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Anatomy of gold catalysts: facts and myths

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This review article covers the main types of gold(I) complexes used as precatalysts under homogeneous conditions in organic synthesis and discusses the different ways of catalyst activation as well as ligand, silver, and anion effects.

1. Introduction

Although a few reports were already published in the thirties on the chlorination of arenes catalysed or mediated by AuCl and $AuCl_3$,[1,2] the first important application of gold(I) complexes in homogeneous catalysis, namely the formation of acetals by addition of methanol to alkynes, was reported by the group of Teles less than 20 years ago.[3] Since then, homogeneous gold catalysis has seen an almost exponential growth leading to the development of many synthetic transformations[4] of considerable importance for the build-up of complex molecular systems.[5]

Although much is known about the basic mechanisms for the activation of unsaturated functional groups, such as alkynes and allenes,[6] there is still a need to more clearly understand the mechanisms of reactions catalysed by gold(I) and gold(III) in order to develop more efficient and selective transformations. This is particularly important in the case of enantioselective gold catalysis, an area in which very little rational design has been reported to date. Furthermore, most of the gold-catalysed reactions are carried out by using stable linear dicoordinated chloride gold(I) complexes [LAuCl], where L is a phosphine or other donating ligand, which are precatalysts that have to be activated by chloride abstraction, leading to species that are often formulated as monocoordinated $[LAu]^+$ complexes. However, no structural proof of the existence of these coordinatively unsaturated d^{12} electron species has yet been obtained.

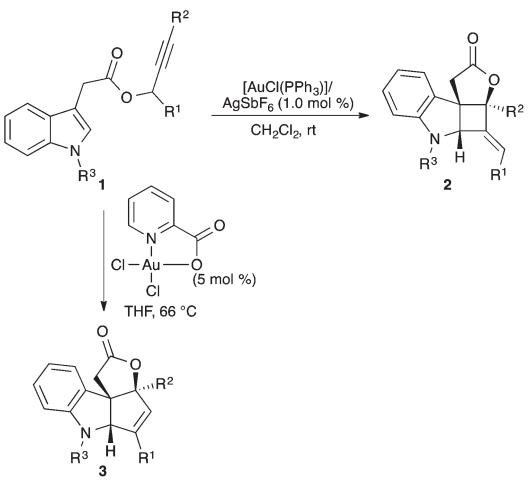
There is also some confusion regarding the particular role of silver(I) salts, often used as co-catalysts, which has led to invoke the so-called "silver effects" in gold(I) catalysis.

This review article covers, mainly from a personal experience, known facts and discusses some "myths" about ligand and counterion effects[7] on gold catalysis, as well as the different activation modes commonly used to generate active species from a stable precatalyst.

2. Gold(I) *vs.* gold(III) catalysis

Most gold-catalysed reactions rely on the use of stable gold(I) precatalysts, whereas gold(III) complexes have been less explored.[8] Switching from gold(I) to gold(III) can have a profound effect, even leading to divergent reaction pathways. This is well exemplified in the reaction of indole **1** with [(PPh_3)-AuCl] in the presence of $AgSbF_6$, which leads to indolenine-fused cyclobutane **2** by a formal [2 + 2] cycloaddition between the indole and an allene formed *in situ*, whereas the use of dichloro(pyridine-2-carboxylato)gold(III) gave **3**, a product of a [3 + 2] cycloaddition (Scheme 1).[9]

A dramatic effect in the reaction outcome was also found in the cyclisation of alkynyl-substituted indoles **4** (Scheme 2).[10] By using gold(I) catalysts, a 7-*exo-dig* cyclisation led to **5**, whereas $AuCl_3$ gave indoloazocines **6** by a formal 8-*endo-dig* cyclisation. Here, it is important to note that the AuCl also provided indo-



Scheme 1 Reactivity of gold(I) *versus* gold(III) in the cyclisation of indole **1**.

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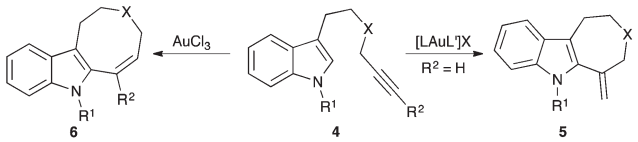
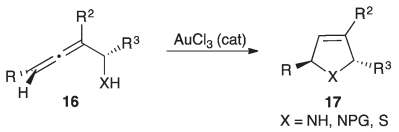


Scheme 2 Formation of seven- and eight-membered indole-fused rings using gold(I) and gold(III).



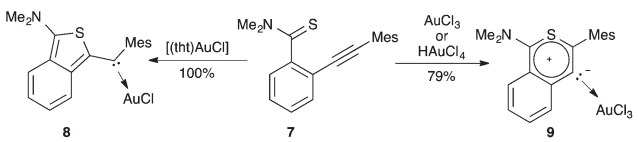
Scheme 5 Gold(III) as a precatalyst in the cycloisomerization of α-amino and α-thioallenes.

loazocines **6**, although the isolated yields were slightly lower. This suggests that chloride as the ligand, more than the oxidation state of the actual catalytic species, is responsible for this change in the cyclisation mode, which has also been observed in the cycloisomerisation of alkynyl cycloheptatrienes.[11]

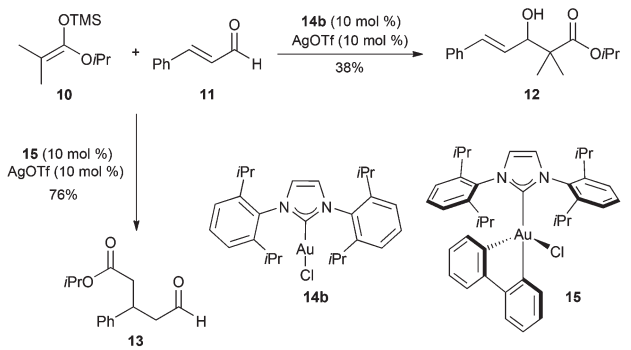
Divergent cyclisation modes were also observed by treating the alkynyl benzothioamide **7** with gold(I) or gold(III), leading to acyclic (aryl)(heteroaryl)carbene gold complex **8** or mesoionic carbene complex **9** respectively (Scheme 3).[12]

The different reactivity found in the reaction between ketene acetal **10** and cinnamaldehyde **11** depending on the oxidation state of the gold catalyst is significant (Scheme 4).[13] Thus, whereas NHC-gold(I) **14b** activated by AgOTf promotes formation of Mukaiyama aldol product **12** by a 1,2-addition, the new gold(III) complex **15** leads to the products of 1,4-addition **13**, in a Mukaiyama–Michael reaction.

In many cases, it is clear that gold(III) salts act as precatalysts that are reduced *in situ* to gold(I),[14] as in the cycloisomerization of α-amino and α-thioallenes **16** to the corresponding 3-pyrrolines and 2,5-dihydrothiophenes **17**, which are most likely catalysed by gold(I) (Scheme 5).[14b,c] The reduction of gold(III) salts to gold(I) takes place with a variety of easily oxidized functional groups, including alcohols[15] and can also take place by a photoinduced electron transfer process.[16]



Scheme 3 Formation of carbenes promoted by gold(I) and gold(III) by 5-*exo*-*dig* or 6-*endo*-*dig* ring closure.



Scheme 4 Different reactivities of NHC gold(I) and gold(III) complexes.

In this context, it may be important to recall that gold(III) salts react with water to form aquo complexes that are Brønsted acids.[17] Cationic gold(I) complexes also coordinate with water[18] or alcohols[19] to form $[LAu(ROH)]^+$ species, or related dinuclear complexes, in which the Lewis acid significantly enhances the Brønsted acidity of ROH.

3. Gold(I) precatalysts

In the early years of gold catalysis, gold(I) as well as gold(III) were mainly used as the chloride salts. However, it was soon realised that ligands play a fundamental role in modulating the reactivity of gold(I) catalysts in the activation of alkynes, allenes, and alkenes.[4–6] In many cases, the careful choice of the ligand is essential to achieve the desired reactivity.

The vast majority of gold(I) complexes show a linear dicoordination,[20] although higher coordination numbers (3 or 4) are also possible.[21] In general, gold(I) complexes with donating ligands that are sterically hindered are the most useful catalysts. Although many phosphine–gold(I) complexes have been prepared,[22] probably the most successful are complexes of commercially available bulky dialkyl biphenyl phosphines, a type of ligands that were initially developed for Pd-catalysed C–C and C–X cross-coupling reactions.[23] Thus, gold(I) complexes such as **18a–d**[24] are very common precatalysts that need to be activated by chloride abstraction with a silver salt to generate active catalysts. Cationic complexes **19a–c** are obtained as stable white salts and are often more convenient catalysts since reactions can be carried out in the absence of silver(I) salts.[25] These complexes bear acetonitrile as a relatively weak coordinating ligand, which has to be replaced by the reactive substrate *via* π-coordination to enter the productive catalytic cycles. Closely related complexes **20a–c** with a weakly coordinating bis(trifluoromethanesulfonyl)amide ligand show similar reactivity (Fig. 1).[26]

The possible existence of a stabilizing arene–gold(I) interaction in complexes **18–20** was studied by comparing the structure of complex **19c** with isoleptic silver(I) and copper(I) complexes **21a–b** (Fig. 2).[27] As expected, the metal–ligand distances decrease in the order Ag > Au > Cu. More interesting is the very significant difference that was observed in the P–M–NCMe angles, from an almost linear coordination for gold(I) complex **19c** (173.1°) to more bent structures for silver and copper complexes **21a** (168.0°) and **21b** (148.8°). Moreover, the closest metal–arene distance for **19c** was much larger (3.04 Å) than that in **21a** (2.89 Å) or **21b** (2.48 Å), the latest two values

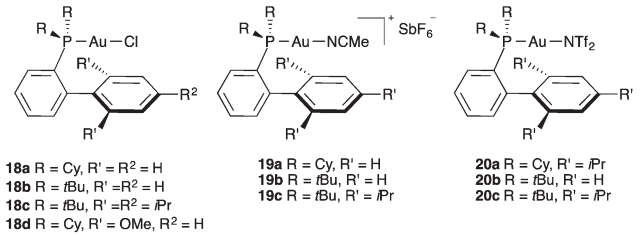


Fig. 1 Gold(I) complexes **18–20** with dialkyl biphenyl phosphine ligands.

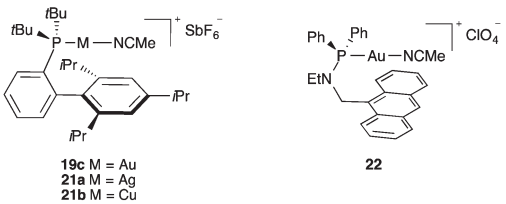


Fig. 2 Isoleptic gold(I), silver(I) and copper(I) complexes **19c**, and **21a–b** and complex **22**.

being characteristic of significant metal–arene interactions. Additional theoretical studies confirmed that in the case of gold(I) complexes of type **19**, the metal centre does not interact significantly with the closest arene ring.[27] Complex **22** and related anthracene complexes show the closest Au–arene distances between 2.96 and 3.246 Å,[28] much longer than those found in well-characterized arene–gold(I) complexes. Very weak interactions were observed in a gold(I) complex related to **19c** but with a pyrimidinium betaine at the *ortho* position.[29]

Well-characterized gold(I)–arene complexes have been found to have the usual linear coordination around gold(I). Thus, cationic η^1/η^2 complexes of type **23** were prepared by exchange of the acetonitrile ligand in complexes of type **19** in an aromatic solvent and were shown to have the shortest Au–arene distances (2.20–2.24 Å) (Fig. 3).[25,27] A similar benzene complex **24** with a sterically demanding cyclic (alkyl)-(amino) carbene showed slightly longer Au–arene distances (2.32–2.34 Å).[30]

The highest electrophilicity is achieved with gold(I) complexes such as **25a–b** with less donating phosphite ligands (Fig. 4).[31] Although less commonly employed, these complexes proved to be far superior to phosphine and NHC-derived gold catalysts for the activation of the less reactive substrates and for enhancing the carbocationic character of the reactive intermediates in the addition of C-nucleophiles of 1,6-enynes[32] and in other processes.[33–37] Other related highly electrophilic complexes have also been developed.[38,39]

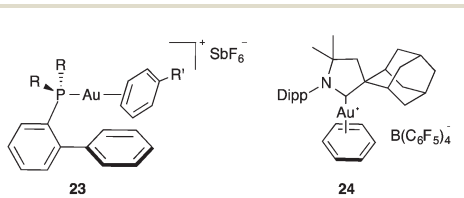


Fig. 3 Arene-gold(I) complexes.

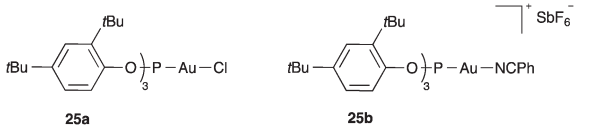


Fig. 4 Phosphite gold(I) complexes.

A variety of chiral mono- and dinuclear phosphine, phosphite, and phosphoramidite gold complexes **26–34** have been developed for the enantioselective activation of alkynes and allenes (Fig. 5).[40–54]

Another important class of gold(I) catalysts bears N-heterocyclic carbenes (NHC), which are two-electron donor bulky ligands with strong σ-donating properties. Gold(I) complexes with highly donating NHC ligands are usually less electrophilic than those with less-electron-donating phosphine ligands, which makes these catalysts more selective in many transformations.[55,56] Complexes of type [(NHC)AuCl] (**14**) can be prepared from the free carbenes[57] or *via* the corresponding silver(I) complexes by transmetalation[58] (Scheme 6). Recently a more

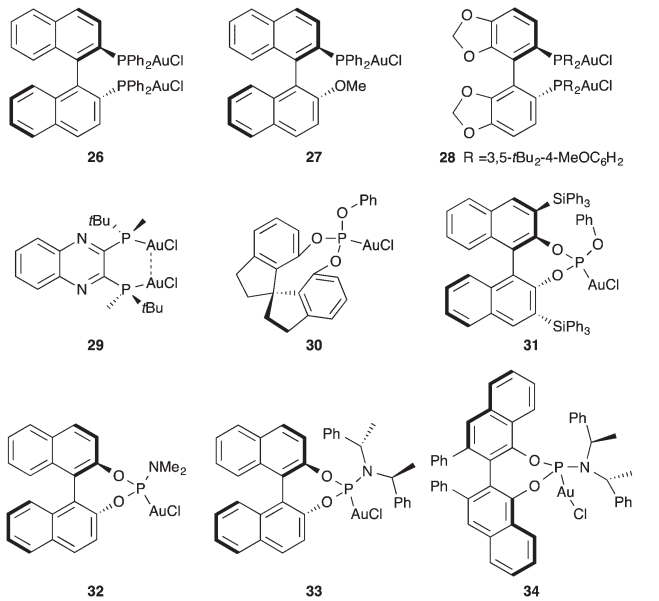
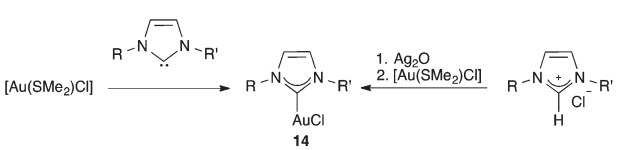


Fig. 5 Representative chiral gold(I) complexes used in enantioselective catalysis.



Scheme 6 Preparation of complexes [(NHC)AuCl].

direct method of synthesis of complexes **14** has been developed from imidazolium salts, which bypasses the preparation of free carbenes by using K_2CO_3 as the base.[59]

By using these procedures, many stable cationic NHC complexes have been prepared.[55,60] In particular, cationic complexes such as **35a–b**,[32] and IPr or IMes neutral complexes with NTf_2 ligands **36a–b**[61] have found widespread applications in homogeneous gold(I)-catalysis (Fig. 6).[62] It is important to recall that the first application of NHC-gold(I) complexes in catalysis was reported in 2003 by Herrmann and co-workers, who showed that one of these complexes was moderately active in the hydration of 3-hexyne to form ketone 3-hexanone.[63]

Complexes **37a–b** with nitrogen acyclic gold(I) carbenes (NAC), readily prepared by the addition of amines to isocyanide gold(I) complexes, have also been prepared and used in catalysis.[64,65] Rotational barriers around the NAC-gold(I) bond have been used to determine the extent of π-back donation of a series of X and L ligands in [(NAC)AuX] and $[(NAC)AuL]^+X^-$ complexes.[66] Chiral complexes **38–41** have also been applied for several gold(I)-catalysed enantioselective transformations (Fig. 7).[67–70]

An interesting class of chiral gold(I) carbene complexes is represented by **42a–b** with axially chiral triazoloisoquinolin-3-ylidene ligands, which have been applied in the enantioselective [2 + 2] cycloaddition of allenamides with dienes

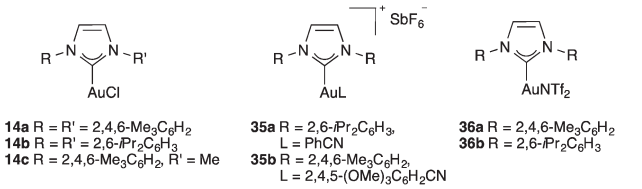


Fig. 6 Representative N-heterocyclic carbene gold(I) complexes.

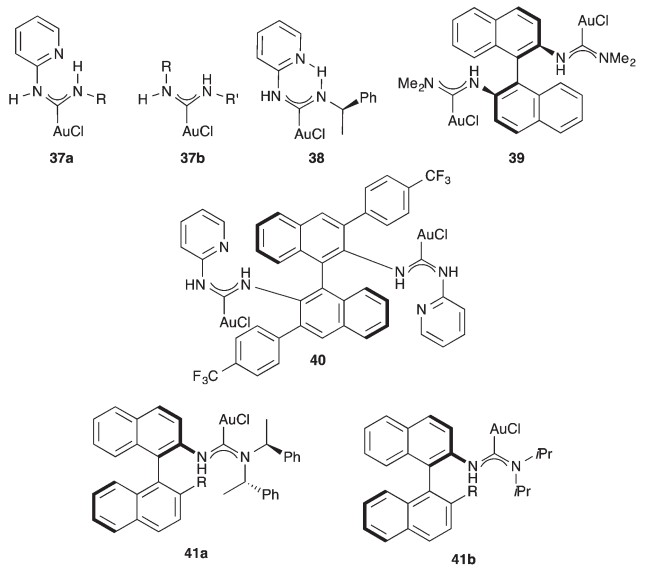


Fig. 7 Acyclic N-heterocyclic carbene gold(I) complexes.

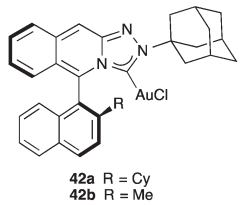
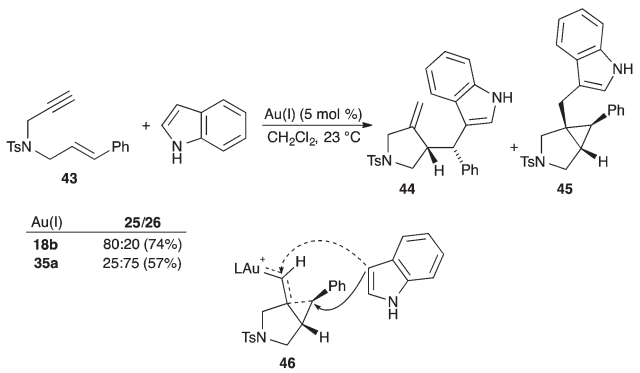


Fig. 8 Chiral N-heterocyclic carbene gold(I) complex.

(Fig. 8).[71] Similarly, other axially chiral NHC-Au(I) complexes have been developed and applied to the asymmetric acetoxycyclization and symmetric oxidative rearrangement of 1,6-enynes.[72]

There are numerous instances in which the selectivity of the reaction can be controlled by the ligand on gold.[4] In a particularly illustrative example, the attack of indole to 1,6-enyne **43** was found to give two adducts **44** and **45** in ratios dependent on the gold(I) complex used as the catalyst (Scheme 7).[32] Adduct **44** became the major product when phosphine gold(I) complex **18b** was used, whereas **45** was the major one with complex **35a** with IPr as the ligand. This different reactivity can be explained by the attack of indole onto the carbene centre of intermediate **46**, which has a carbene-like character due to the higher electron-donating ability of the NHC ligand, while the corresponding intermediate with a phosphine ligand formed using catalyst **18b** possesses a more carbocationic-like character, favouring attack at the benzylic position.

Triazole gold(I) complexes **47–49** have recently been introduced as thermally stable catalysts[73] applied for a variety of synthetic applications[74] (Fig. 9).



Scheme 7 Change in the reaction outcome due to different ligands.

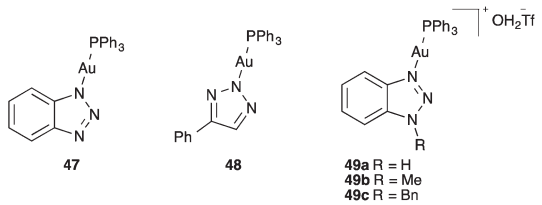
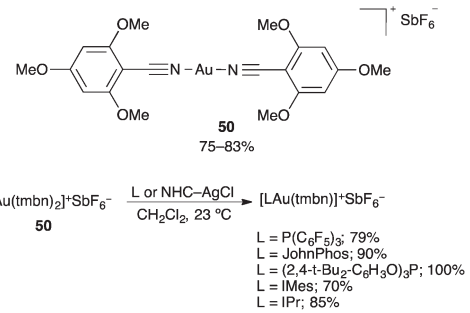


Fig. 9 Triazole gold(I) complexes.



Scheme 8 Precatalyst $[Au(tmbn)_2](SbF_6)$ and generation of active catalysts $[LAu(tmbn)]SbF_6$.

A multipurpose gold(I) precatalyst $[Au(tmbn)_2](SbF_6)$ **50** has been developed with the electron-donating nitrile 2,4,6-trimethylmethoxybenzonitrile as a ligand (tmbn) (Scheme 8).[75] A variety of active catalysts $[LAu(tmbn)]SbF_6$ and $[(L–L)Au_2(tmbn)_2](SbF_6)$ were readily prepared from air-stable precursor **50** by simple ligand substitution with mono- and bidentate ligands. Recently the (η^2-alkyne) complex η^2-alkyne gold(I) complex $[(Ph_3P)Au(t\text{BuC}{\equiv}\text{C}t\text{Bu})]SbF_6$, has been used as a catalyst in some gold-catalysed transformations.[76]

All the above-mentioned precatalysts for the activation of alkynes and other unsaturated functional groups are linear dicoordinated chloride gold(I) complexes [LAuCl]. An interesting different class of tricoordinated gold(I) complexes **51a–b** with *o*-carborane diphosphines has been reported by the group of Bourissou (Fig. 10).[77] Although the application of these complexes for the activation of alkynes has not been reported, these complexes undergo facile oxidative addition with aryl iodides in the presence of $GaCl_3$ or $AgNTf_2$,[77a] a reaction that does not take place with linear complexes [LAuCl].[78] Bulky P,N-ligands such as 4-(2-(diadamanthylphosphanyl)-phenyl)morpholine (Mor-Dalphos) have also been proposed to act as bidentate ligands in certain gold(I)-catalysed reactions.[79]

Complexes **52a–b** have been shown to be more catalytically active than Johnphos gold(I) complex **19b** in the intramolecular [4 + 2] cycloaddition of arylalkynes with alkenes (Fig. 11).[80] These complexes have a *Z*-type boryl ligand, although the Au–B bond distances in the solid state (3.55–3.62 Å) indicate that this interaction is weak. Complex **53** with another *Z*-type boryl ligand is also catalytically active in the cyclisation of enynes.[81] In this last case, presumably a

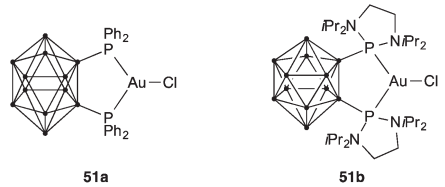


Fig. 10 Tricoordinated gold(I) complexes with *o*-carborane diphosphines.

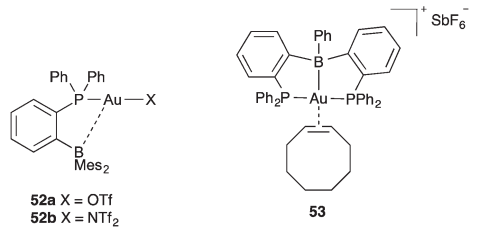


Fig. 11 Tricoordinated gold(I) complexes with *o*-carborane diphosphines.

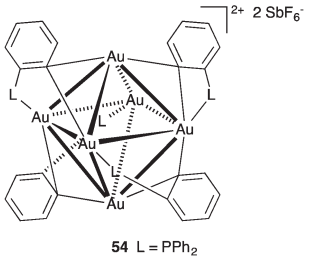


Fig. 12 Catalytically active hexanuclear gold(I) cluster.

stronger interaction exists, as shown in the parent neutral complex with the chloride ligand, which displays a much shorter Au–B bond distance (2.34 Å).

Interestingly, a hexanuclear gold(I) cluster **54** supported by only four phosphine ligands has also been found to be able to activate a variety of alkynyl substrates (Fig. 12).[80]

4. Ligand substitution and activation of gold(I) complexes

Linear dicoordinated gold(I) complexes [LAuX] undergo ligand substitutions by associative mechanisms,[82–88] an aspect that is often overlooked in mechanistic discussions. The alternative dissociative processes would generate a coordinatively unsaturated $[LAu]^+$ cation, which is unlikely under mild conditions. Thus, for example, high energies of activation (78–82 kcal mol^{-1}) have been calculated for chloride dissociation in a series of [(NHC)AuCl] complexes.[89]

In general, commonly used linear dicoordinated chloride gold(I) complexes [LAuCl] are poorly reactive in reactions towards unsaturated substrates and require activation by a silver(I) salt to form insoluble AgCl.[90] There are however instances in which direct dissociation of a chloride anion has been claimed to take place from [LAuCl], although neither structural nor kinetic evidence has yet been provided. Thus, a recent report describes the hydration of terminal alkynes with [(IPr)AuCl] and related complex catalysts which takes place at 110–120 °C for 6–12 h in MeOH–H_2O.[91] However, it is important to remember that the hydration and the analogous alkoxycyclisation of alkynes take place under much milder

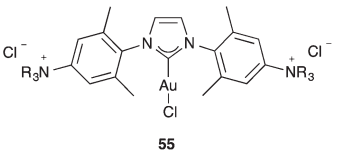


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Fig. 13 Ammonium salt-tagged NHC-gold(I) complexes.

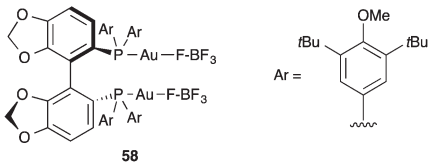

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Fig. 14 Structure of the dicationic complex with tetrafluoroborate anions.

conditions for complexes [LAuX] with less strongly coordinating anions such as tosylates, triflates, or triflimides.[92–94]

It is also somewhat puzzling that ammonium salt-tagged [(NHC)AuCl] complexes **55** (Fig. 13), which are water soluble, are catalytically active in the cyclisation of hydroxy allenes despite the presence of a strongly coordinating chloride anion as the ligand.[95] At very high concentrations inside self-assembled nanospheres, [LAuCl] complexes have also been found to catalyse the intramolecular addition of alcohol to an allene to form a dihydrofuran and the single-cleavage rearrangement of a 1,6-enyne.[96]

Although the structure of most complexes used in homogeneous gold(I) catalysis has been determined by X-ray diffraction, still some uncertainties remain on the structure of the actual catalytically active species that are generated *in situ* by chloride abstraction using different silver salts. This is particularly important in the case of chiral binuclear complexes, where the mono- or dicationic species can actually lead to very different enantioselectivities.[41]

Even in a very crowded environment, complex **56** with a very bulky NHC ligand (IPr**) reacts with $AgNTf_2$ to form neutral species **57** with a covalently bound triflimide ligand (Scheme 9).[97] However, a coordinatively unsaturated species $[LAu]^+BAr^{F-}{}_4$ was proposed to form upon treatment of complex **56** with $NaBAr^{F-}{}_4$ although no structural proof was given for the resulting cationic species.[98]

In this regard, it is important to mention the structure of dicationic digold(I) complex **58**, which was shown to have a covalent structure with the tetrafluoroborate anions bound to the gold(I) centres (Au–F bond distances of approximately 2.1 Å) (Fig. 14).[53] The same structure was retained in solution for **58** and the corresponding bis-perchlorate complex according to DOSY ^{1}H NMR experiments. This result is rather significant, considering that in the series $[R_3PAu–X]$, tetrafluoroborate was found to have the lowest dissociation energy: $CF_3CO_2^- > Cl^- > NO_3^- > TsO^- > TfO^- > BF_4^-$,[99] which points to related covalent structures for many species that are often formulated as ionic species $[LAu]^+X^-$ without structural proof.

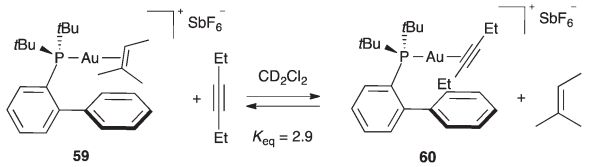
Ligand exchange in well-characterized η^2-alkyne-,[100,101] η^2-alkene-,[102–104] η^2-(1,3-diene)-,[105] and η^2-allene-gold(I) complexes[106,107] takes place by associative mechanisms. Equilibrium constants for ligand substitution in several synthetically important phosphine and NHC gold(I) complexes have been determined in solution.[108] In solution, both alkenes and alkynes coordinate to gold(I), although alkynes are always selectively activated under homogeneous conditions. This high selectivity for alkynes (alkynophilicity) has mainly a kinetic origin, driven by the very low LUMO of the coordinated triple carbon–carbon bond.[109] In general, alkynes coordinate more tightly to gold(I) than do alkenes as shown in the equilibrium between complexes **59** and **60** (Scheme 10), although the differences in binding affinities are low.[100a,110]

In catalytic cycloisomerizations of 1,6-enynes, the kinetic data are also consistent with associative ligand substitution between $[LAu(product)]^+$ and $[LAu(substrate)]^+$ which is the rate-determining step.[111]

Cationic gold(I) species have also been generated by protonolysis of the Au–Me bond in [LAu(Me)] complexes with a strong acid such as methanesulfonic acid, fluoroboric acid, trifluoroacetic acid, or phosphotungstic acid.[112,113] However, it is important to mention that the strong Brønsted acids are not innocent in the presence of alkynes and other unsaturated functional groups and could therefore lead to undesired side reactions. As an alternative, monomeric gold(I) hydroxide complex [(IPr)AuOH] **61**, obtained by treating the neutral complex [(IPr)AuCl] **14b** with KOH,[114] can be activated in the presence of Brønsted acids to form cationic dinuclear hydroxy-gold(I) complex **62** (Scheme 11).

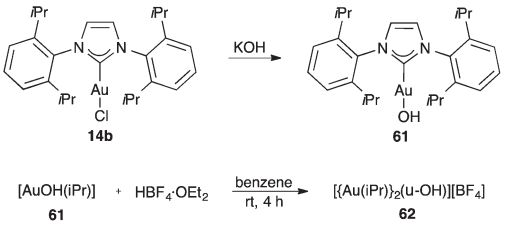
56 R = *p*-*t*BuC$_6$H$_4$ 57 R = *p*-*t*BuC$_6$H$_4$

Scheme 9 Complex **56** with very bulky IPr** ligand and complex **57**.

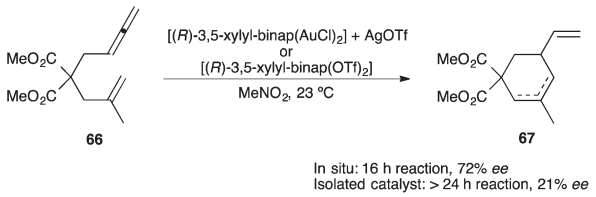


59 60

Scheme 10 Ligand substitution in dialkyl biphenyl phosphine gold(I) complexes.



Scheme 11 Preparation and activation of [(IPr)AuOH] precatalyst.



Scheme 13 The effect of silver(I) on catalytic enantioselective cycloisomerization of enallenes.

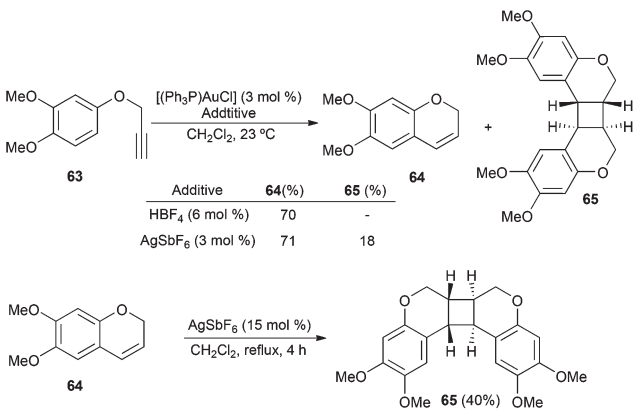
5. On the silver effect

Treatment of [LAuCl] with a stoichiometric amount of a non- or weakly coordinating silver salt AgX is the standard procedure for the *in situ* formation of the active catalyst. In some instances using a high loading of AgX was beneficial.[115]

It is also important to mention that silver salts such as AgOTf used as the chloride abstractors can react with 1,2-dichloroethane, a commonly used solvent in gold(I) catalysis, leading to the formation of triflic acid, which could be the actual catalyst (hidden Brønsted acid catalysis).[116]

Furthermore, silver(I) salts are not totally innocent in gold catalysis. One of the first examples was found in the context of the intramolecular hydroarylation of **63** catalysed by gold(I) to give rise to 2-*H*-chromene **64** (Scheme 12).[117] When **63** was treated with [(Ph_3P)AuCl] and HBF_4, product **64** was formed exclusively. However, by using [(Ph_3P)AuCl] and $AgSbF_6$, dimeric **65** was isolated along with **64**. This [2 + 2] cycloaddition was found to be a silver(I)-catalysed process.

Interestingly, different enantioselectivities were obtained in the cycloisomerization of enallene **66** depending on the manner of activation of the chiral precatalyst (Scheme 13).[118] When the reaction was carried out by using isolated [(*R*)-3,5-xylyl-binap($AuOTf)_2$], product **67** was obtained with much lower enantioselectivity than when the catalyst was generated *in situ* from [(*R*)-3,5-xylyl-binap($AuCl)_2$] and AgOTf.



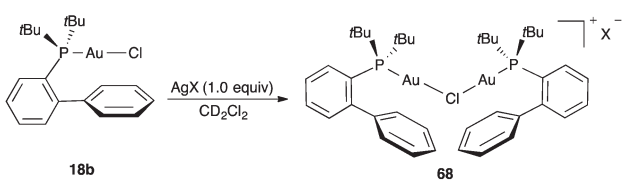
Scheme 12 Gold(I)-catalysed formation of 2-*H*-chromenes and the corresponding dimer.

Several inconsistencies in the experimental results depending on the different procedures used for the activation of neutral gold complexes [LAuCl] by silver salts led to the suggestion of the existence of "silver effects" in gold(I) catalysis.[119] In same cases, it was proposed that the nature of the particular catalytically active species generated *in situ* by mixing a gold catalyst [LAuCl] and AgX depended on whether or not the resulting mixture was filtered through Celite.

An evaluation of this problem by using complex **18b** as a representative phosphine gold(I) complex concluded that most of so-called "silver effects" could be attributed to the ready formation of dinuclear chloride-bridged species such as **68**, which were characterized by X-ray diffraction with different X anions (SbF_6^-, BF_4^-, OTf^-, NTf_2^-) (Scheme 14).[120] Presumably, an associative ligand substitution reaction initiated by coordination of silver(I) to the chloride ligand of [LAuCl] to form transient [LAuCl···$Ag]^+$, followed by addition of a second molecule of [LAuCl] as the incoming ligand leads to [LAuClAuL]$^+$ and AgCl. These dinuclear complexes **68** were readily formed regardless of the counterion when a silver salt AgX was added in the absence of the coordinating substrate in non-coordinating solvents like CH_2Cl_2, and were found to be considerably less catalytically active than cationic complexes [LAu(NCMe)]X towards several transformations of substituted alkynes. On the other hand, when the silver salt was added last, by premixing [LAuCl] with the substrate, formation of dinuclear chloride-bridged species such as **68** could be minimized.

Interestingly, by mixing complex **18b** with $AgSbF_6$ followed by filtration through Celite, complex **69** that shows an additional coordination of silver(I) with the aryl rings could be isolated and characterized by X-ray diffraction (Fig. 15).[121]

Formation of the chloride-bridged species in a gold(I) catalysed reaction was also found in the cycloisomerisation of 1,6-enynes such as **70** in the presence of complex **72** with a sec-



Scheme 14 Formation of the chloride-bridged complexes in a non-coordinating solvent.

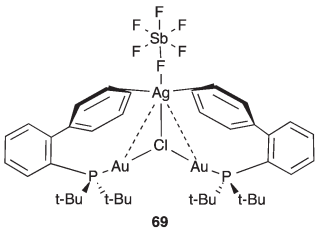
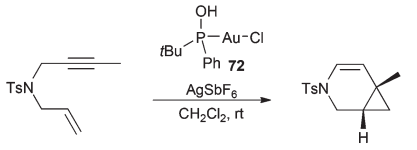


Fig. 15 Structure of an Au–Ag–Au triangular motif.



72 (mol %)	$AgSbF_6$ (mol %)	71 (yield %)
2	2	30
2	4	61

Scheme 15 Effect of the amount of silver salts on the cyclisation of enynes by the SPO-gold(I) complex.

ondary phosphine oxide ligand (Scheme 15).[122] The yield of **71** was significantly increased by using an excess of $AgSbF_6$, which minimized the formation of less reactive $[LAuClAuL]^+$ species, which were detected by ESI mass spectrometry.

The routine use of highly hygroscopic silver salts as halide scavengers can introduce significant amounts of water in the reaction mixtures leading to unwanted hydration of alkynes and hydrolysis reactions. In addition, water reacts with gold(I) complexes to form bridged $[LAu(OH)AuL]^+$ such as **73** [120] and related complexes[108,114c,e] or trinuclear oxonium cations **74** [108,123] (Fig. 16).

More drastic changes can take place in other cases in the presence of silver salts. Thus, upon mixing gold(I) carbene complex **14a** with $AgBF_4$ in a non-coordinating solvent, cationic bis-NHC gold(I) complex **75** was formed (Scheme 16).[124]

As an alternative to silver(I), copper(II) salts, such as $Cu(OTf)_2$, can also be used for the chloride abstraction of gold(I) complexes.[125] Similarly, several Lewis acids of the transition and main group metals can be used for the generation of active species from [LAuCl] complexes.[126]

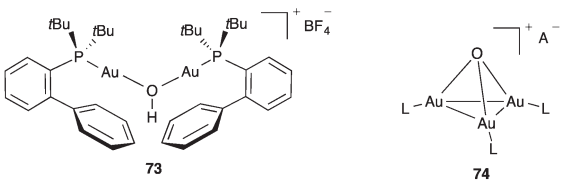
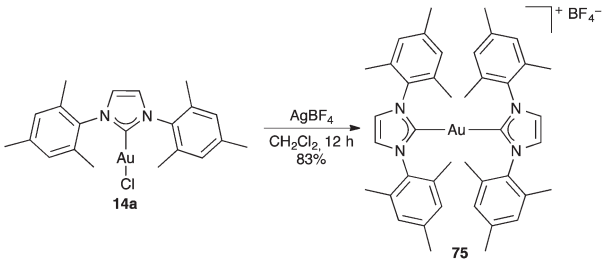


Fig. 16 Hydroxo-bridged complex **73** and trigold(I) oxonium complexes **74**.



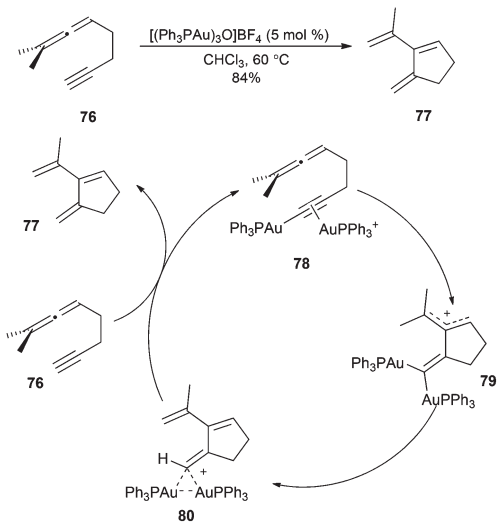
Scheme 16 Formation of bis(IMes) gold(I) complex.

6. Digold complexes

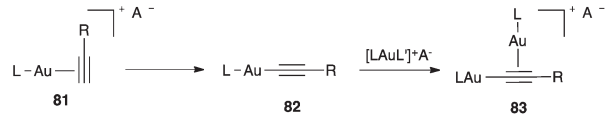
Although digold(I) complexes have been known since the mid seventies,[127] their relevance in homogeneous gold(I) catalysis has only been recognized recently.[128–130] In this section, we will focus only on the findings regarding their role in gold(I)-catalysed transformations.

The first evidence of the dual activation of alkynes *via* σ,π-activation was found in the context of the cycloisomerisation of 1,5-allenynes catalysed by $[(Ph_3PAu)_3O]BF_4$ (Scheme 17).[131] The experimental and computational data for the cyclisation of allenynes **76** to form **77** supported a mechanism in which the coordination of a cationic fragment $[(Ph_3P)Au]^+$ to the gold acetylide in complex **78** promoted a 5-*endo-dig* cyclisation *via gem*-diaurated species **79** and **80**.

The involvement of related σ,π-digold(I) species was proposed in the cycloisomerization of diynes.[132] Although similar species were observed by mass spectrometry under electrospray ionization, their real involvement in the cycloisomerization of 1,6-enynes was questioned.[133] Other alkenyl-[86,134–137] and aryl[138–140] digold complexes with Au_2C three-centre-two-electron bonds have been observed.[141]



Scheme 17 Proposed role of *gem*-diaurated species in the cycloisomerization of 1,5-allenynes.

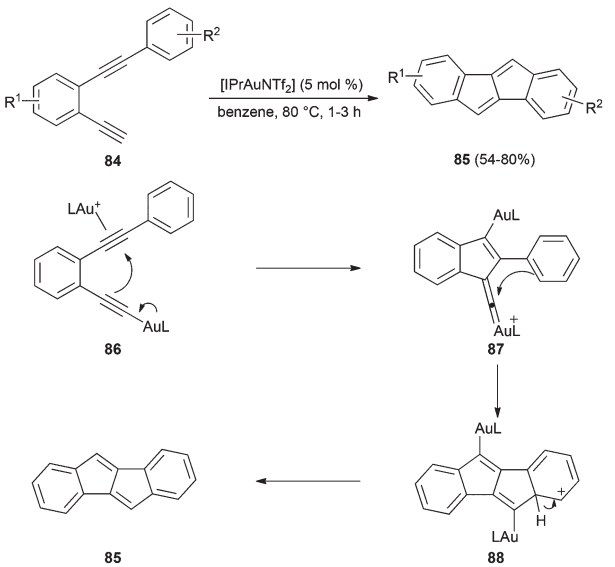


Scheme 18 Formation of digold-alkyne complexes.

σ,π-Digold(I) alkyne digold(I) complexes **83** are easily formed by the *in situ* deprotonation of terminal alkynes in **81** *via* gold(I) alkynyl complexes **82** (Scheme 18).[100b,133,142–144] Complexes of type **83** have been identified as species out of the catalytic cycle in the cycloisomerization of 1,6-enynes,[133] the intermolecular [2 + 2 + 2] cycloaddition of alkynes with oxoalkenes,[143] as well as in the [2 + 2] cycloaddition of alkynes with alkenes.[145]

Importantly, gold(I) binds more strongly to gold(I)-acetylides than to free alkynes,[146] which explains the very low reactivity of digold(I) complexes **83** in the activation of substrates containing alkyne functionalities under catalytic conditions.[143,145] Formation of unproductive σ,π-digold(I) alkyne digold(I) complexes in intermolecular reactions of alkynes with alkenes and related processes could be minimized by changing the counterion of the cationic catalyst from SbF_6^- to the softer anion $BAr^{F-}{}_4$.[143,144]

Although σ,π-digold(I) alkyne complexes **83** are unproductive dead-ends in reactions of alkynes with alkenes, they are excellent catalysts in reactions of diynes in which one of the alkynes is a terminal one, by allowing the simultaneous formation of a σ-alkynyl gold(I) species and a π-alkyne gold(I) that react with each others in a dual-gold(I) catalysed process.[147–149] This apparent contradiction can be explained by the Janus-like character of complexes **83**, which contain, in addition to the usual Lewis acid, a basic gold acetylide. Thus, the annulation of *o*-dialkyne derivatives **84** to form indeno[2,1-*a*]indenes **85** proceeds *via* σ,π-digold(I) alkyne complexes **86**, which give rise to gold(I) vinylidenes **87** that cyclise to **88** (Scheme 19).[136b]



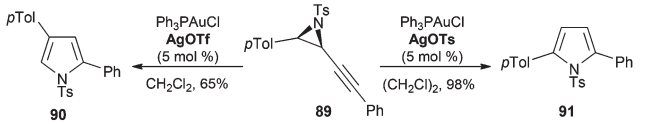
Scheme 19 Annulation *via* σ,π-digold(I) alkyne complexes to form indeno[2,1-*a*]indenes.

7. Anion effects

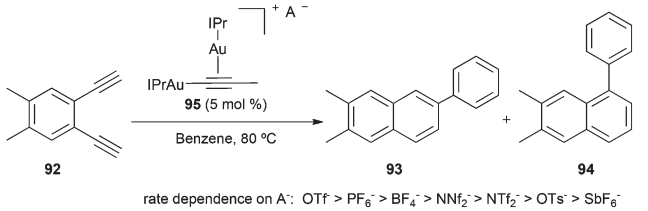
The awareness of the effect of the counterion on gold(I) catalysis has experienced an outbreak recently.[7,150] A particular illustrative example is the reaction of gold(I)-catalysed ring expansion alkynyl aziridines such as **89** to form pyrroles by a tandem cyclisation-opening/Wagner–Meerwein sequence.[151] When the reaction was performed in the presence of AgOTf, product **90** was obtained, whereas using a catalyst with a sufficiently basic counterion such as tosylate, proton elimination and atom transfer took place to give **91** (Scheme 20).

The anion effect was also studied in the gold(I)-catalysed reaction of diyne **92** to give rise to naphthalenes **93** and **94** using σ,π-digold(I) alkyne complexes **95** with different anions (Scheme 21).[152] A fast transformation was observed for TfO^-, although full conversion could not be obtained and, whereas the complex with PF_6^- as the anion gave almost full conversion after 1 h, the corresponding complex with SbF_6^- gave less than 20% conversion after 8 h.

Not surprisingly, ion pairing is responsible for some of the counterion effects. Based on NMR experiments and DTF calculations, the position of the BF_4^- anion in systems [(Ph_3P)Au-(4-Me-styrene)] **96** and [IPrAu(4-Me-styrene)] **97** was studied by ^{19}F–^1H HOESY NMR spectroscopy combined with theoretical modelling (Fig. 17).[153] These results demonstrate that the counterion is placed away from the gold(I) site, although the specific localization strongly depends on the neutral ligand (phosphine or NHC).



Scheme 20 Role of counterions in the ring expansion of alkynyl aziridines.



Scheme 21 Counterion effect in the formation of naphthalenes by σ,π-digold(I) alkyne complexes.

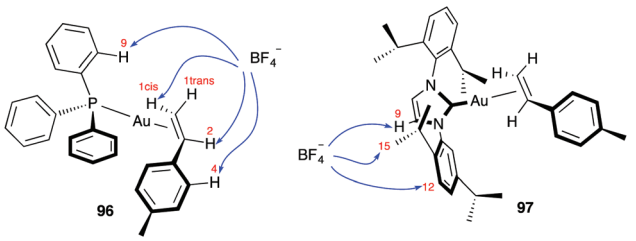
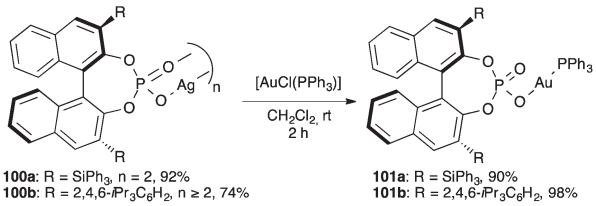


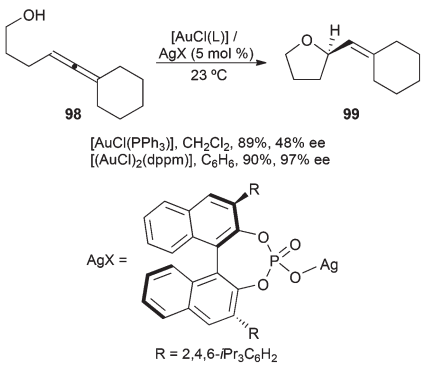
Fig. 17 Key $^{19}F-^{1}H$ HOESY contacts in complexes **97**·BF_4 (left) and **98**·BF_4 (right).



Scheme 23 Synthesis of well-characterized chiral gold(I)-phosphate complexes.

The impact of the anion on the enantioselectivity of gold(I) catalysed reactions has also been investigated.[154,155] This effect was best illustrated in the enantioselective gold(I) catalysed cyclisation of allenols such as **98** to give tetrahydrofuran **99** using achiral complexes [LAuCl] activated by silver(I) binol phosphate salts (Scheme 22) and in other related transformations of allenyl sulfonamides.[154,156] Complexes $[(L–L)(AuX)_2]$ and $[(L–L)Au_2XCl]$ (L–L = bidentate phosphine) were also active in the enantioselective cyclisation of hydroxy- and sulfonamidoallenes.[157] Gold complexes combined with chiral phosphoric acids have also been used in other enantioselective transformations.[158] Interestingly, in the gold(I)-catalysed enantioselective hydroammination by intramolecular addition of tosylamides to allenes, the best results were obtained when using AgOPNB (PNB = *p*-nitrobenzoate), presumably by generating the monocationic gold complex $[((R)\text{-BINAP})Au_2PNB]^+$.[156b]

The above transformations were suggested to proceed in the presence of an ion pair $[LAu]^+X^-$ with a chiral phosphate anion. However, the actual complexes **101a–b**, prepared from the dimeric phosphate silver(I) salts **100a–b**, are very robust covalent species both in the solid-state and in solution. (Scheme 23)[159] Notably, whereas these complexes catalyse the cyclisation of allenol **98** to form tetrahydrofuran **99**, they were surprisingly inactive in the cyclisation of several 1,6-enynes. However, the catalytic activity could be restored upon addition of $[Ag(NCMe)_2]^+SbF_6^-$ or by performing the reaction in the presence of a protic solvent like MeOH. Presumably, in both cases, the associative ligand substitution step generates cationic complexes $[(Ph_3P)Au(S)]^+$ (S = MeCN or MeOH), which are catalytically active. These results show that in order to extend the chiral counterion concept to gold(I)-catalysed activation of alkynes, anionic ligands less basic than phosphates would have to be used.



Scheme 22 Enantioselective cyclisation of allenols with gold(I) catalysts in the presence of chiral phosphate anions.

8. Conclusions

Gold(I) complexes emerged as powerful catalysts for the selective electrophilic activation of multiple bonds under mild conditions. Several aspects have to be taken into account in order to accomplish a gold(I)-catalysed reaction. Thus, although ancillary ligands tune the electronic and steric properties of the gold(I) complex, it is important to remember that precatalysts enter catalytic cycles by associative ligand substitution, which may be rate determining. Anions and anionic ligands also play a significant role in determining the reaction outcome and the enantioselectivity when using chiral catalysts.

In the case of gold(III) precatalysts, uncertainties still exist regarding the actual structure and even the oxidation state of the actual catalytic species since the presence of highly donating chloride as the ligand, more than the oxidation state, seems to be responsible for the observed selectivities.

It is difficult and, in many cases, wrong to overgeneralise in gold(I) catalysis since different substrates require different modes of activation. Thus, although seemingly contradictory, σ,π-digold(I) alkyne species are both dead-ends in reactions of alkynes with alkenes and catalysts in reactions of diynes bearing terminal acetylenes, which are mechanistically very different processes. Similarly, phosphine gold(I) phosphates are good catalysts for the activation of allenes, but very poor ones in cyclizations of enynes.

Finally, particularly in the reactions of the less reactive substrates, premixing the neutral gold complexes [LAuCl] with silver salts leads to the formation of significant amounts of chloride-bridged dinuclear species $[LAuClAuL]^+$ that are poor catalysts. In these cases, premixing [LAuCl] with the substrate, followed by addition of silver salts, minimizes the formation of the unreactive dinuclear complexes. The use of silver-free, cationic $[LAu(S)]^+X^-$ is often the alternative of choice in gold(I) catalysis.

Acknowledgements

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