PREPARATION OF THE FIRST ISOTHIAZOLINYLIDENE COMPLEXES OF Fe, W AND Au

by

MIEKE ANN DESMET

THESIS

submitted in fulfilment of the requirements
for the degree

MASTER OF SCIENCE

in

CHEMISTRY

in the

FACULTY OF SCIENCE

at the

RAND AFRIKAANS UNIVERSITY

SUPERVISOR: PROF. H.G. RAUBENHEIMER

APRIL 1994

OPSOMMING

Hierdie studie behels grotendeels die bereiding en karakterisering van nuwe organo(tio)karbeen-komplekse van yster, wolfram en goud, terwyl 'n nuwe wolframamino(tio)karbeenkompleks asook 'n amino(organo)karbeenkompleks van goud ook beskryf word. Die organo(tio)- en amino(organo)karbeenkomplekse is uniek in die sin dat hulle ontstaan uit σ-komplekse, voorlopers waarin 'n nukleofiliese heteroatom in 'n γ-posisie ten opsigte van die gekoördineerde koolstofatom voorkom. Daarenteen is die meeste bekende Fischer-tipe N-bevattende karbeenkomplekse tot op datum berei vanuit imidoiel-voorlopers waarin hierdie heteroatome in 'n α-posisie ten opsigte van die gekoördineerde koolstofatoom geplaas is.

$[CpFe(CO)_2Cl]$ reageer met 5-isotiasoliellitium om $[CpFe(CO)_2\{\overline{C=CHCH=NS}\}]$ (**1**) te vorm. Behandeling van hierdie verbinding met die elektrofiele reagense CF_3SO_3H of CF_3SO_3Me, lewer die kationiese organo(tio)karbeenkomplekse $[CpFe(CO)_2\{\overline{CCH=CHN(R)S}\}][CF_3SO_3]$ (R= H (**2**) of Me (**3**)). Laasgenoemde kompleks is X-straalkristallografies gekarakteriseer en het 'n Fe-C(karbeen)bindingslengte van 1.952(3) Å.

Die reaksie van 2-tiasoliellitium met $[(CO)_5WCl][NEt_4]$, gevolg deur alkilering met CF_3SO_3Me, lewer die neutrale amino(tio)karbeenkompleks $[(CO)_5W\{\overline{CN(Me)C(Me)=CHS}\}]$ (**4**) op. Hierdie bereiding is uniek aangesien vir die eerste keer 'n wolframchloriedverbinding gebruik is om 'n karbeenkompleks te vorm. Uitbreiding van die metode lei tot die bereiding van 'n wolframorgano(tio)karbeenkompleks, $[(CO)_5W\{\overline{CCH=CHN(Me)S}\}]$ (**5**), deur alkilering op die afgeleë stikstofatoom van die voorloper isotiasolielkompleks. Aansuring in plaas van alkilering vind egter op die metaalgebonde koolstofatoom plaas om 'n stikstof-gekoördineerde kompleks, $[(CO)_5W\{\overline{NCHCH=CHS}\}]$ (**6**), te lewer.

Isotiasoliellitium reageer met [Au(Cl)tht] (tht = tetrahidrotiofeen) om die stabiele bis(isotiasoliel)auraat, $[Au\{\overline{C=CHCH=NS}\}_2]Li$ (**7**), te vorm. Die auraatkompleks word as 'n *in situ* voorloper gebruik vir die sintese van kationiese bis{organo(tio)}karbeengoudkomplekse, $[Au\{\overline{CCH=CHN(R)S}\}_2][CF_3SO_3]$ (R= Me (**8**) of H (**9**)), deur weereens 'n afgeleë stikstofatoom

te alkileer of te protoneer.

Isotiasoliellitium reageer met $[Au(Cl)PPh_3]$ om die neutrale isotiasolielverbinding, $[Au\{\overline{C=CHCH=NS}\}PPh_3]$ (**10**), te vorm wat vervolgens gealkileer kan word om die kationiese mono(karbeen)kompleks, $[Au\{\overline{CCH=CHN(Me)S}\}PPh_3][CF_3SO_3]$ (**11**), te gee. Hierdie kompleks skakel egter spontaan en vinnig om na die homoleptiese goudverbinding, $[Au\{\overline{CCH=CHN(Me)S}\}_2][CF_3SO_3]$ (**8**), en dit was dus alleenlik moontlik om hierdie kompleks eenkeer te isoleer. Die neutrale kompleks **10** is X-straalkristallografies ondersoek en het 'n Au-C(sp_2)bindingslengte van 2.032(7) Å.

Isotiasoliellitium reageer ook met $[Au(C_6F_5)tht]$ om na alkilering die neutrale karbeenkompleks, $[Au(C_5F_5)\{\overline{CCH=CHN(Me)S}\}]$ (**13**), te lewer. Pogings om die voorloper mono(isotiasoliel)-auraatkompleks, $[Au(C_6F_5)\{\overline{C=CHCH=NS}\}]Li$ (**12**), te isoleer, lewer slegs die bis(isotiasoliel)-auraatkompleks **7** op. Die neutrale karbeenkompleks **13** ondergaan ook homoleptiese omskakeling in oplosing om die bis(karbeen)kompleks **8** te vorm. Hierdie omskakeling is met behulp van ^{1}H-KMR-spektroskopie gevolg wat toon dat 'n ewewigsituasie tussen die neutrale mono(karbeen)kompleks **13** en die kationiese bis(karbeen)kompleks **8** bereik word.

Laastens, reageer 1-etielpyrasoliellitium ook met $[Au(Cl)PPh_3]$ om na alkilering van die afgeleë stikstofatoom die kationiese mono{amino(organo)}karbeenkompleks $[Au\{\overline{CCH=CHN(Me)N}(Et)\}PPh_3][CF_3SO_3]$ (**14**) te lewer.

SUMMARY

This study comprises the preparation and characterization of new organo(thio)carbene complexes of iron, tungsten and gold. In addition, the synthesis and characterization of a new tungsten amino(thio)carbene complex as well as a gold amino(organo)carbene complex is also described.

The organo(thio)- and amino(organo)carbene complexes are unique in that they have been prepared from precursors in which the nucleophilic heteroatom is situated γ to the coordinated carbon atom. In contrast, most of the known Fischer-type carbene complexes have resulted from imidoyl precursors in which these heteroatoms are situated α to the coordinated carbon atom.

$[CpFe(CO)_2Cl]$ reacts with isothiazol-5-yllithium to form $[CpFe(CO)_2\{\overline{C=CHCH=NS}\}]$ (**1**). Treatment of this compound with the electrophiles CF_3SO_3H or CF_3SO_3Me gives the cationic organo(thio)carbene complexes $[CpFe(CO)_2\{\overline{CCH=CHN(R)S}\}][CF_3SO_3]$ (R= H (**2**); Me (**3**)). The X-ray crystal structure of the latter complex **3** has been determined and reveals an Fe-carbon(carbene) bond length of 1.952(3) Å.

The reaction of thiazol-2-yllithium with $[(CO)_5WCl][NEt_4]$, followed by subsequent alkylation with CF_3SO_3Me affords the neutral amino(thio)carbenetungsten complex $[(CO)_5W\{\overline{CN(Me)C(Me)=CHS}\}]$ (**4**). This preparation is unique in that a tungsten chloride compound has been used to generate a coordinated carbene compound. Extension of the method leads to the preparation of a tungsten organo(thio)carbene complex $[(CO)_5W\{\overline{CCH=CHN(Me)S}\}]$ (**5**) by subsequent alkylation on the remote nitrogen atom of the precursor isothiazolyl compound. Protonation of the latter compound with CF_3SO_3H, however, occurs on the metal-bonded carbon atom to furnish the nitrogen-donor complex $[(CO)_5W\{\overline{NCHCH=CHS}\}]$ (**6**).

Isothiazol-5-yllithium reacts with [Au(Cl)tht] (tht = tetrahydrothiophene) to form the stable bis(isothiazolyl) aurate compound $[Au\{\overline{C=CHCH=NS}\}_2]Li$ (**7**). The aurate complex has now been used as an *in situ* precursor for the synthesis of the cationic bis{organo(thio)}carbenegold

complexes [Au{$\overline{CCH=CHN(R)S}$}$_2$][CF_3SO_3] (R=Me (**8**); H (**9**)) by alkylation or protonation of the remote nitrogen atom.

Isothiazol-5-yllithium reacts with [Au(Cl)PPh_3] to form the neutral isothiazolyl compound [Au{$\overline{C=CHCH=NS}$}PPh_3] (**10**) which can be alkylated to give the cationic mono(carbene) complex [Au{$\overline{CCH=CHN(Me)S}$}PPh_3][CF_3SO_3] (**11**). This complex however spontaneously rearranges to form the homoleptic gold compound [Au{$\overline{CCH=CHN(Me)S}$}$_2$][CF_3SO_3] (**8**). The X-ray crystal structure of the neutral complex **10** has been determined and reveals a gold-carbon bond length of 2.032(7) Å.

Isothiazol-5-yllithium also reacts with [Au(C_6F_5)tht] to afford upon alkylation, the neutral carbene complex [Au(C_5F_5){$\overline{CCH=CHN(Me)S}$}] (**13**). Attempts to isolate the precursor mono(isothiazolyl) aurate complex [Au(C_6F_5){$\overline{C=CHCH=NS}$}]Li (**12**), yielded the bis(isothiazolyl) aurate complex **7**. The neutral carbene complex **13** also undergoes homoleptic rearrangement in solution to form the bis(carbene) complex **8**. This rearrangement has been followed by ^{1}H NMR spectroscopy which shows that an equilibrium exists between the neutral mono(carbene) complex **13** and the cationic bis(carbene) complex **8**.

Finally, 1-ethylpyrazol-5-yllithium also reacts with [Au(Cl)PPh_3] to afford, upon alkylation of the remote nitrogen atom, the cationic mono{amino(organo)}carbenegold complex [Au{$\overline{CCH=CHN(Me)N(Et)}$}$PPh_3$][$CF_3SO_3$] (**14**).

ACKNOWLEDGEMENTS

I would like to express my gratitude to all who supported and encouraged me during this project. In particular I would like to thank the following people and institutions:

Prof H.G. Raubenheimer for outstanding leadership and guidance

James and Peter for help in editing and proofreading this manuscript

The members of the inorganic chemistry department at RAU (especially Pierre)

My special thanks to Stephanie for all her help and to Paul for his continuous support and patience

My father

The FRD and RAU for financial assistance

CONTENTS

CHAPTER 3

THE SYNTHESIS AND CHARACTERIZATION OF ORGANO(THIO)- AND AMINO(ORGANO)CARBENE COMPLEXES OF GOLD

CHAPTER 4

THE CRYSTALLOGRAPHIC CHARACTERIZATION OF CYCLOPENTADIENYL(ISOTHIAZOLINYLIDENE)IRON(II) AND ISOTHIAZOLYL(TRIPHENYLPHOSPHINE)GOLD(I)

ABBREVIATIONS

	Å	Ångstrom (10^{-10} m)
	Bu	Butyl
	Cp	Cyclopentadienyl
	dppe	$Ph_2PCH_2CH_2PPh_2$
	Et	Ethyl
	IR	Infrared
	MP	Melting point
	MS	Mass Spectrometry
	NMR	Nuclear Magnetic Resonance
	NOE	Nuclear Overhauser Effect
	Ph	Phenyl
	ppm	Parts per million
	TBAB	Tetrabutylammonium bromide
	THF	Tetrahydrofuran
	tht	Tetrahydrothiophene
NMR	br	Broad
	δ	Chemical Shift (ppm)
	d	Doublet
	J	Coupling Constant (Hz)
	m	Multiplet
	q	Quartet
	s	Singlet
	t	Triplet
IR	sh	Shoulder
	st	Strong
	w	Weak
	vw	Very weak

CHAPTER 1

INTRODUCTION AND AIMS

1.1 GENERAL BACKGROUND

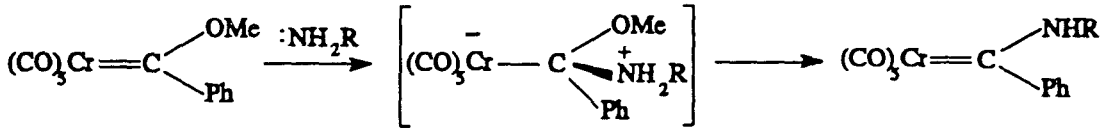
Transition metal organometallic chemistry has become an active and exciting branch of chemistry since the discovery of ferrocene captured the imagination of many chemists in 1951.[1,2] This fascination with organometallic chemistry lies in the tremendously varied chemistry encountered that has led not only to the discovery of new types of reactions, unusual structures and bonding forms, but also to practical applications in industrial catalysis and organic synthesis.

An important and very interesting branch of organometallic chemistry is that of transition metal carbene complexes. These complexes formally contain a metal-carbon double bond and can in general be represented by $L_nM{=}CY^1Y^2$ (L_n = ligands, M = transition metal, C = carbene carbon, Y^1 and Y^2 = substituents on the carbene carbon, such as OR, NR_2, SR, H, CH_2 or R). The first carbene complex, $[(CO)_5WC(Ph)OMe]$, was prepared in 1964 by E.O. Fischer and M.A. Maasböl.[3] Since then, this field of organometallic chemistry has expanded at a rapid rate, and a great variety of preparative routes has led to the synthesis of several hundreds of compounds. Carbenes are important intermediates in metal-catalyzed reactions and they have also found significant applications in organic synthesis.

Conventionally, transition metal carbene complexes may be divided into two categories according to reactivity at the carbene carbon atom, namely the Fischer-[3] and Schrock-type.[4] Each class represents a different type of metal ligand interaction and as a result the ligands exhibit different characteristics.

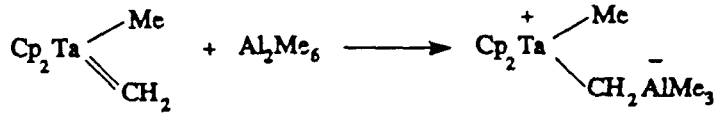
The Fischer-type carbene complexes generally consist of low oxidation state middle and late transition metals with at least one heteroatom substituent, Y^1 and/or Y^2, which is a good π donor (for example OMe, NMe_2 or SMe) on the carbene carbon. The metals commonly contain good

π-acceptor ligands L, such as CO and PR_3, and are characterized by the electrophilic reactivity of the carbene carbon atom. A typical well-studied representative is $[(CO)_5Cr\{C(OMe)Ph\}]$, the first carbene complex to be characterized by X-ray crystallography.[5] This complex readily reacts with a variety of nucleophiles, such as amines and alkyllithiums, to form other carbene complexes. An example is given in Equation 1.1.[6]



Equation 1.1

In contrast, the Schrock-type carbene complexes typically contain higher oxidation state early-transition metals with hydrogen or alkyl substituents on the carbene carbon that are non-π-donors. In this case the carbene carbon shows nucleophilic reactivity and a typical example is $[Cp_2Ta(CH_2)Me]$.[7] The nucleophilicity of the methylene ligand in this complex is illustrated by its complexation with the Lewis acid $AlMe_3$ (Equation 1.2).[8]

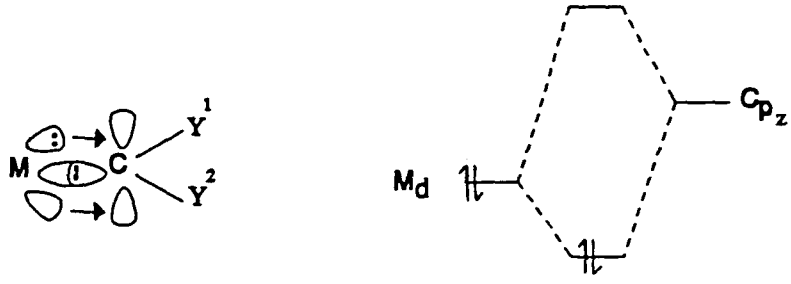


Equation 1.2

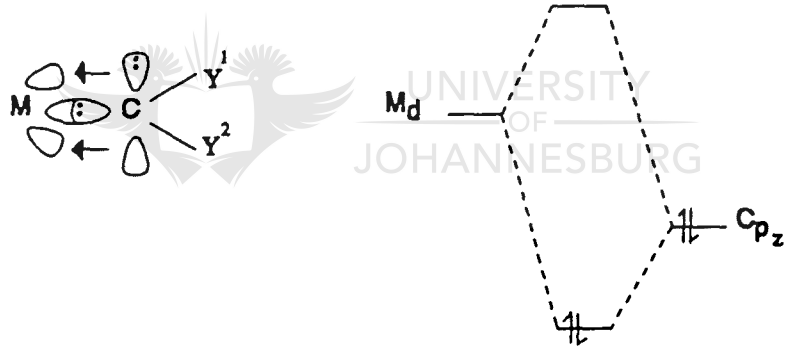
The charge on the carbene carbon is to a large extent controlled by the energy of the M(dπ) orbitals. Since the Fischer carbene complexes mainly consist of middle and late transition metals which are more electronegative, they have more stable M(dπ) orbitals (Scheme 1.1). The presence of π-acceptor ligands L stabilize the M(dπ) levels even more. In forming the metal-carbon σ bond, the ligand donates a lone pair of electrons to the metal from a $[C(sp^2)]$ hybridized carbon atom. The π bond, however, is best described as a M(dπ) to $C(p_z)$ back donation. The π-electron density is largely concentrated on the metal because the vacant $C(p_z)$

orbital is higher in energy than the M(dπ) orbitals. The electron deficient carbene carbon is then further stabilized by the lone pairs of its π-donor substituents.

Fischer-type carbene complex:



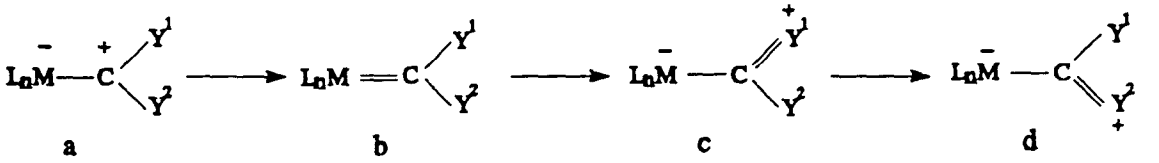
Schrock-type carbene complex:



Scheme 1.1

The Schrock carbene complexes, on the other hand, have less stable M(dπ) orbitals since the early transition metals are more electropositive (greater electropositive character implies that electron loss is easier, which in turn implies that the corresponding orbitals are less stable). The metal-carbon σ bond can be regarded in the same way as in the Fischer carbene complexes but the π bond may be regarded as being polarized towards the carbon, giving an M^{+}-C^{-} charge distribution. The $C(p_z)$ orbital is lower in energy than the M(dπ) orbitals, therefore π-electron density is concentrated on the carbon which becomes nucleophilic in character (Scheme 1.1).

If the metal-carbon bond in Fischer carbene complexes involves σ donation from the carbon to the metal and π back donation in the opposite direction, then π donation from the carbene heteroatom substituents will compete with π donation from the metal. The bonding in Fischer-type carbene complexes must therefore be described by the resonance structures a-d shown in Scheme 1.2.



Scheme 1.2

The relative contributions of the individual resonance forms a, b, c and d depend on the π-donor properties of the substituents Y^1 and Y^2, and the metal at the carbene carbon atom. Thus the relative importance of the various resonance forms varies from complex to complex. However, resonance structure b will be exclusively used to represent carbene complexes throughout the text. The reason for this lies in the classification of carbene complexes as compounds with metal to carbon double bonds and also because it is now accepted amongst 'carbene chemists' to represent carbene complexes in this manner. Resonance form b, however, does not necessarily represent the true structure of all carbene complexes.

The competitive π donation between the metal and the carbene substituents towards the carbene carbon is well supported by x-ray structural data. The distances between the carbene carbon atom and its heteroatom substituents, in complexes such as $[(CO)_5Cr\{C(OEt)NMe_2\}]$[9] and $[(CO)_5Cr\{C(OMe)Ph\}]$,[5] are shorter than single bonds, stressing the importance of resonance forms c or d. Similarly, the metal-carbon bond in certain complexes, such as $[\pi\text{-}C_6H_6(CO)_2Cr\{C(OMe)Ph\}]$,[10] is significantly shorter than a metal-carbon single bond, indicating a contribution from resonance form b. In most Fischer-type carbene complexes, however, the metal-carbon bond is only somewhat shorter than a metal-carbon single bond. This competition is also reflected by the results obtained from temperature dependent NMR spectroscopy. In aminocarbene complexes cis and trans isomers can be detected, usually even

at room temperature, due to restricted rotation about the heteroatom-carbene carbon bond.[11,12] The rotation about the metal-carbene bond is very rapid and therefore rotational isomers can only be detected by NMR spectroscopy if rotation slows down as a consequence of steric hindrance. An example is the cis-bis(carbene) complex [cis-$(CO)_4Cr\{\overline{CN(Me)CH_2CH_2N(Me)}\}_2$].[13]

^{13}C NMR data is also useful in the identification of carbene complexes because the carbene carbon is deshielded and resonates at a very low field strength. It is tempting to ascribe this deshielding to resonance form a (Scheme 1.2), which exhibits a positive charge on the carbene carbon atom, but Schrock carbene complexes which are nucleophilic in character, show similar shifts. The enormous downfield shift is probably a result of the existence of low-energy electronic excited states for the complex which leads to a large 'paramagnetic contribution' to the shift. Therefore reliable predictions of nucleophilic or electrophilic behaviour cannot be made on the basis of ^{13}C NMR spectra.[14]

It should be noted that in the Schrock type carbene complexes, where π donation from the substituents is not significant, the metal-carbon bond is more covalent in nature. Schrock carbenes can almost exclusively be represented by resonance form b (Scheme 1.2). The metal-carbon bond is particularly rigid and thus exhibits considerable double bond character. It is therefore not surprising that the non-equivalence of the methylene protons in the ^1H NMR spectrum of [MeCp(Cp)Ta(CH_2)Me] remains unchanged up to 100°C at which temperature the complex decomposes.[15]

Finally, carbene complexes exist which are intermediate in character between the Fischer and Schrock extremes.[16] Certain carbene complexes reported in the literature exhibit reactivity ranging from electrophilic to nucleophilic and thus suggest that the early 'black and white' classification of transition metal carbene complex reactivity, according to the position of the metal in the periodic table and the nature of the carbene substituents, might be an over-simplification.[17] Presently, however, this classification still serves its purpose. The remainder of the discussion will be confined to Fischer-type carbene complexes.

A large number of preparative methods involving nearly all the transition metals have been developed for the synthesis of carbene complexes. This is reflected in the large series of

comprehensive reviews[18-22] written on the subject, and therefore only a few characteristic synthetic methods have been selected for this section from the abundance of available material.

Carbene complexes may be prepared from non-carbene complex precursors as well as by modification of existing carbene complexes. The following synthetic strategies are available for the synthesis of carbene complexes:

A. From non-carbene complex precursors:

i) Transformation of an existing metal-carbon bond.

ii) Addition of a carbene ligand precursor to a metal complex followed by conversion of the latter into a carbene ligand.

B. From existing carbene complexes:

i) Transfer of a carbene ligand from one metal centre to another.

ii) Modification of a carbene ligand.

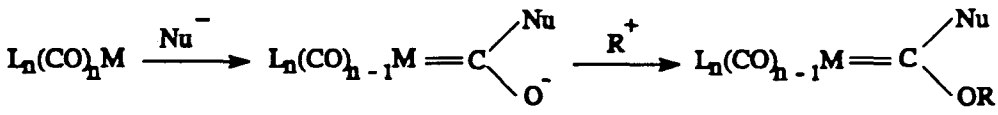
iii) Insertion of an unsaturated organic molecule into the metal-carbene bond.

iv) Oxidation and reduction of carbene complexes.

v) Modification of the metal-ligand framework.

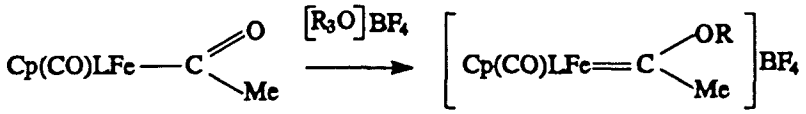
The majority of carbene complexes have been synthesized by transformation of an existing metal-carbon bond, which means that the future carbene carbon is already attached to the metal in the precursor.

The most general preparative method is Fischer's original method which involves the addition of organolithium reagents to a coordinated carbon monoxide molecule in metal carbonyl and substituted metal carbonyl complexes to form acyl complexes. The acyl complexes are then alkylated with electrophiles, such as trialkyl- and triaryloxonium salts, to form alkoxycarbene complexes (Equation 1.3).[22,23] Alkyl iodides instead of oxonium salts have recently been employed as alkylating agents. The advantage of this alkylating agent lies in the procedural ease of a 'one pot' preparation and in the cheaper reagents.[24]



Equation 1.3

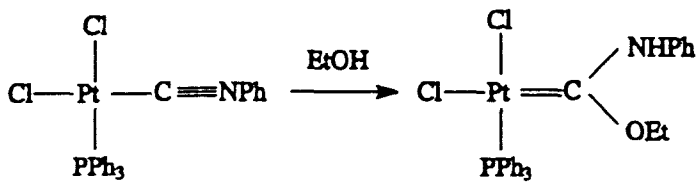
A variant of this procedure is the protonation or alkylation of neutral acyl complexes.[25] For example, acyl(cyclopentadienyl)iron compounds react with trialkyloxonium salts to form cationic alkoxycarbene complexes (Equation 1.4).[26] Thioacyl and imidoyl complexes may similarly be protonated or alkylated to yield carbene complexes with sulphur and nitrogen substituents respectively.[27-29]



L = CO , PPh_3 , $P(C_6H_{11})_3$

Equation 1.4

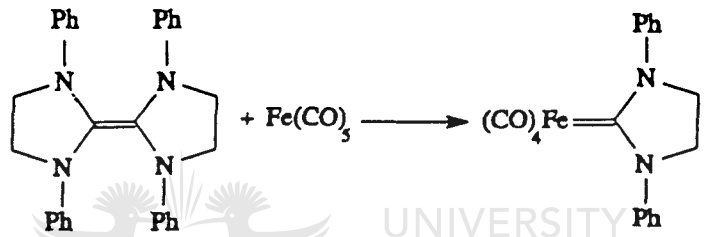
The concept of nucleophilic addition to a metal-bonded carbon atom may also be extended to coordinated isocyanides. Alkoxy(amino)-, amino(thio)- and di(amino)carbene complexes may be obtained by the addition of alcohols, thiols and amines to coordinated isocyanide complexes.[30] An example is shown in Equation 1.5.[31] Other precursors such as coordinated thiocarbonyls,[32,33] vinylidenes,[34] carbynes[35,36] and acetylides[37] can also be used.



Equation 1.5

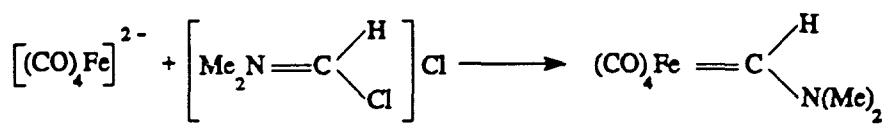
All the synthetic strategies above take advantage of an existing metal-carbon bond which is transformed by various means into a carbene complex. Another approach to the preparation of carbene complexes from non-carbene precursor complexes involves the addition of a suitable carbene ligand precursor which will be attached to a metal complex during synthesis and simultaneously modified. In these types of reactions, the carbene carbon atom is added to the metal in the course of the reaction. Examples of this synthetic strategy are given below.

Transition metal complexes susceptible to nucleophilic attack may be treated with electron rich alkenes, such as 1,1'; 3,3'-tetraphenyl-2,2'-bi-imidazolidinylidene or bis(N-methylbenzo-thiazolinylidene) to form cyclic di(amino)- or amino(thio)carbene complexes. An example is shown in Equation 1.6.[38]



Equation 1.6

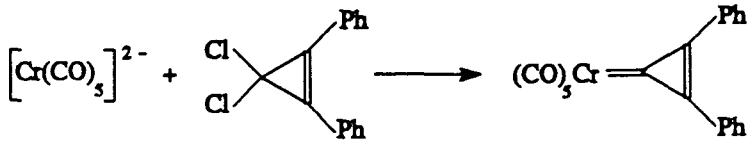
A general synthesis of N-substituted carbene complexes involves the oxidative addition of immonium halides of the type $[Me_2N{=}C(R)Cl]Cl$ (R = H, Cl or NMe_2) to anionic or neutral metal compounds (Equation 1.7).[39]



Equation 1.7

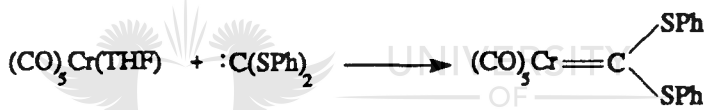
The first carbene complex which was not stabilized by heteroatom substituents was synthesized by a similar method involving the addition of 1,1-dichloro-2,3-diphenylcyclopropene to

$[Na_2][Cr(CO)_5]$ to form a cylopropenylidene complex (Equation 1.8).[40] Similar reaction types involve the addition of imidazolium salts[41,42] and imidoyl chlorides.[43]



Equation 1.8

Only a few examples are known in which anionic organic precursors are used for the preparation of carbene complexes. An example is the trapping of the free carbene $:C(SPh)_2$ on pentacarbonyl complexes of chromium and tungsten. In this manner di(thio)carbene complexes have been formed (Equation 1.9).[44]

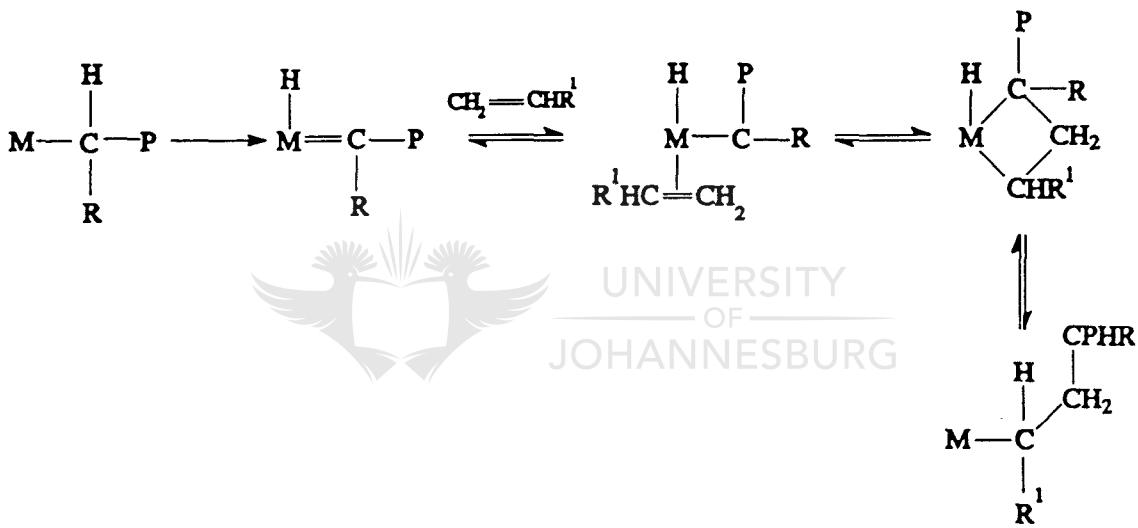


Equation 1.9

Existing carbene complexes may be modified in various ways to yield new carbene complexes. The various methods include changing the substituents on the carbene carbon, transferring the carbene ligand to another metal, electrochemical oxidation of the carbene complex, insertions of carbon-carbon and carbon-nitrogen triple bonds and changing the metal-ligand framework by ligand substitutions, oxidative additions, and isomerizations.[45]

Although new synthetic routes to carbene complexes are still being developed, much attention has shifted from synthesis to reactivity. This is because isolating and understanding these complexes provides mechanistic models for important metal-catalyzed reactions such as the polymerization of alkenes,[46] alkene cyclopropanation,[47,48] alkene metathesis,[49] and the heterogeneous Fischer-Tropsch synthesis.[50-52] Alkene polymerization, for example, is one of the

most important catalytic reactions in commercial use. Here, the Ziegler-Natta catalysts account for the millions of tons of polyethylene and polypropylene produced annually. Green and Rooney[53] have proposed that carbene species, although they have not been isolated, are intermediates in these catalytic reactions. The mechanism first involves the α-hydride elimination of the polymer chain to give a carbene hydride, which then adds ethylene by a metathesis-like mechanism to give a metallacycle which finally opens by reductive elimination with the hydride (Scheme 1.3).[54,55] Cossee, however, has proposed an alternative mechanism in which the polymer chain grows by successive insertions of ethylene.[56,57] Both mechanisms are supported by a number of reactions, and for a particular catalyst or set of reaction conditions either mechanism (or even some other pathway) might prevail.



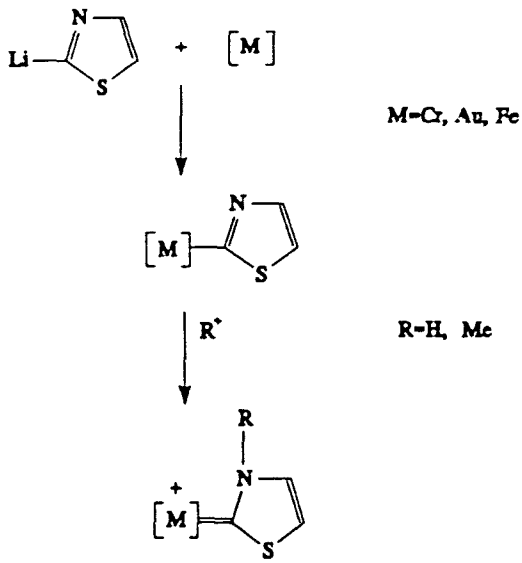
Scheme 1.3

Organometallic carbene complexes currently also play an important role in organic synthesis, particularly in carbon-carbon bond formation.[58-61] They are not only suitable as carbene-transfer agents[62,63] but also undergo interesting cycloadditions[64-66] with other ligands. They are therefore utilized in the synthesis of heterocycles,[67-69] naphthols[70] and natural products such as peptides,[71] vitamins[72-74] and antibiotics.[75] Examples of carbene complexes which have been used in organic synthesis will be discussed in the chapters which follow.

1.2 AIMS AND OBJECTIVES

The preparation of new types of compounds and the development of new synthetic methodologies are important for possible later industrial applications. Recently Hermann[76] expressed it very well by saying that organometallic homogeneous catalysis 'thrives' on the achievements in organometallic chemistry. He remarked that every well-characterized organometallic complex and every clearly described and well understood reaction pathway contributes to the further improvement of homogeneous catalysis. In other words, higher product selectivity and optimum yields in organometallic catalysis may only be obtained by the characterization and structural understanding of as many new organometallic complexes as possible. The fundamental area which receives attention in the present work is that of carbene complexes.

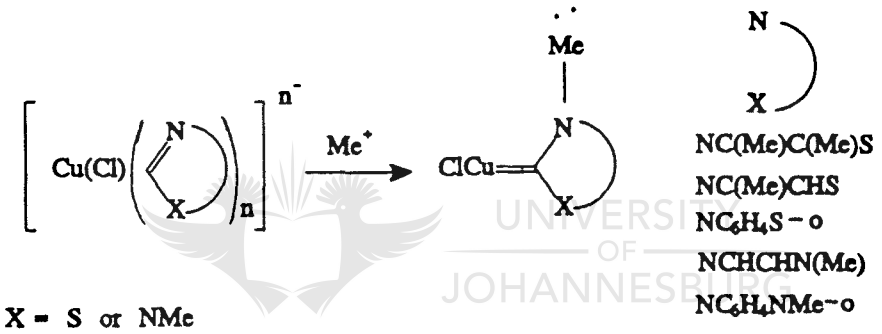
Previous work in our laboratory has shown that lithiated thiazoles readily react with suitable transition metal complexes, such as the chromium Fischer carbene $[CO)_5Cr\{C(OEt)Ph\}]$,[77] the iron(I) chloride $[CpFe(CO)_2Cl]$[78] as well as the gold(I) chlorides [Au(Cl)tht] and $[Au(Cl)PPh_3]$,[79,80] to form thiazolyl complexes which, upon protonation or alkylation of the nitrogen atom, give stable amino(thio)carbene complexes (Scheme 1.4).



Scheme 1.4

This novel synthetic route has been successfully applied to the synthesis of many amino(thio)carbene complexes and will be referred to in the chapters which follow.

Interestingly this route has recently led to the synthesis and characterization of unique mono(carbene) complexes of copper, as well as to the first X-ray structure of a copper carbene complex.[81] The preparation involves the addition of copper(I) chloride to thiazolyllithiums or imidazolyllithiums and the subsequent alkylation of the products formed (Scheme 1.5). The X-ray structure of [Cu{CN(Me)C(Me)C(Me)S}Cl] shows a copper carbene bond length of 1.888(6) Å in the essentially flat, two-coordinate copper complex. There is also an association between the copper atom and the chloride of a neighbouring molecule leading to the apparent dimeric nature of the complex.

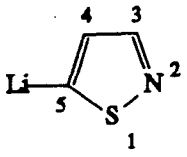


Scheme 1.5

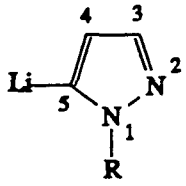
Most of the typical cyclic and acyclic Fischer-type carbene complexes are prepared from precursors in which the nucleophilic heteroatoms are situated α to the coordinated carbon atoms. In the precursor thiazolyl complexes, electrophilic attack also occurs on a heteroatom situated α to the coordinated carbon atom. *This led to the question: Could carbene complexes still form if electrophilic attack occurred on a nucleophilic heteroatom (i.e. N, O or S) which is one, two or even more bond lengths away from the coordinated carbon atom?*

A literature search revealed that ligands such as isothiazole, N-substituted pyrazole and pentachloropyridine could be utilized to realise this idea (Figure 1.1). They all fulfil the requirement that facile deprotonation at a carbon next to a double bond, which is conjugated to

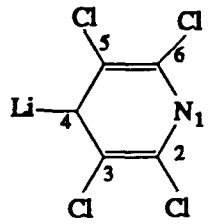
the imine double bond, is possible.



isothiazolyl



1-alkylpyrazolyl

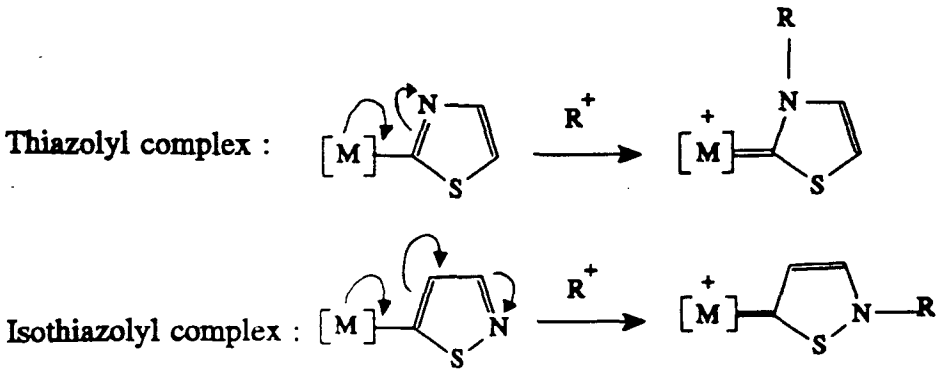


pentachloropyridinyl

Figure 1.1

The fundamentals of this idea may be well illustrated with isothiazole as the ligand. The formation of the isothiazolyl precursor complex would, as in the thiazolyl complexes, involve a simple ligand exchange between a metal chloride complex and a lithiated isothiazole. Subsequent protonation or alkylation of this precursor complex would then yield a new organo(thio)carbene complex. The carbene complexes derived from isothiazolyl precursor complexes would, if formed, differ in two important aspects from those derived from thiazolyl precursor complexes (Scheme 1.6). In the case of the transmetalated thiazolyls, the nitrogen atom is situated α to the coordinated carbon atom and upon protonation or alkylation of this complex an amino(thio)carbene complex is formed, whereas the nitrogen atom in the transmetallated isothiazolyl would be situated γ to the coordinated carbon atom resulting finally in an organo(thio)carbene complex. We consider the nitrogen atom in the isothiazolyl precursor to be in a γ-position with respect to the coordinated carbon by taking into account the formal electron movement in the conjugated carbon chain upon its reaction with an electrophile. Formally, however, it would be more correct to say that the nitrogen atom is situated β to the coordinated carbon atom.

If complexes of this type could be formed they would represent the first examples of heterocarbene complexes formed from a precursor in which the nucleophilic heteroatom is not directly bonded to the coordinated carbon.



Scheme 1.6

The idea mentioned above gave rise to a number of questions which the present work attempts to answer. These question may be formulated as follows:

1) Stable cationic amino(thio)carbene complexes have been prepared by the addition of the iron chloride complex [$CpFe(CO)_2Cl$] to lithiated thiazoles, followed by protonation of the resulting thiazolyl complexes.[78] Could the idea of remote electrophilic attack be applied in a similar manner with ligands such as isothiazole, pentachloropyridine and N-substituted pyrazole to obtain organo(thio)-, di(organo)- and amino(organo)carbene complexes which would all contain nitrogen atoms which are distant from the carbene carbon?

2) Until now tungsten chloride complexes have not been used in substitution reactions to eventually afford carbene complexes. Could a method be developed for the synthesis of tungsten carbene complexes from tungsten chlorides, and could this method then be extended to the synthesis of tungsten carbene complexes from a precursor containing a remote nucleophilic heteroatom?

3) Employing the same strategy as for the iron thiazolinylidene complexes, gold(I) chlorides such as [$Au(Cl)PPh_3$)] and [Au(tht)Cl] as well as the neutral tetrahydrothiophene complex [$Au(C_6F_5)$tht] have been utilized in the synthesis of mono- and bis{amino(thio)}carbene-gold complexes,[79,80] while very recently copper(I) chloride has been utilized in the synthesis of amino(thio)- and di(amino)carbenecopper complexes.[81] Could the idea of electrophilic

attack on a heteroatom which is distant from the coordinated carbon atom be applied to gold and copper metals?

4) Complicating side-reactions such as homoleptic rearrangement, polymerization and protonation or alkylation on carbon rather than nitrogen have been observed during the synthesis of the thiazolinylidene complexes of gold. Would similar side-reactions occur during the synthesis of the new carbene complexes?

5) Only a few thiazolyl precursor complexes have been isolated up to now. Would it be possible to isolate the precursors of the new carbene complexes and, if so, how would they compare to these carbene complexes? For example, would any significant shifts be observed in the NMR spectra when the precursor complex is converted into the carbene complex?

6) How would the new carbene complexes compare with their thiazolinylidene counterparts in terms of structural characteristics? For example, would the C(carbene)-carbon bond contain significant double bond character?

7) The gold thiazolinylidene carbene complexes show interesting Au...Au interactions which have been ascribed to a relativistic effect.[82] Would similar Au...Au interactions occur in the proposed new compounds?

CHAPTER 2

THE SYNTHESIS AND CHARACTERIZATION OF ORGANO(THIO)- AND AMINO(THIO)CARBENE COMPLEXES OF IRON AND TUNGSTEN

2.1 INTRODUCTION

The chemistry of iron and tungsten compounds has been actively studied over the past forty years. This is reflected in the large variety of compounds known and characterized for these metals among which oxide, carbonyl, acetylide, acyl, alkyl, carbene and cluster compounds may be included.[83] Indeed, the field of organometallic chemistry only started to expand after the discovery of ferrocene, while the first carbene complex prepared was a pentacarbonyl tungsten carbene complex.[2,3]

Ever since the discovery of carbene complexes, the growth in the number of useful applications in organic synthesis has been exponential with time. This is particularly true of chromium, tungsten and iron carbene complexes which have found applications in numerous cycloaddition reactions. Applications of iron carbene complexes in organic synthesis include stereospecific intramolecular cyclopropanations utilizing cationic iron carbene complexes of the type $[CpFe(CO)_2\{CY^1Y^2\}]^+X^-$. These cyclopropanation reactions have led to the construction of complex polycyclic ring systems, such as the trans-fused methonodecalin system.[84-87] Similarly, iron complexes of the type $[CpFe(CO)(L)\{CY^1Y^2\}]^+X^-$ may be used for enantioselective cyclopropane synthesis.[88] Further interesting cycloaddition reactions include the synthesis of aminofurans from the reaction of aminocarbeneiron complexes with alkynes;[89] the synthesis of pyrones from the reaction of alkoxycarbene complexes with alkynes;[90] and the synthesis of β-lactams from the reaction of $[(CO)_4Fe\{C(OEt)Ph\}]$ with isocyanides.[91]

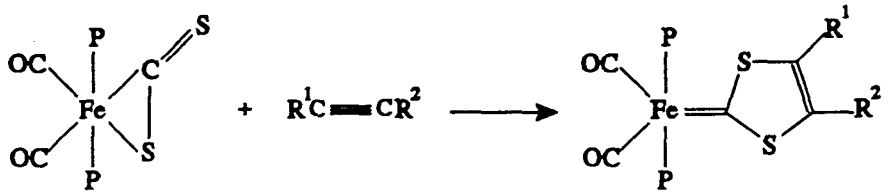
Tungsten carbene complexes have also played an important role in organic synthesis. Perhaps the reaction type of most use is the benzannulation reaction with acetylenes,[92] which has been employed in the synthesis of a number of natural products.[93-96] The Diels-Alder reaction of α,β-unsaturated complexes is another important application of tungsten carbene complexes in organic synthesis. Alkenyl(pentacarbonyl)tungsten complexes of the type $[(CO)_5W\{C(OMe)CR^1{=}CR^2R^3]$ (R^1, R^2, R^3 = H or alkyl) are used in these reactions with esters, aldehydes, ketones, methoxyallenes and simple alkenes, leading to a variety of products. These Diels-Alder reactions occur with rates as well as regio- and stereoselectivity that are normally only associated with the Lewis acid-catalyzed Diels-Alder reactions of esters.[97-102] Furthermore, [3+2] and [2+2] cycloaddditions have also been observed with α,β-unsaturated carbene complexes.[103-105] Organic products from cycloaddition reactions utilizing pentacarbonyltungsten carbene complexes include pyridines, pyridinium salts,[106] pyrazoles,[104,107] bicycloheptanones,[108] 5-ethoxyhydantoids[109,110] and indenes.[111] Although carbene complexes of iron and tungsten have found application in organic synthesis, their use is still open to further investigation.

As the chemistry of carbene complexes has progressed, the development of new synthetic methodologies towards carbene complexes as well as the synthesis of new complexes by modification of existing carbene ligands has become increasingly important. Improved chemo- regio- and stereoselectivity of reactions involving coordinated carbenes can only be accomplished, and new applications developed, after the successful synthesis and characterization of new carbene complexes. The synthesis of new types of carbene complexes and the development of new methodologies towards carbene complexes, receives attention in the present work and iron and tungsten are the metals of choice in this chapter.

A significant number of tungsten and iron heterocarbene complexes have been prepared according to the methods described in Chapter 1 and will not be discussed here in detail again since extensive review articles[19-22] are available. Instead, emphasis here will be directed towards methods employed in the preparation of a few heterocyclic carbene complexes which are relevant to the present investigation.

Among the recent methods used for the synthesis of heterocyclic iron carbene complexes is the unusual reaction of activated acetylenes with carbon disulphide iron complexes to yield

1,3-dithiol-2-ylidene iron compounds (Equation 2.1). This reaction probably takes place by a stepwise mechanism which involves zwitterionic intermediates.[112]

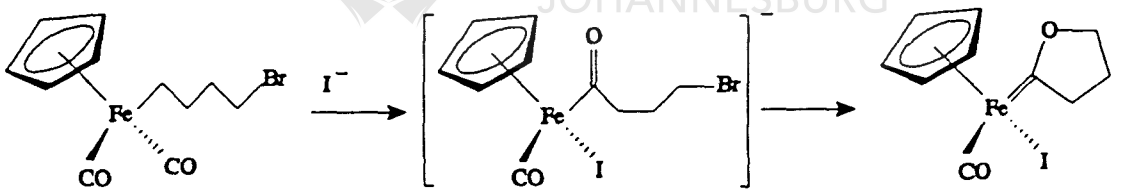


P = $P(OMe)_3$, PMe_3 , PMe_2Ph

R_1 , R_2 = PhCHO , Ph ; Ph , CO_2Me ; H , CO_2Me ; CO_2Me , CO_2Me

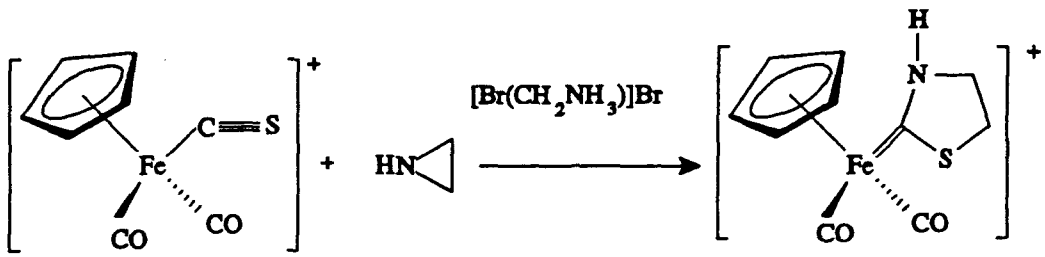
Equation 2.1

In another approach, the reaction of the bromoalkyl complex $[CpFe(CO)_2\{(CH_2)_2Br\}]$ with iodide is utilized (Equation 2.2). The mechanism of carbene formation involves initial attack of the iodide on the bromoalkyl complex, which then induces a migratory insertion step. The resulting anionic acyl species cyclizes affording an alkoxy(organo)carbene complex.[113]



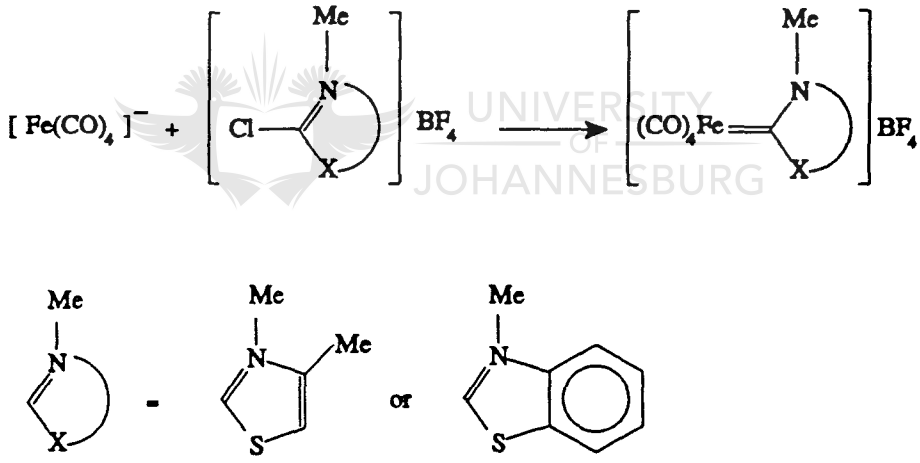
Equation 2.2

The cyclic amino(thio)carbene complex $[CpFe(CO)_2\{\overline{CN(H)(CH_2)_2S}\}][PF_6]$ is formed by the reaction of the cationic thiocarbonyl complex $[CpFe(CO)_2(CS)]^+$ with aziridine in the presence of a halide ion catalyst (Equation 2.3).[114] This complex was previously prepared in lower yield by another route utilizing the reaction of the di(thio)carbene complex $[CpFe(CO)_2\{C(SR)_2\}]$ with β-mercapto-ethylamine $[H_2N(CH_2)_2SH]$.[115] Alkoxy(amino)carbene complexes may be prepared by a similar method as in Equation 2.3 by employing aziridine and the iron carbonyl cation $[CpFe(CO)_3]^+$.[114]



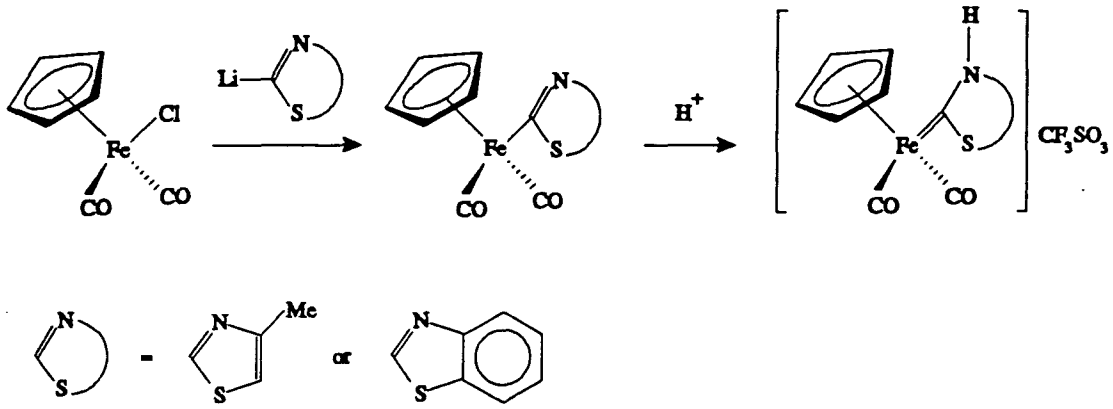
Equation 2.3

Many years ago, Stone and coworkers prepared tetracarbonyl iron amino(thio)carbene compounds by the reaction of the Collman reagent, $Na[Fe(CO)_4]$, with 2-chloro-N,4-dimethyl-1,3-thiazolium and 2-chloro-N-methyl-1,3-benzazolium tetrafloroborate (Equation 2.4). The reaction involves simple nucleophilic displacement of the chloride ion and subsequent formal electron rearrangement.[116]



Equation 2.4

Cationic amino(thio)carbene complexes have recently been prepared in our laboratory. The preparation involves the addition of 4-methyl- or benzothiazolyllithium to an iron chloride complex, $[CpFe(CO)_2Cl]$, to form neutral thiazolyl complexes which can be protonated with CF_3SO_3H to give the corresponding cationic thiazolinylidene complexes (Scheme 2.1).[78]



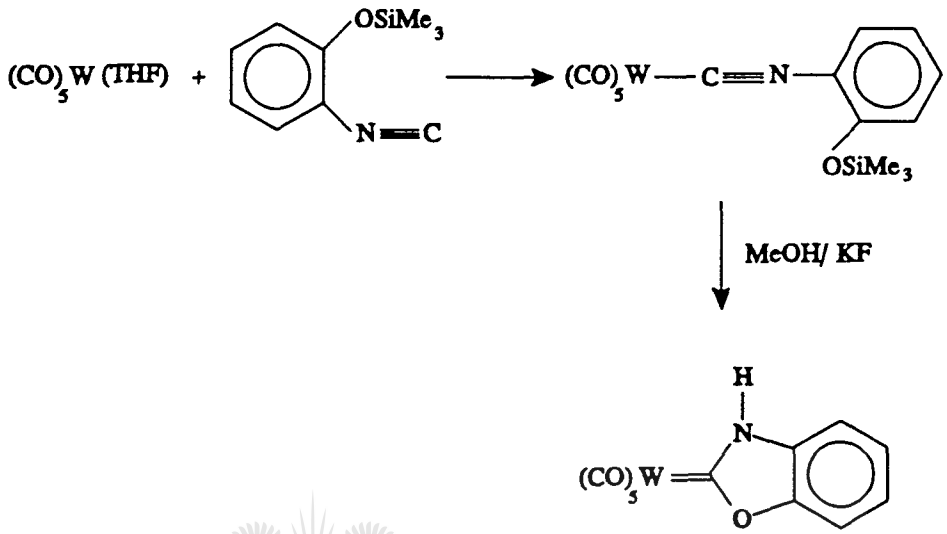
Scheme 2.1

These cyclic thiazolinylidene complexes are prepared from a precursor in which the nucleophilic heteroatom is in an α-position with respect to the coordinated carbon atom. This is typical for the preparation of cyclic and acyclic heterocarbene complexes. As far as could be ascertained, carbene complexes prepared from precursor complexes in which the nucleophilic heteroatom is not directly bonded to the coordinated carbon atom are unknown. One aim of the present work has been to investigate whether such carbene complexes could be prepared and isolated. Carbene complexes containing nitrogen atoms situated α, β and γ to the coordinated carbon atom have already been prepared, but these were not prepared from precursor complexes containing remote nitrogen atoms. Rather, they were prepared by the oxidative addition of N,N'-dimethylazolium iodides to metal salts of the type $[Na_2M(CO)_{10}]$.[117]

The first goal was directed towards preparing new iron carbene complexes from precursors containing remote nucleophilic heteroatoms. In this endeavour, the methodology developed for the synthesis of thiazolinylidene complexes, as illustrated in Scheme 2.1, would be employed by substituting thiazole with isothiazole. This method would result in organo(thio)carbeneiron complexes upon protonation or alkylation of the remote nitrogen atom in the precursor isothiazolyl complex.

Although many pentacarbonyl tungsten carbene complexes are known, only a few cyclic pentacarbonyl tungsten carbenes have been reported, most of which have been synthesized by modification of Fischer carbene complexes.

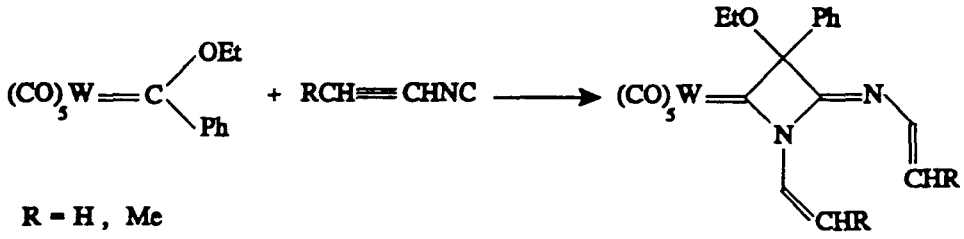
A very recent synthesis of a pentacarbonyl[alkoxy(amino)carbene]tungsten complex involves the addition of 2-trimethyl-siloxyphenyl isocyanide to [$(CO)_5W(THF)$], affording an isocyanide complex in which the Si-O bond is then hydrolysed by the addition of an KF/MeOH mixture (Equation 2.5). The cyclic alkoxy(amino)carbene complex is formed via intramolecular nucleophilic attack of the phenolic oxygen atom at the isocyanide carbon atom.[118]



Equation 2.5

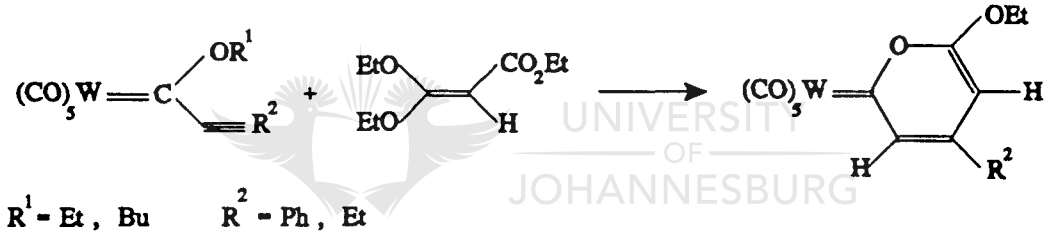
Cyclic pentacarbonyl[di(amino)carbene]tungsten complexes may be prepared from tungsten hexacarbonyls via the cleavage of the carbon-carbon double bond in electron rich olefins (discussed in Chapter 1). Aside from these examples, most cyclic pentacarbonyl(carbene)-tungsten carbene complexes have been prepared from existing Fischer carbene complexes.

Amongst the most recent methods is the synthesis of cyclic amino(organo)carbene complexes by the treatment of the Fischer carbene complex [$(CO)_5W\{C(OEt)Ph\}$] with alkenyl isocyanides (Equation 2.6). These [3+1] cycloaddition reactions are important in organic synthesis, since the cyclic carbene complexes can be oxidatively cleaved to yield β-lactams in high yield.[119]



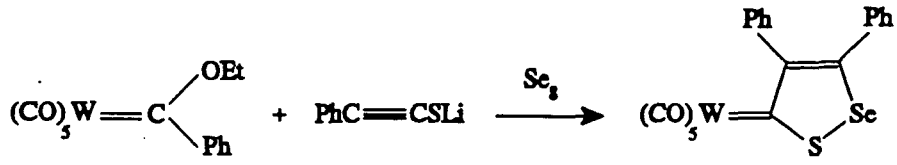
Equation 2.6

Another route for the synthesis of cyclic tungsten heterocarbene complexes involves the reaction of ethyldiethoxyacrylate with alkynal(alkoxy)carbene complexes (Equation 2.7). The mechanism involves a [2+2] cycloaddition, followed by conrotatory opening and final cyclization at the carbene centre. These 6-ethoxy-2H-pyranylidene complexes are also of significance in organic synthesis, since oxidation of the complexes affords 6-ethoxy-2H-pyrones.[120]



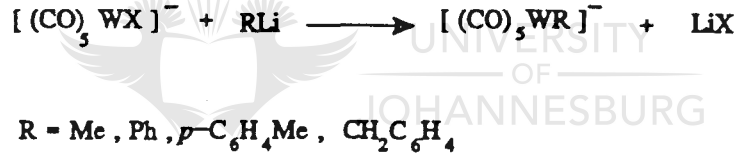
Equation 2.7

Finally, a cyclic pentacarbonyl[organo(thio)]carbene complex of tungsten, may be prepared by the reaction of the Fischer carbene complex [$(CO)_5W\{C(OEt)Ph\}$] with PhC≡CSLi at -30°C followed by the addition of elemental selenium (Equation 2.8). The mechanism of carbene formation involves the unusual C-addition of PhC≡CSLi to the carbene carbon to give an anionic complex. Electrophilic attack of this complex by selenium, loss of ^-OEt, ring closure and coordination of a carbon β to the original carbene carbon results in the cyclic carbene complex.[121]



Equation 2.8

In this chapter the synthesis of carbene complexes by electrophilic attack on remote nitrogen atoms in σ-bonded organometallic precursor compounds is described. Up to now tungsten chlorides have not been used in substitution reactions to eventually afford carbene complexes. However, Casey has developed a complete methodology for the preparation of anionic alkyl- and aryl(pentacarbonyl)tungsten complexes from pentacarbonyltungsten chloride (Equation 2.9) and this method was adapted for the preparation of the precursor isothiazolyl compounds.[122] For comparative purposes, thiazolyllithium was used in the initial experiments.



Equation 2.9

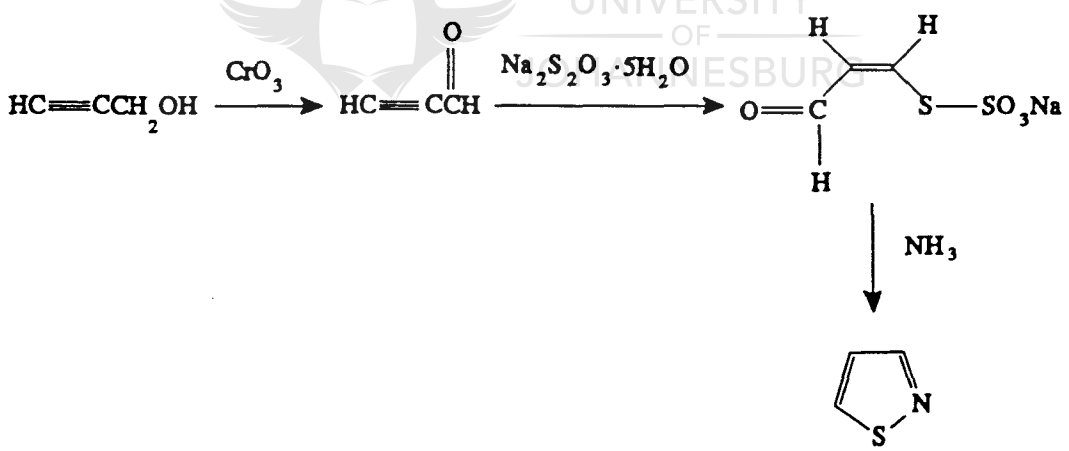
To summarize, the objectives of this investigation are threefold: Firstly, to use the same method previously employed by Cronje[78] in the preparation of iron thiazolinylidene complexes for the preparation of isothiazolinylidene compounds, secondly to develop a method for the synthesis of tungsten carbene complexes from tungsten chlorides, initially by using a thiazolyllithium and eventually an isothiazolyllithium prior to alkylation or protonation, and finally, to compare the structural characteristics of the carbene complexes formed by electrophilic attack on nitrogen atoms situated respectively α and γ to the metal-bonded carbon.

2.2 RESULTS AND DISCUSSION

2.2.1 Isothiazolyl and Isothiazolinylidene Complexes of Cyclopentadienyliron

A. *Preparation of* $[CpFe(CO)_2\{\overline{C{=}CHCH{=}NS}\}]$ **1**, $[CpFe(CO)_2\{\overline{CCH{=}CHN(H)S}\}][CF_3SO_3]$ **2**, *and* $[CpFe(CO)_2\{\overline{CCH{=}CHN(Me)S}\}][CF_3SO_3]$ **3**.

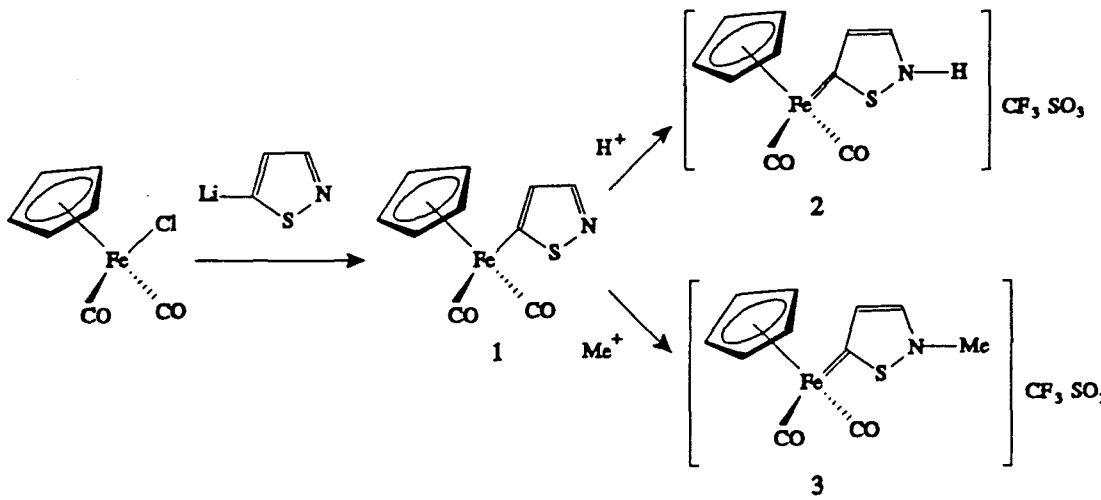
Isothiazole was synthesized according to the method described by Wille and his collaborators.[123,124] It involves the treatment of sodium thiosulphate with propynal (prepared from propargyl alcohol[125]) followed by the addition of liquid ammonia (Scheme 2.2). Isothiazoles, unsubstituted in the 5-position, are readily lithiated in this position in THF at -78°C by n-butyllithium.[126]



Scheme 2.2

The neutral isothiazolyl complex **1** (Scheme 2.3), was prepared by reacting isothiazol-5-yllithium with one molar equivalent of $[CpFe(CO)_2Cl]$ in THF at -78°C. The neutral complex, which is light sensitive and soluble in diethylether and methylene chloride, was obtained as a brown oil

after purification by means of column chromatography and has been characterized.



Scheme 2.3

The isothiazolyl complex **1**, was readily protonated with CF_3SO_3H or alkylated with CF_3SO_3Me in CH_2Cl_2 at 0°C to form the cationic organo(thio)carbene complexes **2** and **3** (Scheme 2.3). After filtration through anhydrous $MgSO_4$, the solutions were concentrated and pentane slowly added. Upon standing at -25°C dark brown crystals of these complexes were obtained.

These organo(thio)carbene complexes represent the first carbene complexes prepared from a precursor complex in which a nucleophilic heteroatom (N in this case) is not directly bonded to the coordinated carbon atom. An X-ray crystal structure of complex **3** was determined. It revealed interesting features which will be discussed and compared to the analogous thiazolinylidene complex $[CpFe(CO)_2\{\overline{CN(H)C(Me)=CHS}\}][CF_3SO_3]$ (Scheme 2.1) in Chapter 4.

B. *Spectroscopic characterization of* $[CpFe(CO)_2\{\overline{C=CHCH=NS}\}]$ **1**, $[CpFe(CO)_2\{\overline{CCH=CHN(H)S}\}][CF_3SO_3]$ **2**, *and* $[CpFe(CO)_2\{\overline{CCH=CHN(Me)S}\}][CF_3SO_3]$ **3**.

1. NMR spectroscopy

The ^1H NMR data for complexes **1**, **2** and **3** (see above) are summarized in Table 2.1. The proton resonances of the cyclopentadienyl ligand in the cationic carbene complexes **2** and **3** are shifted downfield (δ 5.22 and 5.25 respectively) with respect to those in the neutral compound (δ 4.16). This downfield shift is similar to that previously found when the thiazolyl complex was converted into the thiazolinylidene complex $[CpFe(CO)_2\{\overline{CN(H)C(Me)=CHS}\}][CF_3SO_3]$ (Scheme 2.1), and could be ascribed to the increase in positive charge which causes the protons to be less shielded. A small coupling (< 2.60 Hz) between the H_3 and H_4 protons of the isothiazolinylidene ligand was observed for the cationic carbene complexes **2** and **3**, but not for the neutral complex **1**. A broad signal for the NH-proton in complex **2** was observed at δ 14.48 and its chemical shift is, as expected, concentration dependent. This is due to proton exchange and hydrogen bonding as is commonly found for -OH and -NH protons. The NMe protons of complex **3** resonate at δ 4.17, indicating alkylation on the nitrogen atom.

The ^{13}C-$\{^1H\}$ NMR data for the complexes **1**, **2** and **3** are summarized and assigned in Table 2.2. The ^{13}C-$\{^1H\}$ NMR data for the cationic carbene complexes **2** and **3** show that the carbene carbons resonate at δ 189.1 and 189.9 respectively, and that they are shifted downfield with respect to the coordinated carbon of the neutral complex **1**, which resonates at δ 164.0. This downfield shift of the coordinated carbon resonances is similar to that found in the analogous thiazolinylidene complex, in which the coordinated carbon atom shifts from δ 175.1 in the neutral precursor complex to δ 199.5 in the corresponding carbene complex. This is indicative of carbene formation. The carbene carbon in the thiazolinylidene complex appears downfield (10.4 to 9.6 ppm) from the carbene carbons of the isothiazolinylidene complexes. This is expected since the coordinated carbon atom in the neutral thiazolyl complex resonates at δ 175.1, while the coordinated carbon atom in the corresponding isothiazolyl complex resonates at 164.0. The ^{13}C-resonances of the cyclopentadienyl ligand in the cationic carbene complexes **2** and **3** are

also shifted downfield from those in the neutral compound **1**. A similar effect was found when thiazole was the starting material.

Table 2.1

^{1}H NMR data for complexes (**1**) - (**3**)

Complex	δ (Assignment)
1[a]	8.61 (1H, s, H_3); 6.99 (1H, s, H_4); 4.16 (5H, s, Cp).
2[b]	14.48 (1H, br.s, NH); 8.56 (1H, d, $J(H_3\text{-}H_4)$ 1.96 Hz; H_3); 7.41 (1H, d, $J(H_4\text{-}H_3)$ 1.90 Hz; H_4); 5.22 (5H, s, Cp).
3[b]	8.56 (1H, d, $J(H_3\text{-}H_4)$ 2.58 Hz, H_3); 7.31 (1H, d, $J(H_4\text{-}H_3)$ 2.60 Hz, H_4); 5.25 (5H, s, Cp); 4.17 (3H, s, NMe).

[a]Measured in C_6D_6. [b]Measured in CD_2Cl_2.

Table 2.2

^{13}C-{^{1}H} NMR data for complexes (1) - (3)

Complex	δ (Assignment)
1[a]	214.4 (CO); 164.0 (C_5); 157.3 (C_3); 134.9 (C_4); 85.6 (Cp).
2[b,c]	211,5 (CO); 189,1 (C_5, carbene); 150.4 (C_3); 134.5 (C_4); 87.1 (Cp).
3[b,c]	211.4 (CO); 189.9 (C_5, carbene); 153.6 (C_3); 134.7 (C_4); 87.2 (Cp); 40.5 (NMe).

[a]Measured in C_6D_6. [b]Measured in CD_2Cl_2. [c]Pulse delay of 5 seconds.

The carbonyl stretching frequencies of complexes **1**, **2** and **3** (Scheme 2.3) appear in Table 2.3. The ν(CO) absorption bands of complexes **2** and **3** occur respectively at 10 and 18 wavenumbers higher than for the neutral complex **1** from which they were prepared. This effect was also observed when the infrared frequencies of the analogous thiazolyl and thiazolinylidene complexes were measured, and could be ascribed to both an increase in positive charge and to an increase in back donation to the carbene carbon atom.[78]

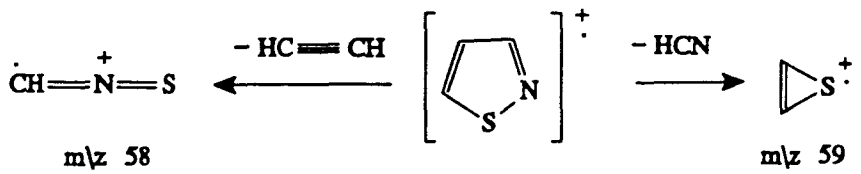
Table 2.3

IR data for complexes (1) - (3)[a]

Complex	ν(CO)/cm^{-1}
1	2036(st); 1986(st).
2	2046(st); 2001(st).
3	2046(st); 2004(st).

[a]Solution spectra recorded in hexachlorobutadiene.

The mass-spectra of complexes **1**, **2** and **3** (Scheme 2.3) are summarized in Table 2.5. It is appropriate to note here that the free isothiazole ligand fragments upon electron impact by two major routes outlined in Scheme 2.4, which involve the loss of neutral acetylene or hydrogen cyanide.[127]



Scheme 2.4

The molecular ion was observed in the mass spectrum of the neutral complex **1** at m/z 261. The fragmentation pattern, as illustrated in Table 2.4, consists of the stepwise loss of two carbonyl ligands, hydrogen cyanide, the C_2HS fragment and finally the cyclopentadienyl ligand. No molecular ion was observed in the mass spectrum of the cationic complex **2**, and the same fragmentation pattern as for complex **1** was observed. The cation was observed at m/z 276 in the mass spectrum of complex **3**. The fragmentation pattern of complex **3**, which is also shown in Table 2.4, involves the stepwise loss of the methyl group, the two carbonyl ligands and the isothiazolinylidene ligand.

Table 2.4

Fragmentation pattern of complexes **1** and **3**

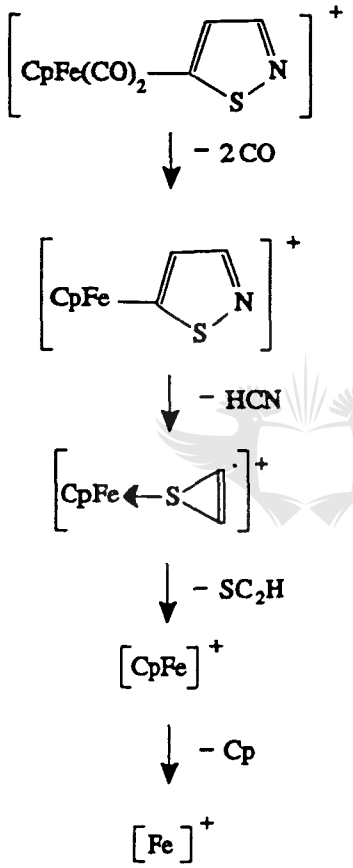
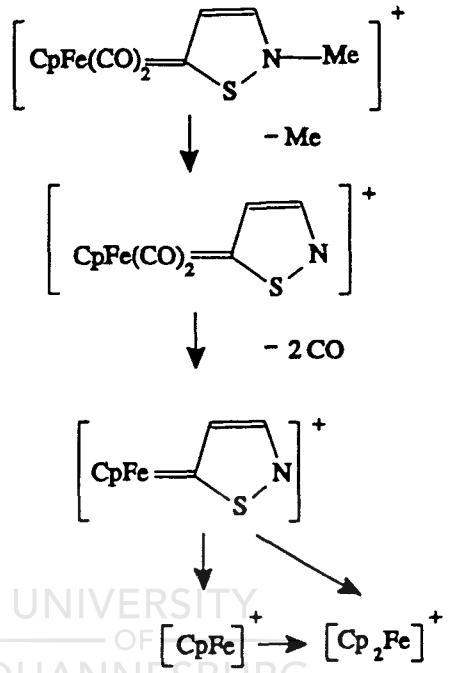
Complex 1	Complex 3
	

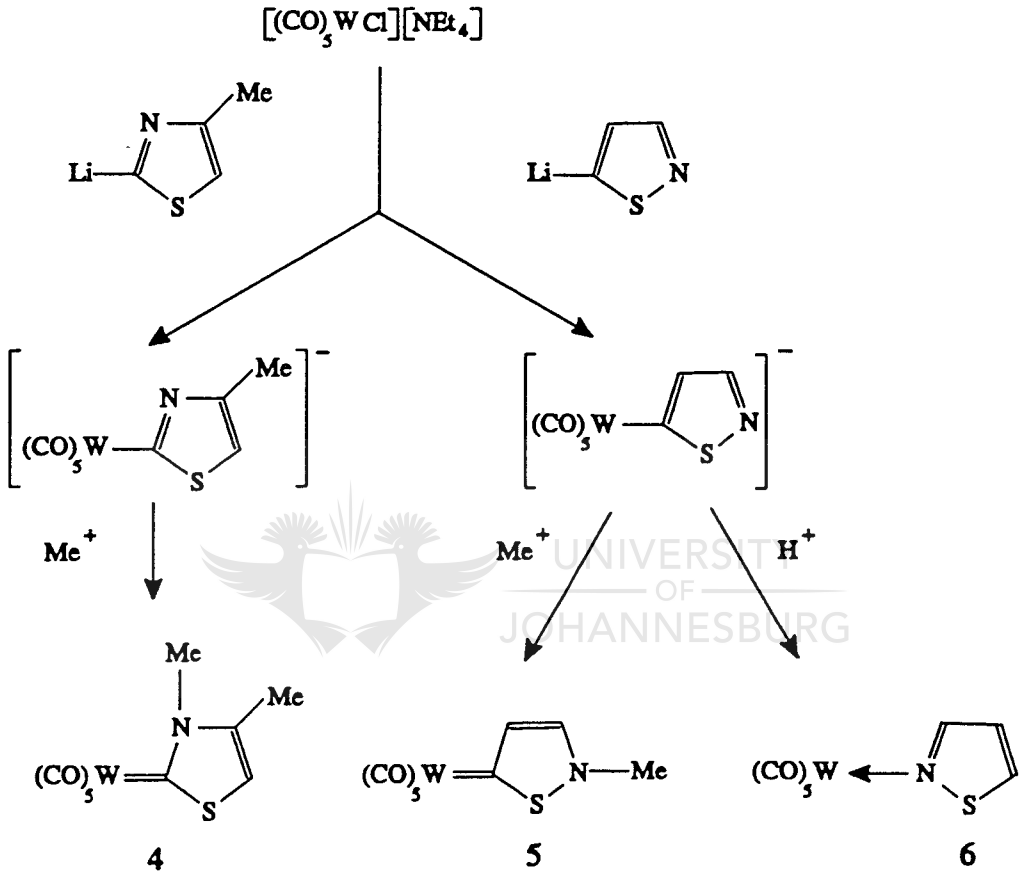
Table 2.5

Mass spectra for complexes (1) - (3)

Complex	m/z	I[a]	Fragment ions
1	261	30	$[CpFe(CO)_2\{\overline{C=CHCH=NS}\}]^+$
	233	85	$[CpFe(CO)\{\overline{C=CHCH=NS}\}]^+$
	205	42	$[CpFe\{\overline{C=CHCH=NS}\}]^+$
	178	100	$[CpFe\{C_2SH\}]^+$
	121	82	$[CpFe]^+$
	56	74	$[Fe]^+$
2	261	16	$[CpFe(CO)_2\{\overline{CCH=CHNS}\}]^+$
	233	63	$[CpFe(CO)\{\overline{CCH=CHNS}\}]^+$
	178	100	$[CpFe\{\overline{CCH=CHNS}\}]^+$
	121	82	$[CpFe]^+$
	56	74	$[Fe]^+$
3	276	5	$[CpFe(CO)_2\{\overline{CCH=CHN(Me)S}\}]^+$
	261	6	$[CpFe(CO)_2\{\overline{CCH=CHNS}\}]^+$
	233	23	$[CpFe(CO)\{\overline{CCH=CHNS}\}]^+$
	205	10	$[CpFe\{\overline{CCH=CHNS}\}]^+$
	186	100	$[Cp_2Fe]^+$
	121	96	$[CpFe]^+$

2.2.2 Thiazolinylidene and Isothiazolinylidene Complexes of Pentacarbonyltungsten

A. *Preparation of* $[(CO)_5W\{\overline{CN(Me)C(Me)=CHS}\}]$ **4** and $[(CO)_5W\{\overline{CCH=CHN(Me)S}\}]$ **5** *and* $[(CO)_5W\{\overline{N=CHCH=CHS}\}]$ **6**



Scheme 2.5

The neutral 4-methylthiazolinylidene complex **4** (Scheme 2.5) was prepared by treating $[(CO)_5WCl][NEt_4]$ with 4-methylthiazol-2-yllithium (obtained from 4-methylthiazole and n-butyllithium in THF at -78°C) and subsequent alkylation of the formed transmetallated anion with CF_3SO_3Me at -78°C. The solvent was removed under vacuum, and complex **4** extracted with pentane. Stripping of the solvent yielded complex **4** as a yellow powder, which was fully characterized. The neutral carbene complex **4** represents the first example of a coordinated

carbene prepared from a chloride complex of tungsten and this constitutes a new facile entry into the field of tungsten carbene complexes.

The same procedure was then used to prepare the isothiazolinylidene complex **5** (Scheme 2.5), which was purified by means of column chromatography. The yellow band was collected and the eluent concentrated. Cooling to -25°C afforded dark brown crystals which were unfortunately not suitable for an X-ray crystallographic study. Attempts at obtaining better quality crystals using different solvents were unsuccessful.

Direct treatment of the isothiazolyl(pentacarbonyl)tungsten anion with CF_3SO_3H at -78°C caused protonation on the metal bonded carbon atom to furnish the nitrogen coordinated complex **6** (Scheme 2.5). Spectral data of this complex were identical to that reported previously by Pannell and co-workers and will not be discussed any further.[128]

B. Spectroscopic characterization of $[(CO)_5W\{\overline{CN(Me)C(Me)=CHS}\}]$ **4** *and* $[(CO)_5W\{\overline{CCH=CHN(Me)S}\}]$ **5**

1. NMR spectroscopy

The ^1H NMR data for complexes **4** and **5** (see above) are summarized in Table 2.6. The NMe protons of complexes **4** and **5** resonate at δ 4.00 and 3.99 respectively, which is once again indicative of alkylation on the nitrogen atom. A small coupling (< 2.84 Hz) between the H_3 and H_4 protons of the isothiazole ligand was observed for complex **5**.

Table 2.6

^{1}H NMR data for complexes **4** and **5**[a]

Complex	δ (Assignment)
4	6.98 (1H, s, H_5); 4.00 (3H, s, NMe); 2.45 (3H, s, Me).
5	7.83 (1H, d, $J(H_3\text{-}H_4)$ 2.84 Hz, H_3); 7.38 (1H, d, $J(H_4\text{-}H_3)$ 2.58 Hz, H_4); 3.99 (3H, s, NMe).

[a]Measured in $CDCl_3$.

The ^{13}C-{^{1}H} NMR data for complexes **4** and **5** are summarized and assigned in Table 2.7. They show that the C_2 and C_5 carbene carbons resonate at δ 208.3 and 197.8 respectively. The carbene carbon of the thiazolinylidene complex **4** appears 10.5 ppm upfield from that of the isothiazolinylidene complex **5**. This is similar to the previously discussed iron complex. The ^{13}C-resonances of the carbene carbons compare well with those observed in a comparable cyclic pentacarbonyltungsten complex $[(CO)_5W\{\overline{CN(H)C_6H_4O\text{-}o}\}]$ (Equation 2.5) in which the carbene carbon resonates at δ 211.6.[118]

The chemical shifts of the cis and trans carbonyl ligands in complexes **4** and **5** occur at δ 202.2 and 197.6, and at δ 203.5 and 197.9 respectively, which corresponds well with the same signals found in the complex $[(CO)_5W\{\overline{CN(H)\text{-}C_6H_4O\text{-}o}\}]$.

Coupling between tungsten-183 (nuclear spin ½, natural abundance 14.3%) and carbon-13 was observed for the carbene and carbonyl carbons of complexes **4** and **5**. The values of the coupling constants $^1J(^{183}W\text{-}^{13}C)$ of the cis and trans carbonyls, compare well with those of other pentacarbonyltungsten complexes. Values between 102.5 and 131.8 Hz for $^1J(^{183}W\text{-}^{13}C)$ have

been observed for complexes such as $[(CO)_5W\{C(Ph)Ph\}]$, $[\{(CO)_5W\{\overline{CN(Me)CH=CHN}(Me)\}]$, $[\{(CO)_5W\{\overline{CN(Me)N=CHN}(Me)\}]$ and $[(CO)_5W\{C(Me)OMe\}]$.[129] The values of the $^1J(^{183}W\text{-}^{13}C)$ coupling constants, involving the carbene carbons, lie between 92.8 and 102.5 Hz for the same complexes. The coupling constant $^1J(^{183}W\text{-}^{13}C)$ 98.1 Hz for the thiazolinylidene complex falls within this range, but the coupling constant of 75 Hz for the isothiazolinylidene complex lies way below these values. Unfortunately coupling constants are not frequently reported and more suitable comparisons cannot be made.

Table 2.7

$^{13}C\text{-}\{^1H\}$ NMR data for complexes **4** and **5**[a]

Complex	δ (Assignment)
4	208.3 ($^1J(^{183}W\text{-}^{13}C)$ 98.1 Hz, C_2, carbene);
	202.2 ($^1J(^{183}W\text{-}^{13}C)$ 127.8 Hz, trans CO);
	197.6 ($^1J(^{183}W\text{-}^{13}C)$ 126.5 Hz, cis CO);
	145.2 (C_4);
	120.7 (C_5);
	42.3 (NMe);
	15.1 (Me).
5	203.5 ($^1J(^{183}W\text{-}^{13}C)$ 137.9 Hz, trans CO);
	197.9 ($^1J(^{183}W\text{-}^{13}C)$ 125.5 Hz, cis CO);
	197.8 ($^1J(^{183}W\text{-}^{13}C)$ 75.0 Hz, C_5, carbene);
	149.3 (C_3);
	133.5 (C_4);
	38.2 (NMe).

[a]Measured in $CDCl_3$.

2. Infrared spectroscopy

The carbonyl stretching frequencies of complex **4** and **5** (Scheme 2.5) are summarized in Table 2.8. In both complexes the $A_1^{(2)}$-band occurs as a shoulder and appears at a higher frequency than the E-band.[130,131] The number of bands observed in the IR spectra and their width often depends on the solvent in which the molecule is dissolved. This can be observed in the IR spectra of complex **5** when measured in hexane or in CH_2Cl_2. In the latter solvent the B_1-band is present, and the $A_1^{(2)}$ and E-bands are degenerate as only one broad peak is visible. There is very little difference in the carbonyl stretching frequencies of complexes **4** and **5**.

Table 2.8

IR spectra for complexes **4** and **5**

Complex	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E
4[a]	2066(w)	1970(vw)	1935(st, sh)	1928(st)
5[a]	2063(w)	——	1938(st, sh)	1928(st)
5[b]	2062(w)	1964(vw)		1922

[a]Solution spectra recorded in hexane. [b]Solution spectra recorded in CH_2Cl_2.

3. Mass spectrometry

The mass-spectra of complexes **4** and **5** are summarized in Tables 2.9 and 2.10. The molecular ions were observed in the mass spectra of both neutral complexes **4** and **5** at m/z 437 and 423 respectively. The fragmentation pattern of complex **4**, which is illustrated in Table 2.9, consists of the stepwise loss of all the carbonyl groups, followed by a methyl group and hydrogen

cyanide. The fragmentation pattern of complex **5** parallels that of complex **4** (Table 2.9). The loss of hydrogen cyanide implies a migration of the metal from the carbon atom to the sulphur atom, these $[W(MeC_2S)]^+$ and $[W(C_2SH)]^+$ fragment ions occur at m/z 255 and 241 in complexes **4** and **5** respectively.

Table 2.9

Fragmentation patterns of complexes **4** and **5**

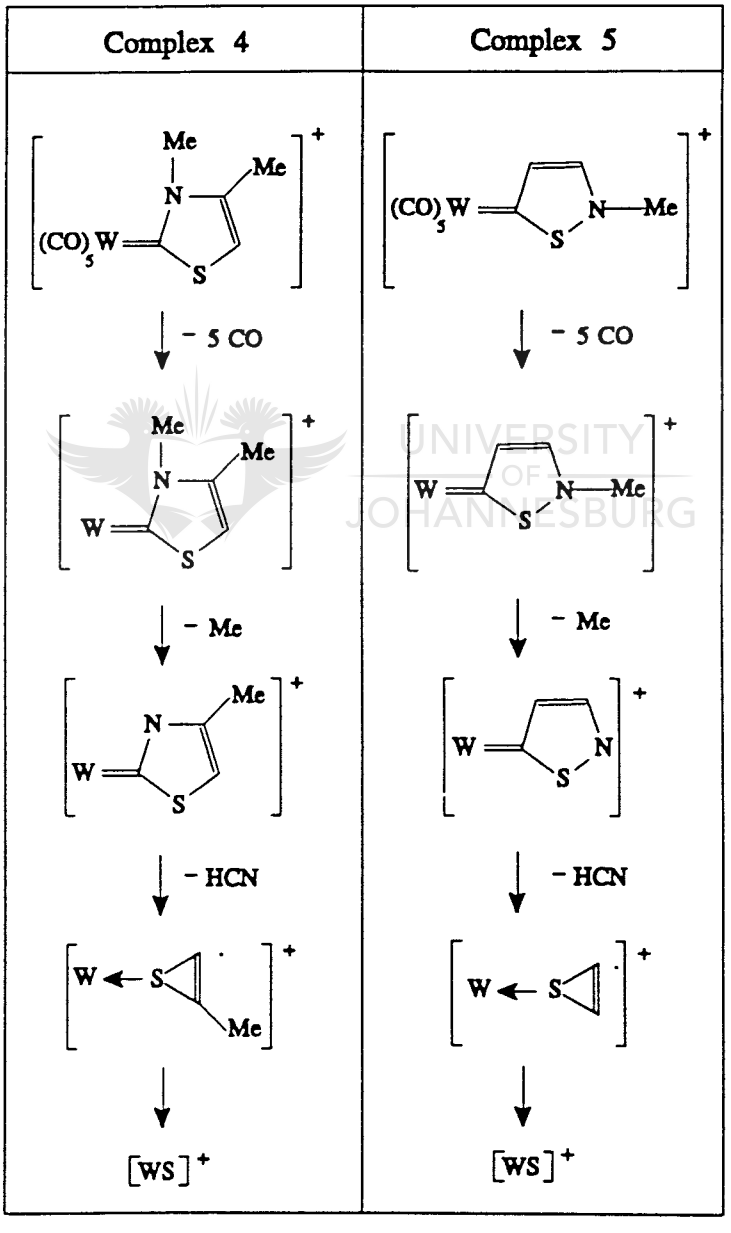


Table 2.10

Mass spectra for complexes **4** and **5**

Complex	m/z	I[a]	Fragment ions
4	437	65	$[(CO)_5W\{\overline{CN(Me)C(Me)=CHS}\}]^+$
	409	22	$[(CO)_4W\{\overline{CN(Me)C(Me)=CHS}\}]^+$
	381	41	$[(CO)_3W\{\overline{CN(Me)C(Me)=CHS}\}]^+$
	353	76	$[(CO)_2W\{\overline{CN(Me)C(Me)=CHS}\}]^+$
	325	73	$[(CO)W\{\overline{CN(Me)C(Me)=CHS}\}]^+$
	297	100	$[W\{\overline{CN(Me)C(Me)=CHS}\}]^+$
	282	9	$[W\{\overline{CNC(Me)=CHS}\}]^+$
	255	29	$[W(MeC_2S)]^+$
	216	10	$[WS]^+$
5	423	11	$[(CO)_5W\{\overline{CCH=CHN(Me)S}\}]^+$
	395	4	$[(CO)_4W\{\overline{CCH=CHN(Me)S}\}]^+$
	367	5	$[(CO)_3W\{\overline{CCH=CHN(Me)S}\}]^+$
	339	8	$[(CO)_2W\{\overline{CCH=CHN(Me)S}\}]^+$
	311	100	$[(CO)W\{\overline{CCH=CHN(Me)S}\}]^+$
	283	17	$[W\{\overline{CCH=CHN(Me)S}\}]^+$
	268	6	$[W\{\overline{CCH=CHNS}\}]^+$
	241	20	$[W(C_2SH)]^+$
	216	8	$[WS]^+$
	184	3	$[W]^+$

2.3 CONCLUSIONS AND FURTHER WORK

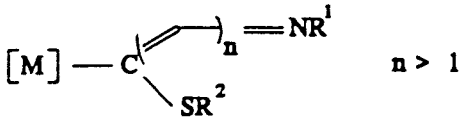
The idea of carbene complex formation by electrophilic attack on a remote nucleophilic nitrogen atom which is conjugated to a metal-bonded carbon in a σ-organometallic complex has for the first time successfully been applied to iron and tungsten compounds which contained isothiazolyl as the carbon bonded σ ligand. Similar reactions with pentachloropyridinyl and 1-ethylpyrazolyl were unsuccessful. Reactions utilizing other cyclic ligands such as pentafluoropyridinyl, isoxazolyl, 2,1-benzisothiazolyl or isoindazolyl might, however, succeed.

The tungsten preparation is unique in that a chloride carbonyl compound has been used to generate a coordinated carbene compound. This method may now be extended to the synthesis of other tungsten carbene complexes.

Further questions which arise from this work are:

a) Could the same type of products be synthesized from acyclic precursors?

b) Could starting materials, and from there complex precursors, be synthesized in which the nitrogen atom is separated from the coordinated carbon atom by several bond lengths, as illustrated in Scheme 2.6?



Scheme 2.6

c) Would it be possible to replace the imine group in such complexes by (=O) or (=S), and the SR_2 group with other heteroatom-containing groups?

d) Most importantly, what kind of reactivity will these complexes possess, and would it be possible to convert them into useful organic products?

2.4 EXPERIMENTAL

2.4.1 General remarks

All reactions involving organometallic reagents were carried out under an atmosphere of nitrogen using standard vacuum-line and Schlenk tube techniques. Clean glassware was taken directly from a drying oven and placed under vacuum before use. For low-temperature reactions dry ice/acetone (-78°C) or ice/salt (-10°C) baths were used.

All solvents were pre-dried in the following manner for two days before use: THF, diethyl ether and diethylene glycol were dried over sodium wire; and pentane, hexane and CH_2Cl_2 over potassium hydroxide. Before use all the solvents were freshly distilled under nitrogen. THF and diethyl ether were distilled from sodium wire and benzophenone, diethylene glycol was distilled from sodium, while pentane, hexane and CH_2Cl_2 were distilled from CaH_2.

Chromatographic purifications were performed under nitrogen using Florisil or Silica gel as the stationary phase in double-layered columns at temperatures lower than -10°C. The stationary phase was placed under vacuum for a minimum of 4 hours before use. Thin layer chromatography (Alugram Sil G/U_{154}) was used to determine the homogeneity of the compounds.

All deuterated solvents and 4-Methylthiazole were obtained from ALDRICH. THF, CF_3SO_3Me and CF_3SO_3H were purchased from FLUKA and n-butyllithium (1.6 M dissolved in hexane) was acquired from MERCK. Isothiazole,[124] $[(CO)_5WCl][NEt_4]$[132,122] and $[CpFe(CO)_2Cl]$[133] were prepared according to published procedures.

The ^1H NMR spectra were recorded on a Varian VXR 200 FT (200.6 MHz) spectrometer. The ^{13}C-{^1H} NMR spectra were recorded on the same instrument at 50.3 MHz. The melting points were determined on a standardised Buchi 535 apparatus and are corrected. The mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument and the infrared spectra on a Perkin-Elmer 841 spectrometer.

2.4.2 Preparation of [CpFe(CO)$_2${C=CHCH=NS}] **1.**

A solution of isothiazole (0.29 cm^3, 1.17 g.cm^{-3}, 4.0 mmol) in THF (40 cm^3) was cooled to -78°C and treated with n-butyllithium in hexane (2.5 cm^3, 1.6 M, 4.0 mmol). The light pink solution was stirred at -78°C for one hour. A solution of [CpFe(CO)$_2$Cl] (0.85 g, 4.0 mmol) in THF (40 cm^3) was added dropwise at -70°C . The mixture was stirred for 2h at 0°C and the solvent removed under vacuum. The residue was extracted with diethyl ether (4 X 50 cm^3). The volume of the extract was reduced and the extract purified by column chromatography at -10°C on florisil with diethyl ether/hexane (1:4 - 5:1) as eluent. The solvent was removed to yield complex **1** as an oily residue.

MP : an oil
Yield : 0.55 g (52%)

2.4.3 Preparation of [CpFe(CO)$_2${CCH=CHN(H)S}][CF_3SO_3] **2.**

A solution of CF_3SO_3H (0.18 cm^3, 1.17 g.cm^{-3}, 2.1 mmol) in CH_2Cl_2 (30 cm^3) was slowly added at 0°C to a CH_2Cl_2 solution of complex **1** (0.55 g, 2.1 mmol). The mixture was stirred for 1h at 0°C and filtered through anhydrous $MgSO_4$. Concentration of the filtrate, slow addition of pentane and cooling to -25°C afforded dark brown crystals of complex **2**.

MP : 91-92°C
Yield : 0.310 g (36%)

2.4.4 Preparation of [CpFe(CO)$_2${CCH=CHN(Me)S}][CF_3SO_3] **3.**

A solution of complex **1** (0.37 g, 1.4 mmol) in CH_2Cl_2 (50cm^3) was cooled to 0°C and treated dropwise with CF_3SO_3Me (0.16 cm^3, 1.45 g.cm^{-3}, 1.4 mmol). The mixture was stirred for 1.5h at this temperature and then filtered through anhydrous $MgSO_4$. Concentration of the filtrate, slow addition of pentane and cooling to -25°C afforded dark brown crystals of complex **3**.

MP : 85-86°C

Yield : 0.24 g (41%)

2.4.5 Preparation of $[(CO)_5W\{\overline{CN(Me)C(Me)=CHS}\}]$ **4.**

A solution of 4-Methylthiazole (0.20 cm^3, 1.1 $g.cm^{-3}$, 2.2 mmol) in THF (20cm^3) was cooled to -75°C and treated with butyllithium (1.38 cm^3, 1.6 M, 2.2 mmol). The yellow solution was stirred at -78°C for 1 hour before it was slowly added over a period of 20 min to a THF solution of $[W(CO)_5Cl][NEt_4]$ (0.98 g; 2.0 mmol) at -75°C. The mixture was stirred for 2h at this temperature and then allowed to reach room temperature over a period of 3h. The mixture was stirred for a further 30 min at room temperature and then re-cooled to -78°C before CF_3SO_3Me (0.25 cm^3, 1.45 $g.cm^{-3}$, 2.2 mmol) was added. The mixture was stirred overnight at this temperature and then allowed to reach room temperature over a period of 3h. The solvent was removed and the residue extracted with pentane (7 X 50 cm^3). Removal of the solvent yielded complex **4** as a yellow powder.

MP : 99°C
Yield : 0.6 g (68%)

2.4.6 Preparation of $[\{(CO)_5W\{\overline{CCH=CHN(Me)S}\}]$ **5.**

A solution of isothiazole (0.15 cm^3, 1.17 $g.cm^{-3}$, 2.05 mmol) in THF (20 cm^3) was cooled to -75°C and treated with n-butyllithium (1.28 cm^3, 1.6 M, 2.05 mmol). The pink solution was stirred at -78°C for 45 min before it was slowly added over a time period of 25 min to a THF solution of $[W(CO)_5Cl][NEt_4]$ (0.98 g; 2.0 mmol) at -70°C. The mixture was stirred for 1h at this temperature and then allowed to reach room temperature over a period of 2h. The mixture was stirred for a further 30 min at room temperature and re-cooled to -78°C before CF_3SO_3Me (0.23 cm^3, 1.45 $g.cm^{-3}$, 2.05 mmol) was added. The mixture was stirred for 1h at this temperature and then allowed to reach room temperature over a period of 12h. The solvent was removed and the residue chromatographed on SiO_2 using pentane/ether (5:1 - 1:1) as eluent. The solvent was removed and the residue redissolved in pentane, cooling to -25°C afforded small brown crystals of complex **5**.

MP : 107-108°C

Yield : 0.62 g (73%)

2.4.7 Preparation of $[(CO)_5W\{\overline{N=CHCH=CHS}\}]$ 6.

A solution of isothiazole (0.14 cm^3, 1.17 $g.cm^{-3}$, 1.86 mmol) in THF (30 cm^3) was cooled to -75°C and treated with n-butyllithium (1.2 cm^3, 1.55 M, 1.86 mmol). The pink solution was stirred at -78°C for 45 min before it was slowly added over a time period of 20 min to a THF solution of $[W(CO)_5Cl][NEt_4]$ (0.89 g; 1.81 mmol) at -70°C. The mixture was stirred for 1h at this temperature and then allowed to reach room temperature over a period of 3h. The mixture was stirred for a further 30 min at room temperature and re-cooled to -78°C before CF_3SO_3H (0.16 cm^3, 1.71 $g.cm^{-3}$, 1.86 mmol) was added. The mixture was stirred for 1h at this temperature and then allowed to reach room temperature over a period of 12h. The solvent was removed and the residue chromatographed on SiO_2 using pentane/ether (5:1 - 1:1) as eluent. The solvent was removed to yield complex **6** as a yellow residue.

MP : 93-94°C

Yield : 0.38 g (51%)

CHAPTER 3

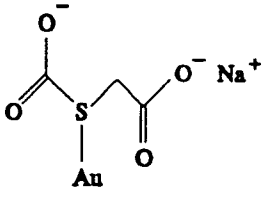
THE SYNTHESIS AND CHARACTERIZATION OF ORGANO(THIO)- AND AMINO(ORGANO)CARBENE COMPLEXES OF GOLD

3.1 INTRODUCTION

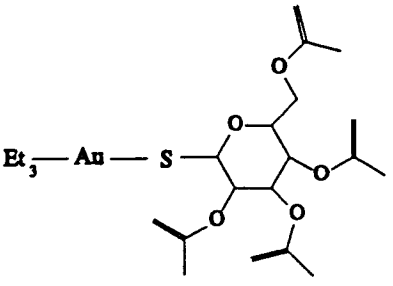
Metallic gold has been valued since the earliest times. The applications of gold, due to its unique physical properties, have long been dominated by its metallic state. The attractive properties of gold have led it to be used as a monetary standard, for jewellery and other decorative uses. Most applications of gold and its compounds have made use of the inertness of gold metal to give longstanding protection of materials against deterioration by chemicals.[134] The durability and ductility of the metal have allowed the production of extremely thin films and wires for such purposes. Gold's high thermal and electrical conductivity have allowed it to be used in the electronics industry.[135,136] However, the chemistry of gold, as such, has remained largely undeveloped, but this is changing. It is now the subject of research in many laboratories and the number of publications has increased vastly.

Crysotherapy (the use of gold based drugs in medicine) is one area that has greatly benefited from this increased interest in gold chemistry. Gold derivatives are of great value in the treatment of rheumatoid arthritis, and very recently compounds effective against cancer have also been found.[137-139] The gold(I) sulphur compounds, Myocrisin[140] and Auranofin[141] (Figure 3.1) have beneficial effects in the treatment of rheumatoid arthritis, however, serious side effects can occur. It is believed that Myocrisin is polymeric in nature with sulphur atoms of the thiol groups linking pairs of gold atoms. Unfortunately the mechanism of action of these drugs is still unknown, but the biochemistry of the transport of gold in the blood stream, into and out of cells

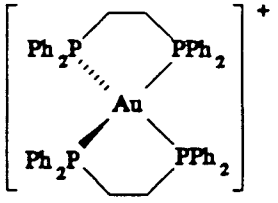
and into the liver and kidneys is becoming clear.[142-144] Bis(diphosphino)gold(I) complexes, such as, $[(dppe)_2Au]Cl$ (Figure 3.1) and $[(Ph_2CH{=}CHPPh_2)_2Au]Cl$, have been found to be effective against particular types of tumours, but give severe toxicity problems.[145]



Myocrisin



Auranofin

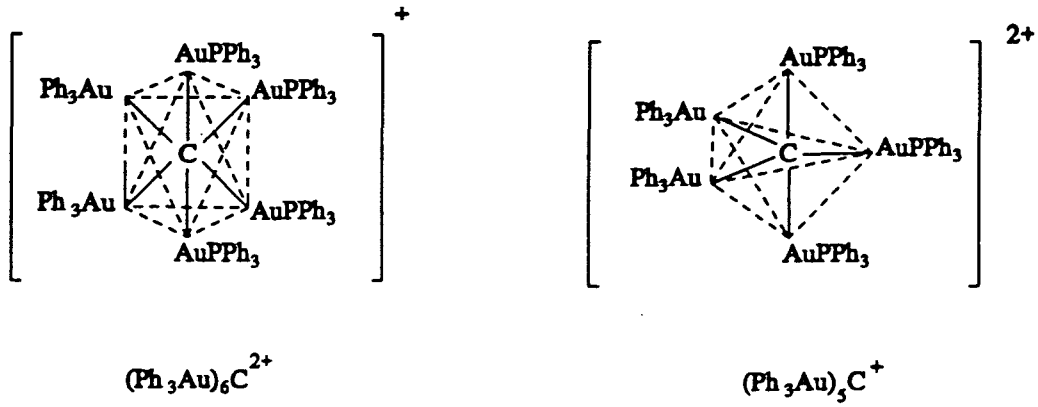


$[(dppe)_2Au]^+$

Figure 3.1

Except for a few gold drugs in medicine, gold compounds have played a minor role compared with the ubiquitous gold metal. Gold is generally regarded as the least useful of the noble metals for catalytic purposes, and few industrial applications of gold-catalyzed reactions are known.[146,147] This situation is likely to change, since recent research shows gold compounds to be effective catalysts in organic synthesis. The latest examples include the synthesis of oxazolines by a gold(I) catalyzed aldol reaction in the presence of chiral ferrocenylamine[148-150] and the synthesis of isoxazole utilizing tetrabutylammonium tetrachloroaurate as catalyst.[151] The latter gold complex is also an effective catalyst for the oxidation of sulfides to sulfoxides.[152]

Interesting developments in the area of gold cluster compounds have recently occurred. Among these are the penta- and hexa(aurio) methanium cations, $(LAu)_5C^+$ and $(LAu)_6C^{2+}$, where L is a tertiary phosphine (Figure 3.2). These cations are trigonal and octahedral gold clusters respectively, and are centred by carbon in both cases.[153-156] Nitrogen can similarly be introduced into such clusters, the most important examples being the compounds $(LAu)_4N^+$ and $(LAu)_5N^{2+}$, with the nitrogen in the centre of a tetrahedron or a trigonal bipyramid respectively.[157,158]



$(Ph_3Au)_6C^{2+}$ $(Ph_3Au)_5C^{+}$

Figure 3.2

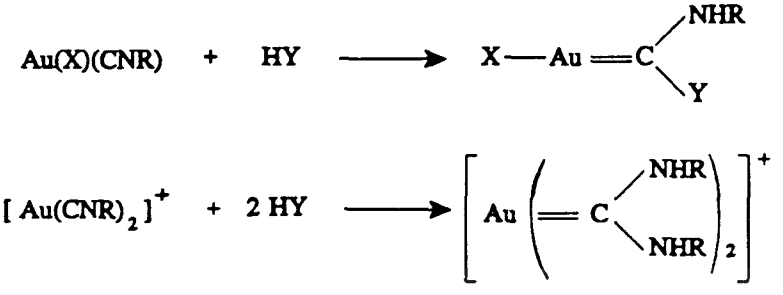
Interest in these gold cluster compounds lies in the Au...Au interactions that have a distance of approximately 3 Å. This strong attractive interaction between gold atoms has been observed in numerous mono- and polynuclear gold(I) compounds. An explanation for these interactions, according to the group of Schmidbaur who synthesized the above mentioned compounds, lies in the so-called relativistic effect. According to these effects, which are only partly understood, the 6s-orbitals and to a lesser extent the 5p-orbitals experience a relativistic contraction. This is accompanied by slight 5d-orbital expansion. The resulting strongly diminished energy gap between the 6s and 5d states facilitate spd-type hybridization. These hybrid orbitals can then participate in effective bond formation between gold atoms.[82,159]

Although none of these recently synthesized gold compounds have found industrial applications, they are important as their characterization has led to a better understanding of gold chemistry. It is this knowledge and understanding that will eventually lead to industrial applications. One of the aims of this chapter has been to contribute towards this understanding of gold chemistry through the synthesis and characterization of new types of gold carbene complexes.

Compared to other noble metals, such as platinum and iridium, few gold(I) carbene complexes have been prepared. The Fischer route, which involves electrophilic addition to metal acyl and related complexes, is not available for gold as only a few of the appropriate gold complexes which could be used as starting materials exist.[22] The major synthetic routes towards gold(I) carbene complexes involve precursor isocyanide complexes, cleavage of the carbon-carbon

double bond in electron rich olefins, and carbene transfer from tungsten pentacarbonyl compounds. More recently, precursor 4-methyl- and benzothiazolyl complexes as well as 2-pyridyl aurate complexes have been used. Although these methods have been discussed in Chapter 1, a few examples relating to gold will be given here.

The most commonly utilized route towards alkoxy(amino)- or di(amino)carbenegold(I) complexes, is the addition of alcohols or amines to gold(I) isocyanide complexes (Equation 3.1 and 3.2). In this manner, a whole series of mono- and bis(carbene) complexes were prepared.[160,161]



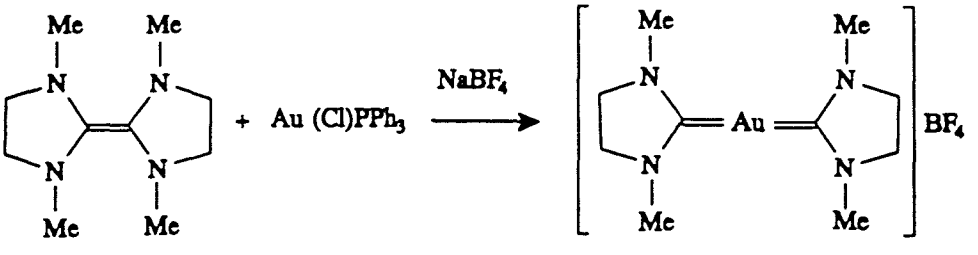
Y = OR, NHR^1

R = alkyl or aryl

X = C_6F_5, Cl

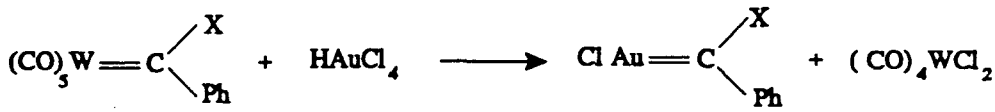
Equation 3.1 and 3.2

An alternative route to the synthesis of bis(carbene) complexes of gold(I) involves the cleavage of the carbon-carbon double bond in electron rich olefins, such as 1,1',3,3'-tetramethyl-2,2'-bi-imidazolidinylidene (Equation 3.3).[38]



Equation 3.3

Furthermore, carbene transfer from alkyl- and aryl(pentacarbonyl)tungsten complexes give the corresponding gold(I) chloride carbene complexes (Equation 3.4). The transfer of the carbene ligand involves a redox process and proceeds by retention of its configuration.[162]



X = OMe , NH_2 , NMe_2 , NHMe

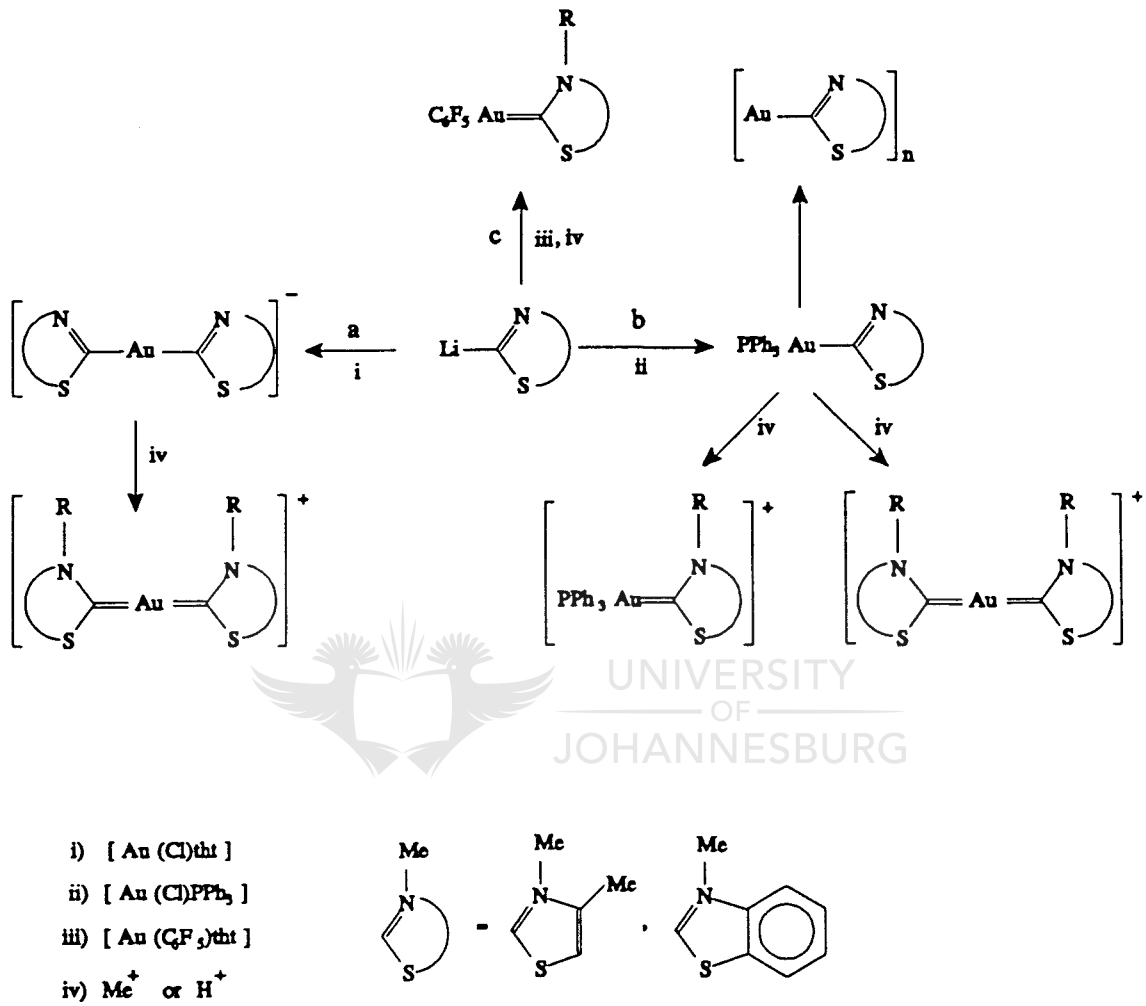
Equation 3.4

Recently in our laboratory a series of new gold(I) carbene complexes have been prepared. A few selected examples are shown in Scheme 3.1. The synthesis of these neutral and cationic amino(thio)carbene complexes involves the addition of lithiated 4-methyl- or benzothiazole to gold(I) chloride or tetrahydrothiophene(pentafluorophenyl)gold complexes followed by the subsequent protonation or alkylation of the products formed. An organo(amino)carbene complex has similarly been prepared by the addition of HCl or HBr to a 2-pyridyl aurate complex. In all these compounds the nucleophilic nitrogen atom is situated α to the coordinated carbon atom.[79,80]

The question to be answered in this chapter is whether, similarly to the results obtained for iron and tungsten in Chapter 2, gold carbene complexes can be obtained from lithiated isothiazoles by protonation or alkylation of a remote nucleophilic nitrogen atom. In this chapter, the preparation and characterization of gold(I) carbene complexes as well as their precursor complexes are of interest.

Thiazolyl aurate complexes have been prepared and isolated by the reaction of [Au(tht)Cl] with lithiated 4-methyl- and benzothiazoles (route a, Scheme 3.1). These aurate complexes can be used as *in situ* precursors for the synthesis of cationic bis{amino(thio)}carbene complexes. One aim was to prepare and isolate an isothiazolyl aurate complex and the corresponding bis{organo(thio)}carbene complexes by protonation or alkylation of the aurate complex. Interestingly, the ^{13}C-{^1H} NMR data of the thiazolyl complexes showed little difference in the chemical shifts of the coordinated carbon atom in the precursor and corresponding carbene

complex. The chemical shifts of these carbons are also of interest in the corresponding isothiazolyl complexes as they could shed light on important characteristics of the bonding in these complexes.



Scheme 3.1

Strongly ligated gold chloride complexes also react with 4-methyl- and benzothiazolyllithium to afford neutral thiazolyl complexes, which upon alkylation yield cationic mono(carbene) complexes (route b, Scheme 3.1). Complicating reactions have been observed in the preparation of these cationic mono(carbene) complexes. The neutral thiazolyl complex decomposed into a polymeric compound, which is believed to exist as a cyclic trimer with n=3, and was thus

difficult to isolate (Scheme 3.1). Furthermore, the mono(carbene) complex was also observed to undergo homoleptic rearrangement (i.e. complexes with mixed ligands spontaneously rearrange to form complexes with homoleptic ligands) to form a bis(carbene) complex. Another objective, was to prepare the corresponding isothiazolyl mono(carbene) complex and to ascertain whether similar rearrangements occur. The neutral isothiazolyl complex would not be expected to polymerize and therefore the aim was also to isolate this neutral precursor complex.

Thiazolyl mono(carbene) complexes containing the anionic $C_6F_5^-$ ligand have also been prepared. $[Au(C_6F_5)tht]$ reacts with 4-methyl- and benzothiazolyllithium to form thiazolyl aurate complexes which can be directly protonated or alkylated to afford the neutral amino(thio)carbene complexes (route c, Scheme 3.1). The third objective was to prepare both the aurate isothiazolyl precursor compound and the corresponding neutral carbene complex.

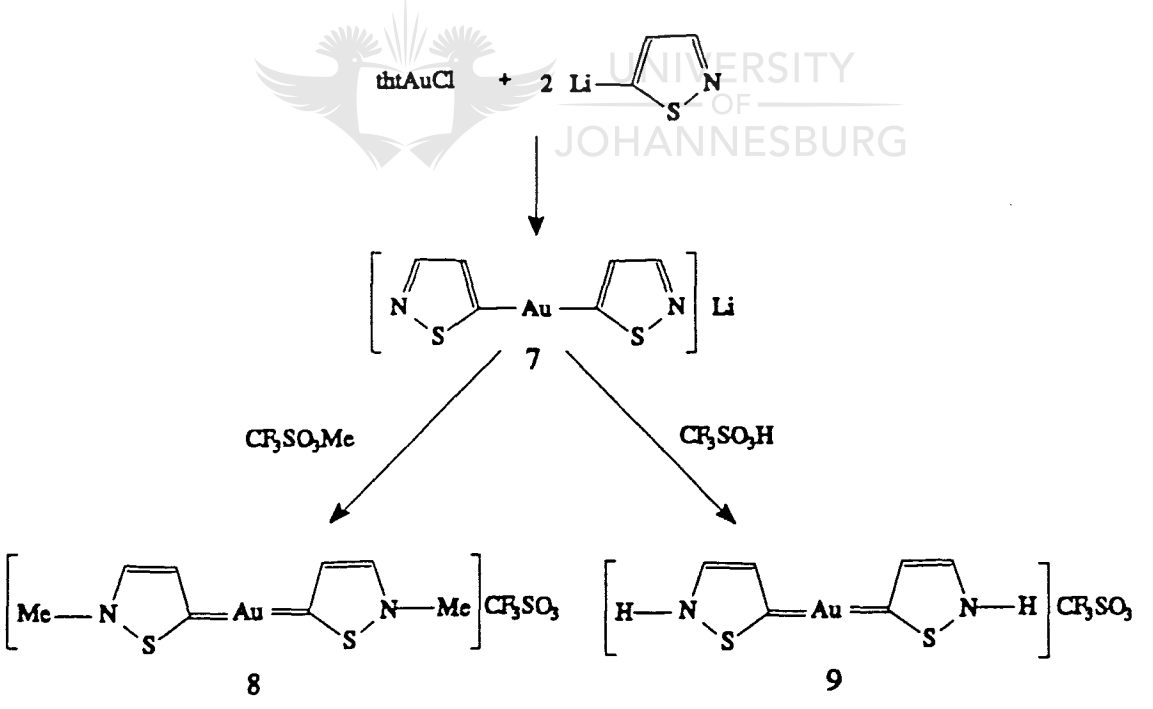
The requirement for the possible deprotonation of a C-H group next to a double bond, which is conjugated to an imine double bond, is fulfilled by 1-ethylpyrazole. If the preparation of a carbene complex utilizing this ligand was successful, it would provide a second example to illustrate the principle of electrophilic attack on a remote nucleophilic heteroatom. A further aim was thus to synthesis amino(organo)carbene complexes employing this ligand while utilizing the same gold starting materials as for the isothiazole ligand.

3.2 RESULTS AND DISCUSSION

3.2.1 Bis(isothiazolyl) Aurate and Cationic Bis(isothiazolinylidene) Complexes of Gold

A. *Preparation of* Li[Au{$\overline{C{=}CHCH{=}NS}$}$_2$] **7**, [Au{$\overline{CCH{=}CHN(Me)S}$}$_2$][$CF_3SO_3$] **8** *and* [Au{$\overline{CCH{=}CHN(H)S}$}$_2$][$CF_3SO_3$] **9**.

The bis(isothiazolyl) aurate complex **7** was prepared by reacting two equivalents of isothiazolyllithium with one molar amount of [Au(Cl)tht] in THF at -78°C. The solution was reduced to dryness and the solid washed several times with diethylether to give complex **7** which has been characterized (Scheme 3.2).



Scheme 3.2

The air sensitive, but thermally stable, aurate is only soluble in THF and acetone. Large quantities of THF were found to be present in the NMR spectra even though the complex was kept *in vacuo* for a twenty-four hour period. The THF, which resonates in its usual position, probably solvates the small lithium counterion. The aurate complex **7** was subsequently used as an *in situ* precursor for the synthesis of the bis(carbene) complexes **8** and **9** (Scheme 3.2).

Direct alkylation or protonation of the aurate complex **7**, at -78°C with two molar amounts of CF_3SO_3Me or CF_3SO_3H respectively, produced yellow solutions of the cationic bis(carbene) complexes **8** and **9** (Scheme 3.2). Upon standing at -25°C long yellow needle-like crystals of the isothiazolinylidene complexes **8** and **9** were obtained.

Complex **8** is soluble in acetone and THF. In microcrystalline form it is thermally stable in air at room temperature when kept in the presence of a few drops of solvent. However, the crystals loose their shape, perhaps by loss of solvent of crystallization, once out of contact with the mother liquor. Complex **9** in its microcrystalline form is much less soluble than its alkylated counterpart, yet the crystals when formed are extremely hygroscopic.

The precipitates of complexes **7** and **9** both display unusual solvent association effects. When the compounds are dry, they are red in colour, otherwise yellow. When exposed to air, the red precipitates change to a yellow colour, possibly due to absorbing atmospheric water.

B. Spectroscopic characterization of $Li[Au\{\overline{C=CHCH=NS}\}_2]$ **7**, $[Au\{\overline{CCH=CHN(Me)S}\}_2][CF_3SO_3]$ **8** *and* $[Au\{\overline{CCH=CHN(H)S}\}_2][CF_3SO_3]$ **9**.

1. NMR spectroscopy

The ^1H NMR data for complexes **7**, **8** and **9** (Scheme 3.2) are summarized in Table 3.1. The ^1H NMR data of compounds **8** and **9** show that the H_3 and H_4 protons are shifted downfield with respect to the H_3 and H_4 resonances of compound **7**. A small coupling between the H_3 and H_4 protons is observed in all three complexes. The NMe protons of complex **8** resonate at δ 4.38,

which is indicative of alkylation on the nitrogen atom. A broad singlet for the NH-proton in complex **9** is observed and its chemical shift is, as expected, concentration dependent. An NOE difference ^{1}H NMR spectrum of complex **8** confirmed the assignment of the H_3 and H_4 protons in all the spectra.

Table 3.1

^{1}H NMR data of compounds (7) - (9)

Complex	δ (Assignment)
7[a]	8.59 (2H, d, J(H_3-H_4) 1.62 Hz, H_3); 7.08 (2H, d, J(H_4-H_3) 1.56 Hz, H_4).
8[a]	9.20 (2H, d, J(H_3-H_4) 2.07 Hz, H_3); 7.40 (2H, d, J(H_4-H_3) 2.63 Hz, H_4); 4.38 (6H, s, NMe).
9[b]	9.15 (2H, d, J(H_3-H_4) 2.41 Hz, H_3); 7.45 (2H, d, J(H_4-H_3) 1.97 Hz, H_4); 6.08 (2H, br.s, NH).

[a]Measured in $(CD_3)_2CO$. [b]Measured in THF-d_8.

The ^{13}C-{^{1}H} NMR data for complexes **7**, **8** and **9** (Scheme 3.2) are summarized in Table 3.2. The carbon atom of the counterion $CF_3SO_3^-$ is not visible in the spectra of complexes **8** and 9 since the signal is split as a result of coupling to the fluorine atoms.

Table 3.2

^{13}C-{^{1}H} NMR data for complexes (7) - (9)

Complex	δ (Assignment)
7[a]	195.0 (C_5);
	155.9 (C_3);
	127.6 (C_4).
8[a]	197.3 (C_5, carbene);
	156.1 (C_3);
	128.9 (C_4);
	40.4 (NMe).
9[b]	197.0 (C_5, carbene);
	152.7 (C_3);
	128.8 (C_4).

[a]Measured in $(CD_3)_2CO$. [b]Measured in THF-d_8.

The carbon-13 spectra of complex 7 and complex 8 are shown in Figure 3.3. All the spectra were measured in $(CD_3)_2CO$. A few interesting features arise when the ^{13}C-{^{1}H} NMR data of the free isothiazole ligand and the complexes 7, 8 and 9 are compared.

The most interesting feature in the carbon-13 spectrum of complex 7 is that the chemical shifts of carbon 3 and carbon 4 show little change compared to free isothiazole. In free isothiazole carbon 4 and carbon 3 resonate at δ 124.4 and 158.1 respectively, while in the isothiazolyl aurate they resonate at δ 127.6 and 155.9 respectively. The coordinated carbon atom, on the other hand, unexpectedly resonates at δ 195 compared to δ 149.1 in the free ligand despite the negative charge on the complex. In this sense complex 7 is similar to the thiazolyl complex (route a, Scheme 3.1) that was previously isolated by Otte.[79]

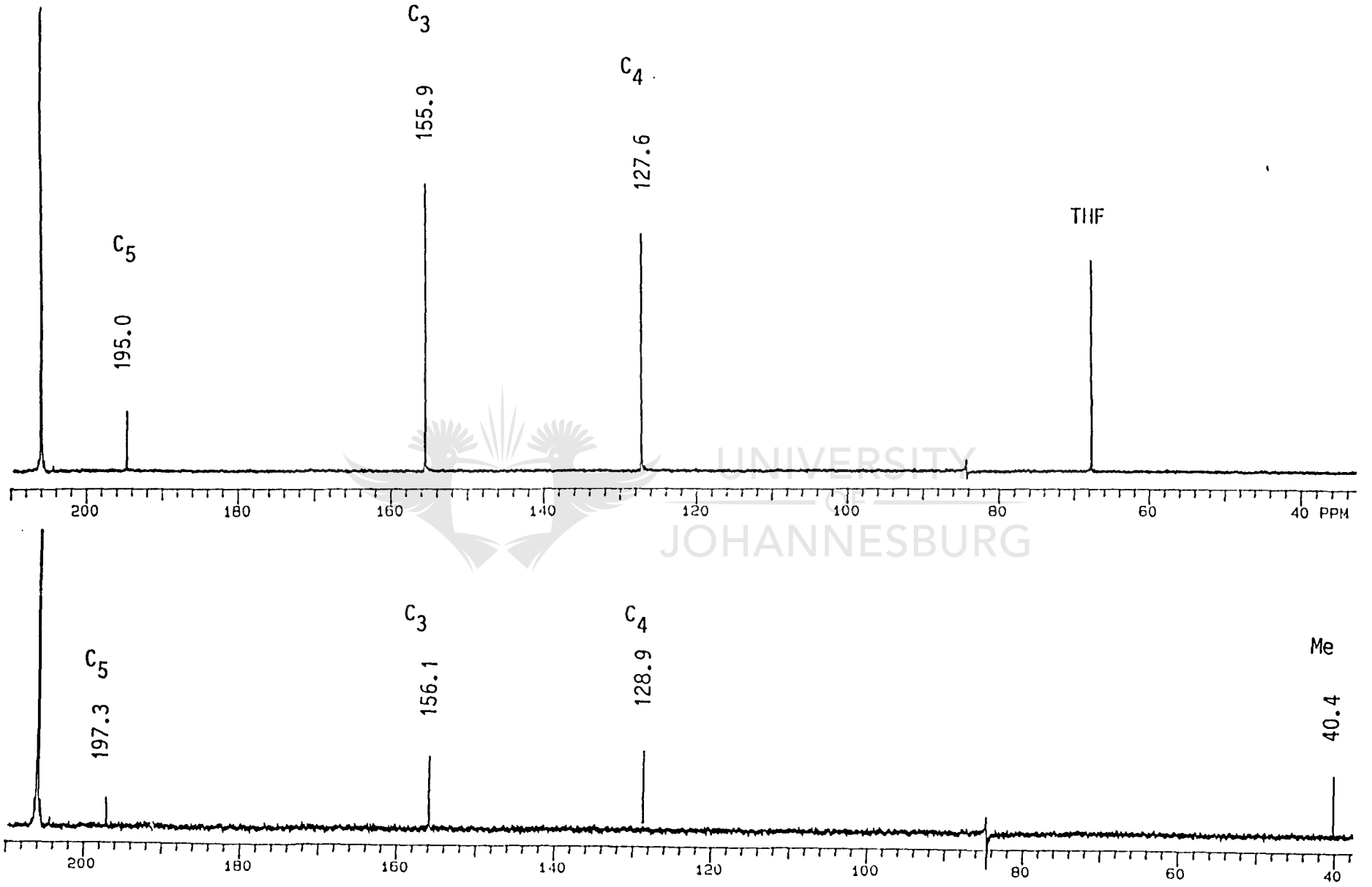
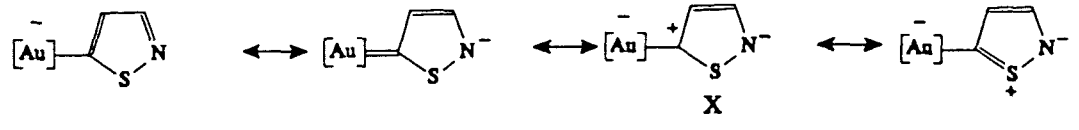


Figure 3.3 The ^{13}C-{^{1}H} NMR spectra of A) Li[Au{$\overline{C{=}CHCH{=}NS}$}$_2$] (7) and B) [Au{$\overline{CCH{=}CHN(Me)S}$}$_2$][$CF_3SO_3$] (**8**)

Another interesting feature in these spectra is the small change in the chemical shifts of the coordinated carbons in the precursor aurate and the corresponding carbene complex. The coordinated carbon in the aurate resonates at δ 195.0 while in the carbene complex it resonates at δ 197.3. This is surprising as a large chemical shift to lowerfield is usually indicative of carbene formation. This was, for example, observed for the isothiazolyl iron precursor and carbene complexes discussed in Chapter 2. Furthermore, the resonances of carbon 3 and carbon 4 also exhibit little change upon formation of the carbene complex. The aurate and carbene complexes are surprisingly similar in nature with respect to their carbon-13 chemical shifts.

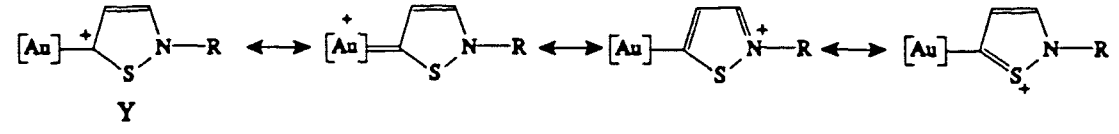
The coordinated carbon atom in the aurate precursor complex resonates at a much lower field (δ 195.0) than expected. This suggests that the observed chemical shift of the coordinated carbon atom in both the precursor aurate complex and the carbene complex is probably due to the contribution of resonance structures x and y in Scheme 3.3, according to which the gold-carbon bond shows dipole character. As mentioned in Chapter 1, however, caution should be used in the interpretation of the carbon-13 chemical shifts since only the diamagnetic contribution to the shift can be correlated to the phenomenon of deshielding.

Isothiazolyl aurate complex



X

Isothiazolinylidene complex



Y

Scheme 3.3

These complexes are delocalized to a large extent and may be represented by many resonance forms. This is not surprising since the ligand is aromatic in nature and the coordinated carbon atom in both complexes is sp^2-hybridized. Evidence for extensive delocalization in these complexes may be found in the analogous thiazolyl mono(carbene) complex [Au{C=NCMe=CHS}{CNHCMe=CHS}]. Although this complex formally consists of one 4-methylthiazole and one 4-methylthiazolinylidene ligand, only one averaged signal for the Au=C and Au-C carbons could be detected.[79]

One could conclude that the manner in which these compounds are generally represented (with a metal-carbon double bond), is not representative of the true nature of these compounds. This is supported by NMR data since the chemical shifts of the carbon atoms (with exception of the coordinated carbon atoms) in both the aurate and the carbene ligands still lie in the aromatic region (δ 155.9 - 128.8). The aromatic character of the ligand is not lost upon formation of the carbene complex.

3. Mass spectrometry

The mass-spectra for complexes **7**, **8** and **9** (Scheme 3.2) are summarized in Table 3.3. The anion was observed in the mass spectra of the aurate complex **7** at m/z 365. Similarly the cation in the di-protonated bis(carbene) complex **9** was observed at m/z 367. The cation of the di-alkylated bis(carbene) complex **8** was, however, not observed. The following three fragments were present in the mass spectra of all three complexes: the dimeric isothiazolyl ion at m/z 168, the isothiazole ligand at m/z 85 and the C_2SH fragment at m/z 57.

Table 3.3

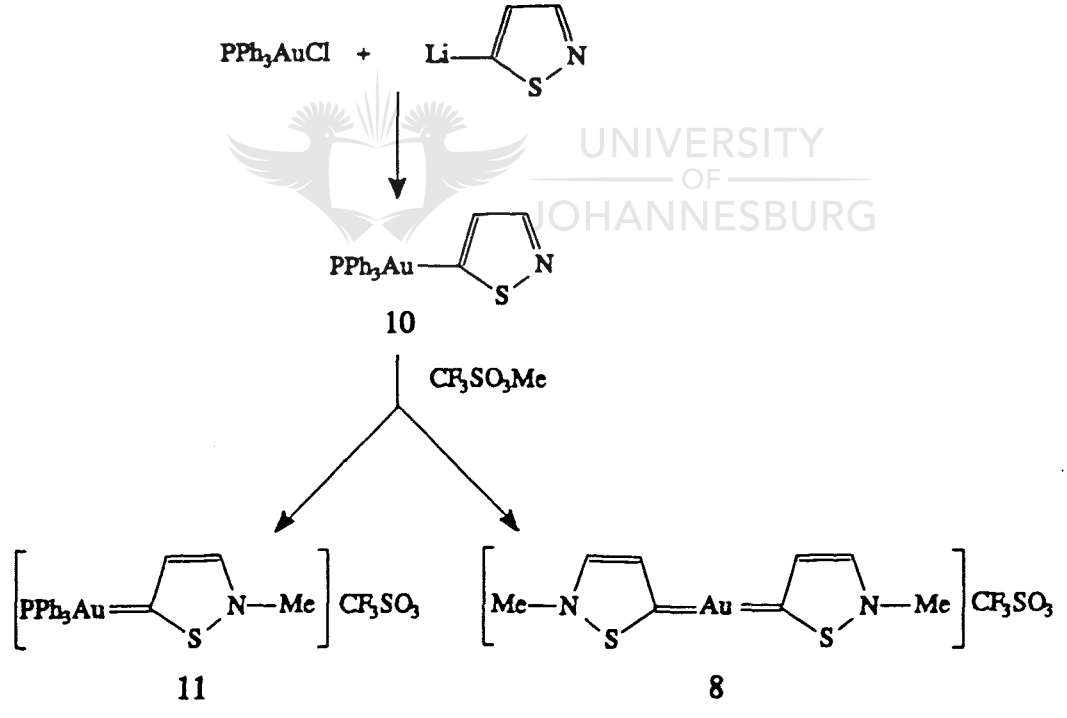
Mass-spectra of complexes (7) - (9)

Complex	m/z	I_a	Fragment ions
7	365	16	$[Au\{\overline{C{=}CHCH{=}NS}\}_2]^+$
	281	3	$[Au\{\overline{C{=}CHCH{=}NS}\}]^+$
	168	4	$[(\overline{C{=}CHCH{=}NS})_2]^+$
	85	100	$[\overline{C{=}CHCH{=}NS}]^+$
	57	91	$[C_2SH]^+$
8	168	50	$[(\overline{C{=}CHCH{=}NS})_2]^+$
	85	100	$[\overline{C{=}CHCH{=}NS}]^+$
	57	83	$[C_2SH]^+$
	45	23	$[CSH]^+$
9	364	2	$[Au\{\overline{CCH{=}CHN(H)S}\}_2]^+$
	282	7	$[Au\{\overline{CCH{=}CHN(H)S}\}]^+$
	251	5	$[Au\{CHCH{=}CHN(H)\}]^+$
	168	100	$[(\overline{C{=}CHCH{=}NS})_2]^+$
	141	20	$[(CCH{=}CHNS)(C{=}CHS)]^+$
	85	50	$[(\overline{C{=}CHCH{=}NS})]^+$
	57	15	$[C_2SH]^+$
	44	10	$[CS]^+$

3.2.2 Neutral Isothiazolyl and Cationic Mono(isothiazolinylidene) Complexes of Triphenylphosphinegold

A. Preparation of [Au{$\overline{C=CHCH=NS}$}PPh_3] **10** *and* [Au{$\overline{CCH=CHN(Me)S}$}PPh_3] [CF_3SO_3] **11**

The neutral isothiazolyl complex **10**, was prepared by reacting [Au(Cl)PPh_3] with lithiated isothiazole in THF at -78°C. The solvent was removed and complex **10** was extracted with methylene chloride, filtered through silica and crystallized at room temperature from benzene using vapour diffusion methods. Off-white prisms of complex **10** were obtained (Scheme 3.4).



Scheme 3.4

Complex **10** is thermally stable in air at room temperature and is soluble in methylene chloride, benzene and most polar organic solvents. The greater solubility of this complex compared to

the isothiazolyl aurate complex **7** and the bis(carbene) complexes **8** and **9**, is probably due to the presence of the neutral PPh_3 group. An X-ray crystal study of complex **10** was undertaken and will be discussed in Chapter 4.

A ^1H NMR study of the reaction mixture before filtration through silica, showed the presence of the bis(isothiazolyl) aurate compound **7** in low concentration. The neutral PPh_3 ligand was displaced by an isothiazolyl ligand. Substitution of the phosphine also occurs in the analogous thiazolyl complexes, which undergo dissociative polymerization. It has been suggested that these polymeric compounds exist as cyclic trimers with n=3 (Scheme 3.1). The neutral isothiazolyl complex, however, does not polymerize as the positions of the nitrogen atoms do not allow for the formation of cyclic trimers and it seems that the potential stability of chains is not sufficient to allow for Au-P bond cleavage.

Depending on the work up conditions, alkylation of the neutral complex **10** with CF_3SO_3Me in THF at -78°C yielded either the cationic mono(carbene) complex **11** or the cationic bis(carbene) complex **8** (Scheme 3.4). Complex **11** was obtained by methylene chloride extraction followed by immediate precipitation by the addition of diethylether, whereas crystals of complex **8** were obtained by allowing the solvent to slowly evaporate. The precursor complex **10** was either prepared *in situ* and directly alkylated, or first isolated and then alkylated. It was only possible to isolate complex **11** once. The preparation could not be repeated since thereafter only crystals of complex **8** were obtained. Furthermore, complex **11** could not be isolated in a pure form or characterized satisfactorily.

There are two possible pathways that could account for the formation of the bis(carbene) complex **8**. During the preparation of the precursor isothiazolyl complex the PPh_3 group could be displaced by the isothiazolyl group to form the bis(isothiazolyl) aurate complex **7**. This complex could then be subsequently alkylated to form complex **8**. In line with this pathway is the presence of complex **7** (detected by ^1H NMR) at this stage. Alternatively, it is possible that the mono(carbene) complex **11** undergoes homoleptic rearrangement during crystallization according to Equation 3.5 (in which the charges have been omitted) to form the bis(carbene) complex **8**.

$$2\,L^{1}AuL^{2} \longrightarrow L^{1}{}_{2}Au + L^{2}{}_{2}Au$$

Equation 3.5

In the first pathway it is very likely that the bis(carbene) complex **8** forms as a result of a slight local excess of lithiated isothiazole as the precursor complex **10** is stable in solution at room temperature and does not decompose into complex **8**. It is therefore highly probable that the second pathway, that is homoleptic rearrangement, is the major cause for the formation of complex **8**. Evidence for this is found in the fact that the reaction mixture slowly turns red in colour as the crystals form.

B. *Spectroscopic characterization of* [Au{$\overline{C=CHCH=NS}$}PPh_3] **10** and [Au{$\overline{CCH=CHN(Me)S}$}PPh_3][CF_3SO_3] **11**

1. NMR spectroscopy

The ^{1}H NMR data for complexes **10** and **11** (Scheme 3.4) are summarized in Table 3.4. The ^{1}H NMR data of complex **11** shows that the H_3 and H_4 protons are shifted downfield with respect to the corresponding resonances of compound **10**, this was similarly the case with the bis(isothiazolyl) aurate complex **7** and the bis(carbene) complexes **8** and **9**. The signal for the phenyl rings appears as a broad multiplet due to J(PH) coupling.

Table 3.4.

^{1}H NMR data of compounds **10** and **11**

Complex	δ (Assignment)
10[a]	8.77 (1H, d, J(H_3-H_4) 1.52 Hz, H_3); 7.54 (15H, m, Ph); 7.29 (1H, d, J(H_4-H_3) 1.46 Hz, H_4).
11[b]	9.27 (1H, d, J(H_3-H_4) 3.19 Hz, H_3); 7.53 (15H, m, Ph); 7.36 (1H, d, J(H_4-H_3) 2.55 Hz, H_4); 4.33 (3H, s, NMe).

[a]Measured in CD_2Cl_2. [b]Measured in $CDCl_3$.

The ^{13}C-{^{1}H} NMR data for complexes **10** and **11** are summarized in Table 3.5. The ^{13}C-{^{1}H} NMR spectrum of complex **10** was repeatedly measured in both $(CD_3)_2CO$ and in CD_2Cl_2. In $(CD_3)_2CO$ all the signals, with exception of the coordinated carbon atom, were present. The signal for the coordinated carbon atom could only be detected using CD_2Cl_2 as the solvent. Furthermore, CD_2Cl_2 was proven to be the 'superior solvent' as it vastly improved the resolution of the peaks.

The ^{13}C-{^{1}H} NMR-spectrum of complex **10** is shown in Figure 3.4. All the signals are split into doublets as a result of coupling with the phosphorus nucleus. The resonances in Table 3.5 assigned to C1, C2,6; C3,5; and C4 refer to the carbon atoms of the phenyl rings. The signal for the C1 carbon of the phenyl ring is observed as a singlet. It is possible, however, that the second peak of the doublet, lies under the δ 129.6 signal, which is assigned to the C3,5 carbons of the phenyl rings. One peak of the doublet of the C_4 carbon atom of the isothiazolyl ligand appears as a shoulder to the δ 129.7 signal, which is also assigned to the C3,5 carbons of the phenyl ring. A similar coupling was also detected in the spectrum run in $(CD_3)_2CO$.

Table 3.5

^{13}C-{^{1}H} NMR data for complexes **10** and **11**

Complex	δ (Assignment)
10[a]	190.6 (^{2}J(PC) 118.4 Hz, C_5);
	155.9 (J(PC) 6.9 Hz, C_3);
	134.6 (J(PC) 13.7 Hz, C2,6);
	131.9 (J(PC) 2.3 Hz, C4);
	129.6 (J(PC) 11.1 Hz, C3,5);
	127.9 (C1);
	130.3 (J(PC) 53.8 Hz, C_4).
11[b]	195.9 (C_5, carbene);
	155.4 (C_3);
	134.1 (C2,6);
	132,2 (C4);
	129.6 (C3,5);
	127.6 (C1);
	128.5 (C_4);
	40.2 (NMe).

[a]Measured in CD_2Cl_2. [b]Mesured in $CDCl_3$.

The value of the coupling constant ^{2}J(P-Au-C) 118.4 Hz of the coordinated carbon atom is not surprising since values between 122.6 and 51.5 have been found for organogold compounds of the type [(R_3P)AuCN], [(R_3P)AuR], [(R_3P)Au{$CH(SiR_3)_2$}] and [(R_3P)Au{$C(SiR_3)_3$}].[163-165]

The ^{13}C-resonance of the coordinated carbon appears in a completely unexpected region since one would have expected this carbon to resonate around δ 165. This agrees with the results obtained for the bis(isothiazolyl) aurate complex **7**, in which the coordinated carbon also resonates at a much lower field than expected.

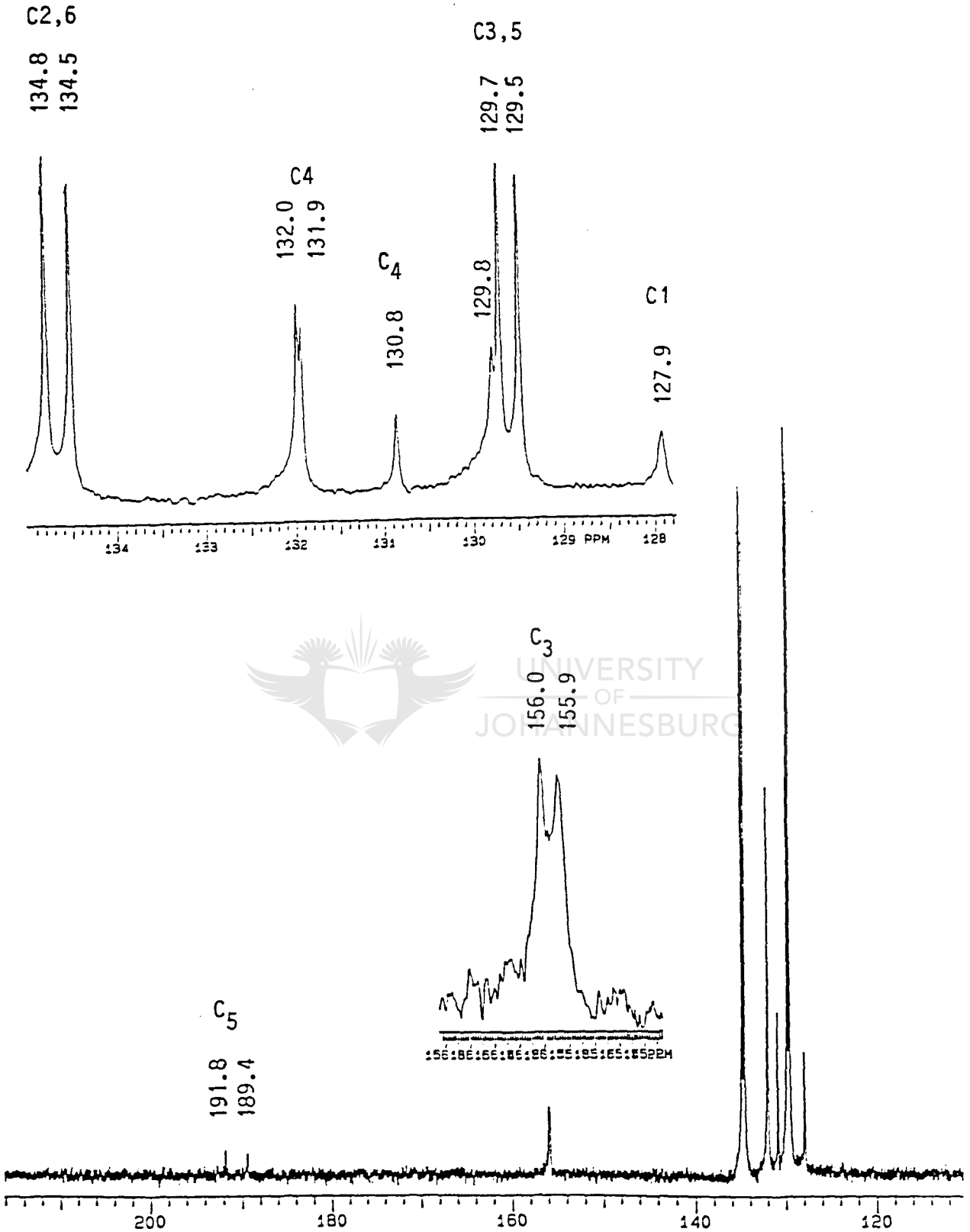


Figure 3.4 ^{13}C-{^{1}H} NMR spectrum of complex [Au{C=CHCH=NS}PPh_3] **10**

The ^{13}C-{^{1}H} NMR spectrum of complex **11** showed poor resolution and as a result the signals are broad and are not split into doublets. The assignment of the carbene carbon at δ 195.9 is uncertain since it was only observed in one spectrum and could not be repeated.

The ^{31}P-{^{1}H} NMR spectra of complexes **10** and **11** are summarized in Table 3.6. Both of the complexes show typical resonances expected for phosphorus atoms coordinated to gold. The resonances of the phosphorus atoms have both shifted downfield with respect to that of [Au(Cl)PPh_3] (δ 33.83; in $CDCl_3$). Since only a single resonance was observed in each case, it is clear that only one type of phosphorus atom is present in solution.

Table 3.6

^{31}P-{^{1}H} NMR data for complexes **10** and **11**

Complex	δ (Assignment)
10[a]	45.59 (s).
11[b]	41.50 (s).

[a]Measured in CD_2Cl_2. [b]Measured in $CDCl_3$.

3. Mass spectrometry

The mass-spectra for complexes **10** and **11** are summarized in Table 3.7. The molecular ion was observed in the mass spectrum of the neutral complex **10**, but the cationic complex **11** showed only peaks corresponding to fragment ions. The fragmentation of both complexes occurs via the initial loss of atoms from the isothiazolyl ligand followed by the systematic loss of phenyl groups.

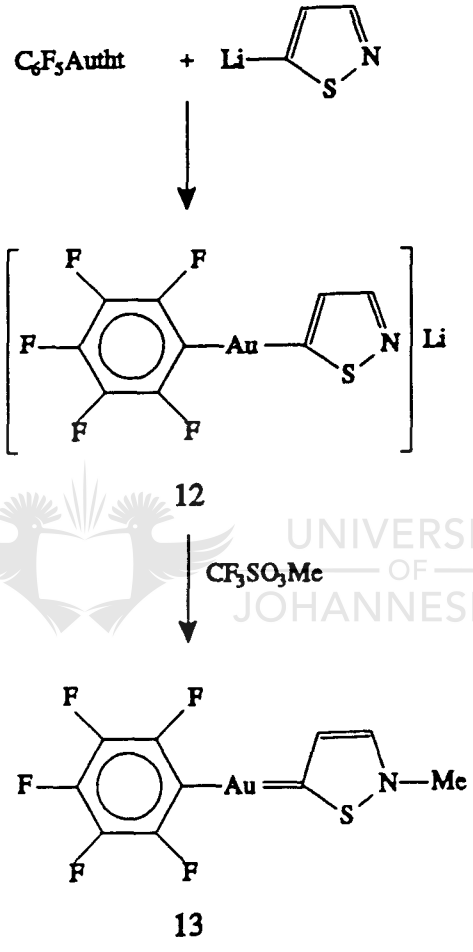
Table 3.7

Mass-spectra of complexes **10** and **11**

Complex	m/z	I[a]	Fragment ions
10	543	2	$[PPh_3Au\{\overline{C=CHCH=NS}\}]^+$
	516	1	$[PPh_3Au\{C=CHS\}]^+$
	459	4	$[PPh_3Au]^+$
	262	100	$[PPh_3]^+$
	185	81	$[PPh_2]^+$
	168	4	$[(\overline{SC=CHCH=N})_2]^+$
	108	45	$[PPh]^+$
	77	14	$[Ph]^+$
11	503	2	$[PPh_3Au\{C=S\}]^+$
	459	4	$[PPh_3Au]^+$
	296	27	$[Au\{\overline{CCH=CHN(Me)S}\}]^+$
	262	90	$[PPh_3]^+$
	198	15	$[(\overline{CCH=CHN(Me)S})_2]^+$
	183	100	$[Ph_3]^+$
	108	45	$[PPh]^+$
	77	32	$[Ph]^+$

3.2.3. A Neutral Isothiazolinylidene Complex of Pentafluorophenylgold

A. Preparation of $[Au(C_6F_5)\{\overline{CCH=CHN(Me)S}\}]$ **13.**



Scheme 3.5

The neutral isothiazolyl mono(carbene) complex **13** (Scheme 3.5) was prepared by treating $[Au(C_6F_5)tht]$ with isothiazolyllithium in THF at -78°C followed by direct alkylation of the aurate complex **12** with CF_3SO_3Me at -65°C. The solvent was removed under vacuum and complex **13** extracted with methylene chloride before filtration through silica gel. Crystallization from methylene chloride/diethylether, however, afforded a mixture of the bis(carbene) complex

8 (p 52) and the neutral carbene complex **13**. After repeated recrystallizations colourless prisms of complex **13** were obtained. The crystals are thermally stable in air, but the complex slowly undergoes homoleptic rearrangement in solution. Complex **13** is soluble in most polar organic solvents.

Attempts to isolate the precursor mono(isothiazolyl) aurate complex **12** yielded the bis(isothiazolyl) aurate complex **7**. Complex **12** is unstable at room temperature since the anionic C_6F_5 ligand is displaced by the isothiazolyl ligand. It is for this reason that the precursor complex **12** was prepared *in situ* at low temperature and directly alkylated to form the carbene complex **13**.

Once again there are two possible pathways that could account for the formation of the bis(carbene) complex **8**. These are:

1) The bis(isothiazolyl) aurate complex **7** forms during the formation of the precursor complex **12** which is subsequently alkylated with CF_3SO_3Me to form the bis(carbene) complex **8**.

2) The mono(carbene) complex **13** undergoes homoleptic rearrangement to form complex **8** and $[Au(C_6F_5)_2]^-$.

The homoleptic rearrangement was followed by a ^1H NMR study. Crystals of complex **13** were dissolved in acetone-d_6 in an NMR-tube and a ^1H NMR spectrum was measured, four days later the same sample was measured and subsequent spectra were collected every 7 days for 4 weeks. Figure 3.5 shows the first three ^1H NMR spectra obtained. After four days 8.3% of complex **13** had rearranged to complex **8**, a week later 16.1% had rearranged to complex **8**, and yet a week later 16.3% had rearranged (in each case an equal amount also rearranges to $[Au(C_6F_5)_2]^-$). Thereafter an equilibrium was established and no further conversion from complex **13** to complex **8** and $[Au(C_6F_5)_2]^-$ occurred. An equilibrium is reached after a ratio of 4.1 : 1 : 1 (complex **13** : complex **8** : $[Au(C_6F_5)_2]^-$) is obtained.

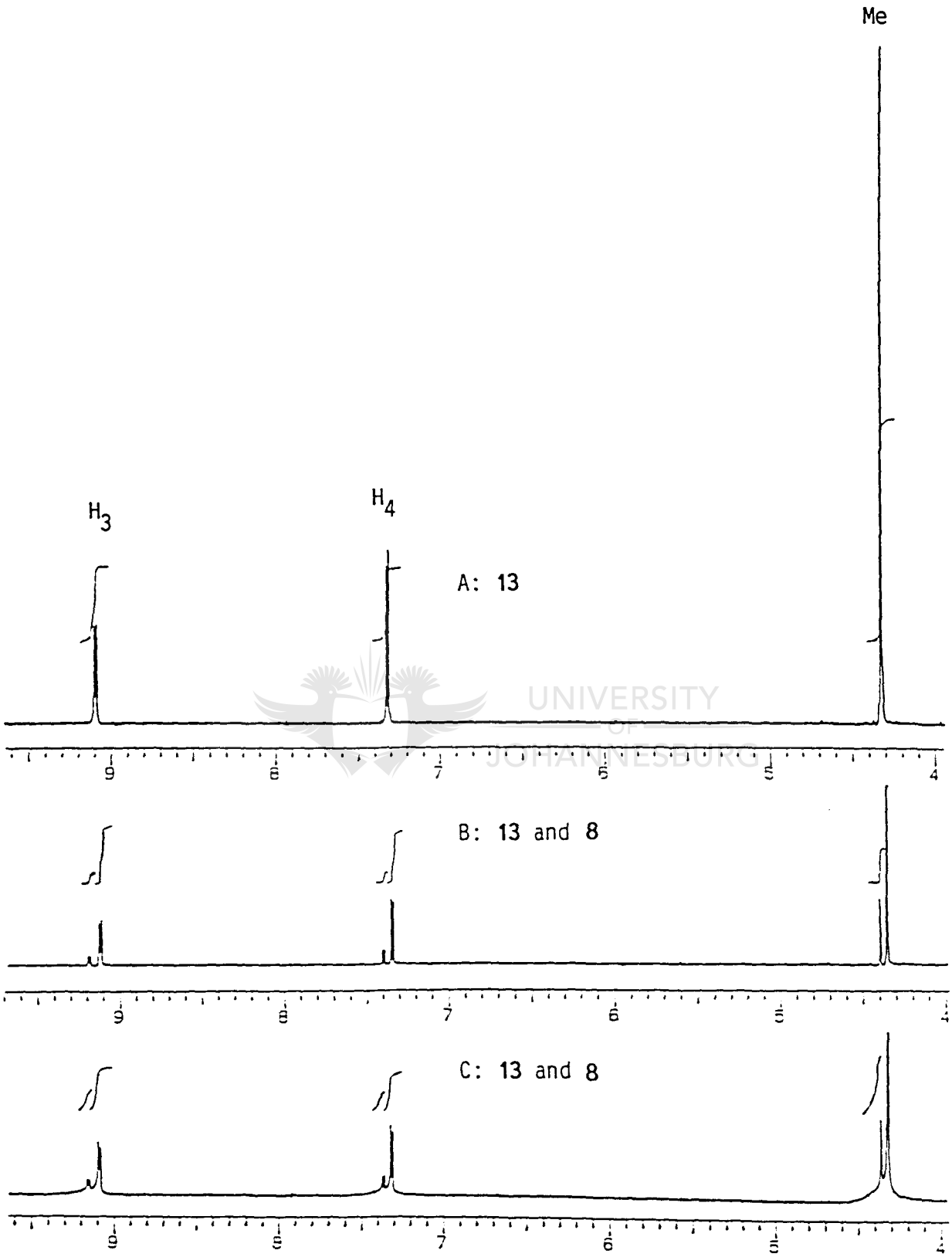


Figure 3.5 The ^{1}H NMR spectra of complex **13** A: day 1 B: day 4 C: day 11

An estimate of the value of the equilibrium constant can be calculated as follows:

$$2[Au(C_6F_5)\{\overbrace{CCH=CHN(Me)S}\}_2] \rightleftharpoons [Au\{\overbrace{CCH=CHN(Me)S}\}_2]^+ + [Au(C_6F_5)_2]^-$$

$$K = \frac{[Au\{\overbrace{CCH=CHN(Me)S}\}_2]^+[Au(C_6F_5)_2]^-}{[Au(C_6F_5)\{\overbrace{CCH=CHN(Me)S}\}_2]^2}$$

$$= \frac{(1)(1)}{(4.1)^2}$$

$$= 5.9 \times 10^{-2} \qquad \text{(in acetone-}d_6\text{ at 23°C)}$$

It should be noted that the value of the equilibrium constant is only an estimate as it is based on the integrals obtained from ^{1}H NMR spectra.

B. Spectroscopic characterization of $[Au(C_6F_5)\{\overbrace{CCH=CHN(Me)S}\}]$ **13**

1. NMR spectroscopy

The ^{1}H NMR- and ^{13}C-{^{1}H} NMR data for complex **13** (Scheme 3.5) are summarized in Table 3.8. In the ^{1}H NMR spectrum allylic coupling between the NMe and H_3 protons of the isothiazolinylidene ligand was detected.

In the ^{13}C-{^{1}H} NMR spectrum of complex **13** the signals of the C_6F_5 ligand are detected as a series of multiplets due to coupling of the ^{19}F nuclei with the carbon nuclei. The carbene carbon resonates at lowfield relative to the other carbene complexes **8, 9** and **11**. Unfortunately it was not possible to compare the chemical shift of the precursor complex **12** and the carbene complex **13**.

Table 3.8

^{1}H and ^{13}C-{^{1}H} NMR data of compound **13**[a]

Spectrum	δ (Assignment)
^{1}H NMR	9.12 (1H, dd, $J(H_3\text{-}H_4)$ 2.47 Hz, $J(H_3\text{-}NCH_3)$ <1 Hz, H_3);
	7.34 (1H, d, $J(H_4\text{-}H_3)$ 2.57 Hz, H_4);
	4.35 (3H, $J(NMe\text{-}H_3)$ <1 Hz, NCH_3).
^{13}C-{^{1}H} NMR	200.8 (C_5, carbene);
	155.5 (C_3);
	127.4 (C_4);
	152.4-151.7 (C_6F_5);
	147.8-147.3 (C_6F_5);
	140.2-139.6 (C_6F_5);
	136.3-134.6 (C_6F_5);
	40.1 (NMe).

[a]Measured in $(CD_3)_2CO$.

3. Mass spectrometry

The mass-spectral data of complex **13** are summarized in Table 3.9. The molecular ion peak at m/z 463 also forms the base peak of the spectrum. The fragmentation pattern consists of the loss of either the isothiazolinylidene ligand or the C_6F_5 ligand. The dimeric isothiazolyl ion is once again present at m/z 168 as well as its di-alkylated counterpart at m/z 198. The N-alkylated isothiazole fragment is also present at m/z 99.

Table 3.9

Mass-spectrum of complex **13**

Complex	m/z	I[a]	Fragment ions
13	463	100	$[Au\{\overline{CCH=CHN(Me)S}\}(C_6F_5)]^+$
	364	18	$[Au(C_6F_5)]^+$
	296	90	$[Au\{\overline{CCH=CHN(Me)S}\}]^+$
	198	13	$[(\overline{CCH=CHN(Me)S}\}_2]^+$
	168	38	$[(\overline{CCH=CHNS})_2]^+$
	99	32	$[\overline{CCH=CHN(Me)S}]^+$

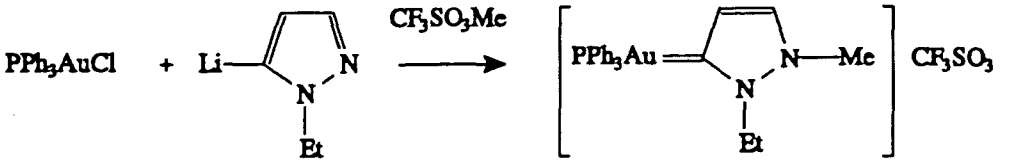
3.2.4. A Cationic Mono(1-ethylpyrazolinylidene) Complex of Triphenylphosphinegold

A. Preparation of $[Au\{\overline{CCH=CHN(Me)N(Et)}\}PPh_3][CF_3SO_3]$ **14**

The preparation of 1-ethylpyrazole from pyrazole is very simple and involves the alkylation of pyrazole with ethylbromide by phase transfer catalysis. A very recent literature method was slightly modified for the preparation.[166] 1-Ethylpyrazole, unsubstituted in the 5 position, is readily lithiated in this position in diethylether at room temperature.[167,168]

The mono(carbene) complex **14** was prepared by treating one equivalent of 1-ethylpyrazolyl-lithium with one equivalent $[Au(Cl)PPh_3]$ in THF at -78°C followed by direct alkylation with CF_3SO_3Me (Scheme 3.6). The solvent was removed under vacuum, and complex **14** extracted with methylene chloride before filtration through Celite. Cooling to -20°C afforded a precipitate, which according to its $^{31}P-\{^1H\}$ NMR spectrum, contained four different phosphorus coordinated gold compounds. After repeated precipitations and recrystallizations, off-white crystals of

complex **14** were isolated. As a result a poor yield of complex **14** was obtained. Attempts to increase the yield of complex **14** by adding 2 equivalents instead of one equivalent 1-ethylpyrazolyllithium were unsuccessful. Complex **14** decomposes slowly in solution, but the crystals are thermally stable at room temperature.



14

Scheme 3.6

Further reactions with 1-ethylpyrazolyllithium as ligand were unsuccessful. With the intention of synthesizing the bis(carbene) complex, two equivalents of 1-ethylpyrazolyllithium was treated with one equivalent [Au(Cl)tht]. This, however, led to the immediate reduction of the gold, even at -78°C. Similarly, when one equivalent [Au(C_6F_5)tht] was reacted with one equivalent of 1-ethylpyrazolyllithium the gold complex was reduced upon alkylation with CF_3SO_3Me.

A possible explanation for the reduction of the gold complexes during these reactions is that upon formation of the precursor complex, the ethyl group of the pyrazole ligand donates electronic charge to the coordinated carbon atom thereby increasing the electron density on the gold. Complete electron transfer would, naturally, lead to the reduction of the gold. The PPh_3 group in [Au(Cl)PPh_3] however compensates for this by removing the electronic charge and thus, in this case, a stable precursor is formed. A phenyl group, which has electron withdrawing properties might be a more appropriate substituent for the N-1 position of the pyrazole ring.

B. Spectroscopic characterization of [Au{CCH=CHN(Me)N(Et)}PPh_3][CF_3SO_3] **14**

1. NMR spectroscopy

The ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR data for complex **14** (Scheme 3.6) are summarized in Table 3.10. The ^1H NMR data of complex **14** show that all the resonances of the protons are shifted downfield with respect to those of free 1- ethylpyrazole (δ 7.56, H_3; 6.16, H_4; 4.16, CH_2; 1.40 Me).

The signal for the coordinated carbon atom in the ^{13}C-{^1H} NMR spectrum of complex **14** could only be detected using CD_2Cl_2 as the solvent. All the signals, with the exception of the ethyl and methyl signals, are split into doublets as a result of coupling with the phosphorus nucleus. The value of the coupling constant, ^2J(P-Au-C) 122.7 Hz, of the carbene atom is once again large as it is in the neutral complex **10**.

The ^{13}C-resonance of the carbene carbon lies at δ 184.3, this however is not surprising since there is a shift of δ 55.6 from the C_5 carbon atom in free 1-ethylpyrazole to the carbene carbon atom in complex **14**. In the case of the isothiazole ligand the corresponding difference is δ 48.2.

The ^{31}P-{^1H} NMR spectrum of complex **14** clearly shows that only one type of phosphorus atom is present, and its value lies in the region expected for phosphorus coordinated to gold.

Table 3.11

^{1}H NMR-data of compound **14**[a]

Spectra	δ(Assignment)
^{1}H NMR	7.89 (1H, d, $J(H_3-H_4)$ 2.73 Hz, H_3);
	7.56 (15H, m, Ph);
	6.50 (1H, d, $J(H_3-H_4)$ 2.69 Hz, H_4);
	4.58 (2H, q, J 7.34 Hz, CH_2);
	4.11 (2H, s, NMe);
	1.57 (3H, t, J 7.28 Hz, Me).
$^{13}C-\{^{1}H\}$ NMR	184.3 (d, J(PC) 122.7 Hz, C_5, carbene);
	136.6 (d, J(PC) 3.7 Hz, C_3);
	135.5 (d, J(PC) 13.7 Hz, C2,6);
	132.4 (d, J(PC) 2.5 Hz, C4);
	129.8 (d, J(PC) 11.4 Hz, C3,5);
	128.6 (C1);
	116.2 (d, J(PC) 3.2 Hz, C_4);
	47.8 (NMe);
	37.5 (CH_2);
	16.4 (Me).
$^{31}P-\{^{1}H\}$ NMR	47.70 (s).

[a]Measured in CD_2Cl_2.

3. Mass spectroscopy

The mass-spectra of complex **14** are summarized in Table 3.14. No molecular ion peak was observed for the complex, and interestingly most of the peaks consisted of the fragmentation of the pyrazole ligand.

Table 3.14

Mass-spectra of complex **14**

Complex	m/z	I[a]	Fragment ions
14	293	5	$[Au\{\overline{C=CHCH=NN}(Et)]^+$
	262	24	$[PPh_3]^+$
	111	100	$[\overline{CH=CHCH=N(Me)N}(Et)]^+$
	96	4	$[\overline{CH=CHCH=NN}(Et)]^+$
	81	27	$[\overline{CH=CHCH=N(Et)N}]^+$
	68	20	$[\overline{CH=CHCH=NN}]^+$
	42	20	$[\overline{CH=CHCHNH}]^+$

3.3 CONCLUSIONS AND FURTHER WORK

In addition to iron and tungsten, gold may also be used to prepare carbene complexes from precursors in which the nucleophilic nitrogen atom is not directly bonded to the coordinated carbon atom.

The present study has shown that isothiazolyllithium reacts with [Au(Cl)tht] to form a bis(isothiazolyl) aurate complex which can be protonated or alkylated to give cationic bis(isothiazolinylidene) complexes. The question here remains whether other electrophiles may be used to generate new carbene complexes and also whether these complexes possess any reactivity. An X-ray crystal structure determination of a bis(aurate) complex and a bis(carbene) compound of this type remains to be determined as it will shed light on the nature of the bonding occurring in these complexes.

Strongly ligated gold chloride complexes such as [Au(Cl)PPh_3] as well as neutral tetrahydrothiophene complexes such as [Au(C_6F_5)tht] also react with isothiazolyllithium to afford, upon protonation or alkylation, cationic or neutral carbene compounds. Homoleptic rearrangement was observed in these syntheses. The exact nature and driving force for this rearrangement remains to be determined.

In addition to isothiazolyl, 1-ethylpyrazolyl has also been used to generate a carbene complex. Only one reaction utilizing this ligand was successful. Reactions with 1-phenylpyrazolyl as well as with other cyclic ligands remain to be carried out.

Further studies to be undertaken which expand upon the idea of remote nucleophilic attack have been discussed in the conclusion to Chapter 2.

3.4 EXPERIMENTAL

6.4.1 General

The same experimental techniques apply as in section 2.4.1.

The following starting materials were prepared according to published procedures: isothiazole,[124] [AuCl(tht)] and [$AuCl(PPh_3)$].[169]

1-Ethylpyrazole[168] and [$Au(C_6F_5)$tht][169] were prepared by slight modification of the published procedures and are described below.

3.4.1.1. Preparation of 1-ethylpyrazole.

In a closed vessel, pyrazole (1.36 g, 20 mmol), TBAB (0.32 g, 5%, 1 mmol) and finely ground potassium hydroxide (2.24 g, 40 mmol) were stirred for 2 hours. The reaction mixture was cooled to -5°C and ethylbromide (1,12 cm^3, 1.46 $g.cm^{-3}$, 15 mmol) was added. The reaction mixture was allowed to stir at this temperature for 6 hours and then allowed to stir at room temperature for a further 20 hours. The product was isolated from the crude mixture by direct sublimation.

Yield : 1,8 cm^3 (92 %)

3.4.1.2 Preparation of [$Au(C_6F_5)$tht].

A solution of bromopentafluorobenzene (0.78 cm^3, 1.97 $g.cm^{-3}$, 6.23 mmol) in diethylether (45 cm^3) was cooled to -78°C and treated with standardized n-butyllithium in hexane (3.9 cm^3, 1.6M, 6.2 mmol). The light pink solution was stirred at -78°C for 1 hour before [AuCl(tht)] (1.92 g, 6.0 mmol) was slowly added. The mixture was stirred for 2 hours before raising the temperature to room temperature over a period of 3 hours. The reaction mixture was filtered through anhydrous magnesium sulphate and silica (1:1) and washed with diethyl ether:methylene chloride (2:1). The solvent was removed and the residue dried under vacuum for one hour.

Yield : 2.12 g (78%)

3.4.1 Preparation of Li[Au{$\overbrace{C=CHCH=NS}$}$_2$] **7.**

A solution of isothiazole (0.29 cm^3, 1.17 g.cm^{-3}, 4.0 mmol) in THF (35 cm^3) was cooled to -78°C and treated with standardized n-butyllithium in hexane (2.5 cm^3, 1.6M, 4.0 mmol). The light pink solution was stirred at -78°C for 45 minutes before [AuCl(tht)] (0.64 g, 2.0 mmol) was added. An immediate colour change to light yellow was observed. The reaction mixture was stirred for 2 hours before raising the temperature to room temperature. The solvent was removed under vacuum and the residue washed with CH_2Cl_2 (3 x 15 cm^3). The powder was dried under vacuum for a 24 hour period.

Yield : 0.605 g (81%)

MP : decomposes slowly between 110-115°C

Note: The yield and melting points are not correct as all the solvent (THF) could not be removed.

3.4.2 Preparation of [Au{$\overbrace{CCH=CHN(Me)S}$}$_2$][CF_3SO_3] **8.**

A solution of isothiazole (0.15 cm^3, 1.17 g.cm^{-3}, 2.1 mmol) in THF (25 cm^3) was cooled to -78°C and treated with standardized n-butyllithium in hexane (1.31 cm^3, 1.6 M, 2.1 mmol). The light pink solution was stirred at -78°C for 45 minutes before [AuCl(tht)] (0.34 g, 1.05 mmol) was added. An immediate colour change to light yellow was observed. The mixture was stirred for 1 hour before raising the temperature to -50°C over a period of 1 hour. The dropwise addition of CF_3SO_3Me (0.24 cm^3, 1.45 g.cm^{-3}, 2.1 mmol) to the reaction mixture at -79°C was accompanied by an immediate colour change from orange to light yellow. The mixture was stirred at -50°C for 1 hour before allowing it to warm up to room temperature. The reaction mixture was filtered through anhydrous magnesium sulphate and Celite (1:1). Cooling to -25°C afforded yellow needle-like crystals of complex **8**.

Yield : 0.37 g (66%)

MP : Decomposition at 159°C

3.4.3 Preparation of $[Au\{\overline{CCH=CHN(H)S}\}_2][CF_3SO_3]$ **9.**

A solution of isothiazole (0.18 cm^3, 1.17 $g.cm^{-3}$, 2.5 mmol) in THF (35 cm^3) was cooled to -78°C and treated with standardized n-butyllithium in hexane (1.56 cm^3, 1.6 M, 2.5 mmol). The light pink solution was stirred at -78°C for 45 minutes before [AuCl(tht)] (0.40 g, 1.25 mmol) was added. An immediate colour change to light yellow was observed. The mixture was stirred for 1 hour before raising the temperature to -50°C over a period of 1 hour. CF_3SO_3H (0.22 cm^3, 1.17 $g.cm^{-3}$, 2.5 mmol) was added dropwise -60°C and the reaction mixture was stirred for 1 hour at -50°C before allowing it to warm up to room temperature. The reaction mixture was filtered through a sinterglass funnel and the precipitate washed with THF (3 x 15 cm^3). The solvent of the filtrate was removed under vacuum and the dry yellow powder washed with diethylether (3 x 115 cm^3) and acetone (1 x 10 cm^3) before being dried under vacuum until the powder had changed completely to a red colour. Redissolving the red powder in THF and cooling to -25°C afforded long yellow needle-like crystals of complex **9**.

Yield : 0.49 g (75%)

MP : A melting point of the crystals was not obtained, as the crystals were extremely hygroscopic.

3.4.4 Preparation of $[Au\{\overline{C=CHCH=NS}\}PPh_3]$ **10.**

A solution of isothiazole (0.15 cm^3, 1.17 $g.cm^{-3}$, 2.0 mmol) in THF (30 cm^3) was cooled to -78°C and treated with standardized n-butyllithium in hexane (1.25 cm^3, 1.6 M, 2.0 mmol). The light pink solution was stirred at -78°C for 45 minutes before [AuCl(PPh_3)] (0.99 g, 2.0 mmol) was added. An immediate colour change to light yellow was observed. The mixture was stirred for 1 hour before raising the temperature to -30°C over a period of 2 hours. The temperature was then allowed to rise to room temperature. The solution was filtered through a short pad of silica gel (prewashed with diethylether) and washed with excess diethylether. The solvent was removed under vacuum, the residue redissolved in a minimum amount of benzene, and crystallized by vapour diffusion technique using pentane at room temperature.

Yield : 0.96 g (83.63%)

MP : 157-158°C

3.4.5 Preparation of [Au{$\overline{CCH=CHN(Me)S}$}PPh_3][CF_3SO_3] **11.**

Complex **10** (0.82 g, 1.5 mmol) was dissolved in THF and cooled to -75°C. The dropwise addition of CF_3SO_3Me (0.17 cm^3, 1.45 $g.cm^{-3}$, 1.5 mmol) to the mixture was accompanied by an immediate colour change from yellow to a brighter yellow. The mixture was stirred for 15 minutes before raising the temperature to -10°C over a period of 1 hour. The mixture was stirred for a further 30 minutes at room temperature and the solvent removed under vacuum. The residue was redissolved in CH_2Cl_2 and filtered through Celite and anhydrous magnesium sulphate (1:1). Concentration of the solution to 10cm^3, addition of 8cm^3 ether and cooling to -20°C afforded a white precipitate. After decanting the solvent, the precipitate was quickly washed with diethylether (2 x 10 cm^3) and dried under vacuum.

Yield : 0.79 g (75%)

MP : A melting point was not obtained as the precipitate would not give a reliable melting point.

3.4.6 Preparation of [Au(C_6F_5){$\overline{CCH=CHN(Me)S}$}] **13.**

A solution of isothiazole (0.15 cm^3, 1.17 $g.cm^{-3}$, 2.0 mmol) in THF (30 cm^3) was cooled to -78°C and treated with standardized n-butyllithium in hexane (1.25 cm^3, 1.6 M, 2.0 mmol). The light pink solution was stirred at -78°C for 45 minutes before [Au(C_6F_5)tht] (0.90 g, 2.0 mmol) was added. An immediate colour change to light yellow was observed. The mixture was stirred for 1 hour before raising the temperature to -50°C over a period of 2 hours. The dropwise addition of CF_3SO_3Me (0.23 cm^3, 1.45 $g.cm^{-3}$, 2.0 mmol) at -65°C to the mixture was accompanied by an immediate colour change from yellow to a brighter yellow. The mixture was stirred for 1 hour before raising the temperature to -30°C over a period of 1 hour. The bright yellow mixture was stirred for a further 30 minutes at room temperature and the solvent removed under vacuum. The residue was redissolved in CH_2Cl_2, filtered through a short pad of silica gel and washed with CH_2Cl_2 (3 x 15 cm^3). Concentration of the solution and crystallization by

vapour diffusion technique using diethylether at 0°C afforded crystals consisting of a mixture of complex **8** and complex **13**. Repeated recrystallizations using the above technique yielded clean crystals of complex **13**.

Yield : 0.30 g (33%)

MP : 178.2°C (with decomposition)

3.4.7 Preparation of $[Au\{\overbrace{CCH=CHN(Me)}\dot{N}(Et)\}PPh_3][CF_3SO_3]$ **14**.

A solution of 1-ethylpyrazole (0.20 cm^3, 0.95 $g.cm^{-3}$, 2.0 mmol) in diethylether (30 cm^3) was cooled to -30°C and treated with standardized n-butyllithium in hexane (1.25 cm^3, 1.6 M, 2.0 mmol). The mixture was stirred for 30 min before raising the temperature to room temperature. The mixture was stirred for a further hour and then added dropwise to a solution of $[AuCl(PPh_3)]$ (0.99 g, 2.0 mmol) in THF at -78°C . An immediate colour change to light yellow was observed. The reaction mixture was stirred for 30 minutes before raising the temperature to -40°C over a period of 2 hours. The mixture was stirred for a further 45 minutes at room temperature. After cooling the solution to -60°C CF_3SO_3Me (0.23 cm^3, 1.45 cm^{-3}, 2.0 mmol) was added, and the solution stirred for a further 1 hour at this temperature before raising the temperature to -40°C over a period of 2 hours. The reaction mixture was allowed to reach room temperature and the solvent was then removed under vacuum. The residue was washed with ether (4 x 15 cm^3), redissolved in CH_2Cl_2 and filtered through silica. Concentration of the solution, addition of diethylether and cooling to -25°C afforded off-white crystals of complex **14**.

Yield : 0.14 g (10%)

MP : 162.3°C (with decomposition)

CHAPTER 4

THE CRYSTALLOGRAPHIC CHARACTERIZATION OF CYCLOPENTADIENYL(ISOTHIAZOLINYLIDENE)IRON AND ISOTHIAZOLYL(TRIPHENYLPHOSPHINE)GOLD

4.1 INTRODUCTION

Single X-ray crystal structure determinations provide valuable information about the structure and, indirectly, the type of bonding occurring in complexes. In this chapter the crystal and molecular structures of complexes $[CpFe(CO)_2\{\overline{CCH=CHN(Me)S}\}][CF_3SO_3]$ (**3**) and $[Au\{\overline{C=CHCH=NS}\}PPh_3]$ (**10**) are discussed. Both X-ray crystal structures unambiguously show the nitrogen atom in the γ-position with respect to the coordinated carbon. The structural characteristics of the isothiazolinylidene complex **3** are compared to those of the analogous thiazolinylidene complex $[CpFe(CO)_2\{\overline{CN(Me)C(Me)=CHS}\}][CF_3SO_3]$ (**15**) (Scheme 2.1) as well as to those of other comparable iron complexes. The Fe-C(carbene) bond length is of special interest as one would like to ascertain whether this bond has any significant double bond character. The structural characteristics of complex **10** are also compared to those of similar compounds.

Only certain aspects of the structures are discussed here. All other crystallographic information is available from Prof G.J. Kruger at the Chemistry Department at RAU, P.O. Box 524, Johannesburg.

4.2 RESULTS AND DISCUSSION

4.2.1 Structure of $[CpFe(CO)_2\{\overline{CCH=CHN(Me)S}\}][CF_3SO_3]$ 3

The molecular structure of compound **3** is shown in Figure 4.1, while selected bond lengths and bond angles are given in Tables 4.1 and 4.2.

The iron atom is pseudo-octahedrally surrounded by a cyclopentadienyl group, two carbonyl ligands and an isothiazolinylidene ligand. The angles between the three monodentate ligands are: C(1)-Fe-C(11) 88.7(2)°, C(1)-Fe-C(10) 96.1(2)° and C(10)-Fe-C(11) 94.0(2)°. This is consistent with distorted octahedral geometry. The analogous thiazolinylidene complex $[CpFe(CO)_2\{\overline{CN(H)C(Me)=CHS}\}][CF_3SO_3]$ (**15**) (Scheme 2.1), which is a structural isomer of complex **3**, shows a similar geometry.[78]

The Fe-C(cyclopentadienyl) distances, which have an average length of 2.089(4) Å, are normal and compare well with similar distances in, for example, $[CpFe(CO)_2\{C(SMe)_2\}]^+$ (average 2.08(3) Å),[170] $[CpFe(CO)_2\{C(=C(CN)_2)CPh=C(CN)_2\}]$ (average 2.086(3) Å),[171] $[CpFe(CO)_2\{\overline{C=C(Me)S(O)OCH_2}\}]$ (average 2.094(11) Å)[172] and complex **15** (average 2.084(4) Å).

The average Fe-CO bond lengths of 1.775(3) Å are consistent with values obtained previously from molecules containing $CpFe(CO)_2$ units.[173] Complex **15** shows a corresponding average bond length of 1.768(3) Å. The Fe-C(carbonyl) bond lengths are significantly shorter (on average 0.18 Å) than the Fe-C(carbene) bond of 1.952(3) Å. A similar effect was found in complex **15**.

The Fe-C(carbene) bond length of 1.952(3) Å is similar to the value of 1.947(3) Å observed in complex **15**. In earlier X-ray data typical Fe-C(sp^3) bond distances fall within the range 2.08 - 2.10 Å,[174] while Fe-C(sp^2) values are most typically in the range 1.97 - 2.00 Å. Examples of Fe-C(sp^2) bond lengths include: 1.972(2) Å in $[CpFe(CO)_2\{C(=C(CN)_2)CPh=C(CN)_2\}]$,[171] 1.981(7) Å in $[CpFe(CO)_2\{C(OMe)=C(Me)PEt_3\}]^+$,[175] 1.971(3) Å in

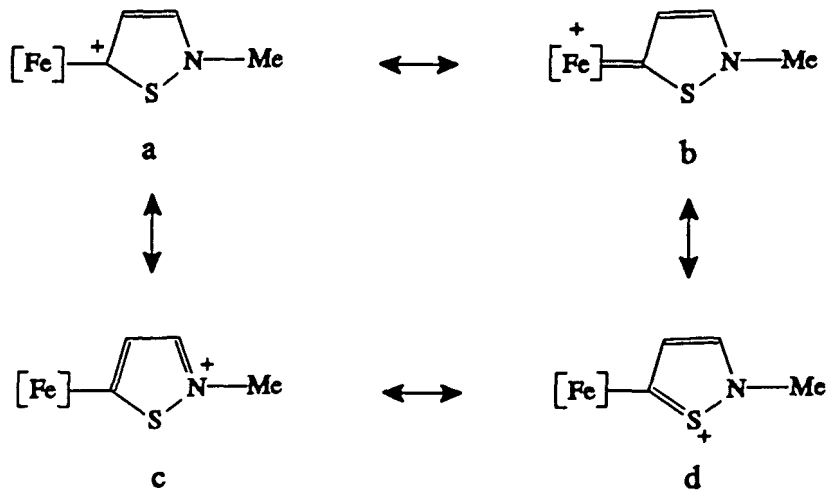
$[CpFe(CO)_2\{C(H)=CHCH=CHBr\}]$[176] and 2.008(7) Å in $[CpFe(CO)_2\{\overline{C=C(Ph)S(O)SCH_2}\}]$.[177] Fe-C(carbene) bond lengths of known carbene complexes occur within the range 1.87 - 2.00 Å and examples here include: 1.88(1) Å in $[CpFe(CO)_2\{C(SPh)H\}]^+$,[178] 2.02(2) Å in $CpFe(CO)_2\{C(SMe_2)\}]^+$ [170] and 197.9(3) Å in $[CpFe(CO)_2\{C_7H_6\}]^+$.[179] All these values suggest that the Fe-C(carbene) bond in complex **3** has double bond character.

The carbon-carbon bond lengths within the isothiazolinylidene ligand are C(1)-C(2) 1.388(4) Å and C(2)-C(3) 1.400(5) Å. The C(1)-C(2) distance is only slightly shorter (0.012 Å) than the C(2)-C(3) distance. In order to ascertain whether the C(1)-C(2) bond has any significant double bond character, the following comparisons were made. Typical carbon-carbon double bond lengths within Fe-C(sp^2)-C(sp^2) fragments occur within the range of 1.30-1.38 Å. Examples of these type of bond lengths include: 1.38(1) Å in $[CpFe(CO)_2\{C(OMe)=C(Me)PEt_3\}]^+$,[175] 1.330 Å in $[CpFe(CO)_2\{\overline{C=C(Ph)S(O)SCH_2}\}]$,[177] 1.312(12) Å in $[CpFe(CO)_2\{\overline{C=C(Me)S(O)OCH_2}\}]$[175] and 1.341(4) Å in $[CpFe(CO)_2\{C(H)=CHCH=CHBr\}]$.[176] The C-C bond length in complex **15**, which does not involve a carbene carbon, is 1.331(4) Å. It may be concluded that the C(1)-C(2) bond length in the isothiazolyl ligand lies within the upper limits of the values listed above and suggests that this bond has only partial double bond character.

The S(1)-C(1) bond length of 1.680(3) Å is 0.03 Å shorter than the corresponding separation in complex **15** [C(carbene)-S 1.708(3) Å, the other C(sp^2)-S bond distance is 1.723(3) Å]. This indicates that some π-bonding does occur between the carbene carbon and the neighbouring sulphur atom in the new compound.

The two carbon-nitrogen bond lengths within the isothiazolinylidene ligand are N(1)-C(3) 1.311(4) Å and N(1)-C(4) 1.463(4) Å. The N(1)-C(3) bond length is significantly shorter (0.152 Å) than the N(1)-C(4) bond length, but this is expected, since the one involves an N-C(sp^2) bond while the other is an N-C(sp^3) bond. In complex **15** the carbon-nitrogen bond lengths are C(carbene)-N 1.328(3) Å and N-C(sp^2) 1.395(3) Å with the carbene carbon-nitrogen bond significantly shorter than the other bond. The N(1)-C(3) bond length in the isothiazolinylidene complex is therefore somewhat shorter than the N-C bonds in the thiazolinylidene complex and indicates that this bond has appreciable double bond character.

Complex **3** may be represented by the various resonance forms shown in Scheme 4.1. All the resonance forms contribute to the structure of complex **3**, but the structure determination indicates that the most important contribution, at least in the solid state, is made by structures a and c.



Scheme 4.1

Table 4.1

Selected bond lengths (Å) for complex **3** with e.s.d.s in parentheses

Fe-C(1)	1.952(3)	C(1)-C(2)	1.388(4)
Fe-C(5)	2.087(4)	C(2)-C(3)	1.400(5)
Fe-C(6)	2.081(4)	N(1)-C(3)	1.311(4)
Fe-C(7)	2.090(3)	N(1)-C(4)	1.463(4)
Fe-C(8)	2.094(4)	S(1)-N(1)	1.674(3)
Fe-C(9)	2.093(4)	S(1)-C(1)	1.680(3)
Fe-C(10)	1.778(3)		
Fe-C(11)	1.773(3)		

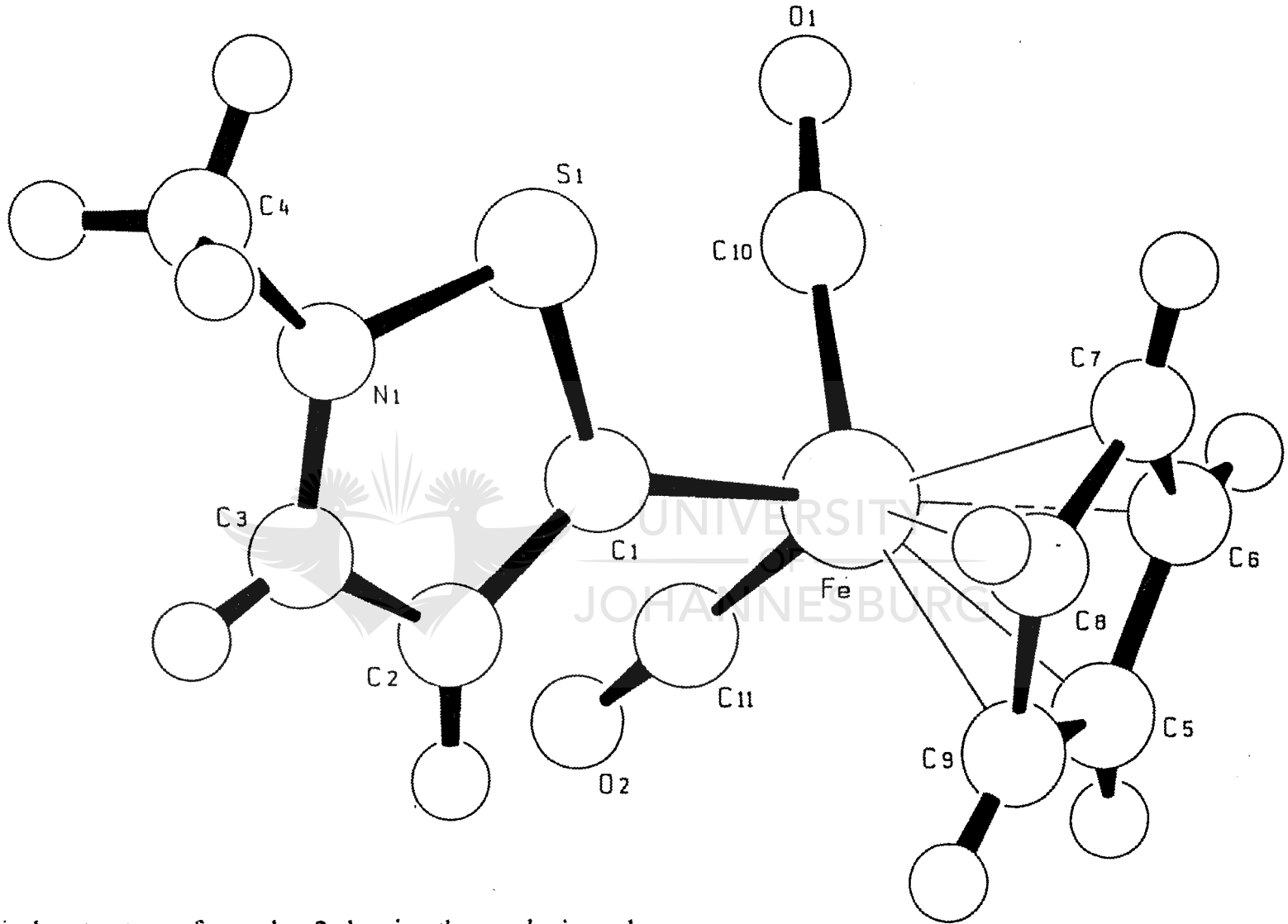


Figure 4.1 Molecular structure of complex **3** showing the numbering scheme

Table 4.2

Selected bond angles (°) for complex **3** with e.s.d.s. in parentheses

C(1)-Fe-C(10)	96.1(2)	S(1)-C(1)-Fe	120.5(2)
C(1)-Fe-C(11)	88.7(2)	C(2)-C(1)-Fe	131.4(2)
C(10)-Fe-C(11)	94.0(2)	C(1)-C(2)-C(3)	112.9(3)
O(1)-C(10)-Fe	175.4(3)	N(1)-C(3)-C(2)	113.5(3)
O(2)-C(11)-Fe	178.6(3)	N(1)-S(1)-C(1)	94.5(2)

4.2.2 Structure of [Au{C=CHCH=NS}PPh$_3$] 10

The molecular structure of complex **10** is shown in Figure 4.2. Selected bond lengths and bond angles are given in Tables 4.3 and 4.4.

The gold atom is linearly coordinated to a phosphorus atom of PPh_3 and to a carbon atom of the isothiazolyl ligand. The P-Au-C angle is 177.1(2)°. Surprisingly, and unlike the cationic thiazolinylidene complex [Au{CN(H)C(Me)C(H)S}PPh_3][CF_3SO_3], no intermolecular gold-gold interactions were observed.[79]

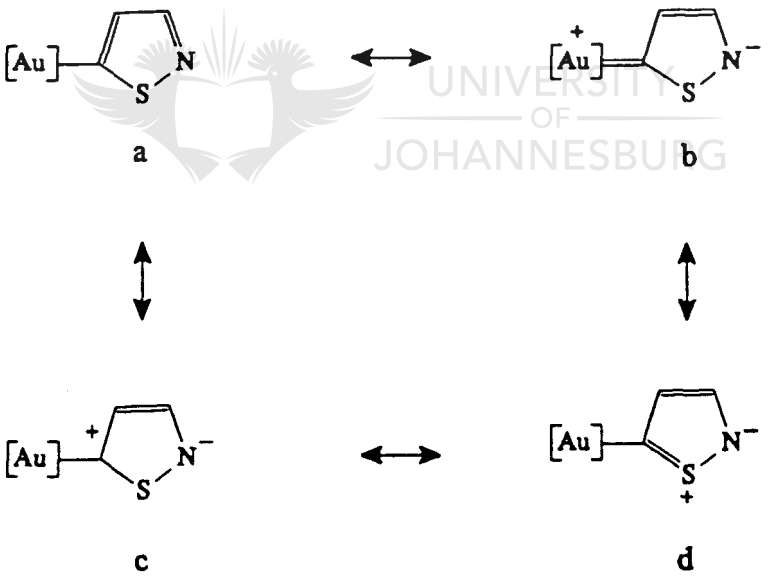
The Au-P bond length of 2.290(2) Å is similar to the distances found in other linear, two-coordinate Au^I complexes, eg. 2.284(1) Å in [Au{$C_6H_3(OMe)_2$}PPh_3],[180] 2.286(3) Å in PPh_3AuPPh_3[181] and 2.291 Å in [Au{$CH_2C(O)Ph$}PPh_3].[182]

The Au-C(sp^2) bond length of 2.032(7) Å is shorter than most other reported Au-C(sp^2) bond lengths, for example, 2.050(4) Å in [Au{$C_6H_3(OMe)_2$}PPh_3],[180] 2.063 Å in [Au(C_6F_5)PPh_3][183] and 2.056(1) Å in [PPh_3Au{C(OMe)=N(p-C_6H_4-Me}].[184] Interestingly, it is more comparable to the formal Au-C(sp^2) double bond distances found in gold(I) carbene complexes such as [Au(C=NC(Me)=CHS)(CN(H)C(Me)=CHS)] (average of 2.03(1) Å),[79] [Au{$CN(CH_2Ph)CH=CHN(H)\}_2$]Cl (average of 2.027(7) Å)[185] and [Au{C(Ph)NMe_2}Cl]

(2.03(3) Å).[186] Ideally one would like to compare this bondlength in complex **10** to that of the analogous isothiazolinylidene complex, but unfortunately suitable crystals of the latter could not be obtained for an X-ray study.

The C(1)-C(2) distance in the isothiazolyl ligand (1.370(8) Å) is only slightly shorter (0.02 Å) than the C(2)-C(3) distance. Both bonds, therefore, show a degree of double bond character. Similarly, the S(1)-C(1) bond of 1.693(7) Å shows some double bond character but is somewhat longer than the 1.680(3) Å in compound **3**, whereas the N(1)-C(3) bond of 1.32(1) Å has a large degree of double bond character.

Complex **10** may, therefore, be represented by the resonance forms shown in Scheme 4.2. The structure determination shows that the most important contributing structure for the neutral complex, at least in the ground state, is a.



Scheme 4.2

Table 4.3

Selected bond lengths (Å) for complex **10** with e.s.d.s in parentheses

Au-P	2.290(2)	C(1)-C(2)	1.370(8)
Au-C(1)	2.032(7)	C(2)-C(3)	1.389(12)
S(1)-N(1)	1.652(6)	P(1)-C(11)	1.839(5)
S(1)-C(1)	1.693(7)	P(1)-C(21)	1.817(4)
N(1)-C(3)	1.320(10)	P(1)-C(31)	1.814(5)

Table 4.4

Selected bond angles (°) for complex **10** with e.s.d.s. in parentheses

P(1)-Au-C(1)	177.1(12)	S(1)-C(1)-Au	122.5(3)
Au-P(1)-C(11)	113.2(2)	C(2)-C(1)-Au	131.1(5)
Au-P(1)-C(21)	113.7(2)	C(1)-C(2)-C(3)	111.7(6)
Au-P(1)-C(31)	111.2(2)	N(1)-C(3)-C(2)	118.2(6)
N(1)-S(1)-C(1)	97.8(3)		

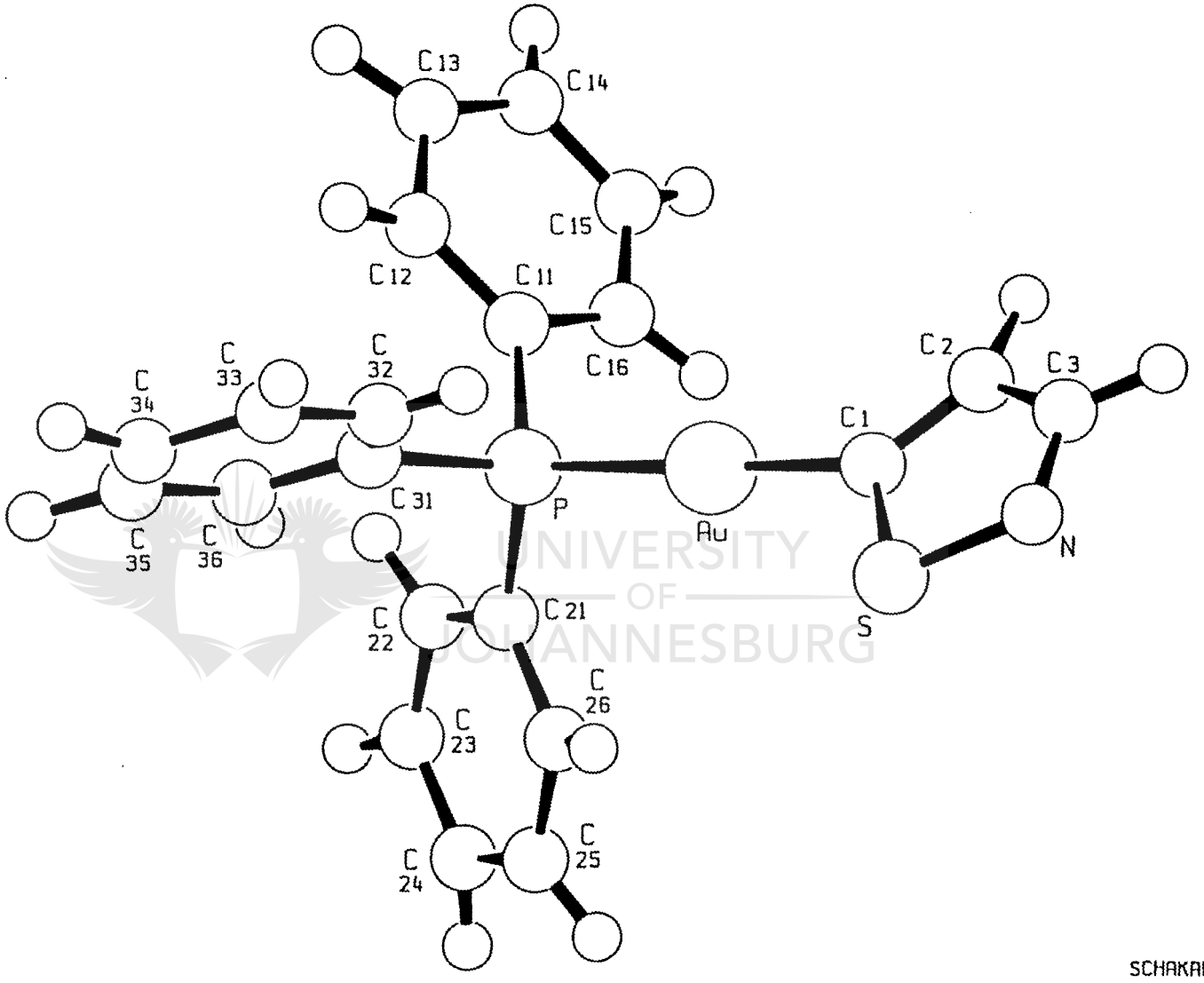


Figure 4.2 Molecular structure of complex **10** showing the numbering scheme

4.3 EXPERIMENTAL

The crystal and molecular structure of complex **3**, $[CpFe(CO)_2\{\overline{CCH=CHN(Me)S}\}][CF_3SO_3]$, was solved by Dr. J.G. Toerien, while the molecular structure of complex **10**, $[Au\{\overline{C=CHCH=NS}\}PPh_3]$, was determined by Prof. G.J. Kruger. The data collection for these complexes was carried out on an Enraf-Nonius CAD4 diffractometer. The cell dimensions were determined from the least-squares refinement of 25 centered reflections using Mo-K_α radiation (λ = 0.71037 Å). The data were corrected, in both cases, for Lorentz polarization and absorption using empirical absorption corrections. No corrections were made for the estimated crystal decay of 2.1% for complex **3** and 3.4% for complex **10**.

The structure of complex **3** was solved using direct methods (SHELX86), followed by difference-Fourier techniques (SHELXL93). All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions.

The position of the gold atom in complex **10** was determined from a Patterson synthesis and subsequent difference maps revealed the rest of the structure (XTAL3.2). All the non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were found from difference maps.

The final atomic coordinates for complexes **3** and **10** appear in Tables 4.5 and 4.6 respectively, while the crystal data for these complexes are summarized in Tables 4.7 and 4.8 respectively.

Table 4.5

Fractional coordinates (x 10^4) and equivalent thermal parameters (x 10^3 Å^2) for complex **3**

Atom	X/a	Y/b	Z/c	U_{eq}
Fe	394(1)	1673(1)	3296(1)	38(1)
S(1)	3337(1)	459(1)	2716(1)	49(1)
N(1)	3586(3)	-109(2)	1633(2)	36(1)
C(1)	1522(3)	843(2)	2400(2)	51(1)
C(2)	1146(4)	518(2)	1442(2)	50(1)
C(3)	2352(4)	-15(2)	1030(2)	52(1)
C(4)	5041(4)	-607(3)	1414(3)	60(1)
C(5)	-925(5)	2906(3)	3148(4)	71(1)
C(6)	-5(6)	2959(3)	3990(3)	68(1)
C(7)	1584(5)	2903(3)	3721(4)	72(1)
C(8)	1560(5)	2810(3)	2651(4)	75(1)
C(9)	-4(6)	2813(3)	2329(3)	71(1)
C(10)	963(4)	1083(2)	4424(2)	49(1)
C(11)	-1307(3)	973(2)	3085(3)	49(1)
O(1)	1286(4)	757(2)	5178(2)	75(1)
O(2)	-2380(3)	507(2)	2949(2)	73(1)
S(2)	5667(1)	2263(1)	1001(1)	45(1)
O(3)	5737(3)	2629(2)	1997(2)	72(1)
O(4)	4158(3)	1905(2)	674(2)	70(1)
O(5)	6997(4)	1697(2)	731(2)	72(1)
C(12)	5887(5)	3298(3)	232(3)	59(1)
F(1)	7283(3)	3697(2)	394(2)	90(1)
F(2)	4819(4)	3942(2)	432(3)	107(1)
F(3)	5752(4)	3089(2)	-732(2)	95(1)
H(2)	194(4)	640(2)	1109(2)	74*
H(3)	2283(4)	-276(2)	392(2)	77*
H(4A)	5753(4)	-569(3)	1983(3)	90*
H(4B)	5515(4)	-323(3)	844(3)	90*
H(4C)	4809(4)	-1255(3)	1270(3)	90*

H(5)	-2017(5)	2929(3)	3128(4)	107*
H(6)	-360(6)	3021(3)	4639(3)	103*
H(7)	2466(5)	2923(3)	4149(4)	109*
H(8)	2429(5)	2756(3)	2248(4)	113*
H(9)	-367(6)	2761(3)	1667(3)	106*

$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (a_i \cdot a_j)$

* Isotropic thermal parameter equal to 1.5 times U_{eq} of the non-hydrogen atom to which the hydrogen atom is attached.

Table 4.6

Fractional coordinates (x 10^4; x 10^5 for Au; x 10^3 for H) and equivalent thermal parameters (x 10^3 Å^2; x 10^5 for Au,P,S) for complex **10**

Atom	X/a	Y/b	Z/c	U_{eq}
Au	37503(2)	22575(2)	100357(2)	*4122(8)
P(1)	3965(1)	2248(1)	8185(1)	*3590(5)
S(1)	1768(2)	2385(2)	11909(2)	*7030
N(1)	2437(7)	2579(7)	13412(5)	*85(3)
C(1)	35390(7)	23660(6)	11694(5)	*51(3)
C(2)	4666(8)	2498(8)	12828(5)	*71(3)
C(3)	3991(9)	2599(9)	13734(6)	*91(4)
C(11)	6036(5)	2455(5)	8253(4)	*38(2)
C(12)	6696(6)	3621(5)	8120(5)	*44(2)
C(13)	8299(7)	3774(7)	8294(6)	*57(3)
C(14)	9210(7)	2763(7)	8575(6)	*62(3)
C(15)	8537(7)	1592(7)	8690(6)	*60(3)
C(16)	6939(6)	1430(6)	8531(5)	*48(2)
C(21)	2976(5)	668(5)	6891(4)	*37(2)
C(22)	3426(6)	225(6)	5849(5)	*49(2)

C(23)	2573(7)	-921(6)	4842(5)	*56(3)
C(24)	1272(7)	-1627(6)	4869(6)	*53(3)
C(25)	806(6)	-1188(6)	5891(6)	*50(3)
C(26)	1654(6)	-52(6)	6892(5)	*43(2)
C(31)	3082(5)	3665(5)	7717(4)	*34(2)
C(32)	2795(6)	4759(6)	8612(5)	*45(2)
C(33)	2075(8)	5807(6)	8277(6)	*56(3)
C(34)	1622(7)	5791(7)	7063(7)	*60(3)
C(35)	1922(7)	4731(7)	6165(5)	*55(3)
C(36)	2642(6)	3672(6)	6498(5)	*46(2)
H(2)	593(6)	208(5)	1302(5)	800
H(3)	470(6)	274(6)	1463(5)	800
H(12)	591(6)	443(5)	759(5)	800
H(13)	882(6)	471(6)	827(5)	800
H(14)	1031(6)	284(6)	876(5)	800
H(15)	928(6)	97(6)	905(5)	800
H(16)	661(6)	52(6)	870(5)	800
H(22)	444(6)	66(5)	582(5)	800
H(23)	280(6)	-135(6)	403(5)	800
H(24)	74(6)	-236(6)	428(5)	800
H(25)	-4(6)	-179(6)	592(5)	800
H(26)	152(6)	29(5)	772(5)	800
H(32)	301(6)	469(6)	944(5)	800
H(33)	197(7)	638(6)	888(5)	800
H(34)	107(7)	632(6)	681(6)	800
H(35)	171(6)	475(6)	529(5)	800
H(36)	279(6)	297(6)	529(5)	800

Table 4.7

Crystal data, collection and refinement details for complex **3**

Formula	$C_{12}H_{10}F_3NO_5S_2Fe$
Molecular mass	425.18
Crystal habit	dark brown needles
Crystal size/mm	0.40 x 0.45 x 0.55
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	8.5118 (6)
b/Å	14.211 (2)
c/Å	13.345 (12)
α/°	90
β/°	91.69 (68)
γ/°	90
Z	4
Volume (U)/Å^3	1613.5 (3)
D_c/g.cm^{-3}	1.750
Radiation	Mo K_α (0.71073 Å)
μ/cm^{-1}	12.5
T/°C	22
F(100)	856
Scan type/ω:2θ	1:1
Scan range/θ°	$3 \leq \theta \leq 30$
Scan angle/°	0.55
Maximum scan rate/°min^{-1}	5.48
Maximum scan time/s per refl.	60
Aperture size/mm	1.3 x 4.0
Zone collected	
h	± 12
k	± 20
l	0,18

Reflections measured	4678
Unique reflections used	3916, $F_o > 4\sigma(F_o)$
Decay/%	2.1
Absorption correction factor:	
Maximum	1.000
Minimum	0.948
Average	0.974
R_{int}	0.027
Parameters refined	217
Max. positional shift/esd	0.001
Residual electron density/e $Å^{-3}$:	
Maximum	0.742
Minimum	-0.672
U_{iso} (H), $Å^2$	*
R	0.053
*w*R	0.150

* Isotropic thermal parameter equal to 1.5 times U_{eq} of the non-hydrogen atom to which the hydrogen atom is attached.

$R = \Sigma(|F_o| - |F_c|/\Sigma|F_o|$

$wR = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{½}$, $w = 1/\sigma^2$

Table 4.8

Crystal data, collection and refinement details for complex **10**

Formula	$C_{21}H_{17}NPSAu$
Molecular weight	543.38
Crystal habit	Off-white prisms
Crystal system	Triclinic
Space group	P-1
a/Å	8.9856 (6)
b/Å	10.1871 (11)
c/Å	12.0069 (6)
α/°	107.588 (7)
β/°	109.034 (6)
γ/°	91.633 (7)
Z	2
Volume (U)/Å^3	980.5 (1)
D_c/g.cm^{-3}	1.847
Radiation	Mo K_α (0.71073 Å)
μ/cm^{-1}	79.16
T/°C	23
F(100)	520
Scan type/ω:2θ	1:1
Scan range/θ°	$3 \leq \theta \leq 30$
Scan angle/°	0.58

Maximum scan rate/°min^{-1}	5.5
Maximum scan time/s per refl.	1200
Zone collected	
h	0.12
k	± 14
l	± 16
Reflections measured	5714
Unique reflections used	5145, $F_o > 3\sigma(F_o)$
Decay/%	3.4
Absorption correction factor:	
Maximum	0.7826
Minimum	0.9992
Average	0.9273
Parameters refined	277
Max. positional shift/esd	0.03 average, 0.44 maximum on H2
Difference map peaks	0.88 Å^{-3} maximum
R	0.035
*w*R	0.028
wR (all hkl's)	0.030

Isotropic thermal parameter of U = 0.08

$R = \Sigma(|F_o| - |F_c|/\Sigma|F_o|$

$wR = [\Sigma[w(F_o - F_c)^2]/\Sigma[w(F_o)^2]]^{½}$, $w = 1/\sigma^2$

REFERENCES

1. T.J. Kealy and P.J. Pauson, *Nature* (London), 1951, 0139.
2. G. Wilkinson, *J. Organomet. Chem.*, 1975, **100**, 273.
3. E.O. Fischer and M.A. Massböl, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 580.
4. R.R. Schrock, *J. Am. Chem. Soc.*, 1974, **96**, 6796.
5. O.S. Mills and A.D. Redhouse, *J. Chem. Soc. A*, 1968, 642.
6. J.S. Miller and A.L. Balch, *Inorg. Chem.*, 1972, **11**, 2069.
7. L.J. Guggenberger and R.R. Schrock, *J. Am. Chem. Soc.*, 1975, **97**, 6577.
8. R.R. Schrock, *Acc. Chem. Res.*, 1979, **12**, 98.
9. G. Huttner and B. Krieg, *Chem. Ber.*, 1972, **105**, 67.
10. U. Schubert, *J. Organomet. Chem.*, 1980, **185**, 373.
11. E. Moser and E.O. Fischer, *J. Organomet. Chem.*, 1968, **15**, 147.
12. C.G. Kreiter and E.O. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 761.
13. C.G. Kreiter, K. Öfele and G.W. Wieser, *Chem. Ber.*, 1976, **109**, 1749
14. R.F Fenske, in *Organometallic Compounds: synthesis, structure, and theory*, (B.L. Shapiro, Ed), Texas A & M University Press, Texas, 1983, 305.
15. R.R. Schrock and P.R. Sharp, *J. Am. Chem. Soc.*, 1978, **100**, 2389.
16. M.A. Gallop and W.R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 121.
17. P.J. Brothers and W.R. Roper, *Chem. Rev.*, 1988, **88**, 1293.
18. D.L. Cardin, B. Cetinkaya and M.F. Lappert, *Chem. Rev.*, 1972, **72**, 545.
19. F.A. Cotton and C.M. Lukehart, *Prog. Inorg. Chem.*, 1972, **16**, 487.
20. F.J. Brown, Prog. *Inorg. Chem.*, 1980, **27**, 1.
21. H. Fischer, in *The Chemistry of the Metal Carbon Bond*, (S. Patai, Ed), Wiley Interscience, New York, 1982, **1**, 181.
22. H. Fischer, K.H. Dötz, K. Weiss, P. Hofmann, U. Schubert and F.R. Kreissl, in *Transition Metal Carbene Complexes*, (P.J. Bieel, Ed), Verlag Chemie, Weinheim, 1982, 2.
23. M.F. Semmelhack and R.J Tamura, *J. Am. Chem. Soc.*, 1983, **105**, 4099.
24. H.R. Thomas, K. Chen and J.R. Vyvyan, *Organometallics*, 1993, **12**, 2806.
25. U. Schöllkopf and F.Gerhart, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 560.

26. M.L.H. Green, L.C. Mitchard and M.G. Swanwick, *J. Chem. Soc. A*, 1971, 794.
27. R.J. Angelici, F.B. McCormick and R.A. Pickering, in *Fundamental Research in Organometallic Chemistry*, (M. Tsutsui, Y. Ishii and H. Yaozeng, Eds), Van Nostrand, New York, 1982, 347.
28. E.D. Dobrzynski, R.J. Angelici, *Inorg. Chem.*, 1975, **114**, 1513.
29. M.A. Gallop and W.R. Roper, *Adv. Organomet. Chem*, 1986, **25**,
30. D.J. Cardin, B. Cetinkaya and M.F. Lappert, *Chem. Rev.*, 1972, **72**, 545.
31. W.P. Felhammer, K.Bartel, U. Plaia, A. Vlokl and A.T. Liu, *Chem. Ber.*,1985, **118**, 2235. W.P. Felhammer, K. Bartel, B. Weinberger and U. Plaia *Chem. Ber.*, 1985, **118**, 2220.
32. R.A. Pickering, R.A. Jacobson and R.J. Angelici, *J. Am. Chem. Soc.*, 1981, **103**, 817.
33. W. Petz, *J. Organomet. Chem.*, 1981, **205**, 203.
34. B.E. Boland-Lussier and R.P. Hughes, *Organometallics*, 1982, **1**, 635.
35. U. Schubert in Ref 21, 233.
36. A.J. Hartshorn and M.F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1976, 761.
37. R.A. Bell, M.H. Chrisholm, D.A. Couch and L.A. Ranhil, *Inorg. Chem.*, 1977, **16**, 677.
38. B. Cetinkaya, P. Dixneuf and M.F. Lappert, *J. Chem. Soc., Dalton. Trans.*, 1974, 1827.
39. B. Cetinkaya, M.F. Lappert and T. Turner, *J. Chem. Soc., Chem. Commun.*, 1972, 851.
40. K. Öfele, Angew. Chem., *Int. Ed. Engl.*, 1968, **7**, 950.
41. K. Öfele, *J. Organomet. Chem.*, 1968, **12**, P42.
42. K. Öfele, *Angew. Chem., Int. Ed. Engl.*, 1968, **8**, 916.
43. M. F. Lappert and A.J. Oliver, *J. Chem. Soc., Dalton. Trans.*, 1974, 65.
44. H.G. Raubenheimer and H.E. Swanapoel, *J. Organomet. Chem.*, 1977, 142, C21.
45. H. Fischer in ref 22, 36.
46. H.W. Turner and R.R Schrock, *J. Am. Chem. Soc.*, 1982, **104**, 2331.
47. M. Brookhark and W.B. Studubaker, *Chem. Rev.*, 1987, **87**, 411.
48. M. Brookhark and Y. Liu, in *Advances in Metal Carbene Chemistry*, (U. Schbert, Ed), Kluwer AAcademic Publishers, Dordrecht, 1989, 251.

49. W.A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 117.
50. E.L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479.
51. C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61.
52. J. Coss, *J. Catal.*, 1982, **5**, 382.
53. M.L.H. Green, *Pure Appl. Chem*, 1978, **50**, 27.
54. K.J. Ivin, J.J. Rooney, C.D. Stewart, M.L.H. Green and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 1978, 604.
55. M.L.H. Green, L.C. Mitchard and M.G. Swanwick, *J. Chem. Soc. A,* 1971, 794.
56. E.J. Arlman and P. Cossee, *J. Catal.*, 1964, **3**, 99.
57. P. Cossee, *J. Catal.*, 1964, **3**, 80.
58. K.H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587.
59. K.H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 644.
60. C.P. Casey, R.A. Boggs and R.L Anderson, *J. Am. Chem. Soc.*, 1972, **94**, 8947.
61. M. Rudler-Chawin and H. Rudler, *J. Organomet. Chem.*, 1981, 212, 302.
62. E.O. Fischer and K.H. Dötz, *J. Organomet. Chem.*, 1972, **36**, C4.
63. J.A. Conner, P.D. Rose and R.M Turner, *J. Organomet. Chem.*, 1973, **55**, 111.
64. W.D. Wulff, in *Comprehensive Organic Synthesis*, (B.M Trost and I. Fleming, Eds), Pergamon press, New York, 1990, **5**, 1065.
65. K.H. Dötz and E.O. Fischer, *Chem. Ber.*, 1972, **105**, 1356.
66. M.P. Doyle, J.H. Griffin, V. Baghiri and R.L. Dorrow, *Organometallics*, 1984, **3**, 53.
67. E.O. Fischer, K. Weiss and K. Buger, *Chem. Ber.*, 1973, **106**, 1581.
68. Y. Ito, I. Ito, T. Hirao and T. Saegusa, *Synth. Commun.*, 1974, **4**, 97.
69. Y. Ito, T. Hirao and T. Saegusa, *J. Organomet. Chem.*, 1977, 131, 121.
70. K.H. Dötz and R. Dielz, *Chem. Ber.*, 1978, **111**, 2517.
71. K. Weiss and E.O. Fischer, *Chem. Ber.*, 1976, **109**, 1868.
72. K.H. Dötz and I. Pruskil, *J. Organomet. Chem.*, 1981, **209**, C4.
73. K.H. Dötz, I. Pruskil and J. Muhlemier, *Chem. Ber.*, 1982, **115**, 1278.
74. K.H. Dötz, W. Kuhn and K. Ackermann, *Z. Naturfursch*, 1983, **B38**, 1351.
75. M.F. Semmelhack, J.J. Bocell, T. Sato, W. Wulff, E. Spiess and A. Zack, *J. Am. Chem. Soc.*, 1982, **104**, 5850.
76. W.A Herrmann, *Kontakte*, 1991, **3**, 29.

77. H.G. Raubenheimer, G.J. Kruger, A. van A. Lombard, L. Linford and J.C Viljoen, *Organometallics*, 1985, **3**, 275.

78. H.G. Raubenheimer, F. Scott, S. Cronje, P.H. van Rooyen and K. Psotta, *J. Chem. Soc., Dalton. Trans.*, 1992, 1009.

79. H.G. Raubenheimer, F. Scott, G.J. Kruger, J.G. Toerien, R. Otte, W. van Zyl, I. Taljaard, P. Olivier and L. Linford, *J. Chem. Soc., Dalton. Trans.*, 1993, submitted for publication.

80. H.G. Raubenheimer, F. Scott, M. Ross and R. Otte, *J. Chem. Soc., Chem. Commun.*, 1990, 1722.

81. H.G Raubenheimer, S. Cronje, P.H. van Rooyen, P.J Olivier and J.G. Toerin. *Angew. Chem., Int. Ed. Engl.*, submitted for publication.

82. H. Schmidbaur, *Gold Bull*, 1990, **23**, 1, 11.

83. F.A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry*, fifth ed, Wiley, New York, 1988.

84. R.S. Iyer, Gee-Hong Kuo and P. Helquist, *J. Org. Chem.*, 1985, **50**, 5898.

85. K.A.M. Kremer and P. Helquist, *J. Organomet. Chem.*, 1985, **285**, 231.

86. P. Seutet and P. Helquist, *Tetrahedron Lett.*, 1988, **29**, 4921.

87. C.P. Casey, W.H. Miles and H. Tukada, *J. Am. Chem. Soc.*, 1985, **107**, 2924.

88. M. Brookhart, D. Timmers, J.R. Tucker, G.D. Williams, G.R. Husk, H. Brunner and B. Hammer, *J. Am. Chem. Soc.*, 1983, **105**, 6721.

89. M.F. Semmelhack and J. Park, *Organometallics*, 1986, **5**, 2550.

90. M.F. Semmelhack, R. Tamura, W. Schnatter and J. Springer, *J. Am. Chem. Soc.*, 1984, **106**, 5363.

91. R. Aummann and H. Heinen, *Chem. Ber.*, 1987, **120**, 1297.

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

93. W.E. Bauta, W.D. Wulff, S.F. Pavkovic and E.J. Saluzec, *J. Org. Chem.*, 1989, **54**, 3249.

94. W.D. Wulff, J.S. M^{c}Callum and F.A. Kunng, *J. Am. Chem. Soc.*, 1988, **110**, 7419.

95. K.H. Dötz and M. Popall, *Chem. Ber.*, 1988, **121**, 664.

96. M.F. Semmelhack, J.J. Bozell, L. Keller, T. Sato, E. Spiess, W.D. Wulff and A. Zask, *Tetrahedron*, 1985, **41**, 5803.

97. W.D. Wulff, W.E. Bauta, R.W. Kaesler, P.J. Lankford, R.A. Miller, C.K. Murray

and D.C. Yang, *J. Am. Chem. Soc.*, 1990, **112**, 3642.

98. W.D. Wullf and T.S. Powers, *J. Org. Chem.*, 1993, **58**, 2381.

99. C.A. Merlic, D. Xu, M.C. Nguyen and V. Truong, *Tetrahedon Lett.*, 1993, **34**, 227.

100. K.H. Dötz, R. Noack, K. Harms and G. Muller, *Tetrahedron lett.*, 1990, **46**, 1235.

101. W.D. Wullf and D.G. Yang, *J. Am. Chem. Soc.*, 1983, **105**, 6726.

102. L.A Paquette, M. Gugelchuk and Yeh-Leh Hsu, *J. Org. Chem.*, 1986, **51**, 3864.

103. K.S Chan and W.D Wulff, *J. Am. Chem. Soc.*, 1986, **108**, 5229.

104. K.L. Faron and W.D. Wullf, *J. Am. Chem. Soc.*, 1990, **112**, 6419.

105. K.L. Faron and W.D. Wulff, *J. Am. Chem. Soc.*, 1988, **110**, 8727.

106. R. Aumann and P. Hinterding, *Chem. Ber.*, 1992, **125**, 2765.

107. F.R. Kreissl, E.O. Fischer and C.G. Kreiter, *J. Organomet. Chem.*, 1973, **57**, C9.

108. A. Parlier, H. Rudler, R. Yefsah and C. Alverez, *J. Organomet. Chem.*, 1987, **328**, C21.

109. R. Aumann and E. Kuckert, *Chem. Ber.*, 1986, **119**, 156.

110. R. Aumann, E. Kuckert and H. Heinen, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 978.

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

112. H. Le Bozec, D. Devanne and P.H. Dixneuf, in *Advances in metal Carbene Chemistry*, (U. Schbert, Ed.), Kluwer Academic Publishers, Nordrecht, 1989, 107. H. Le Bozec, A. Gorgues and P.H. Dixneuf, *Inorg. Chem.*, 1981, **20**, 2486.

113. H. Adams, N.A. Bailey, M. Grayson, C. Ridgway, A.J. Smith, P. Taylor, M.J. Winker and C.E. Housecroft, *Organometallics*, 1990, **9**, 2621.

114. M.M Singh and R.J. Angelici, *Inorg. Chem.*, 1984, **23**, 2691.

115. F.B. M^{c}Cormick and R.J. Angelici, *Inorg. Chem.*, 1979, **18**, 1231.

116. M. Green, F. Gorden, A. Stone and M. Underhill, *J. Chem. Soc., Dalton. Trans.*, 1975, 939.

117. K. Öfele, E. Roos and M. Herberbold, *Z. Naturforsch.*, B, 1976, **31**, 1070.

118. F.E. Hahn and M. Tamn, *J. Organomet. Chem.*, 1993, **456**, C11.

119. R. Aumann, E. Kuckert, C. Krüger and K. Angermund, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 563.

120. F. Camps, J.M. Moreto, S. Ricart, J.M Viñas, E. Molms and C. Miravitlles, *J. Chem. Soc., Chem. Commun.*, 1989, 1560.

121. H.G. Raubenheimer, G.J. Kruger, C.F. Marais, R. Otte and J.T.Z. Hattingh, *Organometallics*, 1988, **7**, 1853.

122. C.P. Casey and S.W. Polichnowski, *J. Am. Chem. Soc.*, 1978, **100**, 7565.

123. F. Wille, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 335.

124. R. Raap, *Can. J. Chem*, 1966, **44**, 1324.

125. J.C. Sauer, *Org. Synth., Coll. Vol. IV*, 1963, 813.

126. M.P.L. Caton, D.H. Jones, R. Slack and K.R.H. Wooldridge, *J. Chem. Soc.*, 1964, 446.

127. K.R.H. Wooldridge, in Advances In Heterocyclic Chemistry, (A.R. Katritzky and A.J. Boulton, Ed), Academic Press, New York, 1972, **14**, 15.

128. K.H. Panell, C. Ching-Yu Lee, C. Parkanyi and R. Redfearn, *Inorg. Chim. Acta*, 1975, **12**, 127.

129. F.H. Köhler, H.J. Kalder and E.O. Fischer, *J. Organomet. Chem.*, 1976, **113**, 11.

130. L.E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

131. F.A. Cotton and C.S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432.

132. E.W. Abel, I.S. Butler and J.G. Reid, *J. Chem. Soc.*, 1963, 2068.

133. W.P Fehlhammer, W.A. Hermann and K. Öfele, in *Handbuch der Präparativen Anorganischen Chemie*, Third Ed, Ferdinand Enke, Stuttgard, 1980, 1953.

134. W.S. Rapson and T. Groenewald, *Gold usage*, Academic Press, London, 1978.

135. C. Bocking and I.R. Christie, *Interdisc. Sci. Rev.*, 1992, **17**, 239.

136. D.M. Jacobson and G. Humpson, ref 131, 244.

137. R.V. Parish and S.M. Cottrill, *Gold Bull.*, 1987, **20**, 3.

138. B.M. Sutton, *Gold Bull.*, 1986, **19**, 15.

139. D.H. Brown and W.E. Smith, *Chem. Soc. Rev.*, 1980, **9**, 217.

140. R.C. Elder, K. Ludwig, J.N. Cooper and M.K. Eidsness, *J. Am. Chem. Soc.*, 1985, **107**, 5023.

141. D.T. Hill and B.M. Sutton, *Acta Crystallogr.,Sect. C*, 1980, **9**, 679.

142. C.F. Shaw III, A.A. Isab, M.T. Coffer and C.K. Mirabelle, *Biochem. Pharmacol.*, 1990, **40**, 1227.

143. R.M. Snyder, C.K. Mirabelle and S.T. Crooke, *Biochem. Pharmacol.*, 1986, **35**,

923.

144. J.E. Laib, C.F. Shaw III, D.H. Petering, M.K. Eidsness, R.C. Elder, J.S. Garvey, *Biochemistry*, 1985, **24**, 1977.

145. S.J. Berners-Price, R. Girand, D.T. Hill, B.M. Sutton, P.S. Jarette, L.F. Faucette, R.K. Johnson, C.K. Mirabelli and P.J. Sadler, *J. Med. Chem.*, 1990, **33**, 1386.

146. J. Schwank, *Gold Bull.*, 1983, **16**, 103.

147. J. Schwank, *Gold Bull.*, 1985, **18**, 2.

148. S.D. Pastor, R. Kesselring and A. Togni, *J. Organomet. Chem.*, 1992, **429**, 415.

149. A. Togni and S.D. Pastor, *J. Organomet. Chem.*, 1990, **381**, C21.

150. M. Sawamura, X. Ito and T. Hayashi, *Tetrahedron Lett.*, 1989, **30**, 2247.

151. F. Gasparrini, M. Giovannoli, D. Misiti, G. Natile, G. Palmieri and L. Maresea, *J. Am. Chem. Soc.*, 1993, **115**, 4401.

152. F. Gasparrini, M. Giovannoli, D. Misiti, G. Natile and G. Palmieri, *J. Org. Chem.*, 1990, **55**, 1323.

153. F. Scherbaum, A. Grohmann, B. Huber, C. Krüger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1544.

154. F. Scherbaum, A. Gromann, G. Muller and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 463.

155. O. Steigelmann, P. Bissinger and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1399.

156. H. Schmidbaur, B. Brachthäuser and O. Steigelmann, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1488.

157. A. Grohmann, J. Reide and H. Schmidbaur, *Nature*, 1990, **345**, 140.

158. YU. L. Slovokhotov and YU. T. Struchkov, *J. Organomet. Chem.*, 1984, **277**, 13.

159. N. Rösch, A. Görling, D.E. Ellis and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1357.

160. G. Minghett and F. Bonati, *Gazz. Chim. Ital.*, 1972, **102**, 205.

161. G. Mighetti, L. Baratto and F. Bonati, *J. Organomet. Chem.*, 1975, **102**, 397.

162. R. Aumann and E.O. Fischer, *Chem. Ber.*, 1981, **144**, 1853.

163. F. Glockling and V.B. Mahale, *J. Chem. Res.(S)*, 1978, **5**, 170.

164. A.L. Hormann-Arendt, C.F. Shaw, *Inorg. Chem.*, 1990, **29**, 4683.

165. H. Schmidbaur and A.M. Aly, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 7.

166. E. Díez-Barra, A. de la Hoz, Ana-Sanchez-Migallón and Jaun Tejeda, *Heterocycles*, 1992, **34**, 1365.

167. D.E. Butler and S.M. Alexander, *J. Org. Chem.*, 1972, **37**, 215.

168. A.R. Katritzky, C. Juyaram and S.N. Vassilatos, *Tetrahedron*, 1983, **39**, 2023

169. A. Hass, J. Helmbrecht and U. Niemann, in *Handbuch der Präparativen Anorganischen Chemie*, Third Ed, Ferdinand Enke, Stuttgard, 1975, 1014.

170. G.N. Glaree, Yingzhany Su, R.A. Jacobson and R.J. Angelici, *Inorg. Chim. Acta*, 1989, **157**, 73.

171. M.I. Bruce, D.N. Duffy, M.J. Liddell, M.R. Snow and E.R.T. Tiekink, *J. Organomet. Chem.*, 1987, **335**, 365.

172. M.R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, 1971, **93**, 354.

173. M.R. Churchill and J. Wormald, *Inorg. Chem.*, 1969, **8**, 1936.

174. P.E. Riley, R.E. Davis, N.T. Allison and W.M. Jones, *J. Am. Chem. Soc.*, 1980, **102**, 2458.

175. W. Malisch, H. Blau, K. Blank, C. Kruger, L.K. Liu, *J. Organomet. Chem.*, 1985, **296**, C32.

176. R. Ferede, M. Noble, A.W. Cordes, N.T. Allision and J. Lay Junior, *J. Organomet. Chem.*, 1988, **339**, 1

177. M.E. Raseta, S.A. Cawood, M.E. Welker and A.L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 8268.

178. C. Knors, Gee-Hong Kuo, J.W. Lcuher, C. Eigenbrot and P. Helquist, *Organometallics*, 1987, **6**, 988.

179. P.E. Riley, R.E. Davis, N.T. Allison and W.M. Jones, *Inorg. Chem.*, 1982, **21**, 1321.

180. P.E. Riley and R.E. Davis, *J. Organomet. Chem.*, 1980, **192**, 283.

181. N.C. Baenziger, K.M. Dittemore and J.R. Doyle, *Inorg. Chem.*, 1974, **13**, 805.

182. Y. Ito, M. Inouye, M. Suginome and M. Murakami, *J. Organomet. Chem.*, 1988, **342**, C41.

183. R.W. Baker and P.J. Pauling, *J. Chem. Soc., Dalton. Trans.*, 1972, 2264.

184. M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio and F. Bonati, *Acta Crystallogr.,Sect. C*, 1985, **41**, 52.

185. F.Bonati, A. Burini, B.R. Pietroni and B. Bono, *J. Organomet. Chem.*, 1987, **375**, 147.

186. U. Schubert, K. Actermann and R. Aumann, *Acta Crystallogr.,Sect. B*, 1982, **11**, 591.