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Gold–alkynyls in catalysis: alkyne activation, gold cumulenes and nuclearity

Connor J. V. Halliday and Jason. M. Lynam*

The use of cationic gold(I) species in the activation of substrates containing C≡C bonds has become a valuable tool for synthetic chemists. Despite the seemingly simple label of 'alkyne activation', numerous patterns of reactivity and product structure are observed in systems employing related substrates and catalysts. The complications of mechanistic determination are compounded as the number of implicated gold(I) centres involved in catalysis increases and debate about the bonding in proposed intermediates clouds the number and importance of potential reaction pathways. This perspective aims to illustrate some of the principles underpinning gold–alkynyl interactions whilst highlighting some of the contentious areas in the field and offering some insight into other, often ignored, mechanistic possibilities based on recent findings.

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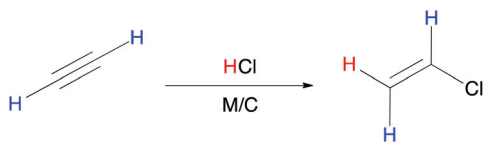
Introduction

Compared to the Platinum Group metals, catalytic processes employing gold are a relatively recent addition to synthetic chemistry. Indeed, gold has traditionally been viewed as being chemically inert,[1] and as such would never be as catalytically useful as its neighbours. This assumption resulted in the omission of gold from catalytic screening processes based on observations of its metallic properties.[2] In 1975 Shinoda conducted an investigation into the activity of various metal chlorides supported on activated carbon in the hydrochlorination of acetylene (Scheme 1),[3] an industrially important route to vinyl chloride monomer. Classically this process was catalysed by mercury(II) chloride however this had numerous drawbacks notably toxicity and rapid deactivation by reduction and loss of both $HgCl_2$ and Hg.[4–6] Shinoda correlated catalyst activity with the metals electron affinity; however, this failed to differentiate between those metals with high electron affinity and high activity and those with high electron affinity and low activity due to their Lewis acidic behaviour. In 1982 Hutchings noted that the process more likely involved the transfer of two electrons, from the π-system of the acetylene to the metal centre, and proposed that a more useful correlation would be to plot the catalyst activity as a function of the metal's standard electrode potential (Fig. 1).[7–9]

This correlation was used predictively and Hutchings proposed that supported gold(III) chloride ($[AuCl_4]^-$) should have a higher activity in the hydrochlorination of acetylene than both the platinum group metals and mercury(II) chloride as gold(III) has a standard electrode potential of +1.52 V, a hypothesis confirmed in subsequent work.[10–13] Alongside the work of Hutchings, studies conducted by the Haruta group also demonstrated the activity of nanoparticulate gold in oxidation processes.[14–16] The realisation of the catalytic potential of gold has spurred theoretical and experimental studies of both hetero- and homogeneous gold systems and resultantly research in this area has increased exponentially with a concomitant increase in understanding of associated reaction mechanisms.[17]



Scheme 1 The hydrochlorination of acetylene by metals supported on activated carbon in the synthesis of vinyl chloride monomer.

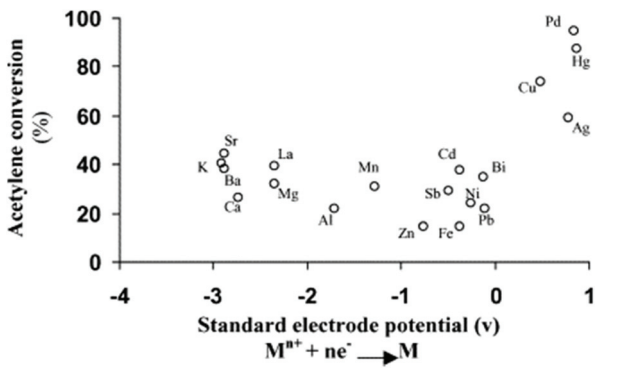


Fig. 1 Acetylene conversion in hydrochlorination as a function of the metal's standard electrode potential (taken from: *Catal. Today*, 2002, 72, p. 12).[7]

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. E-mail: jason.lynam@york.ac.uk; Tel: +44 (0)1904322534

Literature in the area of gold alkyne chemistry is now extensive and cannot be reviewed here comprehensively.[17–34] Further details can be found in Hashmi and Toste's *Modern Gold Catalyzed Synthesis*.[26] In this perspective choice examples have been selected in order to explain the fundamental reactivity of π-activated systems; the main focus however will be the aspects of homogeneous gold-catalysed systems that have come to light more recently with the advent of dual activation catalysis and the implication of the involvement of gold cumulenes and other oligonuclear gold species.[27,35]

Bonding, structure and reactivity

Alkyne activation in modern homogeneous gold-catalysis is typically conducted using gold salts ($Au^{I}X$ or $Au^{III}X_3$) or cationic gold (I) species of the type $[LAu^{+}X^{-}]$, where L is a neutral donor ligand, often a phosphine,[36–42] or N-heterocyclic carbene (NHC).[31,32] It is these $[LAu^{+}X^{-}]$ type species that will be focused upon due to their preponderance in gold–alkynyl systems.

π-complexes

The interaction between the π-system of an alkyne and the LAu^{+} fragment can be viewed as consisting of a σ-donor interaction from the π-bonding orbital of the alkyne to vacant d-orbitals at the metal centre alongside a π-accepting interaction between occupied metal d-orbitals and a vacant π*-antibonding orbital of the alkyne, in accordance with the Dewar–Chatt–Duncanson bonding model (Fig. 2).[43] There is also an electrostatic component to bonding between the cationic gold species and the electron rich π-system.

Ab initio calculations by Teles *et al.* suggested that π-complexes of this type were key intermediates in the activation of alkynes towards nucleophilic attack.[36] Toste *et al.* were the first to isolate and fully characterise an example of a cationic gold η^2–π-complex using a phosphine with a tethered silyl-alkyne moiety resulting in the dimeric species as seen in Fig. 3.[44] As well as the gold complex the analogous silver complex and a monomeric copper complex were prepared utilising the same ligand. Notably, whilst the copper centre binds symmetrically to the alkyne moiety (Cu–C distances of 2.029(2) Å and. 2.024(2) Å), in both the gold and silver systems the bound metal is slipped toward the triisopropylsilyl-bound carbon (Au–C distance of 2.197(5) *vs.* 2.270(5) and 2.217(5) Å *vs.* 2.287(5) Å in the non-centro symmetric gold dimer; Ag–C distances of 2.294(3) Å *vs.* 2.445(3) Å), a characteristic associated with increased

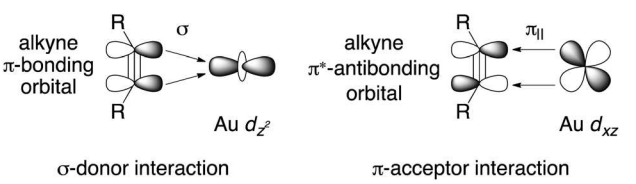


Fig. 2 The Dewar–Chatt–Duncanson model of binding showing the in plane interaction of an alkyne with a gold centre.

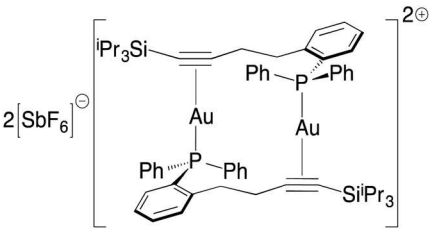


Fig. 3 Dimeric gold η^2–π-complex as isolated and characterised by Toste *et al.*[44]

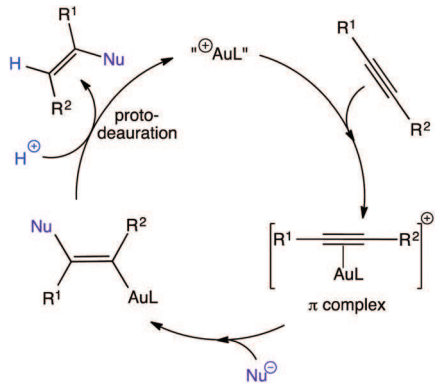
electrophilicity of the bound unsaturated species.[45,46] Toste and co-workers used Density Functional Theory (DFT) to probe the bonding in simplified versions of these systems and found that the σ-donor interaction was the dominant interaction in all three systems (Cu, Ag, Au) and that both the σ-donor interaction and π-acceptor interaction were strongest for gold (237 kJ mol^{-1} and 56 kJ mol^{-1} respectively) as well as displaying the largest difference (181 kJ mol^{-1}) between them.[44]

This dominance of σ-donation *versus* π-backbonding (which is also supported by a Charge–Displacement analysis)[47] in these systems has been interpreted as resulting from the alkyne π* being too high in energy with respect to the closed shell configuration of the metal centres. This effect is more dominant in gold than the other coinage metals due to its increased shielding as a result of the lanthanide contraction, coupled with the relativistic effects of the period six transition metals.[48,49]

This greater removal of electron density from the alkyne ligand on binding LAu^{+}, in combination with the induction of an overall positive charge and the reduction in symmetry caused by the slipped binding of the metal presumably underlies the observed electrophilicity of the alkyne ligand in the gold system when compared to both silver and copper. In agreement with this the calculated LUMO (containing the metal–π* π-acceptor interaction) was found to be 17 kJ mol^{-1} lower in energy in the gold system compared to the analogous silver system, further supporting the observed superiority of gold as a π-activation catalyst.[44]

Nucleophilic addition to π-activated alkynes

Nucleophilic addition to π-activated alkynes is by far the most studied form of homogeneous gold-catalysis in modern chemistry.[17,22,50] The prototypical mechanism involves initial binding of gold to the π-system followed by a concerted attack of a nucleophilic species and slipping of the metal to form an η^1-vinyl species. This species then undergoes protodeauration to give the corresponding alkene (Scheme 2). These kinds of processes have resulted in the successful hydration,[38] hydroalkoxylation,[36,51,52] hydroamination,[53] hydrofluorination[54] and hydrocarboxylation[55] of alkynes in homogeneous gold systems, all utilising an LAu^{+} catalyst. The interaction of the LAu^{+} species with propargyl esters, as originally described by Toste and co-workers,[56] however, proceeds *via* the initial formation of a reactive gold carbene species due to migration of the ester group (Scheme 3a). This transient reactive species is "trapped"

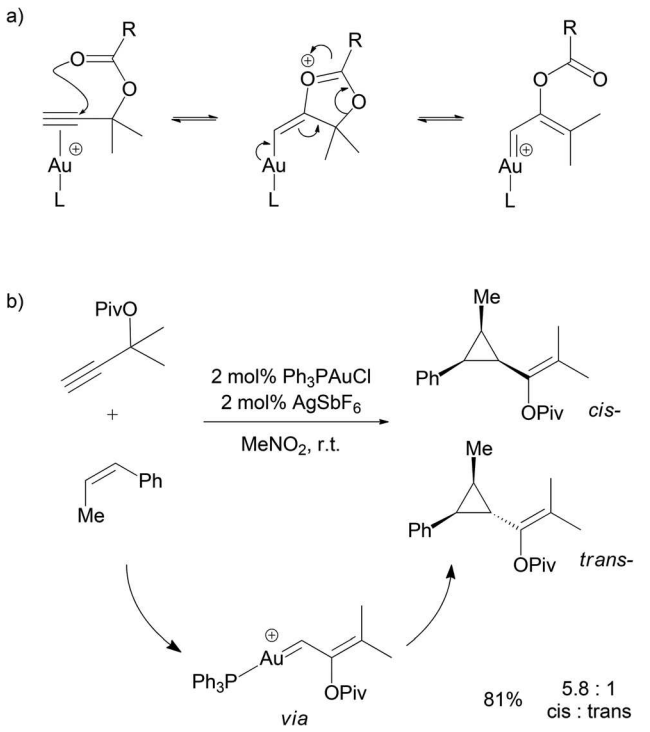


Scheme 2 The catalytic addition of nucleophiles (NuH) to alkynes activated by cationic gold species.

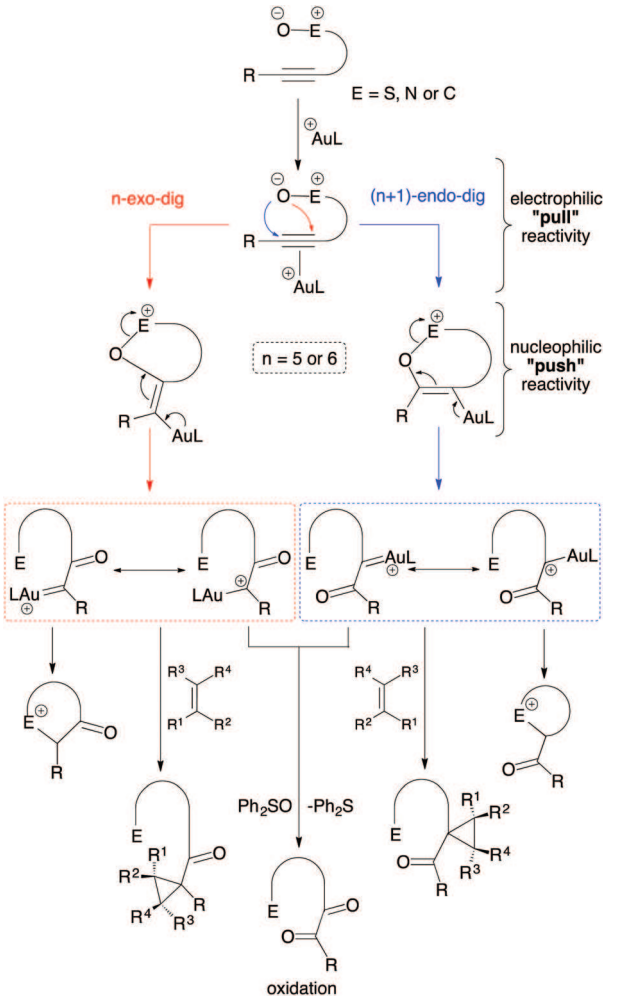
by a nucleophilic alkene stereoselectively generating *cis*-cyclopropane products, consistent with a concerted carbene transfer process as observed in classical transition metal–carbenoid systems (Scheme 3b).[57,58]

This methodology has also been applied in an intramolecular fashion to enynes by the groups of both Liu and Fürstner,[59,60] the latter subsequently utilising it in their total synthesis of the terpene sesquicarene.[61] Sequential intra- then intermolecular reactions have also been demonstrated by Echavarren and co-workers to generate complex molecules containing two cyclopropane moieties.[62] More recently, propargyl esters tethered to furan functionalities have been shown to undergo gold-catalysed cycloisomerisations to generate complex oxygen-containing frameworks.[63]

An important class of reactions in the formation of heteroatom-containing frameworks proceeds *via* the generation of α-oxo gold carbene species formed when a functionality containing a polar element–oxygen (E–O) bond oxidises a gold-activated alkyne; the gold then acts in an "electron-donating" capacity (*vide infra*), eliminating the originally bound element (E).[29,34] These highly reactive gold carbene species are then free to be attacked in an intra- or intermolecular fashion by nucleophiles such as the now coordinatively unsaturated eliminated atom (E), migrating alkyl/hydride groups and arene or alkene-containing species; oxidation is also possible (Scheme 4).[64] These addition–elimination reactions have been observed for sulfoxides,[65–68] epoxides,[69,70] nitrones,[71] nitro substituted species,[72] and both amine,[73,74] and pyridine *N*-oxides.[75–77] Recently the group of Roithová conducted an in-depth investigation into reactions of this type, focussing on the reaction of alkynes with pyridine *N*-oxide in the presence



Scheme 3 (a) The mechanism of gold induced propargyl ester isomerisation (b) the gold catalysed formation of cyclopropanes from propargyl esters and alkenes as observed by Toste *et al.*[56] (Piv = $[C(O)C(CH_3)_3]$).



Scheme 4 The general mechanism of α-oxo carbene formation and their subsequent trapping by various nucleophilic species. Specified reactivity refers to the gold centre.

of $[IPrAu]^+$.[78] In this system it was found that although the naked carbene was present in the gas phase, in the condensed phase the pyridine "traps" the highly reactive species forming an α-oxo gold carbenoid which acts as a synthetic surrogate for the carbene on elimination of pyridine (Scheme 5).

The ambiguity in these systems has sparked debate as to whether the cationic organometallic species generated in these reactions is best described as a gold carbene or a gold-stabilised carbocation.[79] The vast majority of systems isolated have been shown to fall into the latter of the two categories structurally, requiring the positive charge to be resonance-stabilised by heteroatoms,[80–85] stabilised by π-delocalisation[86] or protected from external attack by bulky substituents,[87] in order to be suitably stable for isolation and study. Gold-coordinated carbocationic species without stabilising substituents have however been detected in gas-phase nucleophilic addition reactions.[78,88–90]

Despite these structural observations the propensity of gold to demonstrate nucleophilic "push" reactivity (as shown in Scheme 4) mimics that of a more π-basic metal. Calculations suggest that relativistic components to bonding play a significant role; the contracted s-orbitals increase shielding and result in more diffuse d- and f-orbitals. This shortens and strengthens bonds which would suggest an increase in orbital overlap.[91,92] This relativistic effect on orbital overlap may explain the uncharacteristic reactivity of gold when compared to other d^{10}-metal centres however it then becomes difficult to explain the minimal degree of gold–carbon π-bonding character observed in isolated gold carbene systems. Recently an example of a 'true' gold carbene was published by Bourissou and co-workers that utilises an *o*-carborane diphosphine ligand (Fig. 4a).[93] Due to the bent binding mode of the ligand the energy of the d_{xz} orbital of the coordinated gold(I) centre is increased allowing overlap with higher energy vacant orbitals.[94,95] The result of this effect is a far greater participation of gold in backbonding, a property demonstrated by the formation of the first gold-based classical carbonyl species *i.e.* with an observed lowering of ν(CO) from that of free CO on

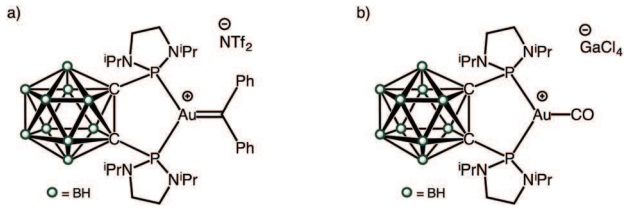


Fig. 4 The (a) gold carbene, and (b) gold carbonyl, complexes isolated by Bourissou and co-workers.[93]

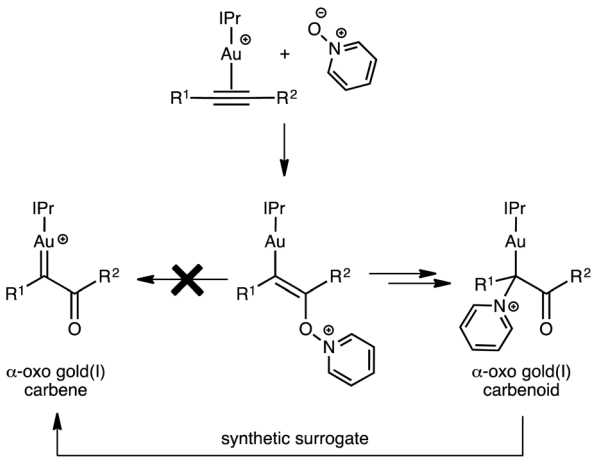
binding (from 2143 cm^{-1} to 2113 cm^{-1}) caused by the partial occupation of the CO π* orbitals (Fig. 4b).

The application of gold carbenes of the type isolated by Bourissou and co-workers to catalysis will likely open up new avenues of reactivity, therefore expanding the versatility of homogeneous gold systems. It will also allow a more definitive comparison of reactivity between systems classified as gold-stabilised cations and those with gold–ligand backbonding. At the very least, it provides detailed insight into the fundamentals of gold coordination chemistry.

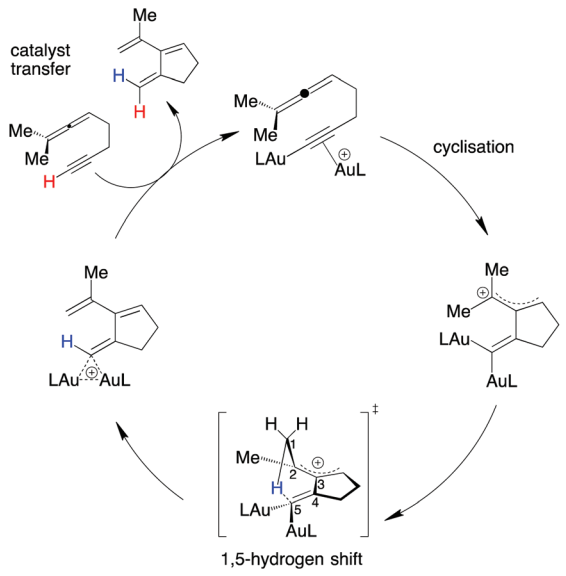
The bonding in these systems should be viewed as a continuum between that of a gold stabilised singlet carbene, as in the Bourissou example, and a metal coordinated carbocation as appears to be the case for the majority of known examples.[96–98] The precise position on this continuum being determined by ancillary ligands and carbene substituents.

Dual activation catalysis – the role of σ-complexes (gold alkynyls)

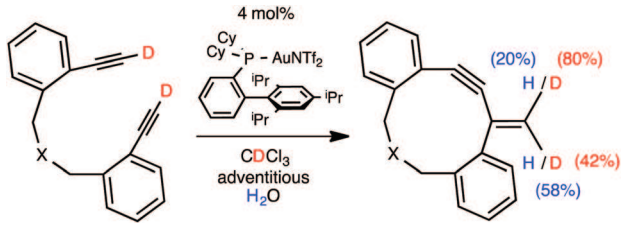
In 2008 Toste and Houk proposed a then unique mechanism whilst studying the cycloisomerisation of 1,5-allenynes.[99] The conditions employed only resulted in the cycloisomerisation of substrates containing terminal alkynes and a detailed experi-



Scheme 5 The preferential formation of the α-oxo gold(I) carbenoid species over the 'naked' α-oxo gold(I) carbene.[78]



Scheme 6 The proposed mechanism of the gold catalysed cycloisomerisation of 1,5-allenynes (L = PPh_3).[99]



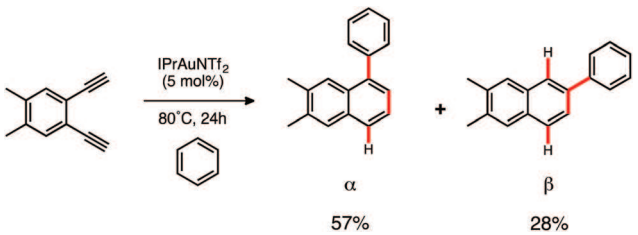
Scheme 7 The observed proton–deuterium exchange as a result of reversible gold alkynyl formation in the cycloisomerisation of diynes.[100] (X = $C(CO_2Me)_2$).

mental and computational study led to the proposal of the catalytic cycle shown in Scheme 6. This was the first indication that more than one gold centre may be involved in a catalytic cycle.

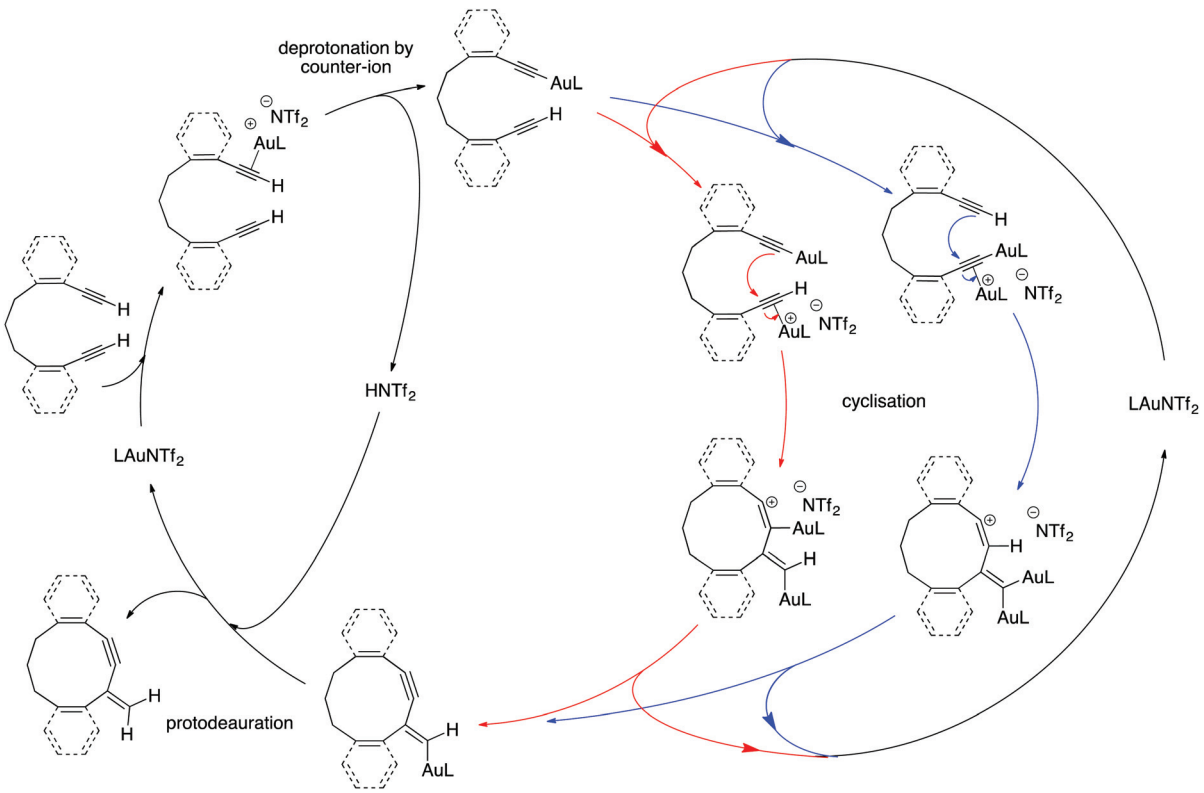
In 2009 Gagosz *et al.* reported the cycloisomerisation of diynes in the formation of medium-sized cyclic alkynes.[100] In deuterium labelling studies, the reactant terminal alkyne exchanged with the solvent system resulting in a mixture of proteo- and deutero-dialkyne starting material and products, again suggesting the presence of gold alkynyls (Scheme 7). Gagosz proposed four potential mechanisms with two possibilities satisfying the results of isotope labelling studies and varying only in the binding-selectivity of a second equivalent of gold, binding to either the alkyne or alkynyl moiety (Scheme 8).

Despite experimental evidence being insufficient to differentiate between these two mechanistic routes Gagosz proposed that the route proceeding *via* alkynyl activation would be more favourable, based on the calculations of Toste and co-workers.[99] This methodology has subsequently been employed in an intermolecular fashion with both terminal alkynes and haloalkynes.[101,102]

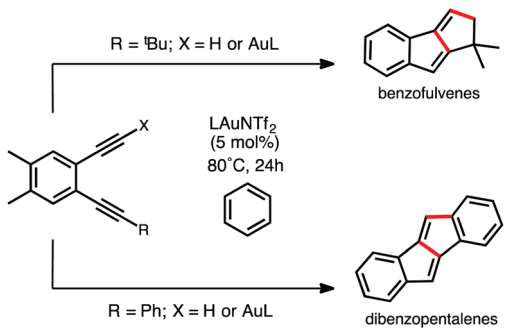
In 2012 the group of Hashmi noted unusual reaction products in the gold catalysed cyclisation of unsubstituted 1,2-dialkynylarenes.[103] In addition to the expected α-substituted naphthalene product, an unexpected β-substituted naphthalene was also isolated (Scheme 9). A subsequent kinetic study showed that initial rapid production of the α-substituted



Scheme 9 The expected α-substituted naphthalene, the result of a 6-*endo*-dig cyclisation onto a gold activated alkyne, accompanied by the unexpected β-substituted product.[103] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene).



Scheme 8 Gagosz's proposed mechanisms for the gold catalysed cycloisomerisation of diynes.[100] Red: π-activation of alkyne rather than alkynyl disfavoured by *ca.* 92 kJ mol^{-1} according to DFT calculations;[99] blue: π-activation of gold alkynyl is more energetically favourable and in agreement with prior calculations. (L = XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl).



Scheme 10 The formation of benzofulvenes and dibenzopentalenes from tertiary butyl and phenyl substituted starting material (or corresponding alkynyls) respectively (L = IPr).

product decreased considerably as production of the β-substituted product began. This was indicative of a change in mechanism and led to the implication of an initial slow formation of the gold alkynyl. In agreement with this, exposure of the corresponding gold alkynyl to catalytic amounts of LAu^+ gave exclusively the β-substituted naphthalene product.

Although alkynyls could be implicated the selectivity of the reaction did not correlate to those previously observed or hypothesised by Toste or Gagosz. Mechanistic clues arose when one of the alkyne moieties was substituted; the groups of both Zhang and Hashmi conducted studies on tertiary-butyl-substituted compounds which yielded benzofulvenes as products[37,104] whilst Hashmi and co-workers also observed the formation of dibenzopentalenes when a phenyl-substituted substrate was employed (Scheme 10).[37,104–106] Both dibenzopentalenes and benzofulvenes showed obvious evidence of an initial five membered ring formation.

Based on the experimental observation of various tricyclic systems formed from 1,2-dialkynylarene substrates and an in-depth computational study of a simplified system, Zhang proposed that the reaction proceeded *via* the formation of a high energy gold–vinylidene intermediate (Scheme 11a).[37] Based on this proposal, Hashmi *et al.* were able to explain the formation of the observed β-substituted naphthalenes *via* the intermolecular attack of a nucleophile at the highly electrophilic α-carbon of the vinylidene; a subsequent hydrogen transfer, shown to occur through isotope labelling studies, would generate a reactive gold carbene which would then undergo a ring expansion to generate the fused six rings as seen in the product (Scheme 11b).

Further evidence for vinylidene-type intermediates was given by the gold-catalysed reaction of 1,2-dialkynylarenes with alkenes which, in agreement with the reaction of carbenes,[47–49,51] undergoes a stereoselective cyclopropanation.[107] The stereoselective nature of the reaction eliminates the possibility of electrophilic attack by a carbenium ion and instead supports the concerted 'trapping' of the alkene by a vinylidene-type species followed by a gold-catalysed cascade of ring expansions to generate benzocyclobutenes (Scheme 12). The radical trapping alkene 1,4-cyclohexadiene also reacted in this manner, excluding the possible involvement of Bergman cyclisation pathways that typically occur in ene/arene–diyne systems.[108–110]

Despite the mounting evidence for the presence of vinylidene intermediates in selected gold-catalysed reactions, it should be noted that vinylidene formation relies on the π-activation of the alkyne moiety rather than the alkynyl (species **A**/**A′** Scheme 11), an energetically disfavoured process as initially noted by Toste and Houk[99] and reinforced by numerous subsequent studies.[35,100,106,111,112] Furthermore vinylidene formation is even more energetically disfavoured than carbene formation as, whilst backbonding remains negligible, the charge on the α-carbon can no longer be stabilised by substituents. These factors have presumably hindered the isolation of a stable gold vinylidene.

Natural bond order (NBO) calculations by Hashmi and Vilhelmsen show that, in the same way that gold carbene species are best described as gold-stabilised carbocations, these vinylidene species are essentially very high energy gold-stabilised vinyl cations.[106] This results in the observed high electrophilicity of the α-carbon which, as can be seen from the calculated LUMO (Fig. 5), possesses a vacant p-orbital. In agreement with this, DFT calculations by Lynam and Fey show that, in comparison to the more π-basic metals ruthenium and rhodium (which, given an appropriate ligand set, can readily form vinylidenes due to their greater backbonding abilities) gold has essentially no thermodynamic propensity to tautomerise to the vinylidene when presented with an alkyne (Fig. 6).[113] Despite this there is experimental evidence to suggest this tautomerisation does occur in rare cases[114] and in the cross coupling of

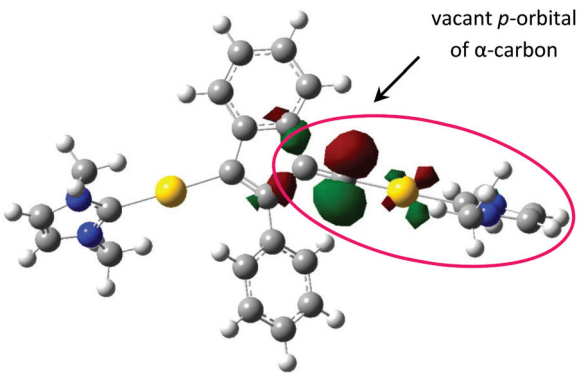
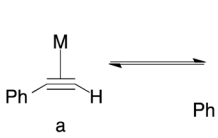
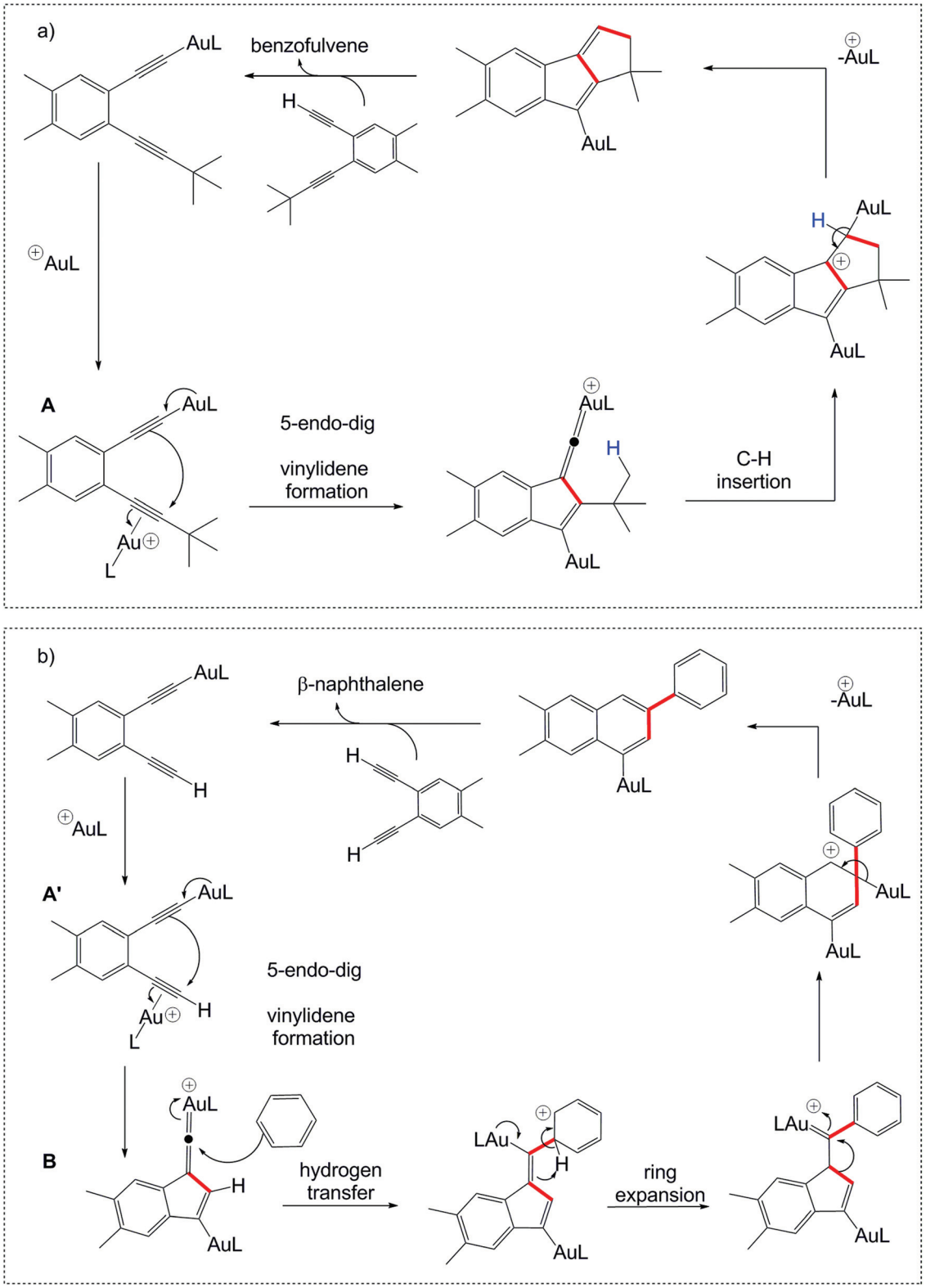


Fig. 5 The calculated LUMO of the intermediate gold(I) vinylidene of the dibenzopentalene synthesis highlighted is the vinylidene ligand (taken from: *Acc. Chem. Res.*, 2014, 47, p. 873).[35]

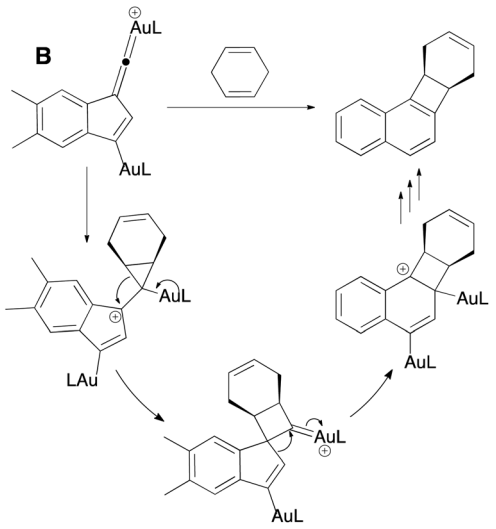


M	$\Delta E_{(v\text{-}a)}$/kJ mol^{-1}
$[RuCl_2(PH_3)_2]$	- 67.44
$[RhCl(PMe_3)_2]$	- 16.53
$[AuIMes]^{\oplus}$	+ 77.29

Fig. 6 The energy difference between the η^2–π-complex (a) and the vinylidene (v) tautomer for d^6-Ru, d^8-Rh and d^{10}-Au.[113] (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene).



Scheme 11 (a) The intramolecular trapping of a high energy gold vinylidene resulting in the observed fused 5-ring motif (L = BrettPhos);[37] (b) attack of the highly electrophilic vinylidene α-carbon by nucleophilic benzene showing the subsequent hydrogen transfer and ring expansion to generate β-substituted naphthalene products (L = IPr).[103]



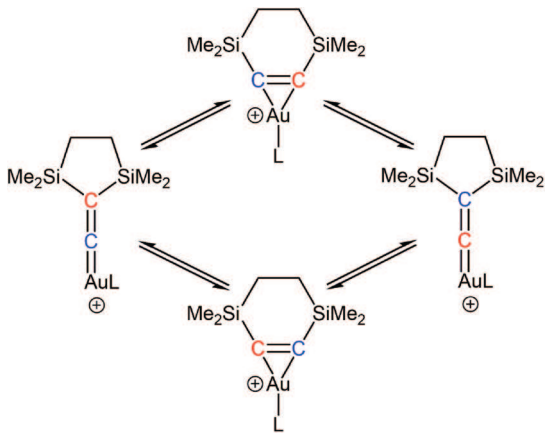
Scheme 12 The stereospecific reaction of vinylidene intermediate B (Scheme 11b) with 1,4-cyclohexadiene showing the subsequent gold-catalysed ring expansion cascade (L = IPr).[107]

enamines and terminal alkynes it has even been postulated that a single gold centre may support both a carbene and a vinylidene ligand simultaneously which reductively eliminate to generate the observed allene products.[115]

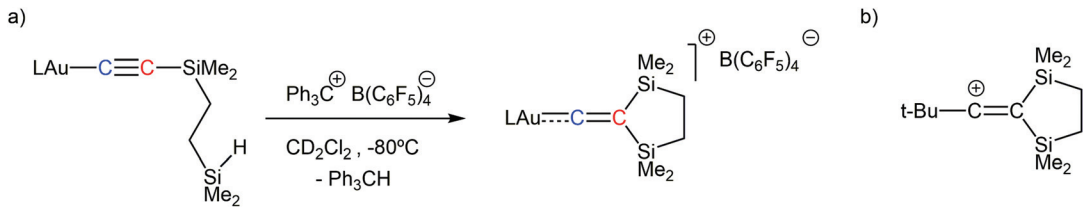
Recently Widenhoefer and Harris synthesised and characterised the first example of a gold(I) vinylidene.[116] This complex was accessed *via* hydride abstraction from a gold (disilyl)-ethylalkynyl complex, $[(L)Au\{\eta^1\text{-}C^1{\equiv}C^2Si(Me)_2CH_2CH_2SiMe_2H\}]$, which cyclises to generate the (β,β-disilyl)vinylidene complex $[(L)Au{=}C^1{=}C^2\overline{Si(Me)_2CH_2CH_2Si}(Me)_2]^+$ (L = P(^{t}Bu)$_2$*o*-biphenyl) (Scheme 13a). Previously Ozawa observed the stabilising effect of silyl substituents at the β carbon in the rhodium-based vinylidene complexes [*trans*-RhCl{=C=C(R)(SiMe$_3$)}(P^{i}Pr$_3$)$_2$] in which vinylidene stability increased in the order R = Ph < ferrocene < SiMe$_3$ leading him to suggest the involvement of β-SiC hyperconjugation in the stabilisation of these complexes.[117] This theory of stabilisation by (σ–π)p hyperconjugation is further supported by analysing complexes bearing tin-substituted vinylidene ligands, study of the crystal structure of the manganese complex $[Mn(\eta^5\text{-}C_5H_5)(Me_2PCH_2CH_2PMe_2)\text{–}\{{=}C{=}C(Ph)(SnMe_3)\}]$ reveals considerable distortion at the β carbon, with the tin centre sitting closer to the α-carbon ($C_\alpha{=}C_\beta$–Sn = 115.2(4)°; $C_\alpha{=}C_\beta$–C = 123.8(5)°);[118] similar structural distortions were also predicted computationally by Lynam and Fey in the optimised structures of vinylidene ligands bearing an SnMe$_3$ group.[113]

The method employed by Widenhoefer and Harris[116] to prepare the gold(I) vinylidene utilises the stabilising effect of β-SiC hyperconjugation[119] in order to dissipate the localised charge of the α-carbon over two silicon centres, as demonstrated by the observed downfield shift in the ^{29}Si NMR spectrum after cyclisation when compared to the neutral precursor alkynyl ($\Delta\delta$ = +54 ppm). Comparison of this value to the related β,β-disilyl-α-*tert*-butyl vinyl cation $[^t\text{Bu-C}^+{=}C\overline{Si(Me)_2CH_2CH_2Si}(Me)_2]$ ($\Delta\delta$ = +86 ppm)[120,121] (Scheme 13b) demonstrates the greater electron donating capacity of the LAu fragment when compared to a tertiary butyl substituent however, it also demonstrates that the main driving force of vinylidene formation is not the ability of gold(I) to stabilise the α-carbon but the silicon centres, verifying the NBO calculations of Hashmi and Vilhelmsen in the nature of the α-carbon.[106]

Although the vinylidene species in Scheme 14 could not be isolated, it was identified by NMR spectroscopy and found to be highly fluxional with C^1 and C^2 undergoing facile interconversion even at −90 °C. It was proposed that interconversion occurs *via* a gold η^2-disilacyclohexyne intermediate, $[(L)Au\{\eta^2\text{-}C{\equiv}C\overline{Si(Me)_2CH_2CH_2Si}(Me)_2\}]^+$ (Scheme 14), based on related phenomena in β,β-disilylvinyl cations bearing α-SiR$_3$ or α-GeR$_3$ groups.[121] Interestingly similar interconversion phenomena have also been observed in the trinuclear ruthenium



Scheme 14 The proposed interconversion of C^1 and C^2 *via* an intermediate η^2-disilacyclohexyne species (L = P(*t*Bu)$_2$*o*-biphenyl).



Scheme 13 (a) Hydride abstraction from a gold (disilyl)ethylalkynyl complex generating a (β,β-disilyl)vinylidene complex;[86] (b) the β,β-disilyl-α-*tert*-butyl vinyl cation (L = P(*t*Bu)$_2$*o*-biphenyl).

complex[122] $[\{Ru(CO)_2(\eta^5\text{-}C_5H_5)\}_3(\eta^1:\eta^2\text{-}C{\equiv}C))]^+$ and the binuclear iron complex[123] $[\{Fe(CO)_2(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C{\equiv}CH)]^+$ the unifying feature between each of these apparently disparate complexes is that the species bound to the $[C{\equiv}C]^{2-}$ motif *i.e.* $[SiR_3]^+$, $[GeR_3]^+$, $[Ru(CO)_2(\eta^5\text{-}C_5H_5)]^+$ and $[Fe(CO)_2(\eta^5\text{-}C_5Me_5)]^+$ can all be considered isolobal to the proton. The same can also be stated of the LAu^+ fragment and as such it should perhaps be of little surprise that it behaves in a similar fashion. Di- and trinuclear gold(I) alkynyl systems also display highly fluxional solution behaviour (*vide infra*),[35,99,100,112,124–126] a contributing factor in the difficulty of determining the catalytically useful species in known systems.

The nature of gold cumulenes has further been explored through the synthesis of a series of gold allenylidenes. In 2013 Hashmi reported the first example of a gold(I) allenylidene complex[127] followed subsequently by the group of Che who published the first gold(III) example.[128] Very recently the Bertrand group has extended the library of gold allenylidenes to include a formally gold(0) as well as homoleptic gold(I) examples.[129] Further work from the Che group outlined the synthesis of a further four examples of homoleptic gold(I) allenylidene complexes (Fig. 7).[130] It is worth noting that the *in situ* formation of gold allenylidenes, on protonation of either *ortho*- or *para*-pyridylethynyls appended to Au_8 clusters, has also been proposed by Konishi *et al.* in order to explain the observed greater perturbation in their electronic properties when compared to that with an appended *meta*-pyridylethynyl ligand.[131]

The groups of both Hashmi and Che elected to utilise a method of allenylidene preparation developed by Fischer and co-workers in which the corresponding metal propiolamide, pyridyl or NHC-based ethynyl complex is methylated at the ligand to generate the corresponding allenylidene complex.[132] In Hashmi's example analysis of the solid-state structures of both the allenylidene complex and the corresponding propiolamide precursor complex show that upon methylation, whilst there is a slight decrease in the Au–C_α distance (1.978(4) Å *vs.* 1.996(4) Å), there is no appreciable lengthening in the C_α–C_β distance (1.196(5) Å *vs.* 1.191(6) Å) which remains in the range of a C≡C bond.[133] This apparent minor reduction in bond order is corroborated on analysing the ν(C≡C) IR frequency which shift only marginally to lower energy ($\Delta\nu$ = 2 cm^{-1}). Methylation also results in a significant contraction in the C_γ–N bond distance (1.28(1) Å *vs.* 1.337(5) Å) suggesting an increase in bond order. Overall this suggests that the stability of the complex is provided primarily by the π-donating nature of the pyrrolidine substituent and that the dominant resonance form is that of a stabilised propargyl cation (structure **II**, Scheme 15) with very little Au–C multiple bonding character.[127]

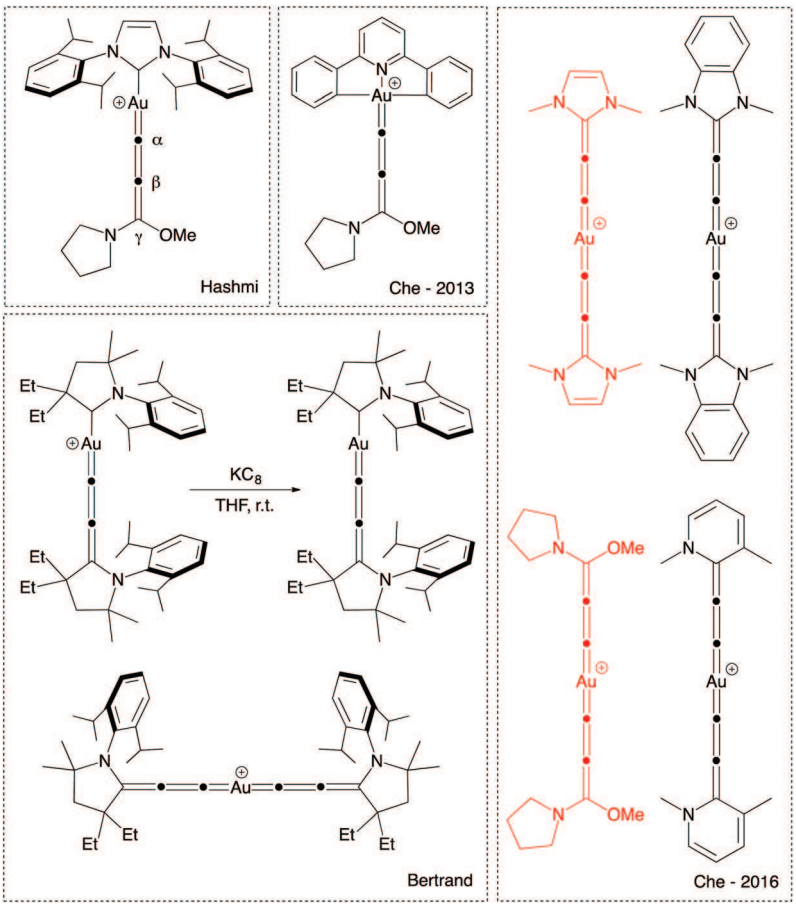
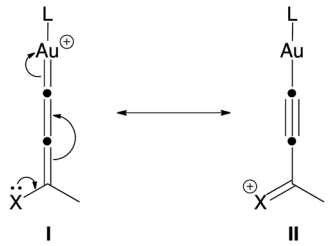


Fig. 7 Isolated gold allenylidene complexes isolated by the groups of Hashmi,[127] Che[128,130] and Bertrand.[129]



Scheme 15 Relationship between allenylidene I and π stabilised propargyl cation II.

Similar conclusions can be reached on studying the gold(III) allenylidene reported by Che and co-workers in 2013.[128] Although the solid-state structure of the propriolamide precursor was not determined the calculated Wiberg bond orders for the allenylidene complex were reported as: Au–C_α = 1.03, C_α–C_β = 2.61, C_β–C_γ = 1.19, C_γ–N = 1.57, C_γ–O = 1.38. It is apparent that the C_α–C_β bond retains triple bond character and this is supported experimentally by the small shift to lower energy observed for the ν(C≡C) IR frequency upon methylation ($\Delta\nu$ = 5 cm^{-1}). Methylation is also once again accompanied by an increase in the bond order between the γ-carbon and the π-donor substituents appended to the allenylidene ligand again suggesting that resonance structure **II** is the dominant one.

Bertrand *et al.* successfully utilised a hydride abstraction methodology in order to synthesise the three related systems seen in Fig. 7.[129] Unfortunately the solid-state state structures of both mono-allenylidene complexes (gold(I) and gold(0)) contained two superimposed molecules in the unit cell, preventing the accurate comparison of the geometric parameters, DFT calculations and Muliken spin density analysis suggest that the reducing electron, on going from the cationic to the neutral complex (Fig. 7), sits on the allenylidene ligand with 93.9% of the spin density occupying the C_α–C_β–C_γ fragment meaning that the complex is best described as a gold(I) centre bearing a paramagnetic, anionic, "allenylidene" ligand. The solid-state structure of Bertrand's homoleptic allenylidene complex however allows analysis of bond lengths, again demonstrating the dominance of resonance structure **II** displaying C_α–C_β distances typical of a C≡C bond at 1.176(8) Å and 1.201(8) Å which are accompanied by shorter C_γ–N bonds (1.298(8) Å and 1.303(8) Å respectively) than would be expected of a C–N single bond. These observations are reiterated by the recent homoleptic examples published by the Che group.[130] Interestingly however, comparison of the calculated structures of both the ground state and the triplet-excited state of two of the homoleptic complexes isolated by Che (Fig. 7: red) showed that promotion of an electron from the C_α–C_β centred HOMO to the Au–C_α centred LUMO resulted lengthening of the C_α–C_β bond and shortening of the Au–C_α bond. This suggests greater delocalisation *i.e.* allenylidene character in the triplet-excited state, an aspect highlighted by the increased planarity of the optimised excited state structures. In summary it can be seen that, as with both gold carbenes and vinylidenes, gold allenylidenes possess very little π-bonding character between the gold centre and the α-carbon of the ligand; the stability of the species arising primarily from delocalisation of the positive charge at the ligand to π-donor substituents appended to the γ-carbon.

Bronsted-acid *vs.* π-acid catalysis

Classically the activation of unsaturated species requires harsh, Brønsted acid conditions;[134] softer methods of catalysis were sought resulting in the application of carbophilic π-acidic transition metal fragments, namely those isolobal to the proton such as mercury(II) and, on realisation of its potential, gold(I).[4,135]

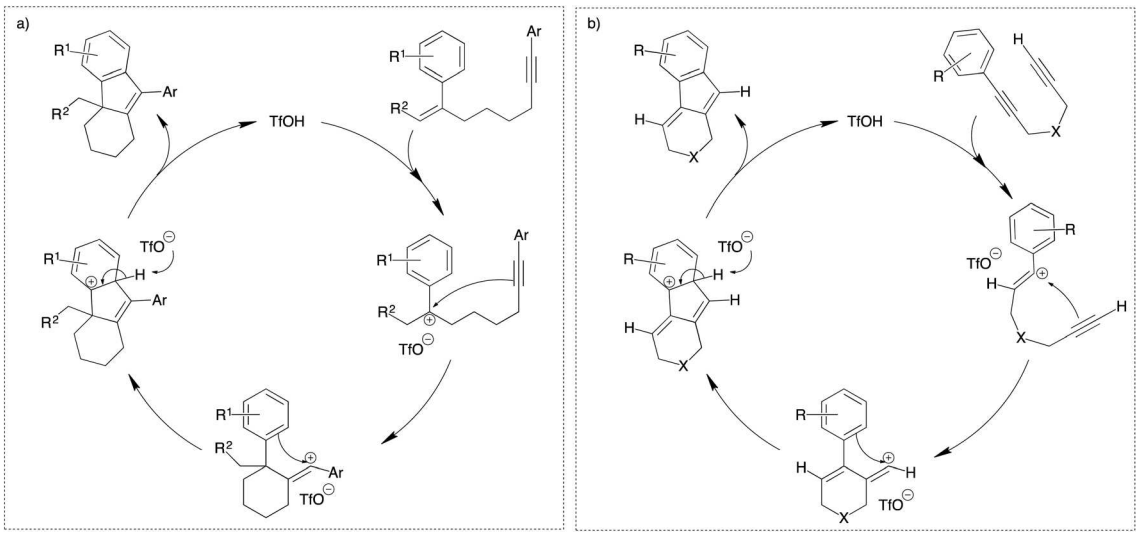
Examples have come to light of strong acids, generated *in situ* by a transition metal complex, catalysing reactions rather than the transition metal itself.[136,137] Work by Jin and Yamamoto has even demonstrated that catalytic amounts of triflic acid successfully catalyses the cycloisomerisation of enynes to give polycyclic frameworks through vinyl cation intermediates (Scheme 16a).[138,139] Related chemistry could easily be envisaged for diynes and would give structures analogous to those of the vinylidene pathways (Scheme 16b). Liu and co-workers have proposed that the gold-catalysed cycloaddition of substituted diynes relies on activation by both π-acidic gold and a strong Brønsted acid generated *in situ* (Scheme 17).[140]

Generation of a gold alkynyl from a terminal alkyne results in the formation of a strong Brønsted acid. The role of the counter-ion as a possible proton shuttle was initially proposed by Gagosz (Scheme 8) and whilst the generated $HNTf_2$ was ruled out as the sole catalytic species, its secondary involvement was not considered.[100] The formation of a gold–alkynyl does not necessarily imply its direct involvement or that it constitutes the only activating species present in the system.

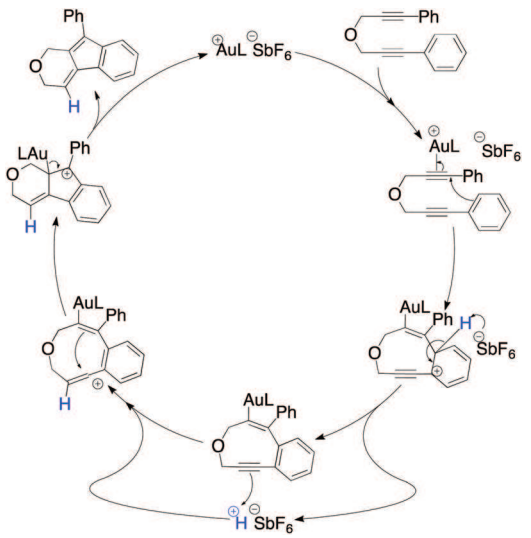
Evidence in favour of this 'fallacy of false cause' argument was recently provided by Echavarren and Obradors who, whilst studying the gold-catalysed cycloaddition of alkynes with oxoalkenes noted that the majority of the gold species added was, at room temperature, in a dinuclear (σ,π) form in solution, as determined by $^{31}P\{^1H\}$ NMR.[141] When the σ,π-complex was isolated and added in catalytic amounts, only 9% conversion was achieved after heating at 50 °C for nineteen hours. On addition of substoichiometric amounts of $HSbF_6$ however, re-equilibration and regeneration of the terminal alkyne (and subsequent π-complex) allowed catalysis to occur; clear evidence that the σ,π-complex is actually a resting state outside of the catalytic cycle in this particular system (Scheme 18) and highlighting the potential role of strong Brønsted acids in this chemistry, either as a catalyst or co-catalyst.

Nuclearity in gold–alkynyl systems

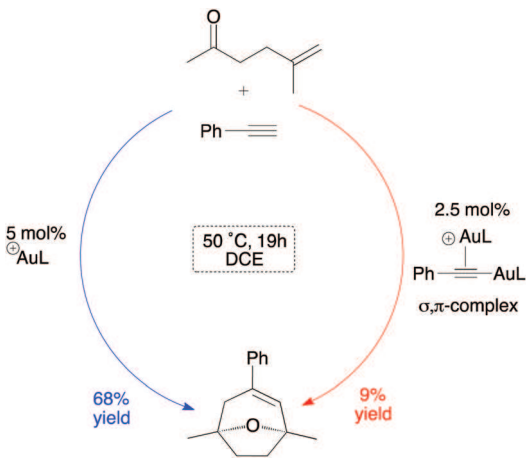
Numerous groups have studied the interaction of LAu^+ species with terminal alkynes in order to try and determine the nature of the active species present in systems believed to proceed *via* dual activation catalysis.[124–126] The solid state products of these reactions typically take the form of dinuclear σ,π



Scheme 16 (a) The Brønsted acid catalysed cycloisomerisation of enynes as reported by Jin and Yamamoto;[138,139] (b) application of the same principle to diynes (hypothetical).



Scheme 17 The cycloisomerisation of substituted diynes as proposed by Liu *et al.* (L = PPh_3). Note the similarities in structure of the substrate and product in comparison to the vinylidene pathway (Scheme 11a).[140]

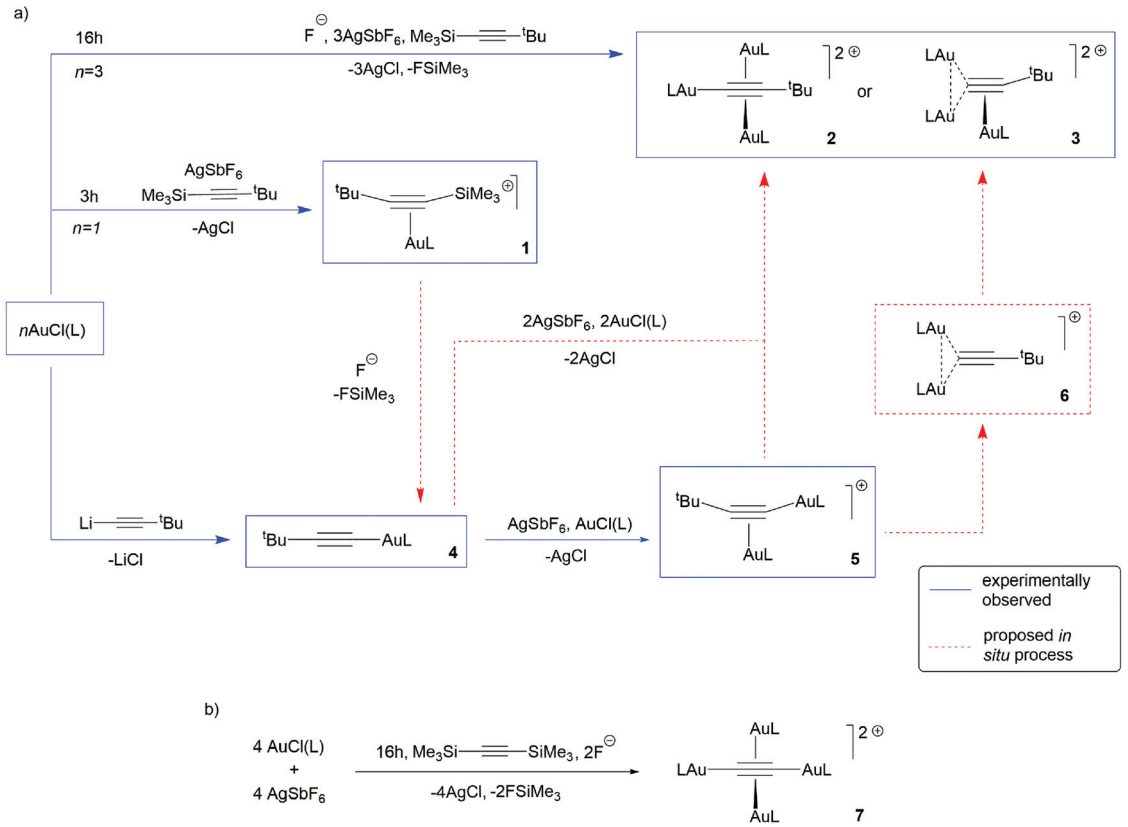


Scheme 18 Schematic showing the reduced catalytic efficacy of the σ,π-species with respect to the AuL^+ species (L = ^{t}BuXPhos).[141]

complexes (see Scheme 18 for the general structure of a σ,π complex) a reflection of the lower energy product on LAu^+ binding to a gold alkynyl ligand as opposed to the substrate alkyne.[35,99,100,106,111,112] These observations have led to the implication of σ,π complexes as important intermediates in a number of catalytic cycles.[35,100,106]

Importantly however the solution state behaviour in the interaction of LAu^+ fragments with terminal alkynes exhibit highly fluxional behaviour and is suggested to assume a range of different mono- and dinuclear species all of which may, and have been proposed to, play a role in catalysis.[35,99]

The diverse nature of binding in LAu^+–C≡C systems is demonstrated neatly by the (^{t}Bu$_3$P)Au^+ examples explored by Russell *et al.*, summarised in Scheme 19a.[126] Addition of AuCl (P^tBu_3) and $AgSbF_6$ to a solution of ^{t}Bu-C≡C–$SiMe_3$ at room temperature resulted in the monocationic π-complex **1** after three hours. Whilst the solid-state structure of **1** was too disordered to accurately assess the geometric parameters, the ^{29}Si $\{^1H\}$ DEPT NMR spectrum displayed a single resonance at δ = −5.2 ppm. Comparison to the unbound alkyne, δ = −18.8 ppm, reveals a shift to higher frequency of 13.6 ppm. This downfield shift, as with the (β,β-disilyl)vinylidene complex (*vide supra*), is caused by the placement of a partial positive charge upon the silicon. This suggests that the silicon atom is involved in (σ–π)p hyperconjugation to the tertiary butyl bound carbon



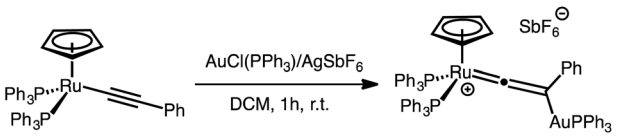
Scheme 19 (a) The relationship between the mono-, di- and trinuclear species isolated by Russell *et al.* (b) The related tetranuclear species isolated by Russell *et al.* (L = P^tBu_3).[126]

atom, itself possessing partial positive charge due to the slipped binding of the gold centre towards the silicon bound carbon.

Repetition of the reaction with three equivalents of AuCl(P^tBu_3)/$AgSbF_6$, stirred at room temperature for 16 h, resulted in the related trinuclear dicationic complexes **2** and **3** isolated in two separate crystallisation experiments. In order to explain the formation of **2** and **3**, Russell proposed that the increase in electrophilicity at silicon allows desilylation of **1** by way of a fluoride ion delivered from the SbF_6^- counter-ion leading to the *in situ* formation of the gold alkynyl complex **4**. Preparation of **4** *via* the salt metathesis of AuCl(P^tBu_3) and ^{t}Bu-C≡C–Li allowed its isolation and characterisation. Subsequent reaction of **4** with one equivalent of AuCl(P^tBu_3)/$AgSbF_6$ lead to the formation of the dinuclear σ,π complex **5** which, on binding a further equivalent of (^{t}Bu$_3$P)Au$^+$ can be envisioned to form **2**. The solid-state structure of **5** reveals that the gold centre bound to the π system shows considerable slipped binding towards the (^{t}Bu$_3$P)Au bound carbon (2.209(5) Å *vs.* 2.307(6) Å) a common motif in σ,π complexes.[112,125,126,141–144] If the bound (^{t}Bu$_3$P)Au$^+$ were to continue to slip it would result in the formation of the *gem*-diaurate complex **6** to which a further equivalent of (^{t}Bu$_3$P)Au$^+$ could bind resulting in complex **3**.

The isolation and structural characterisation of complexes **1–5** indicates that the potential energy surface on which these complexes sit is flat. This is supported by the observation that on redissolving any of the multinuclear complexes only a single resonance is observed in the $^{31}P\{^1H\}$ NMR spectra of these compounds. Russell and co-workers successfully synthesised the tetranuclear complex **7** by stirring Me_3Si–C≡C–$SiMe_3$ with four equivalents of AuCl(P^tBu_3)/$AgSbF_6$ over sixteen hours Scheme 19b. Despite characterisation in the solid-state when redissolved only a single $^{31}P\{^1H\}$ resonance is observed at δ = 93.1 ppm down to temperatures as low as −80 °C. When taken in conjunction with the observation that LAu$^+$ fragments bind preferentially to gold alkynyls over the corresponding terminal alkyne it becomes apparent that even at catalytic loadings once the initial gold alkynyl is formed the nuclearity at the activated substrate molecule is far from restricted to dinuclear complexes theorised to be of such importance.

Recently the groups of Lynam and Fey conducted an investigation into the interaction of the (Ph_3P)Au$^+$ fragment with ruthenium and gold alkynyl complexes in order to study the metal effect on the preferred nuclearity in multinuclear systems.[112] Reaction of AuCl(PPh_3)/$AgSbF_6$ with the ruthenium alkynyl complex [Ru(η^5-C_5H_5)(PPh_3)$_2$(–C≡C–Ph)] led to the clean formation of the corresponding mixed metal vinylidene complex [Ru(η^5-C_5H_5)(PPh_3)$_2$(=C=C(Ph){Au(PPh_3)})]SbF_6 mirroring the reactivity of [Ru(η^5-C_5H_5)(PPh_3)$_2$(–C≡C–Ph)] previously observed for other electrophiles (Scheme 20).[145–147]



Scheme 20 The addition of $[(PPh_3)Au]SbF_6$ to $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(-C{\equiv}C-Ph)]$ to generate $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(=C=C(Ph)\{Au(PPh_3)\})]SbF_6$.[112]

DFT calculations conducted by Fey suggested that d^8-gold(III) may be more adept at stabilising a vinylidene ligand when compared to closed shell d^{10}-gold(I) however attempts to form a gold(III)–gold(I) vinylidene species proved unsuccessful, instead addition of $(Ph_3P)Au^+$ to a gold(III) alkynyl in toluene led to the formation of the corresponding σ,π complex (Scheme 21). Unexpectedly dissolution of the isolated σ,π complex in dichloromethane (DCM) or repetition of the reaction using DCM as the solvent led to the spontaneous formation of a trinuclear $\sigma\text{–}\pi^2\text{–}\sigma$ complex. DFT calculations showed a small energy difference between the σ,π and $\sigma\text{–}\pi^2\text{–}\sigma$ complexes in DCM with the latter being formed preferentially as a result of π–π stacking interactions between the pincer ligands of the gold(III) centres and the formation of a stable gold bis-phosphine by-product (Scheme 21).

Further calculations indicated that trinuclear species of this type may be accessible in gold(I) alkynyl systems which was subsequently demonstrated experimentally by analysing the reaction mixtures in the reaction between gold(I) alkynyls and $(Ph_3P)Au^+$ in DCM by electrospray ionisation mass spectrometry. Interestingly related systems employing more σ-donating ligands appear not to form these trinuclear species,[124–126] further demonstrating the effect that ligand choice may have in selecting the particular species present in solution.

These observations serve to demonstrate further that the solution state chemistry of gold can be effected by numerous factors that may not typically gain much attention, notably solvent choice and the role of dispersion interactions, both of which have been shown to alter the favoured nuclearity in solution and may have profound effects on reactivity as a result.

Conclusions

The nature of gold is ambiguous, as illustrated by the seemingly conflicting patterns of structure and reactivity exhibited by the gold cumulenes.[134] There are examples in which the possibility of Brønsted-acid catalysis is not rigorously excluded and, whilst the evidence in support of gold vinylidene complexes is extensive, it is important to realise that the solution behaviour of gold species is complex and are often dependent on ancillary ligand, substrate[96–98] and solvent choice;[78,112] currently unknown gold species may provide a lower energy pathway to the same products.[148–150] The discovery and characterisation of these solution species is an important future direction, although homogeneous gold-catalysis continues to result in more atom-efficient transformations,[52,61,151–154] it is only with mechanistic understanding that design can begin to be applied allowing the expansion of the available synthetic toolbox.

Acknowledgements

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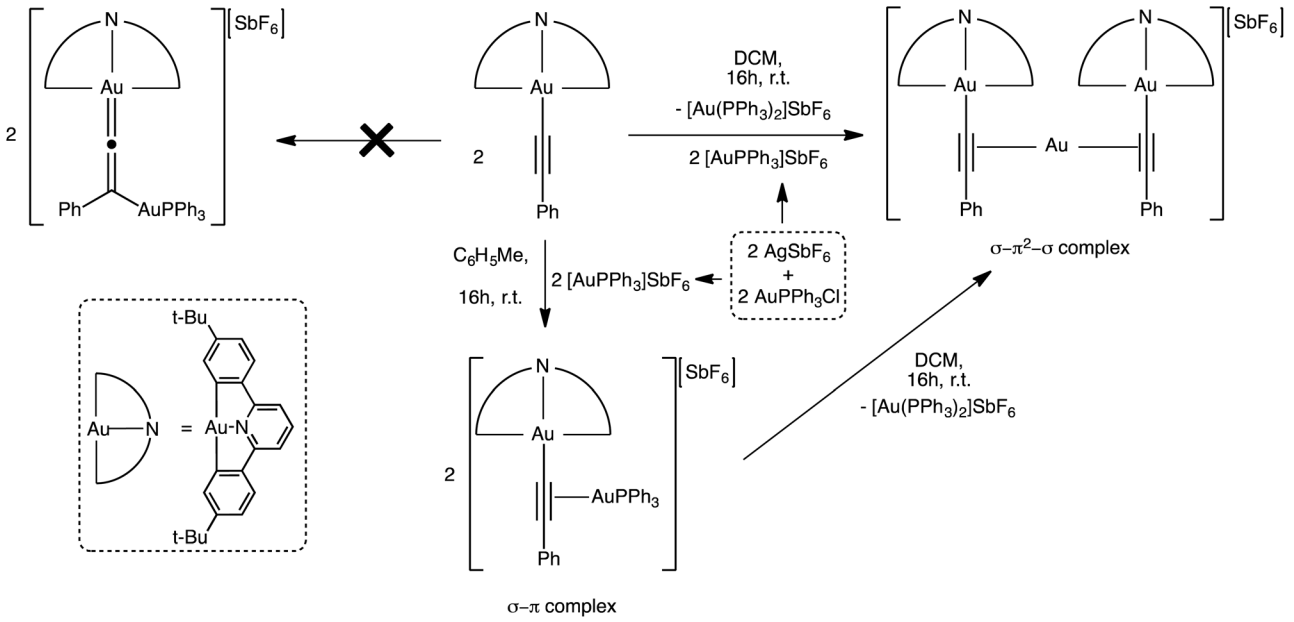

Scheme 21 The experimentally observed solvent effect on gold alkynyl framework nuclearity.[112]

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