ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 617–618 (2001) 170–181

Journal of Organometallic Chemistry

Mini Review

Carbene complexes derived from lithiated heterocycles, mainly azoles, by transmetallation

Helgard G. Raubenheimer *, Stephanie Cronje

Department of Chemistry, University of Stellenbosch, Private Bag XI, Matieland, Stellenbosch 7602, South Africa

Received 4 September 2000; accepted 25 September 2000

Abstract

Heterocyclic carbene complex formation can be achieved by lithiation of CH-acidic azoles, transmetallation involving a variety of transition metal complexes and, finally, protonation or alkylation. This article describes the synthetic methodology involved with a special emphasis on unexpected or (presently) unusual features of the reactions or products. The procedure can be extended to allow carbene complex formation by reaction at remote heteroatoms and also for diorgano(carbene) complex formation. Certain azolyls do not substitute but add to coordinated carbonyls and the resulting anionic Fischer-type carbene complexes can function as bidentate ligands. With gold(I) as central metal, many azolyls as well as carbene complexes participate in homoleptic rearrangement. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbene complexes; 2,3-Dihydro-thiazol-2-ylidene complexes; 2,3-Dihydro-1*H*-imidazol-2-ylidene complexes; 2,5-Dihydro-isothiazol-5-ylidene complexes; 2,5-Dihydro-1*H*-pyrazol-5-ylidene complexes; 1,2-Dihydro-pyridin-2-ylidene complexes

1. Introduction

The discovery of stable free carbenes by Arduengo in 1991 [1] has led to furious activity by Kuhn [2], Arduengo himself [3] and others [4] to prepare heterocyclic carbene complexes, a continuation of excellent research carried out by Öfele and co-workers [5–7], Wanzlick et al. [8], Lappert and his group [9], and Stone et al. [10] in the late sixties and early seventies. Stable carbenes and their application as ligands in transition metal complexes have been extensively reviewed [11,12], and even discussed in the more popular literature [13].

The transmetallation method for the preparation of 2,3-dihydro-1*H*-imidazol-2-ylidene complexes of gold was utilized by Burini and co-workers in 1989 [14]. Their attempts to isolate silver and copper analogues were, however, unsuccessful. Mononuclear gold(I) carbene complexes also form when trimeric gold(I) imidazolyl reacts with ethyl chlorocarbonate or ethyl iodate [15].

Our efforts in this field since 1985 [16] involve the initial deprotonation of an azole followed by transmetallation and protonation or alkylation to afford carbene complexes. This procedure has led to a large number of compounds with interesting characteristics and some highlights of the work are discussed here. The advantages of this approach are firstly that in certain situations the (azolyl) metal complex is isolable and, secondly, that the protonation option can be utilized. Apart from the preparation and characterization of new compounds a major goal of our endeavour has been to discover new, unexpected reactions or physical attributes of the products. We report in this review amongst others on:

1. The formation of carbene complexes containing a distant nitrogen atom compared to an α-N in Fischer-type amino(carbene) complexes.
2. Cyclopentadienyl deprotonation by coordinated thiazolyl and subsequent bonding to iron.
3. Homoleptic rearrangements of ligands attached to gold(I).

---

* Corresponding author. Tel.: +27-11-4892365; fax: +27-11-4892363.

E-mail address: hgr@land.sun.ac.za (H. G. Raubenheimer).

PII: S0022-328X(00)00704-X

4. Heterometallocyclic ring formation by nucleophilic CO attack of the distant nitrogen atom.
5. Thiazolyl Fischer-type carbene complexes as bidentate ligands.
6. Ligand substitution by the isocyanide tautomer of a lithiated oxazole.

Whereas carbene ligands in typical Fischer- or Schrock-type complexes can be functionalised or applied in catalysis, dihydro-azol-ylidenes are of the inert type, very much like the well established phosphines or amines. Due to their inherent stability they coordinate strongly and even metal systems that have in the past defied isolation as carbene complexes, can now be prepared. Carbene complexes of copper(I) fall into this category [17–19]. Our complexes are related to Fehlhammer's 2,3-dihydro-oxazol-2-ylidenes, reported in a series of publications since 1974 [20].

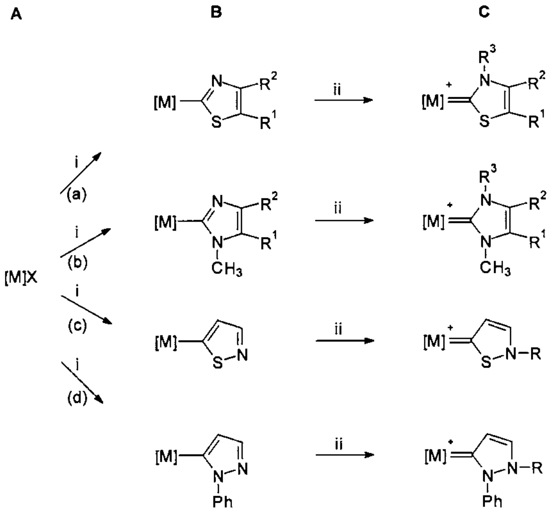
2. Heterocyclic carbene complexes

2.1. Preparation of mono(heterocyclic) carbene complexes

These compounds are derived from lithiated thiazoles, imidazoles, isothiazole, a pyrazole and pyridine.

2.1.1. The standard transmetallation route

Certain transition metal complexes containing halides or other labile ligands react readily with lithiated azoles. Subsequent protonation or alkylation furnishes dihydro-azol-ylidene compounds (Scheme 1). The complex fragment [M] itself may carry a negative charge or be neutral implying that $[M]^+$ in Scheme 1 could be neutral or positively charged. Examples are given in Table 1 and it is indicated that only a few azolyl complexes have been isolated. The azolyl complexes are often unstable at room temperature (r.t.) and have to be converted to the carbene compound at very low temperatures (−78°C) in order to obtain a stable, characterizable product.



Scheme 1. (i) Lithiated azole; (ii) acid or alkylating agent.

Somewhat surprising is the carbene (Table 1, reaction no. 1) and carbonyl (Table 1, reaction no. 8) substitutions by certain carbanions since these ligands are not labile and normally a nucleophilic attack on carbon should be expected. Metal carbonyls, however, differentiate between imidazolyls and thiazolyls: the first react by substitution and the latter by addition to CO (vide infra). These carbene and carbonyl substitutions probably result from free, partly anionic, heterocyclic carbene formation (Scheme 2) as proven by Boche and co-workers [32,33].

In the last two classes of reactions [(c) and (d) in Table 1], the organo-thio and amino-organo carbene complexes are formed by electrophilic attack on a remote (3 bonds removed from the coordinated carbon) nitrogen atom.

2.1.2. Other preparative routes and complicating reactions

All transmetallation reactions are, however, not straightforward and some unexpected observations have been made in the course of our investigations. In addition, all preparations do not necessarily involve a transmetallation or only a transmetallation. Certain products are unstable, and protonation does not only occur on a nitrogen atom.

2.1.2.1. Carbene complexformation by addition (aggregate formation). When a suspension of CuX (X = Cl or I) is used for the preparation of 2,3-dihydro-thiazol-2-ylidene and 2,3-dihydro-imidazol-2-ylidene complexes, the halide is retained even though an excess of azolyl is used, suggesting the formation of an aggregate of the type shown in Scheme 3 [17,18]. In addition, only alkylation affords carbene complexes whereas acidification gives a dinuclear, halide-bridged, imine complex [19].

Similar arguments according to Scheme 4 [28] are applicable to the formation of carbene(cyano)gold(I) compounds from AuCN, a starting material which is insoluble in THF.

2.1.2.2. Deprotonation of coordinated thiazoles. *N*-coordinated thiazoles can rearrange upon deprotonation to afford carbene complexes after subsequent alkylation (Scheme 5) [16,22].

2.1.2.3. Mono (carbene) complexes from di(azolyl) compounds. Addition of a solution of a thiazolyllithium to half a molar amount of ClAu(THT) produces the corresponding soluble aurate complexes (Fig. 1), having typical carbene-like ^{13}C-NMR resonances for their C^2 carbons (vide infra).

Table 1
Mono(dihydro-azol-ylidene)complexes [a]

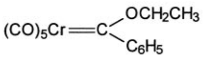
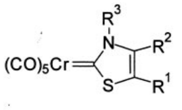
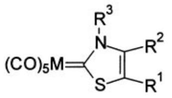
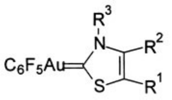
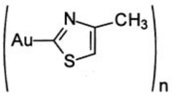
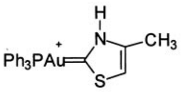
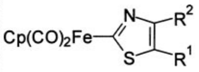
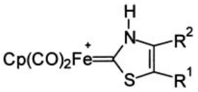
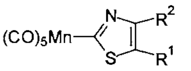
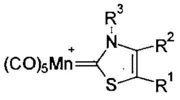
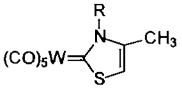
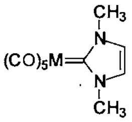
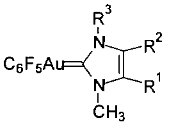
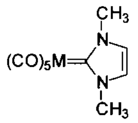
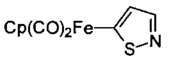
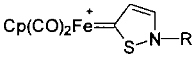
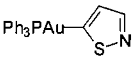
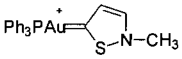
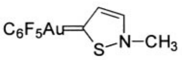
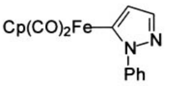
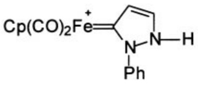
Reaction no	[M]X (**A**)	Azolyl (**B**)	Carbene complex (**C**)	References
(a)				
1	 $(CO)_5Cr{=}C(OCH_2CH_3)(C_6H_5)$	not isolated	 $R^1 = H, R^2 = CH_3$; $R^1R^2 = CH{=}CHCH{=}CH$; $R^3 = CH_3$ or CH_2CH_3	[16]
2	$(CO)_5M(THF)$ M = Cr, Mo, W	not isolated	 $R^1 = H, R^2 = CH_3$; $R^1R^2 = CH{=}CHCH{=}CH$; $R^3 = CH_3$ or CH_2CH_3	[16, 22]
3	$C_6F_5Au(THT)$	not isolated	 $R^1 = H, R^2 = CH_3$; $R^1R^2 = CH{=}CHCH{=}CH$; $R^3 = H$ or CH_3	[23, 24]
4	Ph_3PAuCl	decomposition to 		[24]
5	$Cp(CO)_2FeCl$	 $R^1 = H, R^2 = CH_3$; $R^1R^2 = CH{=}CHCH{=}CH$	 $R^1 = H, R^2 = CH_3$; $R^1R^2 = CH{=}CHCH{=}CH$	[25]
6	$(CO)_5MnBr$	 $R^1 = R^2 = H$; $R^1 = H, R^2 = CH_3$	 $R^1 = R^2 = H$; $R^1 = H, R^2 = CH_3$; $R^3 = H$ or CH_3	[26]
7	$(CO)_5WCl^-$	not isolated	 R = H or CH_3	[27]
(b)				
8	$(CO)_5M(CO)$ M = Cr, Mo, W	not isolated		[22]

Table 1 (*Continued*)

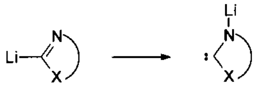
9	$C_6F_5Au(THT)$	not isolated	 $R^1 = R^2 = H$; $R^1R^2 = CH{=}CHCH{=}CH$; $R^3 = H$ or CH_3	[28]
10	$(CO)_5MCl^-$ M = Cr or W	not isolated		[22]
(c)				
11	$Cp(CO)_2FeCl$		 R = H or CH_3	[29]
12	Ph_3PAuCl			[30]
13	$C_6F_5Au(THT)$	not isolated		[30]
(d)				
14	$Cp(CO)_2FeCl$			[31]

Careful single protonation or alkylation affords monocarbene complexes, Fig. 2.This reaction does not occur with imidazolyl aurates and only bis(carbene) complexes can be isolated [26]. General reviews of gold carbene complexes appear in references [34] and [35].

2.1.2.4. Cyclopentadiene deprotonation by azolyl complexes. The in situ prepared $14e^-$ thiazolyl complexes $(LL)FeR_2$ [LL = dppm, dppe, R = $C{=}NC_6H_4S$-*o* or $C{=}NC(CH_3){=}CHS$] deprotonate monocyclopentadiene facilitating cyclopentadienyl coordination and monocarbene complex formation. In the process one of the heterocyclic rings is protonated and, subsequently, H-bonded to the other while one of the phosphorous atoms simultaneously detaches itself from the metal (Scheme 6) [25].

The product in Scheme 6 is related to a hydrogen bonded bis(pyridyl)gold(III) compound prepared previously by Komiya et al. [36] according to Scheme 7.

2.1.2.5. C rather than N protonation of the azolyl metal compounds. Not only the thiazolyl and imidazolyl copper compounds (vide supra) are protonated on the metallated carbons, it also happens to other anionic imidazolyl compounds and an isothiazolyl tungsten complex according to Scheme 8 22 and Scheme 9 [27] forming the corresponding imine adducts.

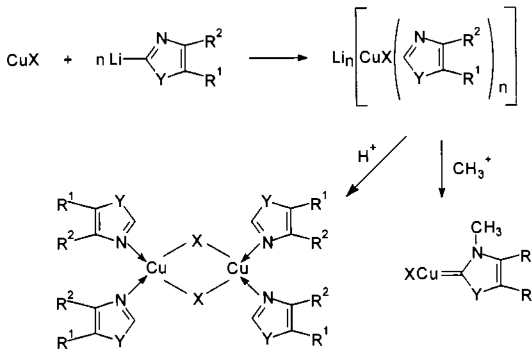


X = S or NR

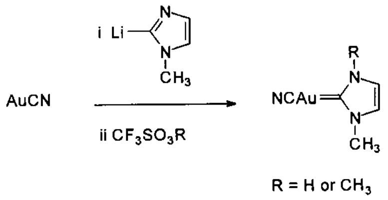
Scheme 2.

---

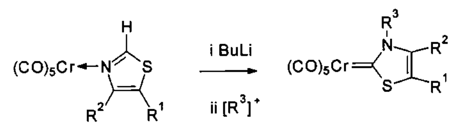
[a] The use of double bonds in drawings of metal carbene compounds is purely formalistic and does not necessarily represent the real bonding situation in these systems especially for copper(I) and gold(I) complexes. A donor/acceptor arrow or a dipolar formula is more representative of the true bonding situation in most carbene compounds [21]. For 1,2-dihydro-pyridin-2-ylidene gold(I) complexes containing more delocalized ring systems (Schemes 7 and 10) the latter method of representation is preferred.



Scheme 3. X = Cl or I, Y = S or NCH_3, R^1R^2 = H, CH_3 or CH_3, CH_3 or CH=CHCH=CH.



Scheme 4.



Scheme 5. R^1R^2 = H, CH_3 or CH=CHCH=CH; R^3 = CH_3 or CH_2CH_3.

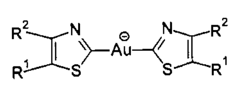


Fig. 1. R^1R^2 = H, CH_3 or CH=CHCH=CH.

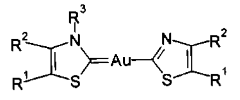


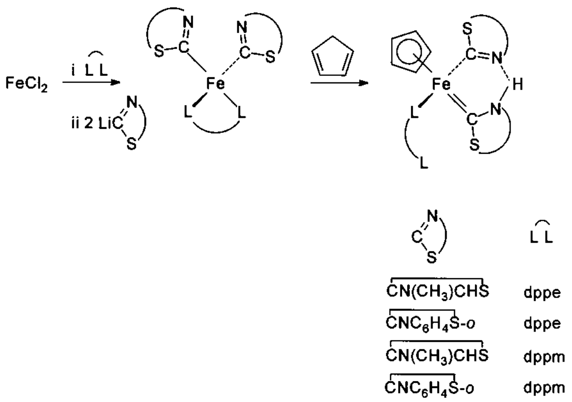
Fig. 2. R^1R^2 = H, CH_3 or CH=CHCH=CH; R^3 = H or CH_3.

2.1.2.6. A mono(carbene) complex of AuCl derived from pyridine. A gold carbene complex comparable to that of copper discussed above (Scheme 3), can be prepared by another route. Treatment of ClAu(THT) with an equimolar amount of 2-lithiated pyridine affords the 2-pyridyl trimer previously prepared by different methods the earliest of which dates back to 1970 [37,38]. Later Bonati et al. used mass spectroscopy as a basis for proposing trimeric structures for related structures derived from lithioimidazoles [14]. Addition of HCl in diethyl ether to a stirred suspension of the gold-pyridyl oligomer affords the soluble, neutral, chloro(1,2-dihydro-pyridin-2-ylidene) complex according to Scheme 10 [39].

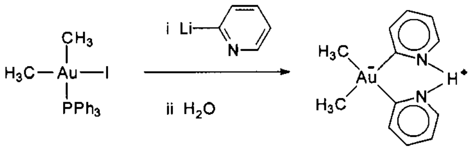
2.1.2.7. Homoleptic rearrangement. We have called reactions of the type:

$$2AuL^1L^2 \rightarrow AuL^1_2 + AuL^2_2$$

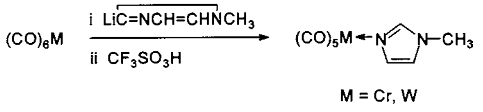
which have previously been described for cyanide containing, mixed ligand gold compounds, homoleptic rearrangements [40]. Examples of such reactions occurring in solution when attempts are made to prepare mixed-ligand complexes are illustrated in Schemes 11 and 12 [30].



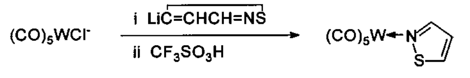
Scheme 6.



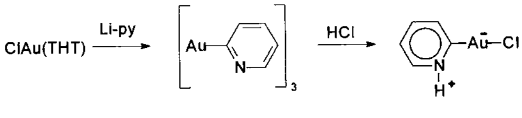
Scheme 7.



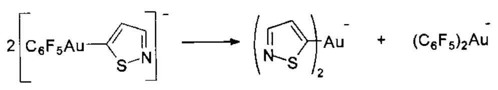
Scheme 8.



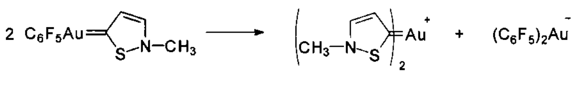
Scheme 9.



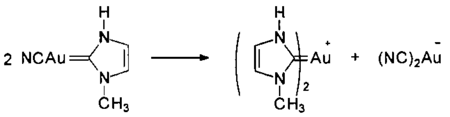
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

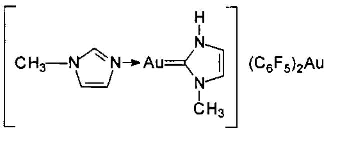
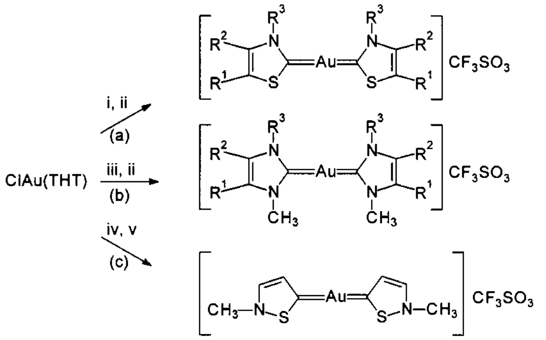
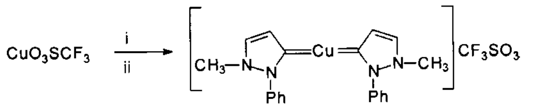


Fig. 3.



Scheme 14. (i) LiC=NCR^2=CR^{1}S (R^{1}R^2 = H and CH_3, CH=CHCH=CH); (ii) $CF_3SO_3R^3$(R^3 = H or CH_3; (iii) LiC=NCR^2=CR^{1}NCH$_3$ (R^{1}R^2 = H and CH_3 or CH=CHCH=CH); (iv) LiC=CHCH=NS; (v) $CF_3SO_3R^3$ (R^3 = CH_3).



Scheme 15. (i) LiC=CHCH=NNPh, (ii) $CF_3SO_3CH_3$.

The first reaction is fast, whereas the latter slow process can be followed by ^{1}H-NMR measurements and equilibrium is established only after 18 days. Equilibrium is also attained for the reaction in Scheme 13 [28] for which $K = 6.7 \times 10^{-1}$ in acetone-d_6 at 23°C. The homoleptic rearrangement of C_6F_5Au-[CNHCH=CHN(CH_3)] is accompanied by rapid proton migration from nitrogen to the initially coordinated carbon to give the carbene-imino complex in Fig. 3 [28].

2.2. Preparation of bis(dihydro-azol-ylidene) complexes

Although many gold(I)bis(carbene) complexes are obtained by homoleptic rearrangement of the carbene precursor or mono(carbene) compound, bis(carbene) compounds have also been obtained for gold(I), copper(I) and silver(I) according to rational synthetic methods.

2.2.1. The transmetallation route

In general, the transmetallation route towards bis(carbene) complexes involves the initial formation of metallate complexes. Subsequent double protonation or alkylation then affords cationic carbene complexes. Only one example is known wherein alkylation as well as protonation could be utilized for carbene formation in the same compound. Typical examples of reactions [26,28,30] are given in Scheme 14.

The above mentioned mixed carbene complex forms when a specific quantity of the di(imidazolyl)gold anion [formed in reaction (b)], is successively treated with equimolar quantities of $CF_3SO_3CH_3$ and CF_3SO_3H.

Starting from copper(I)triflate, homoleptic bis(carbene) complexes of copper derived from thiazole, imidazole and pyrazole [41] can be prepared in a similar fashion to gold (Scheme 15).

Although similar silver(I) compounds also form, they are light and air sensitive [42].

2.2.2. Other methods

As mentioned before, bis(carbene) complexes of gold(I) can also be obtained by homoleptic rearrangement of monocarbene complexes, e.g. when Ph_3PAu-C=NCR^2=CR^{1}NCH$_3$ (R^{1}R^2 = H and H or CH=CHCH=CH) is alkylated or by dissolving the mono(carbene) complex (CN)AuCNHCH=CHNCH$_3$ in THF at r.t. [28]

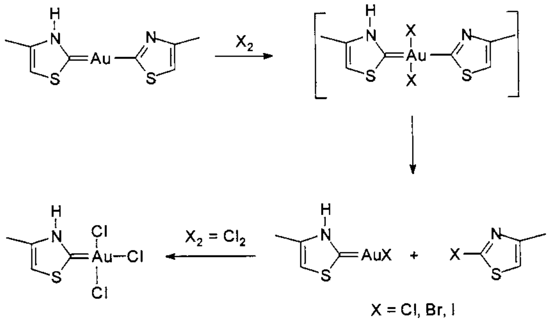
Substitution of the halide in $M(CO)_5Cl^-$ (M = Cr, W) by 1-methylimidazol-2-yllithium afforded upon alkylation the neutral monocarbene complexes (Table 1, reaction no. 10). Additional CO substitution affords the tetracarbonyl bis(carbene) complexes previously reported by Öfele and co-workers [6,7].

2-Lithiated pyridine reacts similarly to the azolyls in Scheme 14 with ClAu(THF) to form the corresponding bis(carbene) complexes by subsequent double protonation or alkylation [39].

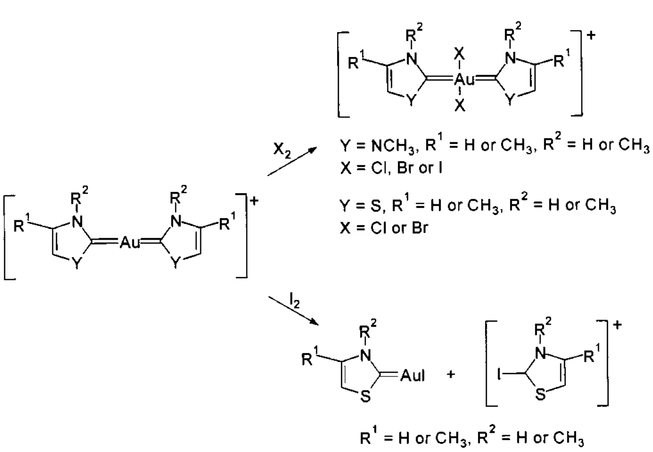
2.3. Redox chemistry of simple heterocyclic gold(I) bis(carbene) complexes

Bonati [43,44] and Laguna [45,46] have reacted acyclic diamino(carbene) complexes of gold with halogens to obtain gold(III) compounds. This approach is also applicable to dihydro-azolylidene compounds with some unexpected results.

Firstly, the mono(carbene)thiazolylgold(I) compound in Scheme 16 can be oxidized by halogens but then immediately undergoes a reductive elimination of the 2-halothiazole to form mono(carbene) halogold compounds [47]. Excess Cl_2 leads to the formation of a 2,3-dihydrothiazol-2-ylidene(trichloro) gold compound [47].



Scheme 16.



Scheme 17.

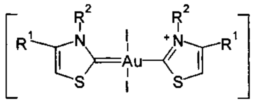
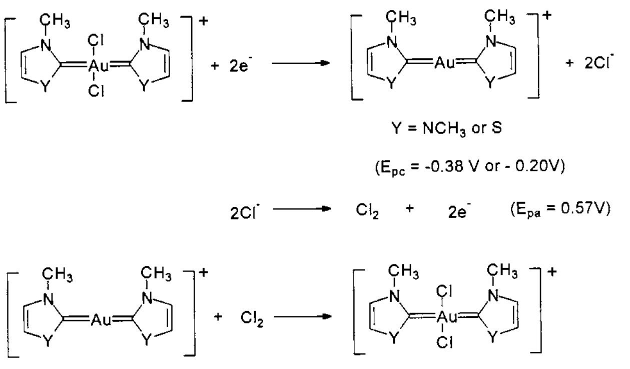


Fig. 4. $R^1 = H$ or CH_3, $R^2 = H$ or CH_3.



Scheme 18.

Secondly, chlorine and bromine oxidatively add to cationic bis(carbene) complexes derived from thiazoles and imidazoles, but whereas iodine reacts similarly with 2,3-dihydro-imidazol-2-ylidene complexes, the 2,3-dihydro-thiazol-2-ylidene compounds form monocarbene(iodo) gold complexes (Scheme 17) [47].

The formation of the latter compound by a rare kind of reductive elimination is explained when the gold(III) compounds are written in one of their more important contributing forms, as shown in Fig. 4.

Both Au(I) and Au(III) bis(2,3-dihydro-imidazol-2-ylidene) and bis(2,3-dihydro-thiazol-2-ylidene) complexes have been studied by cyclic voltammetry [48]. Unlike the ligands in some gold(I)phosphine compounds, the carbene ligands do not dissociate from the metal upon oxidation to gold(III). No Au(II) intermediates could be detected in the oxidation and reduction processes. The cyclic voltammograms indicate successively the reduction of the gold(III) compounds, the oxidation of formed halides to halogens and finally chemical oxidation of the gold(I) carbene complexes by these halogens. The consecutive reaction steps (for X = Cl) can be written as in Scheme 18.

Bis(carbene)gold(I) complexes, therefore, show no oxidation or reduction waves over the potential range (Fc/Fc^+) (Fc = ferrocene) 1.5 to −2.4 V. A cathodic wave is only visible after scanning through the oxidation of added halide thus effecting oxidative addition to the bis(carbene) complexes.

3. Physical characterization of the azole-derived heterocyclic carbene complexes

Mass spectrometry, infrared spectroscopic measurements and nuclear magnetic resonance chemical shifts have been utilized in the characterization of these carbene complexes. Although the latter reveals the most about the bonding in these substances, molecular ions of most neutral complexes, cations of all cationic mono- and bis(carbene) complexes as well as the molecular ions of the copper 2,3-dihydro-imidazol-2-ylidene and 2,3-dihydro-thiazol-2-ylidene triflates are detectable in the mass spectrometer. Carbonyl infrared vibrations are of interest for the carbonyl compounds (vide infra), and are well described in the literature [5–7].

The carbene carbon in most carbene complexes prepared from thiazoles, isothiazoles and also pyridine resonate at δ ca. 200 ± 10 ppm in ^{13}C-NMR spectra. It is safe to state that the signals for 2,5-dihydro-isothiazol-5-ylidene complexes are found upfield from comparable 2,3-dihydrothiazol-2-ylidenes and that substitution of a thiazolyl group by chloride or iodide in a mono(carbene) complex also effects an upfield shift of the carbene carbon resonance. 2,3-Dihydro-imidazol-2-ylidene and 2,5-dihydro-pyrazol-5-ylidene complexes have their carbene carbon resonance at higher field strength (δ-values of approximately 180 ppm). No significant differences are found between mono- and bis(carbene) complexes in spite of the positive charge difference.

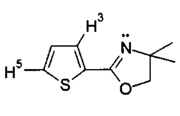
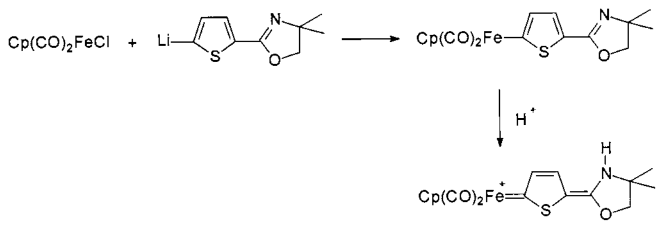


Fig. 5.



Scheme 19.

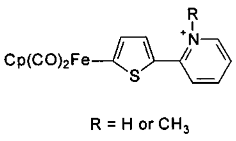


Fig. 6.

It needs to be mentioned that a very small chemical shift difference exists between the coordinated carbon in the carbene complex precursor and the carbene complex itself for gold(I) compounds [15,28]. The carbene complexes derived from thienes (vide infra) differ in this respect. Furthermore, oxidative addition of halogens to bis(carbene) gold(I) complexes results in an upfield chemical shift of the coordinated carbon atoms [47]. This shift is larger for bromide than for chloride. In the trichloro gold compound (Scheme 16) the carbene carbon is shifted $\Delta\delta$ 24.8 ppm upfield with respect to the corresponding monochloro gold(I) compound.

In contrast, for dicarbonyl(cyclopentadienyl)iron(II) complexes (compare reaction no. 5, 11 and 14 in Table 1), significant downfield shifts occur during carbene formation. Shifts of $\Delta\delta$ 24.4 for 4-methylthiazolyl versus 2,3-dihydro-4-methylthiazol-2-ylidene, $\Delta\delta$ 27.4 for benzothiazolyl versus 2,3-dihydro-benzothiazol-2-ylidene, $\Delta\delta$ 25.9 for isothiazolyl versus 2,5-dihydro-isothiazol-2-ylidene and $\Delta\delta$ 19.1 ppm for pyrazolyl versus 2,5-dihydropyrazol-2-ylidene complexes [and concomitant shifts to higher energy for the v(CO) absorption bands] are observed [25,31].

4. Results from crystal structure determinations

Some generalizations based on crystal structure determinations of heterocyclic carbene complexes derived from azoles and pyridine are possible:

1. Metal-C(sp^2) separations for azolyls and dihydroazol-ylidene complexes are similar.
2. All these bond lengths in gold(I) and gold(III) compounds are approximately 2 Å [39,49–51]. Somewhat shorter distances are found in the copper (av. 1.88 Å) [17,18] and iron compounds (av. 1.96 Å) [25,29,31].
3. Intermolecular Au···Au interactions are indicated by distances around 3 Å [52,50,24]. In the compound $[\mathrm{Au}(=\overline{\mathrm{CN(CH_3)CHCHS}})_2]\mathrm{O_3SCF_3}$ two different gold–gold interactions determine the arrangement of the complex ions in the lattice. Alternating Au···Au interactions are characterized by 3.19 and 3.48 Å separations [50].

Calculations using the hybrid HF/DFT Beckes Half-and-Half (BHANDH) and Becke3LYP (B3LYP) methods give structures in close agreement with the crystal structure determinations of gold(I) and gold(III) carbene complexes [47].

5. Carbene complexes derived from thiophene that contains an azolyl functional group

In the context of carbene chemistry and specifically with reference to the transmetallation preparative method, the bifunctional compound, 4′,5′-dihydro-4′,4′-dimethyl-2′-(2-thienyl)oxazoline (Fig. 5), previously utilized by Carpenter and Chadwick [53] for the preparation of coordination compounds, has special significance.

First, it can be deprotonated in the 3 or 5 position (Fig. 5) depending on the solvent and base used. Second, it contains an imine nitrogen atom for coordination or reaction and third, the nitrogen atom is conjugated with both the 3 and 5 carbons of the thiene system and, therefore, mediates carbene formation on protonation or alkylation subsequent to transmetallation.

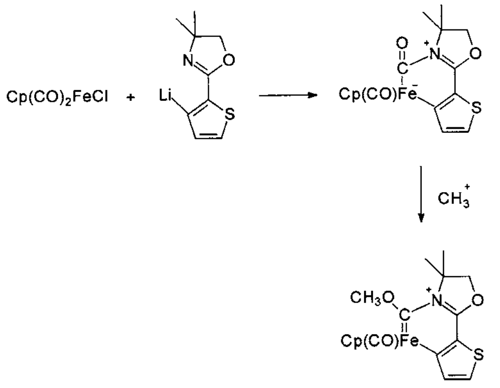
With CpFe(CO)$_2$Cl two product types are formed. 5-Lithiation, transmetallation and protonation afford a cationic organo-thio carbene complex. Protonation takes place on a nitrogen atom in the oxazolinyl ring far removed from the coordinated carbon atom (Scheme 19) [31].

The carbene complex in Scheme 19 resonates at δ 177.4 ppm representing a downfield shift of $\Delta\delta$ 29.3 ppm compared to the neutral precursor complex. Carbene formation is also reflected in 27 and 35 cm^{-1} v(CO) frequency shifts towards higher wavenumbers for the cation. A much smaller ^{13}C-NMR downfield shift of only ca. 10 ppm occurs between similar pyridyl-5-thienyl compounds of iron (Fig. 6) upon protonation or alkylation. It can be concluded that more typical pyridinium salts rather than true carbene complexes are formed.

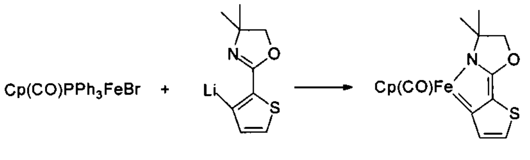
Transmetallation of 2-(4′,5′-dihydro-4′,4′-dimethyloxazoline)-3-thienyllithium with $Cp(CO)_2FeCl$ and nucleophilic attack of the nitrogen atom on a carbonyl ligand affords a heterometallacyclic complex [31]. Alkylation of the six-membered chelate affords a true Fischer-type cyclic carbene complex. Analysis of ^{13}C-NMR data indicates that the resonance structure used in Scheme 20 is the most important one (δ C^3, respectively, 149.7 and 151.7 ppm for the thienyl rings in the two products isolated).

A similar reaction starting with a monocarbonyl(phosphine) complex of iron gives a neutral nitrogen coordinated metal chelate complex by phosphine substitution. Here the coordinated carbon in the thienyl ring exhibits true carbene character (δ 192.4 ppm) (Scheme 21).

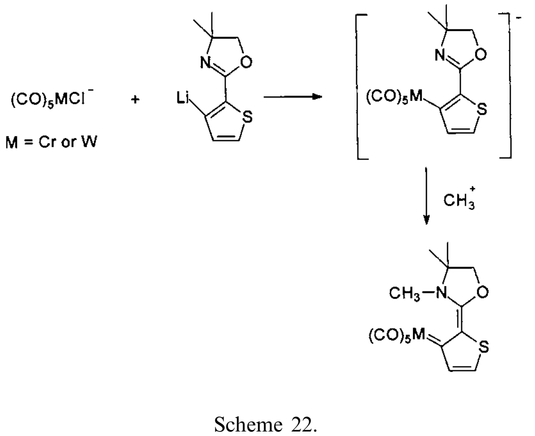
The same reagent can be used to prepare divinylcarbene, complexes of Group 6 metals (Scheme 22) [54].



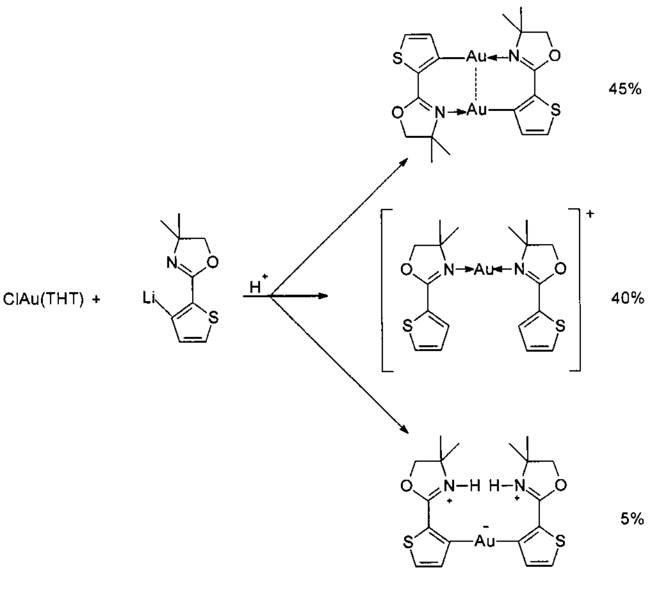
Scheme 20.



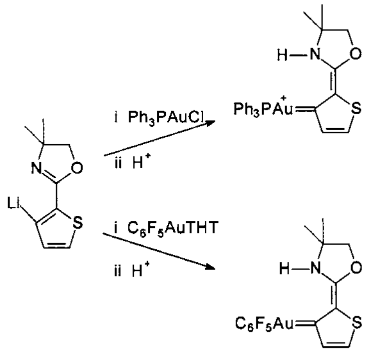
Scheme 21.



Scheme 22.



Scheme 23.



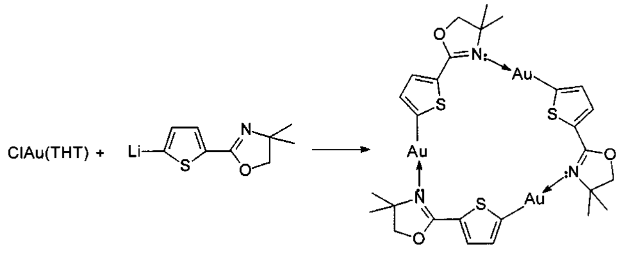
Scheme 24.

Initial attempts to similarly prepare cationic bis(divinylcarbene) complexes of gold from ClAu(THT) were unsuccessful and the reaction mixture (after protonation) contains only 5% of the sought after product (based on NMR studies). It mainly consists of a neutral dimeric gold compound (45%) and a diimine complex (40%), indicating that C rather than N protonation occurred (Scheme 23) [51].

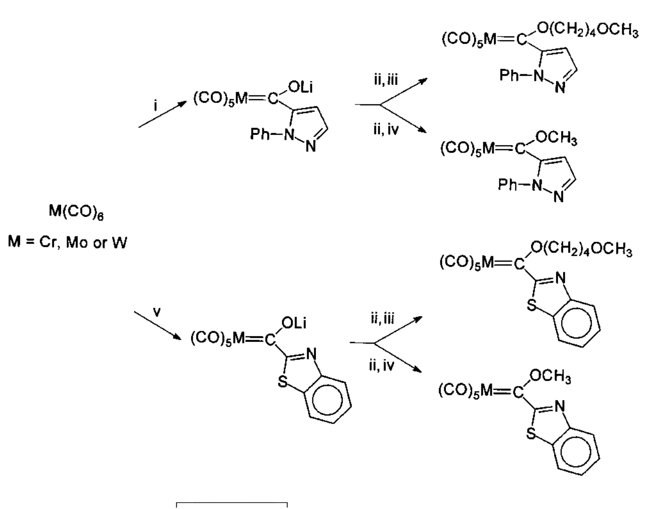
The first isolated diorganogold compounds are formed according to the reactions in Scheme 24 [51].

The two carbene ^{13}C-NMR signals appear at δ 190.9 and 195.5 ppm, respectively. In the neutral precursor to the cationic product formed in the reaction with Ph_3PAuCl, the coordinated carbon has a chemical shift of δ 175.8 ppm. No homoleptic rearrangement occurs in either of these preparations.

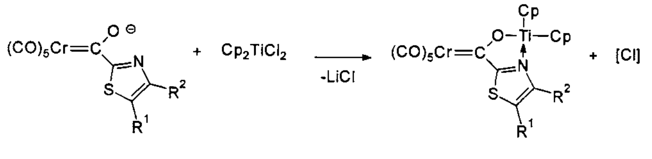
The C^5-lithiated thienyl(oxazoline) cannot not be used for carbene complex preparation with gold(I). Protonation after reaction with $C_6F_5Au(THT)$ occurs on C^5 and an imine complex ensues. With ClAu(THT) a neutral trimeric, 18-membered gold-thienyl complex forms (Scheme 25) that decomposes upon protonation.



Scheme 25.



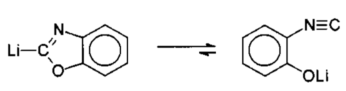
Scheme 26. (i) LiC=CHCHNNPh, (ii) $CF_3SO_3CH_3$, (iii) THF, (iv) CH_2Cl_2, (v) $LiC{=}NC_6H_4S$-*o*.



Scheme 27. R^1R^2 = H, CH_3 or CH_3, CH_3 or CH=CHCH=CH.

6. Fischer-type carbene complexes containing azolyl groups

Since lithium aryls react with metal carbonyls it is not unexpected that lithiated pseudo aromatic compounds will do the same. Pyrazolyllithium or benzothiazolyllithium compounds react with $M(CO)_6$ (M = Cr, Mo or W) to afford neutral carbene complexes after alkylation with $CF_3SO_3CH_3$ or $[(CH_3)_3O]BF_4$ [22,16]. When these reactions are carried out in THF, the alkylating agent first attacks this cyclic ether and generates $CH_3O(CH_2)_4^+$ as an effective alkylating agent (Scheme 26). This reaction is mentioned in a patent [55] but is not reproducible with carbene anions without heterocyclic substituents.



Scheme 29.

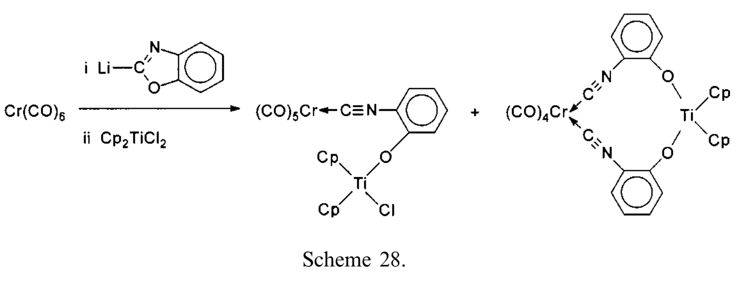
It has previously been shown [56,57] that anionic Fischer-type carbenes can function as ligands towards transition metal complexes leading for example to complexes of the type $(CO)_5Cr[C(OTiCp_2Cl)C_6H_5]$, $(CO)_5$ $Cr[C(OTiCp_2Cl)N(CH_3)_2]$, $(CO)_5Cr\{C[OTi\{C_5(CH_3)_5\}_2Cl]CH_3\}$ and $(CO)_5Cr[C(OZrCp_2Cl)CH_3]$. Recent results obtained in our group show that such complexes containing Zr are active oligomerization catalysts for 1-pentene in the presence of MAO [58].

With a thiazolyl substituent on the carbonyl as in the complexes mentioned above, an unexpected conversion occurs with Cp_2TiCl_2 (Scheme 27). The crystal structure of the paramagnetic Ti(III) product has been determined by X-ray methods [59]. We now believe that the titanium(IV) has been reduced by unreacted thiazolyllithium according to a reaction previously proposed independently by Martin and Jellinek [60] and Atwood [61].

Attempts to replace the thiazolyl group with benzoxazolyl and further reaction with Cp_2TiCl_2 as above, brings one into a dynamic area of chemistry developed by Fehlhammer [20] and more recently carefully extended and studied by Boche [62] and Hahn [63]. The formal CO substitions by the isocyanide tautomer of lithiated benzoxazole is shown in the reactions in Scheme 28 [64].

The ^{13}C-NMR data obtained by Boche and co-workers [62] shows a 95 ± 5% presence of the acyclic isomer in the isomerization equilibrium in Scheme 29. These results can be used to explain the formation of the compounds in Scheme 28.

The oxophilic titanium center plays an integral part in stabilizing the isocyanide form and in preventing carbene formation. The diisocyanide titanoxy complex



Scheme 28.

functions as a bidentate ligand towards chromium in the latter product. The result is somehow reminiscent of the bis(carbene) complex formation when $Cr(CO)_6$ reacts with carbenes derived from imidazoles [5–7,22].

References

[1] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[2] (a) N. Kuhn, T. Kratz, Synthesis, 1993, p. 561. (b) N. Kuhn, J. Fahl, D. Bläser, R. Boese, Z. Anorg. Allg. Chem. 625 (1999) 729.

[3] (a) A.J. Arduengo III, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530. (b) A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese, F. Davidson, Organometallics 12 (1993) 3405. (c) A.J. Arduengo III, F. Davidson, H.V.R. Dias, J.R. Goerlich, D. Khasnis, W.J. Marshall, T.K. Prakasha, J. Am. Chem. Soc. 119 (1997) 12742.

[4] (a) F.E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, Angew. Chem. Int. Ed. Engl. 39 (2000) 541.(b) K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier, P. Kiprof, J. Organomet. Chem. 498 (1995) 1. (c) T. Weskamp, F.J. Kohl, W.A. Herrmann, J. Organomet. Chem. 582 (1999) 362. (d) F.R Kreissl, T. Lehotkay, C. Ogric, E. Herdtweck, Organometallics 16 (1997) 1875.

[5] (a) K. Öfele, J. Organomet. Chem. 12 (1968) P42. (b) K. Öfele, Angew. Chem. 80 (1968) 1032.

[6] K. Öfele, E. Roos, M. Herberhold, Z. Naturforsch. 31b (1976) 1070.

[7] K. Öfele, W.A. Hermann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer, J. Mink, J. Organomet. Chem. 459 (1993) 177.

[8] (a) H.W. Wanzlick, E. Schikora, Angew. Chem. 72 (1960) 494. (b) H.W. Wanzlick, H.J. Kleiner, Angew. Chem. 73 (1961) 493.

[9] (a) M.F. Lappert, Coord. Chem. Rev. 358 (1988) 185. (b) D.J. Cardin, B. Cetinkaya, E. Cetinkaya, M.Y. Lappert, J. Chem. Soc. Dalton Trans. (1973) 514.

[10] (a) P.J. Fraser, W.R. Roper, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1974) 761. (b) C.H. Game, M. Green, F.G.A. Stone, J. Chem. Soc. Dalton Trans. (1975) 2280.

[11] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.

[12] W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2162.

[13] A.J. Arduengo III, R. Krafczyk, Chem. Unserer Zeit 32 (1998) 6.

[14] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 375 (1989) 147.

[15] F. Bonati, A. Burini, B.R. Pietroni, B. Bovio, J. Organomet. Chem. 408 (1991) 271.

[16] H.G. Raubenheirner, G.J. Kruger, A. van A. Lombard, L. Linford, J.C. Viljoen, Organometallics 4 (1985) 275.

[17] H.G. Raubenheimer, S. Cronje, P.H. van Rooyen, P.J. Olivier, J.G. Toerien, Angew. Chem. Int. Ed. Engl. 33 (1994) 672.

[18] H.G. Raubenheimer, S. Cronje, P.J. Olivier, J. Chem. Soc. Dalton Trans. (1995) 313.

[19] H.G. Raubenheimer, S. Cronje, G.J. Kruger, P.J. Olivier, Polyhedron 14 (1995) 2389.

[20] (a) K. Bartel, W.P. Fehlhammer, Angew. Chem. Int. Ed. Engl. 13 (1974) 599. (b) U. Plaia, H. Stolzenberg, W.P. Fehlhammer, J. Am. Chem. Soc. 107 (1985) 2171. (c) W.P. Fehlhammer, M. Fritz, Chem. Rev. 93 (1993) 1243.

[21] H.G. Raubenheimer, S. Cronje, in: H. Schmidbaur (Ed.), Gold: Progress in Chemistry, Biochemistry and Technology, Gold Halides, Pseudohalides and Related Compounds, Wiley, London, 1999, p. 615.

[22] H.G. Raubenheimer, Y. Stander, E.K. Marais, C. Thompson, G.J. Kruger, S. Cronje, M. Deetlefs, J. Organomet. Chem. 590 (1999) 158.

[23] H.G. Raubenheimer, F. Scott, M. Roos, R. Otte, J. Chem. Soc. Chem. Commun. (1990) 1722.

[24] H.G. Raubenheimer, F. Scott, G.J. Kruger, J.G. Toerien, R. Otte, W. van Zyl, I. Taljaard, P. Olivier, L. Linford, J. Chem. Soc. Dalton Trans. (1994) 2091.

[25] H.G. Raubenheimer, F. Scott, S. Cronje, P.H. van Rooyen, K. Psotta, J. Chem. Soc. Dalton Trans. (1992) 1009.

[26] A. Neveling, M.Sc. Thesis, University of Stellenbosch, 1999, p 73.

[27] H.G. Raubenheimer, M. Desmet, J. Chem. Res. (S) (1995) 30.

[28] H.G. Raubenheimer, L. Lindeque, S. Cronje, J. Organomet. Chem. 511 (1996) 177.

[29] J.G. Toerien, M. Desmet, G.J. Kruger, H.G. Raubenheimer, J. Organomet. Chem. C 479 (1994) C12.

[30] H.G. Raubenheimer, M. Desmet, G.J. Kruger, J. Chem. Soc. Dalton Trans. (1995) 2067.

[31] H.G. Raubenheimer, M. Desmet, P. Olivier, G.J. Kruger, J. Chem. Soc. Dalton Trans. (1996) 4431.

[32] G. Boche, C. Hilf, K. Harms, A Marsch, J.C.W. Lohrenz, Angew. Chem. Int. Ed. Engl. 34 (1995) 487.

[33] C. Hilf, F. Bosold, K. Harms, J.C.W. Lohrenz, M. Marsch, M. Schimeczek, G. Boche, Chem. Ber. 130 (1997) 1201.

[34] See Ref. [21], p 608.

[35] (a) H. Schmidbaur, A. Grohmann, M.E. Olmos, A. Schier, in: S. Patai, Z. Rappoport (Eds.), The chemistry of organic derivatives of gold and silver, Wiley, Chichester, 1999, p 227. (b) H. Schmidbaur, in: A. Slawisch (Ed.), Gmelin Handbuch der Anorganischen Chemie, Organogold Compounds, Springer Verlag, Berlin, 1980, p 169.

[36] S. Komiya, S. Meguro, A. Shibue, S. Ozki, J. Organomet. Chem. 328 (1987) C40.

[37] L.G. Vaughan, J. Am. Chem. Soc. 92 (1970) 730.

[38] P. Jutzi, H. Hensler, J. Organomet. Chem. 114 (1976) 265.

[39] H.G. Raubenheimer, J.G. Toerien, G.J. Kruger, R. Otte, W. van Zyl, P. Olivier, J. Organomet. Chem. 466 (1994) 291.

[40] H.G. Raubenheimer, S. Cronje, in: H. Schmidbaur (Ed.), Gold: Progress in Chemistry, Biochemistry and Technology, Gold Halides, Pseudohalides and Related Compounds, 1999, p. 603 and references therein.

[41] H.G. Raubenheimer, M. Desmet, L. Lindeque, J. Chem. Res. (S) (1995) 184.

[42] M. Desmet, Ph.D. Thesis, Rand Afrikaans University, 1996, p 146.

[43] G. Minghetti, F. Bonati, J. Organomet. Chem. 54 (1973) C62.

[44] G. Minghetti, F. Bonati, G. Banditelli, Inorg. Chem. 15 (1976) 1718.

[45] R. Usón, A. Laguna, J. Vicente, J. García, B. Bergareche, P. Brun, Inorg. Chim. Acta 28 (1978) 237.

[46] R. Usón, A. Laguna, Coord. Chem. Rev. 70 (1986) 1.

[47] H.G. Raubenheimer, P.J. Olivier, L. Lindeque, M. Desmet, J. Hrušak, G.J Kruger, J. Organomet. Chem. 544 (1997) 91.

[48] P. Kühlkamp, H.G. Raubenheimer, J.S. Field, M. Desmet, J. Organomet. Chem. 552 (1998) 69.

[49] G.J. Kruger, P.J. Olivier, L. Lindeque, H.G. Raubenheimer, Acta Crystallogr. Sect. C 51 (1995) 1814.

[50] G.J. Kruger, P.J. Olivier, H.G. Raubenheimer, Acta Crystallogr. Sect. C 52 (1996) 624.

[51] M. Desmet, H.G. Raubenheimer, G.J. Kruger, Organometallics 16 (1997) 3324.

[52] G.J. Kruger, P.J. Olivier, R. Otte, H.G. Raubenheimer, Acta Crystallogr. Sect C 52 (1996) 1159.

[53] A.J. Carpenter, D.J. Chadwick, J. Chem. Soc. Perkin Trans. 1 (1985) 175.

[54] Y. Stander, M. Sc. Thesis, Rand Afrikaans University, 1996, p 110.

[55] A. Yamashita, H.G. Johnson, US Patent No. 4 737 519 A, 1988.
[56] H.G. Raubenheimer, E.O. Fischer, J. Organomet. Chem. 91 (1975) C23.
[57] E.V. Anslyn, B.D. Santarsiero, R.H. Grubbs, Organometallics 7 (1988) 2137.
[58] A. Neveling, M.Sc. Thesis, University of Stellenbosch, 1999, p 54.
[59] L. van Niekerk, M.Sc. Thesis, University of Stellenbosch, 2000, p 51.
[60] (a) H.A. Martin, F. Jellinek, J. Organomet. Chem. 8 (1967) 115. (b) H.A. Martin, F. Jellinek, J. Organomet. Chem. 12 (1968) 149.
[61] J.L. Atwood, G.K. Barker, J. Holton, W.E. Hunter, M.F. Lappert, R. Pierce, J. Am. Chem. Soc. 99 (1977) 6645.
[62] C. Hilf, F. Bosold, K. Harms, M. Marsch, G. Boche, Chem. Ber. 130 (1997) 1213.
[63] (a) F.E. Hahn, M. Tamm, J. Chem. Soc. Chem.Comm. (1993) 482. (b) F.E. Hahn, M. Tamm, T. Lügger, Angew. Chem. Int. Ed. Engl. 33 (1994) 1419. (c) M. Tamm, T. Lügger, F.E. Hahn, Organometallics 15 (1996) 1251. (d) M. Tamm, F.E. Hahn, Coord. Chem. Rev. 182 (1999) 175.
[64] L. van Niekerk, M.Sc. Thesis, University of Stellenbosch, 2000, p 123.