)	H(16A)-C(16)-C(17)	109.9(4)
H(16B)-C(16)-C(17)	109.8(4)	H(16A)-C(16)-O(11)	109.9(3)
H(16B)-C(16)-O(11)	109.7(3)	C(16)-C(17)-H(17A)	108.2(4)
C(16)-C(17)-H(17B)	122.3(4)	H(17A)-C(17)-H(17B)	109.5(0)
C(16)-C(17)-H(17C)	97.0(4)	H(17A)-C(17)-H(17C)	109.5(0)
H(17B)-C(17)-H(17C)	109.5(0)	H(19A)-C(19)-H(19B)	109.5(0)
H(19A)-C(19)-C(20)	109.6(4)	H(19B)-C(19)-C(20)	109.7(5)
H(19A)-C(19)-O(12)	109.9(3)	H(19B)-C(19)-O(12)	109.8(3)
C(19)-C(20)-H(20A)	102.0(4)	C(19)-C(20)-H(20B)	130.6(4)
H(20A)-C(20)-H(20B)	109.5(0)	C(19)-C(20)-H(20C)	93.9(5)
H(20A)-C(20)-H(20C)	109.5(0)	H(20B)-C(20)-H(20C)	109.5(0)

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Table 8 Bond Lengths (Å) Involving the Hydrogen Atoms

C(12)-H(12)	1.080(0)	C(13)-H(13)	1.080(0)
C(16)-H(16A)	1.080(0)	C(16)-H(16B)	1.080(0)
C(17)-H(17A)	1.080(0)	C(17)-H(17B)	1.080(0)
C(17)-H(17C)	1.080(0)	C(19)-H(19A)	1.080(0)
C(19)-H(20B)	1.080(0)	C(20)-H(20A)	1.080(0)
C(20)-H(20B)	1.080(0)	C(20)-H(20C)	1.080(0)

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Appendix 2

Crystallographic Data of $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$

Table 1 Crystallographic Data of $(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5$, (2)

	2
Empirical Formula	$C_{20}H_{12}W_2O_{12}S$
Molecular Weight	844.069
Crystal Dimensions, mm	0.25 x 0.26 x 0.45
Space Group	P21/n (14)
Cell Dimensions	
a, Å	14.731(1)
b, Å	12.016(1)
c, Å	15.087(2)
α, °	90
β, °	111.08
γ, °	90
Z	4
Volume	2492(1)
D (calc), g.cm^{-3}	2.219
μ, cm^{-1}	9.00
Radiation (λ, Å)	Mo-K$_\alpha$, (0.7107)
T, °C	23(1)
F(000)	1568
Scan Type (ω:2θ)	1:1
Scan Range (θ°)	$3 \leq \theta \leq 30$
Zone Collected:	
h	0.20
k	0.16
l	-21, 21
Max. scan speed (deg. min^{-1})	5.48
Max. scan time, sec.	60

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Scan angle ($\omega + 0.34 \tan \theta$) °	0.48
Aperture size (mm)	1.3 x 4.0
Reflections collected	7811
Decay, %	7.0 (corrected)
EAC correction factor: Maximum Minimum Average	 1.000 0.883 0.946
Unique reflections used (> 3 σ (I))	5449
R_{int}	0.021
Parameters refined	323
Max. positional shift/esd	0.106
Residual electron density ($eÅ^3$): Maximum Minimum	 1.946 -1.946
$U_{iso}(H)$, $Å^2$	0.084(12)
R	0.056
R_w	0.046

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Table 2 Fractional Coordinates (x 10^4) and Equivalent Thermal Factors (x 10^3 Å^2)

	x / a	y / b	z / c	U_{eq}
W(1)	4836(1)	2219(1)	1148(1)	43(1)
W(2)	937(1)	7957(1)	48(1)	40(1)
S	4061(2)	6095(2)	1361(2)	47(1)
C(1)	2814(7)	6313(9)	847(8)	41(2)
C(2)	2364(8)	5361(9)	374(8)	44(3)
C(3)	3018(8)	4474(9)	474(8)	49(3)
C(4)	3986(7)	4733(8)	978(7)	37(2)
C(5)	4841(7)	4012(10)	1207(8)	50(3)
O(1)	5572(5)	4727(6)	1525(6)	58(2)
C(6)	6598(9)	4375(10)	1887(11)	78(4)
C(7)	7221(9)	5252(12)	2327(11)	83(4)
C(8)	3703(10)	9279(11)	2827(8)	70(4)
C(9)	2922(9)	9064(9)	1923(9)	63(3)
O(2)	3055(6)	7932(6)	1625(6)	55(2)
C(10)	2360(8)	7377(9)	930(7)	41(3)
C(11)	3975(10)	2219(12)	-165(12)	79(4)
O(3)	3456(8)	2223(11)	-981(8)	118(4)
C(12)	3605(9)	2214(9)	1539(12)	79(4)
O(4)	3046(8)	2185(9)	1850(9)	113(4)
C(13)	4825(9)	608(10	1097(10)	61(4)
O(5)	4792(8)	-390(8))	1070(8)	91(3)
C(14)	5738(9)	2099(11)	2561(11)	66(4)
O(6)	6211(7)	1991(10)	3327(7)	89(3)
C(15)	6068(9)	2108(10)	785(10)	61(4)
O(7)	6659(6)	1913(8)	554(7)	77(3)
C(16)	348(11)	6584(9)	359(8)	61(4)
O(8)	-145(7)	5883(7)	522(7)	77(3)
C(17)	610(8)	8703(10)	1161(9)	51(3)

O(9)	347(7)	9079(8)	1677(6)	73(3)
C(18)	-404(9)	8461(10)	-858(9)	52(3)
O(10)	-1149(6)	8730(8)	-1356(6)	72(3)
C(19)	1450(10)	9406(9)	-226(9)	63(4)
O(11)	1773(7)	10212(8)	-421(7)	82(3)
C(20)	1179(9)	7198(12)	-1106(9)	65(4)
O(12)	1236(7)	6837(9)	-1743(7)	96(3)

$$\underline{U}_{eq} = \tfrac{1}{3}\,\Sigma_i \Sigma_j \underline{U}_{ij}\, \underline{a}_i^* \underline{a}_j^* (a_i \cdot a_j)$$

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Table 3 Bond Lengths (Å)

W(1)-C(5)	2.156(12)	W(1)-C(11)	1.93(2)
W(1)-C(12)	2.099(13)	W(1)-C(13)	1.937(12)
W(1)-C(14)	2.07(2)	W(1)-C(15)	2.079(11)
W(2)-C(10)	2.154(11)	W(2)-C(16)	1.997(13)
W(2)-C(17)	2.105(11)	W(2)-C(18)	2.048(13)
W(2)-C(19)	2.000(13)	W(2)-C(20)	2.106(12)
S-C(1)	1.738(10)	S-C(4)	1.725(10)
C(1)-C(2)	1.385(13)	C(1)-C(10)	1.470(13)
C(2)-C(3)	1.407(13)	C(3)-C(4)	1.390(13)
C(4)-C(5)	1.464(13)	C(5)-O(1)	1.325(12)
O(1)-C(6)	1.473(13)	C(6)-C(7)	1.40(2)
C(8)-C(9)	1.46(2)	C(9)-O(2)	1.468(11)
O(2)-C(10)	1.349(12)	C(11)-O(3)	1.19(2)
C(12)-O(4)	1.085(14)	C(13)-O(5)	1.200(13)
C(14)-O(6)	1.122(14)	C(15)-O(7)	1.074(12)
C(16)-O(8)	1.194(14)	C(17)-O(9)	1.086(12)
C(18)-O(10)	1.131(13)	C(19)-O(11)	1.162(14)
C(20)-O(12)	1.085(13)		

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Table 4 Valence Angles (°)

C(5)-W(1)-C(11)	92.5(5)	C(5)-W(1)-C(12)	88.9(4)
C(11)-W(1)-C(12)	88.5(6)	C(5)-W(1)-C(13)	179.6(3)
C(11)-W(1)-C(14)	88.1(6)	C(12)-W(1)-C(13)	90.7(5)
C(5)-W(1)-C(14)	92.0(5)	C(11)-W(1)-C(14)	175.9(6)
C(12)-W(1)-C(14)	90.5(6)	C(13)-W(1)-C(14)	87.9(6)
C(5)-W(1)-C(15)	94.9(4)	C(11)-W(1)-C(15)	92.5(6)
C(12)-W(1)-C(15)	176.0(4)	C(13)-W(1)-C(15)	85.5(5)
C(14)-W(1)-C(15)	88.2(5)	C(10)-W(2)-C(16)	89.9(5)
C(10)-W(2)-C(17)	95.5(4)	C(16)-W(2)-C(17)	85.5(5)
C(10)-W(2)-C(18)	176.5(4)	C(16)-W(2)-C(18)	90.3(5)
C(17)-W(2)-C(18)	88.0(4)	C(10)-W(2)-C(19)	93.0(5)
C(16)-W(2)-C(19)	175.2(5)	C(17)-W(2)-C(19)	90.4(5)
C(18)-W(2)-C(19)	87.1(5)	C(10-W(2)-C(20)	87.4(4)
C(16)-W(2)-C(20)	93.1(5)	C(17)-W(2)-C(20)	176.8(5)
C(18)-W(2)-C(20)	89.2(4)	C(19)-W(2)-C(20)	91.0(5)
C(1)-S-C(4)	93.6(5)	S-C(1)-C(2)	109.8(8)
S-C(1)-C(10)	122.3(8)	C(2)-C(1)-C(10)	127.9(9)
C(1)-C(2)-C(3)	112.9(10)	C(2)-C(3)-C(4)	114.6(10)
S-C(4)-C(3)	109.0(8)	S-C(4)-C(5)	122.4(8)
C(3)-C(4)-C(5)	128.6(10)	W(1)-C(5)-C(4)	126.3(8)
W(1)-C(5)-O(1)	130.8(8)	C(4)-C(5)-O(1)	102.7(10)
C(5)-O(1)-C(6)	122.7(9)	O(1)-C(6)-C(7)	111.8(11)
C(8)-C(9)-O(2)	107.6(10)	C(9)-O(2)-C(10)	123.2(9)
W(2)-C(10)-C(1)	126.9(7)	W(2)-C(10)-O(2)	128.2(7)
C(1)-C(10)-O(2)	104.7(9)	W(1)-C(11)-O(3)	178.9(14)
W(1)-C(12)-O(4)	171(2)	W(1)-C(13)-O(5)	178.1(11)
W(1)-C(14)-O(6)	177.1(13)	W(1)-C(15)-O(7)	170.3(12)
W(2)-C(16)-O(8)	168.3(11)	W(2)-C(17)-O(9)	172.9(11)
W(2)-C(18)-O(10)	179.3(11)	W(2)-C(19)-O(11)	175.7(11)

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W(2)-C(20)-O(12)	174.5(12)		

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Table 5 Anisotropic Thermal Factors (x 10^3 Å^2)

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
W(1)	39(1)	39(1)	58(1)	-2(1)	26(1)	4(1)
W(2)	33(1)	42(1)	47(1)	0(1)	17(1)	5(1)
S	34(1)	41(2)	63(2)	-4(1)	13(1)	3(1)
C(1)	27(5)	45(6)	48(7)	5(5)	8(5)	4(5)
C(2)	34(6)	41(6)	60(8)	-5(6)	19(5)	-3(5)
C(3)	48(7)	35(6)	67(8)	-9(6)	23(6)	0(5)
C(4)	34(6)	37(6)	41(6)	7(5)	15(5)	4(5)
C(5)	22(5)	75(8)	52(7)	14(6)	14(5)	6(6)
O(1)	36(4)	47(5)	90(7)	-8(5)	20(5)	3(4)
C(6)	46(8)	50(8)	129(14)	-7(9)	21(9)	-5(7)
C(7)	41(8)	87(11)	110(13)	-14(10)	15(8)	-13(8)
C(8)	64(9)	70(9)	69(9)	-24(8)	18(8)	-5(8)
C(9)	65(9)	26(6)	86(10)	-16(6)	12(8)	1(6)
O(2)	47(5)	51(5)	64(5)	0(4)	17(4)	12(4)
C(10)	41(6)	42(6)	45(6)	-5(5)	20(5)	-5(5)
C(11)	55(9)	60(9)	120(14)	-7(10)	29(9)	7(8)
O(3)	86(9)	156(12)	97(9)	-9(9)	14(7)	25(9)
C(12)	56(8)	23(6)	176(16)	-9(8)	63(10)	4(6)
O(4)	82(8)	93(8)	207(13)	1(8)	105(9)	0(7)
C(13)	49(7)	49(7)	99(11)	-12(8)	43(8)	-1(6)
O(5)	106(9)	66(7)	124(9)	-11(7)	67(8)	9(6)
C(14)	48(8)	57(8)	101(11)	12(9)	36(8)	9(7)
O(6)	69(7)	135(10)	61(6)	20(7)	22(6)	16(7)
C(15)	59(8)	40(7)	101(11)	14(7)	50(8)	14(6)
O(7)	67(7)	92(7)	101(7)	17(6)	64(6)	22(6)
C(16)	98(11)	32(6)	51(8)	-4(6)	25(8)	10(7)
O(8)	73(7)	59(6)	113(9)	4(6)	50(6)	-9(5)
C(17)	50(7)	47(7)	57(8)	-6(6)	21(6)	7(6)

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O(9)	86(7)	79(7)	74(7)	-16(5)	53(6)	5(6)
C(18)	53(7)	47(7)	65(8)	-18(6)	33(7)	0(6)
O(10)	45(5)	80(7)	75(7)	5(5)	3(5)	17(5)
C(19)	89(11)	29(6)	66(9)	2(6)	20(8)	28(7)
O(11)	81(7)	68(7)	104(8)	7(6)	42(6)	4(6)
C(20)	45(7)	92(11)	58(8)	-18(8)	20(7)	-2(7)
O(12)	97(8)	137(10)	69(7)	-27(7)	49(7)	13(7)

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Table 6 Coordinates of the Hydrogen Atoms (x 10^3)

	x/a	y/b	z/c	U
H(2)	1593(8)	5304(9)	-29(8)	84(12)
H(3)	2785(8)	3658(9)	181(8)	84(12)
H(6A)	6786(9)	4074(10)	1300(11)	84(12)
H(6B)	6689(9)	3713(10)	2396(11)	84(12)
H(7A)	7997(9)	5110(12)	2614(11)	84(12)
H(7B)	6947(9)	5294(12)	2900(11)	84(12)
H(7C)	7072(9)	6026(12)	1937(11)	84(12)
H(8A)	3542(10)	10057(11)	3097(8)	84(12)
H(8B)	4467(10)	9251(11)	2927(8)	84(12)
H(8C)	3530(10)	8596(11)	3204(8)	84(12)
H(9C)	2226(9)	9130(9)	2007(9)	84(12)
H(9B)	2955(9)	9657(9)	1397(9)	84(12)

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Appendix 3

Crystallographic Data of (η^1:η^5-$C_4H_3SC(OEt)W(CO)_5)Cr(CO)_3$, (9)

Table 1 Crystallographic Data of (η^1:η^5-$C_4H_3SC(OEt)W(CO)_5)Cr(CO)_3$

	9
Formula	$C_{15}H_8Cr_1O_9S_1W_1$
Space group	$P\bar{1}$
a, Å	6.938(2)
b,Å	10.855(4)
c, Å	12.847(3)
α, deg	88.92(2)
β,deg	82.39(2)
γ, deg	86.44(2)
V, Å^3	957
Z	2
F(000)	568
d_{calc}, g/cm^3	2.08
Crystal size, mm	0.40 x 0.15 x 0.05
μ(Mo-K_α), cm^{-1}	68.2
Data collection instrument	Nicolet R3mV
Radiation	Mo-K_α (λ = 0.71073 Å)
Orientation reflections: no.;	28
range (2θ)	$14 \le 2\theta \le 24°$
Temp., K	293
Data measured	3666
Unique data	3313
No. of unique with $I \ge 3.0\sigma$ (I)	2460
No. of parameters	244
R [a]	0.0409
R_w [b]	0.0435

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Weighting scheme	$\omega^{-1} = \sigma^2 (F) + 0.000961F^2$
Largest shift/esd, final cycle	0.001
Largest peak	0.6

[a] $R = \Sigma[|F_0| - |F_c|] / \Sigma|F_0|$

[b] $R_w = \Sigma w^{½}. [|F_0| - |F_c|] / \Sigma w^{½}. |F_0|$

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Table 2 Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å ^{2} x 10^3)

	x/a	y/b	z/c	$\underline{U}_{eq}$
W(1)	8359(1)	-3893(1)	8005(1)	49(1)
Cr(1)	8597(2)	385(2)	7522(1)	48(1)
S(1)	5454(4)	136(2)	7073(2)	53(1)
C(1)	5683(16)	1193(9)	8030(9)	59(4)
C(2)	6403(15)	633(9)	8921(8)	52(3)
C(3)	6938(13)	-639(8)	8779(7)	44(3)
C(4)	6583(13)	-1053(8)	7797(7)	41(3)
C(5)	6988(14)	-2291(8)	7291(7)	43(3)
O(1)	6311(11)	-2150(6)	6388(5)	54(2)
C(7)	6544(21)	-3113(11)	5597(8)	69(4)
C(8)	5632(22)	-2649(14)	4707(9)	89(6)
C(11)	9236(19)	1892(12)	6869(10)	76(5)
O(11)	9627(19)	2819(9)	6464(9)	127(6)
C(21)	10496(17)	484(12)	8360(9)	67(4)
O(21)	11638(14)	531(12)	8937(7)	100(5)
C(31)	10303(17)	-496(12)	6501(9)	64(4)
O(31)	11299(15)	-1018(11)	5880(8)	108(4)
C(41)	10484(22)	-2922(12)	8489(10)	74(5)
O(41)	11764(18)	-2436(11)	8731(10)	120(5)
C(51)	9490(25)	-5415(14)	8667(10)	91(6)
O(51)	10104(23)	-6285(10)	9050(9)	143(7)
C(61)	10244(20)	-4283(11)	6645(9)	66(4)
O(61)	11331(41)	-4539(10)	5949(7)	89(4)
C(71)	6312(20)	-4966(10)	7614(8)	63(4)
O(71)	5122(18)	-5608(9)	7438(7)	99(4)
C(81)	6539(22)	-3564(10)	9365(9)	71(5)
O(81)	5558(18)	-3413(9)	10139(7)	98(4)

$\underline{U}_{eq} = \frac{1}{3} \Sigma_i \Sigma_j \underline{U}_{ij}\, \underline{a}_i^* \underline{a}_j^* (a_i \cdot a_j)$

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Table 3 Bond Lengths (Å)

W(1)-C(5)	2.173(9)	W(1)-C(41)	2.039(15)
W(1)-C(51)	2.011(15)	W(1)-C(61)	2.076(11)
W(1)-C(71)	2.005(13)	W(1)-C(81)	2.036(12)
Cr(1)-S(1)	2.360(3)	Cr(1)-C(1)	2.176(10)
Cr(1)-C(2)	2.205(10)	Cr(1)-C(3)	2.183(9)
Cr(1)-C(4)	2.152(9)	Cr(1)-C(11)	1.875(13)
Cr(1)-C(21)	1.819(12)	Cr(1)-C(31)	1.879(11)
S(1)-C(1)	1.726(11)	S(1)-C(4)	1.780(9)
C(1)-C(2)	1.420(15)	C(2)-C(3)	1.416(13)
C(3)-C(4)	1.404(13)	C(4)-C(5)	1.499(13)
C(5)-O(1)	1.311(11)	O(1)-C(7)	1.458(12)
C(7)-C(8)	1.446(18)	C(11)-O(11)	1.154(17)
C(21)-O(21)	1.158(16)	C(31)-O(31)	1.122(15)
C(41)-O(41)	1.140(20)	C(51)-O(51)	1.141(19)
C(61)-O(61)	1.118(14)	C(71)-O(71)	1.160(18)
C(81)-O(81)	1.137(15)		

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Table 4 Bond Angles (°)

C(5)-W(1)-C(41)	93.8(4)	C(5)-W(1)-C(51)	177.3(6)
C(41)-W91)-C(51)	88.8(6)	C(5)-W(1)-C(61)	92.5(4)
C(41)-W(1)-C(61)	87.5(5)	C(51)-W(1)-C(61)	88.5(5)
C(5)-W(1)-C(71)	91.0(4)	C(41)-W(1)-C(71)	175.0(5)
C(51)-W(1)-C(71)	86.4(6)	C(61)-W(1)-C(71)	93.6(5)
C(5)-W(1)-C(81)	89.6(4)	C(41)-W(1)-C(81)	92.3(5)
C(51)-W(1)-C(81)	89.4(5)	C(61)-W(1)-C(81)	177.9(5)
C(71)-W(1)-C(81)	86.4(5)	S(1)-Cr(1)-C(1)	44.5(3)
S(1)-Cr(1)-C(2)	69.9(3)	C(1)-Cr(1)-C(2)	37.8(4)
S(1)-Cr(1)-C(3)	71.0(3)	C(1)-Cr(1)-C(3)	65.6(4)
C(2)-Cr(1)-C(3)	37.6(4)	S(1)-Cr(1)-C(4)	46.2(3)
C(1)-Cr(1)-C(4)	70.3(4)	C(2)-Cr(1)-C(4)	64.9(4)
C(3)-Cr(1)-C(4)	37.8(3)	S(1)-Cr(1)-C(11)	102.5(4)
C(1)-Cr(1)-C(11)	88.9(5)	C(2)-Cr(1)-C(11)	112.2(5)
C(3)-Cr(1)-C(11)	149.9(4)	C(4)-Cr(1)-C(11)	148.6(5)
S(1)-Cr(1)-C(21)	158.0(4)	C(1)-Cr(1)-C(21)	119.7(5)
C(2)-Cr(1)-C(21)	88.9(4)	C(3)-Cr(1)-C(2)	88.5(4)
C(4)-Cr(1)-C(21)	119.6(5)	C(11)-Cr(1)-C(21)	90.9(6)
S(1)-Cr(1)-C(31)	105.1(4)	C(1)-Cr-C(31)	148.4(5)
C(2)-Cr(1)-C(31)	156.5(5)	C(3)-Cr(1)-C(31)	118.9(4)
C(4)-Cr(1)-C(31)	94.6(4)	C(11)-Cr(1)-C(31)	91.3(5)
C(21)-Cr(1)-C(31)	91.8(5)	Cr(1)-S(1)-C(1)	62.1(4)
Cr(1)-S(1)-C(4)	60.7(3)	C(1)-S(1)-C(4)	90.6(5)
Cr(1)-C(1)-S(1)	73.4(4)	Cr(1)-C(1)-C(2)	72.2(6)
S(1)-C(1)-C(2)	112.4(7)	Cr(1)-C(2)-C(1)	70.0(6)
Cr(1)-C(2)-C(3)	70.4(5)	C(1)-C(2)-C(3)	112.7(9)
Cr(1)-C(3)-C(2)	72.0(5)	Cr(1)-C(3)-C(4)	69.9(5)
C(2)-C(3)-C(4)	112.1(8)	Cr(1)-C(4)-S(1)	73.1(3)
Cr(1)-C(4)-C(3)	72.3(5)	S(1)-C(4)-C(3)	111.8(7)

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Cr(1)-C(4)-C(5)	122.0(6)	S(1)-C(4)-C(5)	117.3(7)
C(3)-C(4)-C(5)	131.0(8)	W(1)-C(5)-C(4)	124.6(6)
W(1)-C(5)-O(1)	131.2(6)	C(4)-C(5)-O(1)	104.2(7)
C(5)-O(1)-C(7)	122.7(8)	O(1)-C(7)-C(8)	108.0(10)
Cr(1)-C(11)-O(11)	179.8(11)	Cr(1)-C(21)-O(21)	176.5(10)
Cr(1)-C(31)-O(31)	178.8(11)	W(1)-C(41)-O(41)	175.5(11)
W(1)-C(51)-O(51)	178.8(14)	W(1)-C(61)-O(61)	175.7(11)
W(1)-C(71)-O(71)	176.7(9)	W(1)-C(81)-O(81)	177.7(11)

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Table 5 Anisotropic Displacement Parameters (Å x 10^3)

	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
W(1)	70(1)	41(1)	39(1)	-5(1)	-19(1)	5(1)
Cr(1)	52(1)	47(1)	44(1)	-10(1)	6(1)	-12(1)
S(1)	57(2)	43(1)	59(1)	1(1)	-11(1)	2(1)
C(1)	59(7)	38(5)	72(7)	-11(5)	16(6)	-3(5)
C(2)	51(6)	49(6)	53(5)	-17(5)	10(5)	-11(5)
C(3)	40(5)	41(5)	50(5)	-11(4)	6(4)	-14(4)
C(4)	39(5)	43(5)	41(4)	-6(4)	0(4)	-6(4)
C(5)	51(6)	38(5)	39(4)	1(4)	-1(4)	-4(4)
O(1)	88(5)	40(4)	38(3)	-13(3)	-31(3)	10(3)
C(7)	110(10)	57(7)	45(5)	-15(5)	-30(6)	3(7)
C(8)	111(11)	108(11)	48(6)	-28(6)	-29(7)	31(9)
C(11)	77(9)	68(8)	76(8)	-29(6)	29(7)	-10(7)
O(11)	176(12)	59(6)	127(9)	4(6)	59(8)	-38(7)
C(21)	50(7)	92(9)	57(6)	-17(6)	5(6)	-20(6)
O(21)	67(7)	166(11)	72(5)	-19(6)	-16(5)	-34(6)
C(31)	58(7)	78(8)	56(6)	-16(6)	2(6)	-12(6)
O(31)	100(7)	129(9)	81(6)	-39(6)	38(6)	13(7)
C(41)	96(10)	61(7)	69(7)	-7(6)	-29(7)	9(7)
O(41)	113(8)	108(9)	158(10)	-22(7)	-87(8)	-11(7)
C(51)	135(13)	85(10)	57(7)	-21(7)	-49(8)	38(9)
O(51)	256(17)	84(7)	101(8)	0(6)	-97(10)	63(9)
C(61)	85(9)	62(7)	50(6)	-1(5)	-11(6)	8(6)
O(61)	79(6)	109(8)	73(6)	-14(5)	9(5)	21(5)
C(71)	98(9)	44(6)	50(5)	-1(5)	-20(6)	-13(6)
O(71)	149(10)	76(6)	83(6)	-1(5)	-38(6)	-44(7)
C(81)	123(11)	38(6)	50(6)	7(5)	-10(7)	-1(6)
O(81)	145(9)	79(6)	63(5)	-9(5)	17(6)	-14(6)

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Table 6 Hydrogen Atom Coordinates (x 10^4) and Isotropic Displacement Parameters (Å x 10^3)

	x/a	y/b	z/c	U
H(1A)	5318	2058	7979	80
H(2A)	6625	1087	9523	80
H(3A)	7517	-1151	9286	80
H(7A)	5935	-3839	5879	80
H(7B)	7900	-3323	5381	80
H(8A)	5748	-3257	4166	80
H(8B)	4279	-2441	4937	80
H(8C)	6254	-1922	4437	80

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