



Gold carbene complexes and beyond: new avenues in gold(I)-carbon coordination chemistry

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Abstract

The different coordination modes in carbon-gold(I) complexes are spotlighted with a focus on gold(I). The emergence of gold carbene complexes and their critical discussion in the community is presented, and an overview of their bonding fundamentals and synthetic procedures is given. Several intriguing and sometimes highly reactive gold-carbon coordination complexes that were recently synthesised and isolated are reviewed and a critical outlook into their potential applications is provided. This includes vinylidene and higher cumulenyliidene complexes, free carbenes with gold substituents, carbodicarbene complexes, and non-Fischer/Schrock sesquicarbene complexes.

Keywords Gold carbenes · Gold carbenoids · Sesquicarbene complexes · Alkylgold complexes · Gold catalysis

Catalysis intermediates and new coordination complexes

Gold and its complexes have had to deal with the longstanding prejudice of being extraordinarily unreactive. We know now that the element has yet to be created for which the combined creativity of global chemistry and physics communities would fail to find an application. Rich chemical applications of homogeneous gold compounds have been found, especially in the catalytic activation of multiple bonds to give a manifold of products, including materials for organic electronics, natural products, and pharmaceuticals [1–9].

Even though gold(I) complexes are widely employed in highly selective C–C multiple bond activations even in the presence of air and moisture, it was still not until the advent of modern ligand systems that organogold intermediates of such activations were easily prepared. In early gold organometallics, mono-coordinated gold(I) complexes were found

to react vigorously with water and other Lewis bases to form ate complexes with anions of $[\text{AuX}_2]^-$ type [10]. LAu(I)X complexes are typically inert to oxygen and water if the X-type ligands are strongly coordinating, which is one of the reasons why such complexes were perceived to be not catalytically useful. But low reactivity of species is not always a crux. It is rather one of the main features that allowed the application of cationic gold complexes in the stabilisation of exotic species, and it also allows the use of air-stable catalysts and precursors for π -activation reactions. A manifold of catalytic intermediates such as carbene and higher cumulene complexes have been isolated, some of which even represent previously unknown coordination modes of carbon (Fig. 1).

The discovery of gold's potential in homogeneous catalysis

One of the reasons for the initial misconception of the reactivity of gold complexes is that the classification of transition metals in triads is misleading in group 11. Gold behaves differently to both silver and copper. This difference can be attributed to the onset of significant acceleration of electrons in the 1 s orbital of gold atoms. With 79 protons being close to the core electrons, Einstein's relativity theory must be considered when describing gold's electronic structure. Pyykkö described this in detail in 2004 and stressed that this effect even gives a powerful contraction of the outermost

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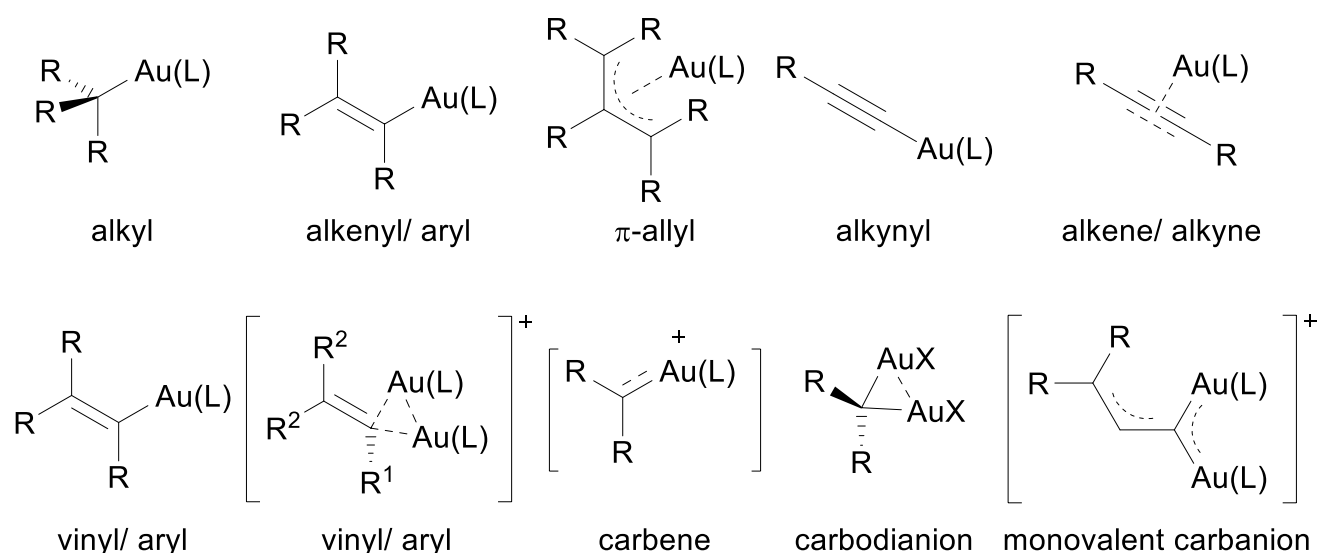


Fig. 1 Coordination modes in gold(I) complexes and their formal organic parent compounds

6s orbital [11]. This effect propagates to the valence shell and leads to a contraction and lowered energy level of the valence 6 s orbital and a significant expansion and destabilisation of the 5d orbitals. Gold, thus, acts as a far stronger π -acid than one may have expected.

A consequence of this property is that gold is a surprisingly reactive catalyst for the activation of π -bonds. The oxidation states +I, +II, and +III of gold have all been shown to be useful in homogeneous catalysis. Gold(II) has been proposed as a transient intermediate in photocatalysis, and work is ongoing on discovering ways of employing and generating homogeneous gold(II) species. We still have limited access due to redox instability [12, 13]. However, in the case of gold(I) and gold(III), both species can well be stabilised by donor ligands such as phosphines, amines, and carbene ligands like *N*-heterocyclic carbenes, making them practical and often air-stable synthesis tools [14].

Researchers had found gold to be useful as π -acid already in the rearrangement of strained carbocycles in the 1970s [2]. Homogeneous gold complexes gained increasing attention when their usefulness was subsequently shown in asymmetric aldol reactions in 1986 by Ito and Hayashi [15, 16], in Teles' finding of their high activity for the addition of nucleophiles to alkynes in 1998 [17, 18], and Hashmi's discovery of catalytic C–C bond formation reactions in 2000 [2, 19, 20]. The investigation of the mechanisms of these reactions brought the field of gold-carbon coordination chemistry into the spotlight of the contemporary research. Simple gold(III) salts were often employed in early works, while more elaborate and more stable homogeneous complexes of gold(I) dominated the research landscape in the following years [4, 21, 22]. A typical example of a reaction cycle in gold(I) catalysis is given in Fig. 2. A cationic gold(I) complex **1**

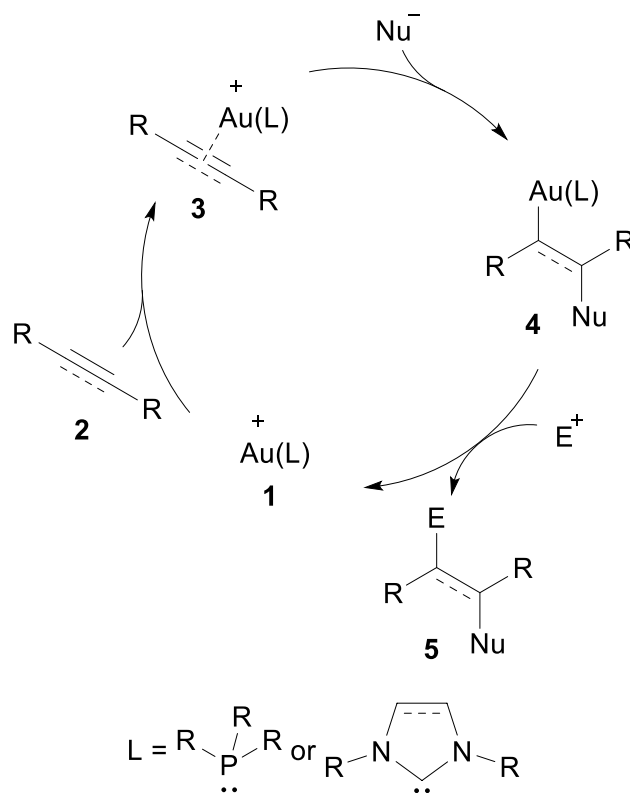


Fig. 2 A schematic typical gold(I) catalysed π -activation

typically coordinated by a single phosphine or *N*-heterocyclic carbene ligand with an open coordination site is used to form a π -complex **3** with an alkyne or alkene **2**. A nucleophile such as an amine then attacks the activated π -bond leading to a vinyl complex **4** by element-auration (e.g. aminoauration). The catalytic cycle is closed by electrophilic

substitution of the gold moiety which recovers the cationic gold fragment $(L)Au^+$ **1** and produces a 1,2-disubstituted alkene or alkane **5**.

Gold(I) carbene complexes

Synthesis

The simple example shown before can satisfyingly be explained with simple π - and σ -coordinated gold fragments but it was observed that gold(I) fragments effectively function as electron-donating group (EDG) leading to initially unexpected behaviour of the intermediates generated by π -coordination. Gold carbene complexes soon appeared as peculiar mechanistic suggestion in such reactions [3, 23, 24]. These complexes have been discussed before that alongside the establishment of other carbene ligands that we nowadays consider commodity ligands in catalysis [25, 26]. The ensuing discussion focussed on carbocations bound to a gold centre carrying another neutral ligand which may be a phosphine ligand, an *N*-heterocyclic carbene ligand, or other related ligand systems.

Convincing amounts of evidence have been gathered that gold carbene complexes are key intermediates in the activation of π -bonds and are crucial for explaining the observed distinct reactivity of gold with multiple bonds. As gold was expected to have a limited π -backbonding ability, this suggestion was viewed critically. It soon became clear that this concept can be used for broadening the scope of gold's applications in homogeneous catalysis and several synthetic methods have been established for isolating gold carbene complexes (Fig. 3) [27–30]. Direct access can be furnished from diazo compounds **6** which can also be first captured with other metal centres to afford **8**. The transfer of the resulting carbenes to cationic gold(I) complexes gives **7**.

Bonding in gold(I) carbene complexes: carbene or carbenoid?

The nature of the chemical bonding in gold(I) carbenes has caused disputes of an extraordinary nature (Fig. 4a) [27]. They can be described by a σ -bond and a classical π -backbond to a cationic carbon's empty p-orbital but the relevance of the backbond appeared to be unclear at the time (Fig. 4b). Several groups isolated formal gold carbene complexes with different aims. Some studies wanted to prove the critics wrong by showing the existence of "true" gold carbene complexes with a relevant double bond character. Others objected and showed the low contribution of π -backdonation in isolated complexes experimentally. Depending on the working hypothesis, both of these aims were fulfilled because both hypotheses were completely

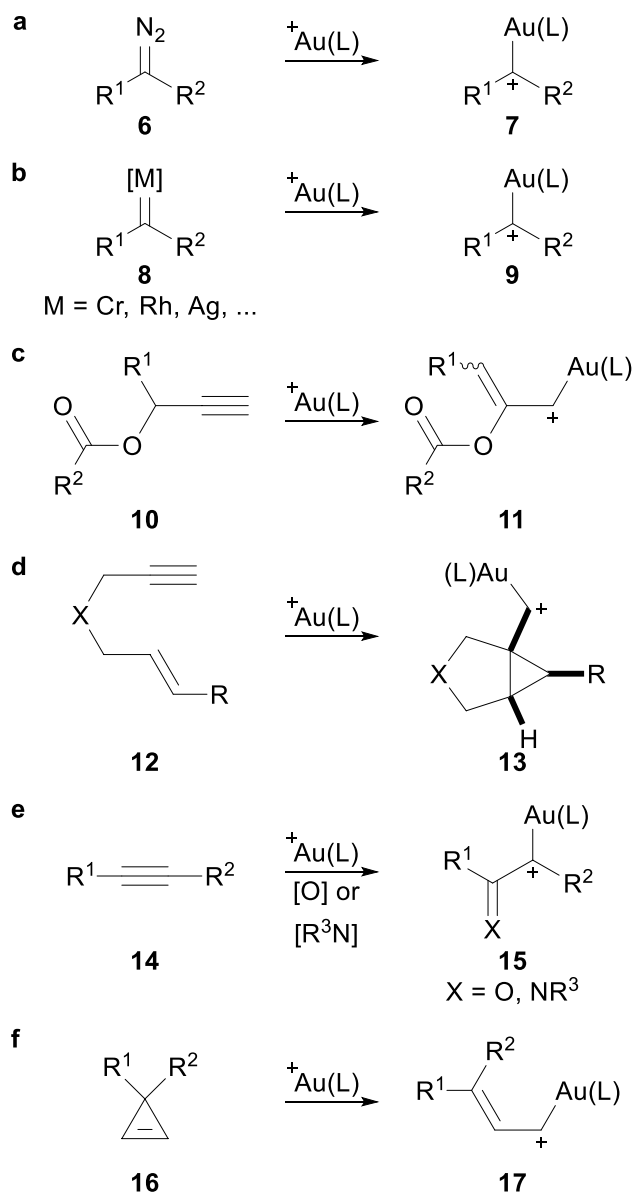
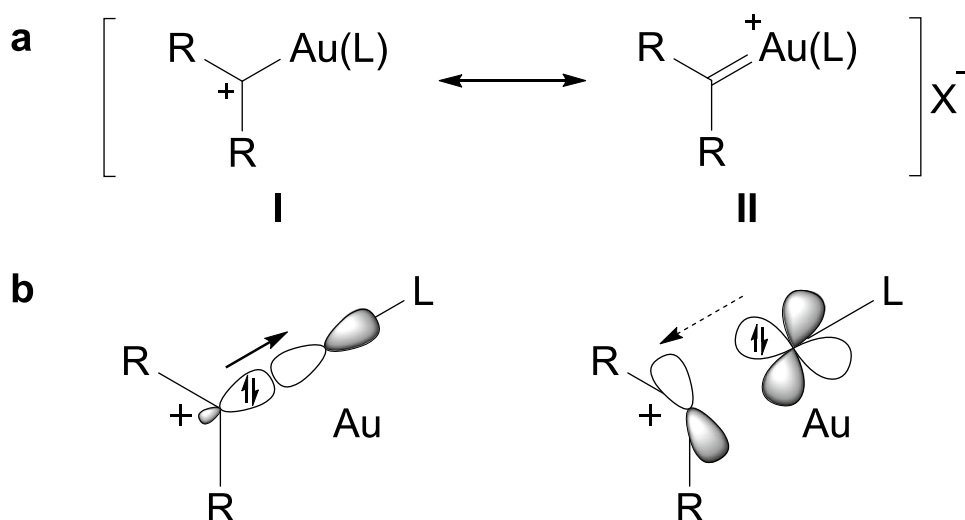


Fig. 3 a–f Selected synthesis methods for gold carbenes

correct without contradicting each other. Several remarkable gold carbene complexes have been isolated, a selection of which is discussed later. Their publications have been used as a venue for discussing the relevance of the carbene resonance structure **II**.

One shall carefully absorb the following paragraphs as history lesson. While a background motif of the dispute regarding gold carbenes has been the relevance and strength of π -backbonds in gold carbenes, the predominating theme of this disaccord was purely semantic. The terms gold carbene and gold carbenoid were used to voice opinions on the relevance of the π -backbond. Gold carbene implies a two-electron donor with two orbitals involved in bonding [31]. They are usually classical Fischer carbene complexes

Fig. 4 Limiting structures of gold carbene complexes on the continuum ranging from σ -coordinated carbocations to carbon–metal double bonds (a). Binding orbital interactions in gold(I) carbene complexes (b)



with low oxidation state metals and π -donors on the carbene ligand. The lowest unoccupied molecular orbital (LUMO) constitutes the π -backbond to the carbene carbon which acts electrophilic and will be partially occupied depending on the electronic features of the complex. Typical gold carbenes contain weak π -backbonds, meaning that they are better described as metalated carbocations. While the backbonds in gold complexes are especially weak, one shall note that this is true for any Fischer carbene complex.

The term carbenoid was a poor way of describing gold carbene complexes. It was used to explicitly state the low relevance of the π -backbond. This name is broadly defined as “Complexed carbene-like entities that display the reactivity characteristics of carbenes, either directly or by acting as sources of carbenes.” in the IUPAC goldbook [32]. Any carbene complex can reasonably be viewed as carbenoid based on this definition which happened within this context, while the involved parties obviously meant that the complexes were like carbene complexes but not carbene complexes. It should be easy to see that this distinction is based on a subjectively selected discrete point on a continuous attribute. Now that the discussions seem settled, it can be summarised that the case of gold carbenes has once more brought to our attention the fragility of nomenclature definitions and Lewis representations of chemical structures.

As Echavarren stated more recently, it seems much more useful to restrict the term carbenoid to LAuCXR_2 **18** species that are related to Simmons-Smith carbenoids which may release a gold carbene complex **19** by elimination of X or it may release a carbene by α -elimination of LAuX (Scheme 1) [27]. We agree that this distinction makes the use of distinct terms relating to carbene reactivity more useful. Care is still advised both when reading and using the term “carbenoid” as it remains poorly defined. Highlighting the carbene reactivity from a carbenoid by this definition, Steinborn showed that $[(\text{PPh}_3)\text{Au}(\text{CH}_2\text{I})]$ decomposes quickly at room temperature to give ethylene and $[(\text{PPh}_3)\text{AuI}]$ [33]. Fürstner recently reported that such carbenoids can even be used for the transfer of formal difluorocarbenes [34]. The term “gold carbene complex” shall be considered gold coordinated by a carbene. Gold carbenes push the extremes towards the Fischer side of carbenes and are best described as metalated carbocations with most stabilisation originating from heteroatom or unsaturated substituents.

Isolated gold carbene complexes

Fürstner isolated the dianisole-stabilised gold carbene complex **22**, calling it carbenoid at the time (Fig. 5) [35]. They employed an indirect synthesis method by first isolating a

Scheme 1 Gold carbenoids and gold carbene complexes

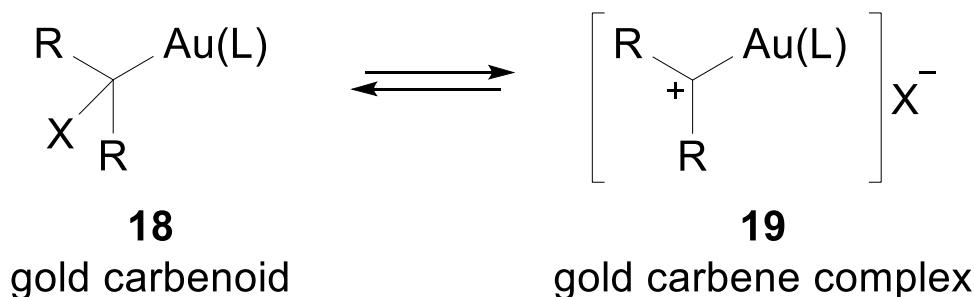
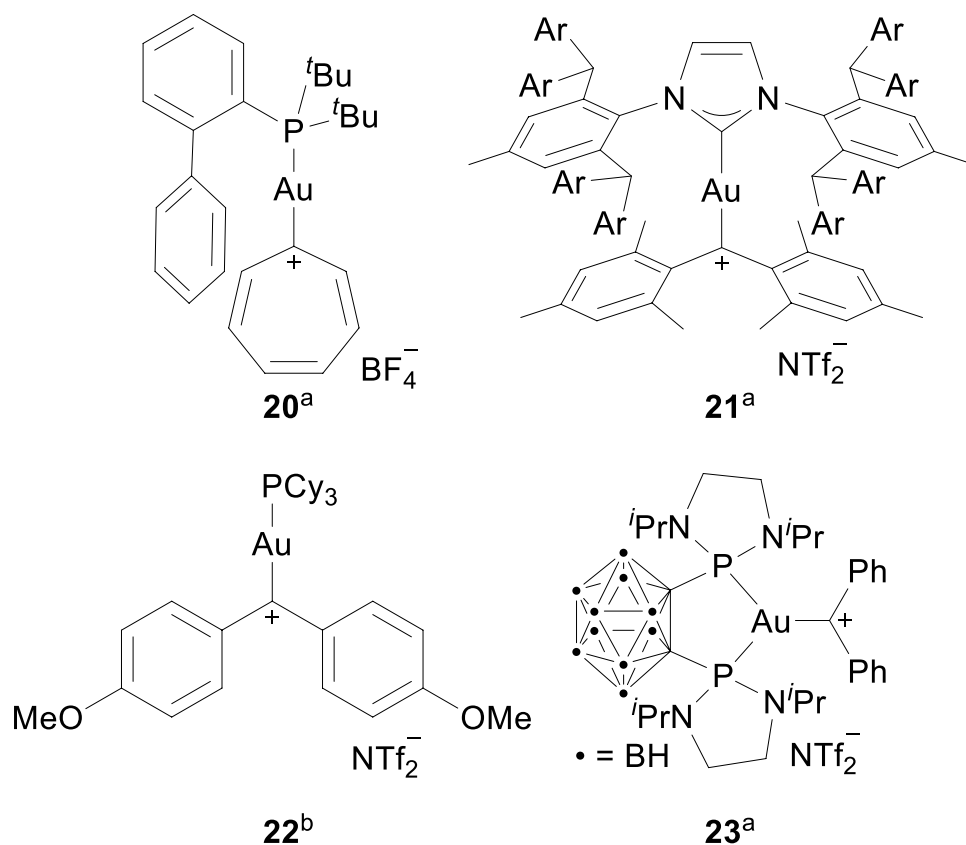


Fig. 5 Notable isolated gold(I) carbene complexes. Synthesis method as shown in ^aFig. 3a, ^bFig. 3b



rhodium carbene complex generated from the diazonium precursor. Then, they transmetalated the carbene to gold. He would later with the isolation of another carbene complex note that the relevance of the carbene resonance structure **II** is low and that the discussion is of primarily semantic nature [36]. This dispute about the nature of gold carbene bonding has triggered the hunt for complexes with stronger and stronger carbene character to show the existence of true gold carbene complexes. Several non-heteroatom stabilised species were isolated in the following directly from diazonium precursors such as the tropylium-derived complex **20** by Widenhoefer [37], the bulky imidazole-protected dimesityl-stabilised carbene complex **21** by Straub [38], and Miqueu, Amgoune, and Bourissou's carbene **23**. [39]

Even though biscarbene complexes of gold(III) have been known since 1973, the landscape of gold(III) carbon/carbene complexes is underdeveloped compared to gold(I). Gold(III) carbene complexes with N-heterocyclic carbenes (NHC) of the type [(NHC)₂AuX₂] act as oxidants and react to the respective gold(I) complexes [(NHC)₂Au]⁺X⁻. [40, 41] Only in 2017 Mézailles and co-workers synthesised reactive neutral gold(III) carbene complexes by adding a carborane to a dicationic gold(III) moiety and showed that these complexes are capable of carbene transfer reactions [42]. It was recently found again that gold(III) carbenes can efficiently give completely different products in catalyses

with otherwise identical starting materials [43, 44]. Further elaboration of the carbon coordination chemistry of gold(III) and the in situ interconversion of gold(I) and gold(III) is expected to enhance the scope of homogeneous gold catalysis even further.

Trigonal planar gold(I) coordination allows the stabilisation of new complexes

Among all this progress, surprisingly little of what one would consider basic inorganic chemistry in transition metal coordination chemistry has yet been uncovered in well-defined molecular gold chemistry. Just over the last decade a manifold of π -complexes of gold(III) with C–C multiple bonds was reported [45, 46]. Bourissou has reported a π -allyl complex of gold(III) [47]. Much of this chemistry remains to be investigated in molecular gold(I) complexes. Significant strides forward have been reached, however, with the introduction of ligands that force gold(I) in trigonal planar geometry.

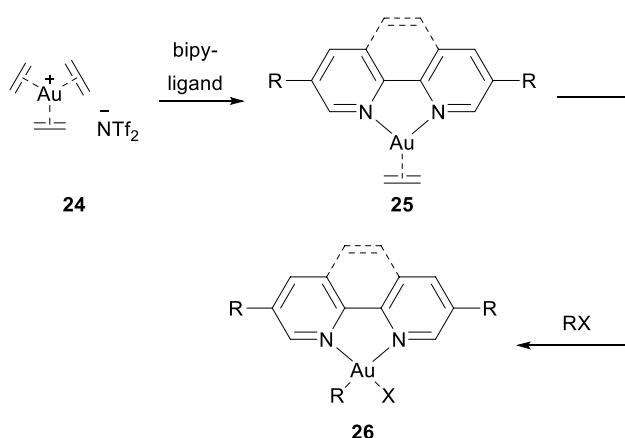
Bourissou's carbene **23** already gave an outlook into this emerging field in gold's coordination chemistry [34]. The employed *o*-carborane diphosphine ligand forced gold(I) into an unusual trigonal planar geometry which was rare at the time. Trigonal planar gold(I) complexes were found to

enable enhanced access to gold's redox chemistry and even enabled oxidative addition reactions on gold(I) [48–50]. The first key step in both the activation of alkynes and alkenes is the π -coordination of the multiple bonds. Only limited structural information on such gold(I) complexes had been garnered [51]. Gold showed C–C hopping in π -complexes too rapidly for nuclear magnetic resonance analysis. Russel and later Hashmi and their co-workers have been able to isolate well-defined trigonal planar ethylene complexes **25** only in 2018 and 2019, respectively (Scheme 2) [49, 52]. Both found in these studies different modes to unlock oxidative addition/reductive elimination chemistry in these gold(I) complexes via the gold(III) complexes **26**. [49, 52, 53] The hemilabile P/N-ligand MeDalPhos (di(1-adamantyl)-2-dimethylaminophenylphosphine) has been established in the meantime as gold standard for unlocking oxidative addition on gold(I) complexes, effectively merging the two rich fields of gold(I) and gold(III)-catalysed reactions [54–56].

Higher cumulenes of gold(I) carbene complexes

Sometimes several exotic species need to be considered in a single mechanism. When two gold centres are employed, we can directly activate 1,5-diyne. The pre-catalysts that have proven most promising are the ones that are already pre-configured for the job, i.e. one gold atom is σ -coordinated (alkynyl complex) and one is π -coordinated (alkyne complex) to propynyl. These are now called dual activation catalysts (DAC) [57]. This double activation is one of the methods to directly create gold carbenes in situ. A σ,π -complex such as **27** is formed when such catalysts are reacted with 1,5-diyne (Fig. 6a).

The regioselectivity of such gold-catalysed cyclisation reactions follows the Zimmerman-Traxler model. This



Scheme 2 Gold(I) ethylene complexes with bipyridine ligands unlock oxidative additions in gold(I) complexes

means that *5-endo-dig* cyclisation is usually kinetically favoured over other options. This directly leads to a mixed organogold species containing a σ -bound gold centre and a gold vinylidene **28**. CH-insertion can then be utilized for the annulation of further ring systems [58]. This selectivity can be overpowered by using a 5-membered ring as backbone for the diyne system. Two fused 5-membered rings are less stable than 5-membered rings fused to 6-membered rings which leads to the preference of a typically hindered *6-endo-dig* cyclisation to give **29**. [59]

The vinylidene intermediate **28** is a higher cumulene of a gold carbene: a gold carbene complex containing a double bond to the neighbouring carbon centre (Fig. 6b). Synthetic access was even found to allenylidenes containing two cumulated C–C double bonds and a gold carbene bond. This was enabled by electrophilic addition reactions to the oxygen atom in 3-oxoalkynylgold complex **30** which led to the rearrangement of the π -system to give the target allenylidene complexes **31**. [60] Further analysis showed that the weak π -interaction with the gold centre leads to an electronic structure that is intermediary between a propargylic cation and an allenylidene.

Aurated carbenes

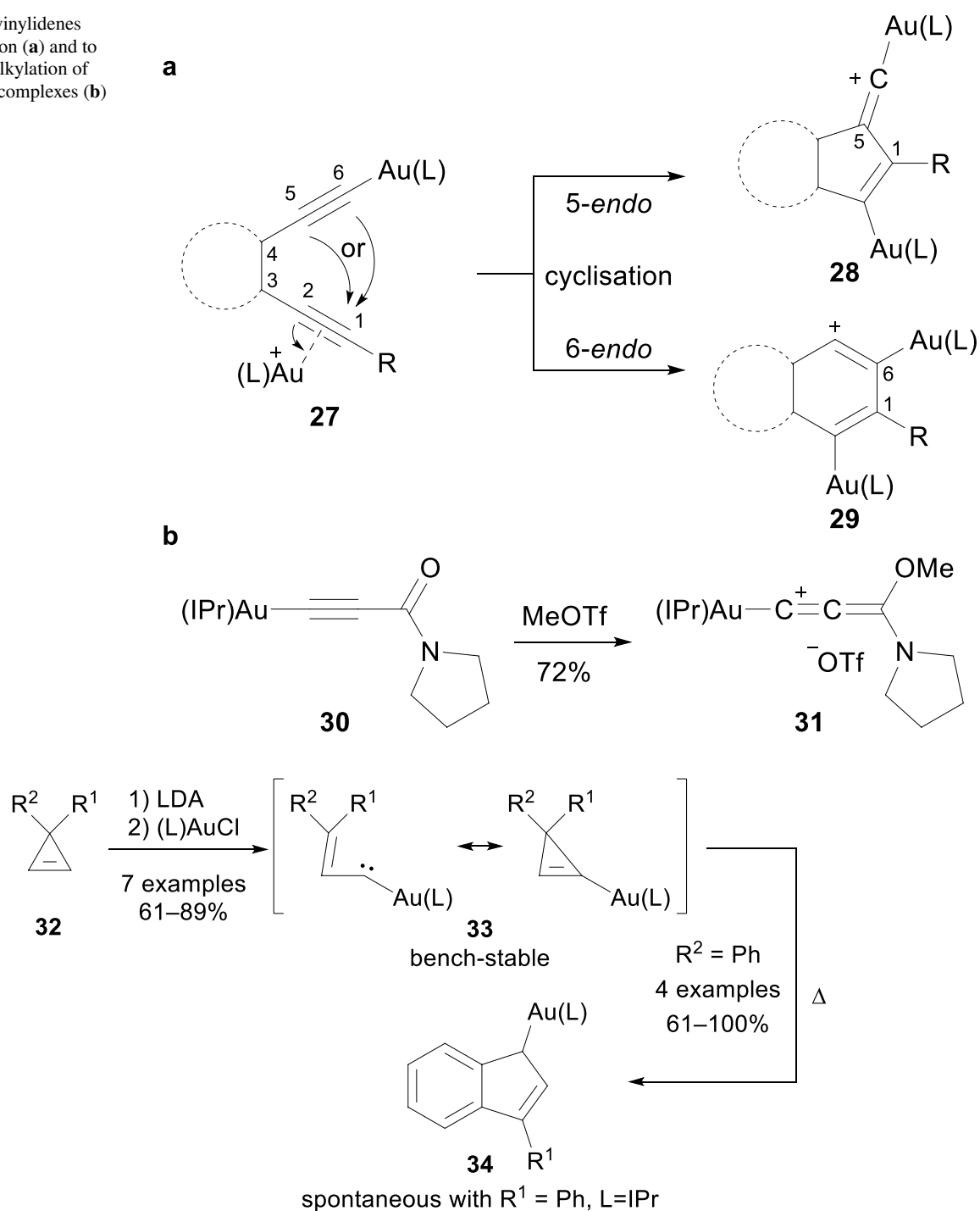
Whereas the previously discussed reactive species were mostly discovered and isolated in efforts of understanding mechanistic intricacies of known gold-mediated reactions, gold's stabilising nature has been found useful in quests for novel carbon-based compounds as well. For example, vinylic gold(I) was calculated to have a strong stabilising effect similar to cyclopropyl and phenyl substituents on the ring strain energy (*RSE*) in cyclopropenes [61].

Ring strain energy *RSE* for R = F > H \approx OMe > Et \approx *i*-Pr > *c*-Pr >

Ph \approx AuP(OMe)₃ \approx Au(IPr) > Au(PMe)₃ > *t*-Bu

We discovered that the steric demand of gold centres, while decreasing the ring strain energy, leads to strongly distorted rings in cyclopropen-1-ylgold(I) complexes **33** (Scheme 3) [61]. Similar pre-activation was found in (NHC) (tricyclo[4.1.0.0^{2,7}]hept-1-yl)gold(I) complexes that contain an aurated bicyclobutane unit [62]. Both of these systems tend to undergo ring-opening reactions that lead to terminally bound gold moieties. This is both due to steric demand and due to gold stabilising the intermediates. Ring-opening of the cyclopropenyl complexes lead to an interesting arrangement: an aurated carbene wherein the carbon atom that is bound to gold(I) is a free carbene itself. This carbene intermediate was shown to be easily accessible at room temperature or with mildly elevated temperatures whereas non-aurated cyclopropenes would show the same reactivity

Fig. 6 Access to vinylidenes by diyne-cyclisation (**a**) and to allenylidenes by alkylation of 3-oxoalkynylgold complexes (**b**)



Scheme 3 Cyclopropenylgold(I) complexes derived from cyclopropenes and their rearrangement to indenylgold(I) complexes with an allylic gold centre

only at temperatures of $> 180^\circ\text{C}$. The rearrangement to 1*H*-inden-1-ylgold(I) complexes **34** succeeded with phenyl substituents installed in 3-position in the cyclopropenylgold(I) complexes.

These indenylgold complexes **34** were the first isolated examples of allylgold(I) species [61]. Gold(I) had been

proposed by computational efforts and based on indications from catalysis to show allylic substitution reactivity [63]. Indeed, the isolated indenyl complexes would favour the formation of indenes via an electrophilic S_E' mechanism under rearrangement even with an aggressive proton

as electrophile from hydrogen chloride. We are still looking forward to the discovery of π -allylgold(I) complexes and further σ -allylgold(I) and their investigation regarding β -H-elimination and electrophilic addition mechanisms.

Bent allene and allenyl complexes

Schmidbaur has isolated and stabilised carbodiphosphoranes in the 1970s as digold complexes showing that allene-analogues **III** with strong mesomeric donor substituents (+M) act as double ylides **IV** with formally dianionic central carbon atom that is capable of η^1 - σ -coordination (Fig. 7) [64–67]. $(\text{Me}_3\text{P}^+)\text{C}^{2-}(\text{P}^+\text{Me}_3)$ was successfully reacted with $\text{MeAu}(\text{PMe}_3)$ to give $(\text{Me}_3\text{P}^+)_2\text{C}(\text{AuMe})_2$ **35**. This concept later saw a resurgence with upcoming investigations of carbodicarbenes in 2007 [68–71]. The donor atom X in carbodicarbenes is carbon which is substituted with π -donors and can be considered a carbene ligand for the central carbon atom of the allene. While not the focus of this article, it should be noted in the context of digold complexes that Schmidbaur also discovered aurophilic interactions in related work with the digold complexes of bis(diphenylphosphino) methane with AuCl , AuI , and AuMe [72–75]. This effect reasoned by relativistic effects in the d^{10} -gold(I) complexes leads to changed reactivity and to the observation of shortened bond lengths of down to 2.5 Å compared to the ion's

van der Waals radius 3.8 Å [76]. $(\text{Me}_2\text{N})_2\text{C}=\text{C}=\text{C}(\text{NMe}_2)_2$ by Fürstner's group can be regarded as transient carbodicarbene. The molecule itself is linear along the allene carbon atoms, whereas η^1 -coordination with gold(I) leads to $[(\text{Me}_2\text{N})_2\text{C}]^+\text{C}^-\text{AuPPh}_3$ with a bent allene (carbodicarbene) ligand. The Bertrand group extended the concept to a purely carbon-based carbodicyclopropenylidene that was trapped with gallium, boron, and gold (**36**) [77]. Diauration was not found in these carbon-based examples. The discovery of these compounds was intimately intertwined with the coordination chemistry of gold and now they are an emerging class of ligands for their strong σ -donation and their interesting feature of potentially allowing double coordination at a single carbon centre [78–80].

Related structures based on gold donors were synthesised from dilithiated propargylbenzene and phenylallene, respectively [81]. The lithiated reactants are easily accessible from the two triple bond isomers prop-1-yn-1-ylbenzene and prop-2-yn-1-ylbenzene and can be reacted with NHC gold(I) chloride precursors to give **37** and **38** (Fig. 8). Protodeauration succeeded selectively at C3 in both cases. The application of these promising entry points in further reactions remains to be investigated. **37** is a plausible access point toward a 3-metalated allenylidene by hydride abstraction. The resulting complex may also behave like an α -goldalkynyl gold carbene complex. **38** is a prototype carbodicarbene based on metallic π -backdonation rather than group 15 π -donation. **38** and analogues with a higher metalation grade or stronger π -donating metals are an interesting alternative to current generation carbodicarbenes and may tackle their stability issues and enable easier synthetic access.

1,1-Digoldallylium complexes

Just recently in 2020, Bertrand identified mono-coordinated monovalent carbanions as a feasible goal for future isolation [82]. A year prior to that, we reported that the known gold carbene complex synthesis method via ring-opening of cyclopropenes (Fig. 3f) can be used in conjunction with the cyclopropen-1-ylgold(I) complexes **32** to generate the digold(I) complexes **39** derived from said monovalent carbanions (Fig. 9a) [83]. Reacting **39** with dimethylsulfoxide (DMSO) quantitatively leads to the sulfoxonium salt **40** which was crystallised and appeared to

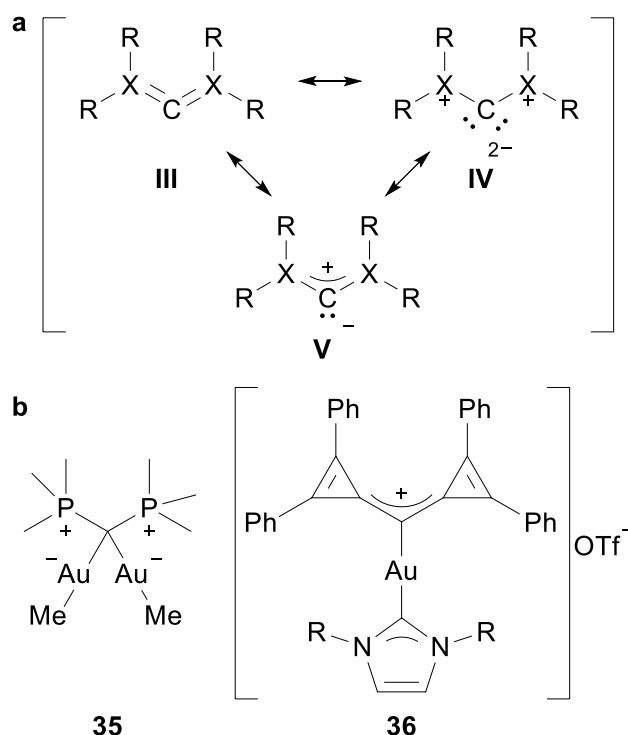


Fig. 7 Limiting structures of carbodicarbenes (a). Isolated gold carbodicarbenes complexes (b)

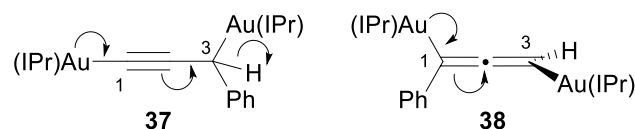


Fig. 8 Isolated allene isomeric alkynyl-propargyl digold complex and allen-1,3-diyl digold complex and plausible π -donation scenarios

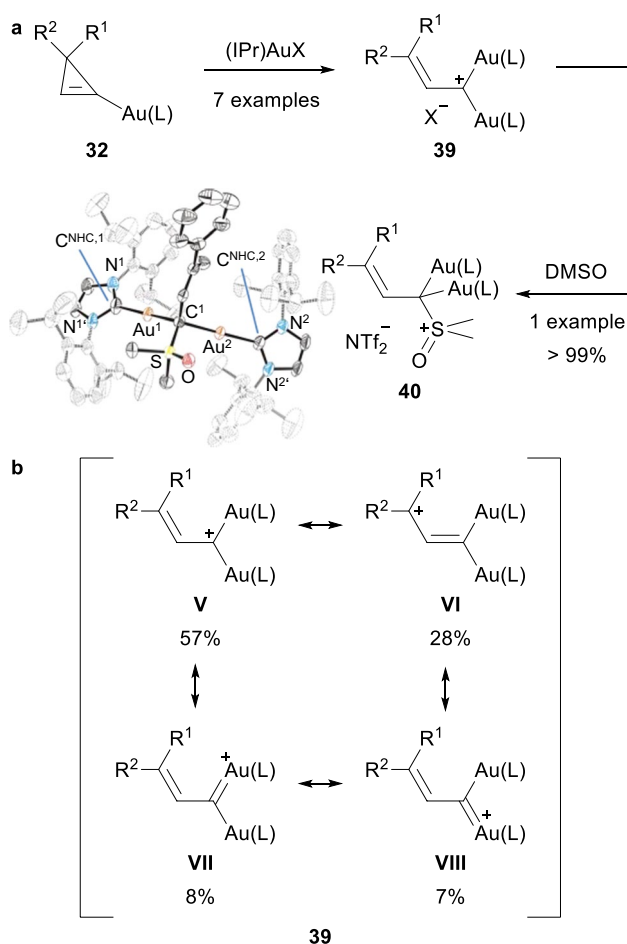
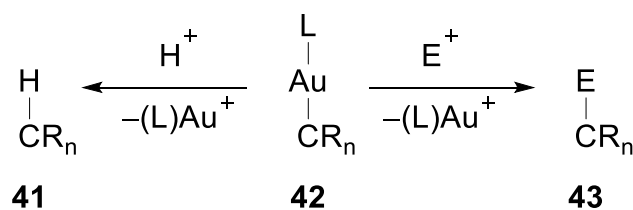


Fig. 9 1,1-Digoldallylium complexes also termed sesquicarbene complexes (**a**). Limiting structures of gold sesquicarbene complexes and their average weights determined by intrinsic bond orbital calculations (**b**)

be stable towards air and moisture for months. The optical properties indicate that comparably strong π -backbonding is present and a later computational study confirmed that both gold centres participate similarly strong in this (Fig. 9b). Each of the gold atoms donates back about as much as found in an average gold carbene complex which leads to a strong total backbonding and a first optical excitation in the near infrared spectrum [84]. It is interesting to note that this complex breaks the Fischer/Schrock carbene classification as the heteroatom-stabilisation is both weak and coming from a transition metal participating in carbene-bonding itself. The calculations furthermore showed that stabilisation by the allylic domain overpowers stabilisation by the second metal moiety by a factor of 3–4. This is an exotic addition to the portfolio



Scheme 4 Protodeauration versus electrophilic substitution with other reactants

of homodinuclear gold complexes [85], but more importantly a new coordination mode of carbon itself.

Future goals

The relatively young history of homogeneous gold catalysis has seen a spiralling rise based on initially identified applications in the first decade of our century. While the next decade brought increasingly elaborate applications, we have seen a particular interest in the mechanistic intricacies and in the isolation of unusual reactive species. Some fundamental blind spots on the map of gold(I)'s carbon coordination chemistry still exist, such as σ - and π -allylgold(I) complexes. We look forward to another golden decade of discovery that will utilize the toolbox that we have discussed:

- Carbene complexes with comparably strong π -backbond
- Ethylene complexes
- Vinylidene and higher cumulenyliidene complexes
- Free carbenes with gold substituents
- Carbodicarbene complexes with formally dianionic carbon ligand
- Precursors for cumulenyliidenes/carbodicarbenes chemistry based on auric π -backdonation
- Non-Fischer/Schrock-type sesquicarbene complexes

It must be acknowledged that the by far most important contribution that gold-carbon coordination chemistry can currently make to the field of gold catalysis is the establishment of useful transformations based on organogold complexes (Scheme 4). An astonishing amount of established gold catalyses are terminated by a simple protodeauration rather than by the introduction of additional value from the resulting organogold species. It is highly desirable to establish simple standard protocols for avoiding the protodeauration of products such as **42** to introduce a non-proton electrophile **E** in **43**. Direct (dissociative) substitution reactions are difficult due to the low polarity of C–Au bonds; however, C = Au and N = Au bonds can be utilized in carbene and nitrene transfer reactions under certain conditions [5]. There have been efforts directed towards circumventing this

problem by transmetalation to other metal centres [86–92]. This would effectively unlock the cross-coupling chemistry or element-metal exchange chemistry of these other metal centres in lieu of protodeauration for the termination of gold catalyses [93–95]. Another promising way of achieving this is on the horizon with our increasing understanding of the interconversion of gold's oxidation states. Gold(III) is typically tetracoordinate which allows for associative substitution or oxidative addition reactions which can release **43** by reductive elimination [9]. Further work is needed for the establishment of broadly applicable solutions.

One major advantage of gold(I) catalyses is that they often do not require any special procedures and can be performed in air which is not true for the discussed reactive species (yet). Their potential is currently severely limited due to partially elaborate synthetic methods and due to our limited understanding of their reactivity. The discussed portfolio of compounds extends our development platform for follow-up reactions of most conceivable catalysis products, but further research is needed to improve their synthesis and application. The primary goals for implementing these species are:

- 1) Generate the organogold species in situ for enabling sustainable and procedurally convenient investigation and application
- 2) Establish the complexes as reagents by developing useful and clean follow-up chemistry making use of the unique potential for multiple simultaneous bond formations
- 3) Close catalytic cycles with the in situ generation of organogold species and useful follow-up chemistry
- 4) Stabilise the carbon-gold(I) complexes against air and moisture either by electronic and steric tuning of the molecular structure or by establishing the complexes as short-lived intermediates in gold(I)-mediated or -catalysed reactions

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Code availability Not applicable.

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Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Conflict of interest The author declares no competing interests.

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