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Authors: Huey-San Melanie Siah and Anne Fiksdahl

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FULL PAPER

Preparation and catalytic activity of novel σ,π-dual gold(I) acetylide complexes

Huey-San Melanie Siah[a] and Anne Fiksdahl*[a]

Abstract: Synthesis, characterisation and catalytic activity of a series of novel σ,π-dual gold(I) acetylide complexes are presented. σ,π-Dual gold(I) complexes based on the JohnPhos ligand or the bridging chiral MeO-BIPHEP ligand were generated from terminal alkynes in the presence of an organic base. The catalytic activity of the complexes was explored in a range of gold(I)-catalysed reactions of propargylic alcohol derivatives and their catalytic and enantioselective potential were compared to corresponding monogold(I) phosphane and chiral digold(I) diphosphane species.

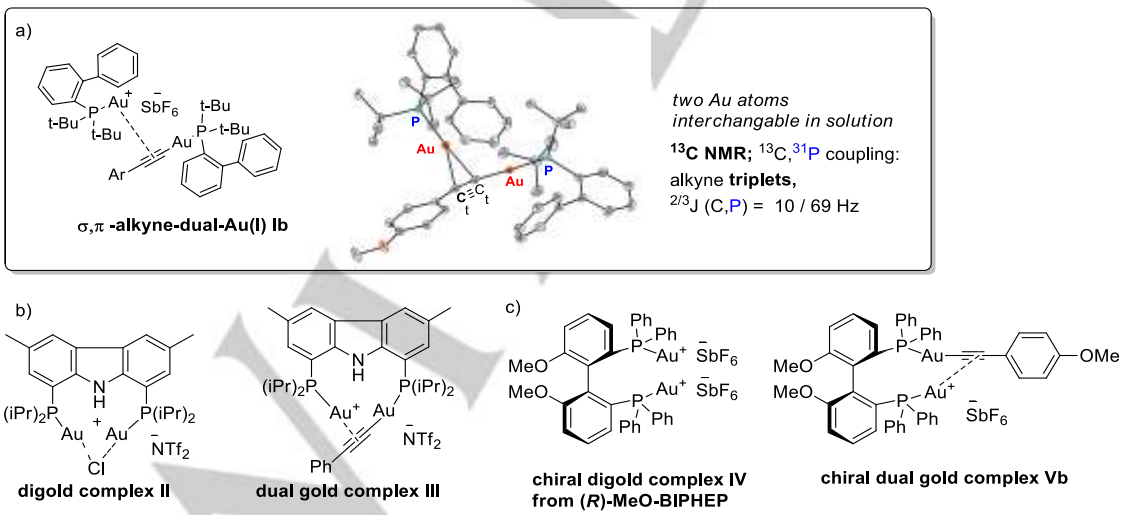
Introduction

σ,π-Dual gold(I) acetylide complexes, mainly based on NHC ligands, have been reported to be active catalytic species in organic transformations, and there is a growing interest for use of such complexes.[1] Investigations of isolated σ,π-dual gold catalysts show different catalytic activity or regioselectivity when compared to monogold complexes.[1a, 2] The Fiksdahl group has previously identified dual gold complexes as the catalytically active species in electrophilic trifluoromethylation of terminal alkynes (Figure 1).[3] It was proposed that the JohnPhos σ,π-dual-Au(I) complex **Ib** (Figure 1a) promoted alkyne-CF_3 product formation in a catalytic manner by transfer of a $[LAu]^+$ fragment from the σ,π-dual-Au complex to the alkyne substrate, activating for trifluoromethylation.

The structures of digold complex **II** and σ,π-dual gold complex **III** (Figure 1b) have recently been reported. The catalytic ability of digold complex **II** has been tested in one reaction,[4] while the catalytic potential of bridged σ,π-dual gold complexes has not been explored so far. In contrast to chiral bridged σ,π-dual gold complexes, such as complex **Vb** (Figure 1c), chiral digold complex **IV** and similar complexes have been applied in enantioselective reactions.[5] Bridged chiral σ,π-dual gold acetylide complexes can be generated from chiral digold complexes and alkynes and may have potential to give different catalytic activity, including enantioselectivity.

The aim of the present study was to acquire more knowledge on the synthesis and properties, as well as the catalytic ability, of new σ,π-dual gold complexes. We also wanted to observe whether the two closer gold atoms in chiral σ,π-dual gold(I) acetylide complexes would provide different regioselectivity or enantioselectivity from the corresponding monogold JohnPhos phosphane complex **VI** and the chiral digold diphosphane complex **IV** (Scheme 1a,b). We hereby present further studies on synthesis and characterisation of novel σ,π–dual gold(I) complexes. Their catalytic activity in different gold(I)-catalysed propargyl reaction is discussed, as well.

Figure 1. a) σ,π-Dual gold(I) acetylide complex **Ib**, reported by the Fiksdahl group.[3] Structures of b) digold and dual gold complexes[4] (**II**, **III**) and c) chiral digold and dual gold complexes (**IV**, **Vb**).



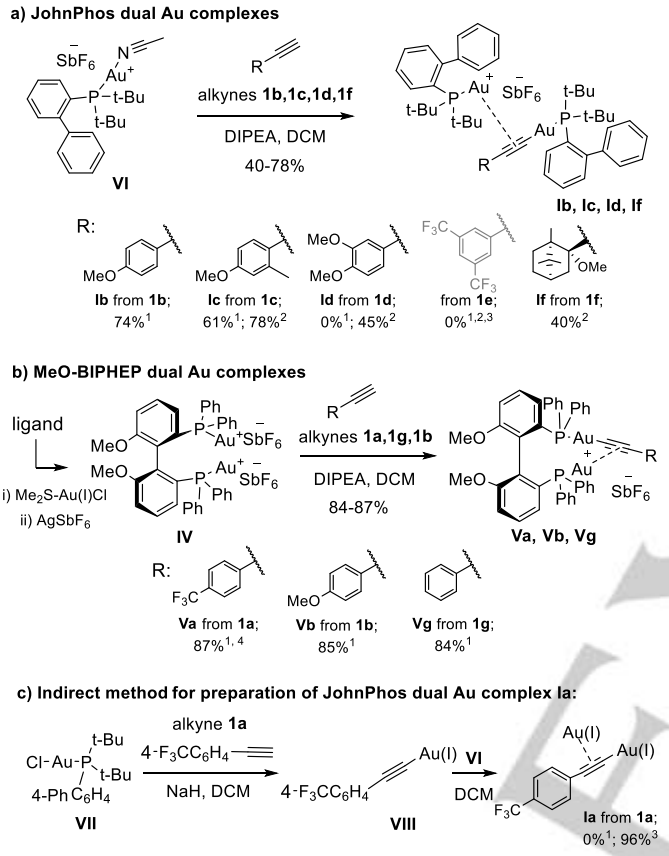
[a] H.-S. M. Siah and prof. dr. A. Fiksdahl
Department of Chemistry, Norwegian University of Science and Technology, Hoegskoleveien, NO-7491 Trondheim, Norway
E-mail: anne.fiksdahl@ntnu.no
Homepage: https://www.ntnu.edu/gold/

Supporting information for this article is given via a link at the end of the document.

Results and Discussion

Synthesis of JohnPhos and MeO-BIPHEP σ,π–dual gold complexes I and V

In order to probe the catalytic activity in reactions of propargylic alcohol derivatives, a series of σ,π-dual gold(I) complexes, with coordinated JohnPhos ligand or the bridging chiral MeO-BIPHEP ligand were synthesised from a range of alkynes, including a chiral alkyne (Scheme 1a-c).



1) direct method; 1:1 ratio; **VI**:alkyne or **IV**:alkyne;
2) direct method; 2:1 ratio; **VI:**alkyne;
3) indirect formation of **Ia**, yield over two steps;
4) dual gold complex unstable in solution

Scheme 1. Preparation of a) JohnPhos dual gold complexes and b) chiral MeO-BIPHEP σ,π-dual gold complexes. c) Indirect preparation method. Yields calculated from amount of gold complex used.

*JohnPhos dual gold complexes **I***

The complexes were prepared from aryl alkynes (**1b**, **1c** and **1d**) and the chiral alkylalkyne **1f** by a procedure based on our previous experience from trifluoromethylation studies (Scheme 1a).[3] By mixing the JohnPhos-Au(I) cationic species **VI** with the appropriate alkyne (**1b**, **1c**, **1d**, **1f**; 1:1 or 2:1 ratio) in the presence of diisopropylethylamine, the dual gold complexes **Ib, Ic, Id** and **If** were obtained in moderate to high yields (40-78%) in a single step. The most electron-rich alkyne **1d**, required excess of the Au(I) source (2:1 ratio **VI**:**1d**), as only the gold-acetylide was formed using a 1:1 ratio. A similar 2:1 ratio of **VI:**alkyne **1c** improved the yield of the dual gold complex **Ic** (from 61% to 78%).

The electron-deficient alkyne **1a** initially failed to give a dual gold complex via the direct method (Scheme 1a), as only the gold-acetylide was formed. However, an indirect method (Scheme 1c), via the gold-acetylide intermediate **VIII** (generated from alkyne **1a** and sodium hydride, and chloride replacement of the JohnPhos gold(I) chloride species **VII**) and final π-coordination of a second cationic gold unit **VI**, gave excellent yield of the desired JohnPhos dual gold complex **Ia** (96% over two steps).

The formation of dual gold complex from the most electron-deficient alkyne **1e** was not successful with any of the methods, as only gold-acetylide was obtained, with no further coordination of a second gold unit. This demonstrates how the nature of the alkyne may favor either dual gold complex or gold-acetylide formation.

*(R)-MeO-BIPHEP bridged dual gold complexes **V***

In initial studies, digold complexes, such as (*R*)-MeO-BIPHEP-digold **IV** (Scheme 1b), were generated *in situ*[5e] from five chiral diphosphane ligands ((*R*)-BINAP, (*R,R*)-DIOP, (*R*)-Phanephos, (*R*)-MeO-BIPHEP and (*S*)-iPr-MeOBIPHEP) by complexation with gold chloride (Me_2S-Au(I)Cl) and counterion exchange, as shown by NMR (Figure 2). The digold complexes were identified by ^{1}H and ^{31}P NMR. Synthesis of the target bridged dual gold complexes from the digold complexes and alkyne **1b** gave products with varied purity and stability (NMR, MS). However, the stable bridged (*R*)-MeO-BIPHEP σ,π-dual gold complex **Vb** was successfully obtained from digold species **IV** and alkyne **1b.**

Thus, mixing the digold species **IV** with the appropriate electron-rich or electron deficient arylalkyne (**1a**, **1b** and **1g**) (1:1 ratio **IV**:alkyne) in the presence of diisopropylethylamine, afforded the (*R*)-MeO-BIPHEP bridged dual gold complexes **Va, Vb** and **Vg** in high yields in a single step (84-87%, Scheme 1b). The dual gold complexes were characterised and identified by NMR (^{1}H, ^{19}F, ^{13}C, ^{31}P) and HRMS.

NMR studies

The dual gold(I) complex **Ib** has previously been studied by the Fiksdahl group.[3] The crystal structure (XRD, Figure 1a) confirmed the σ,π-coordination of the gold units in the solid state, while NMR data indicated that the gold units are interchangeable in solution, as both alkyne ^{13}C NMR signals were recorded as triplets (^{13}C-^{31}P coupling). Only a single set of proton signals and a single phosphorous signal from the gold ligand was seen in ^{1}H and ^{31}P NMR, in accordance with previous reports.[6] Similar NMR observations were made for complexes **Ia**, **Ic, Id, If** and **Va**, **Vb**, **Vg** in the present study.

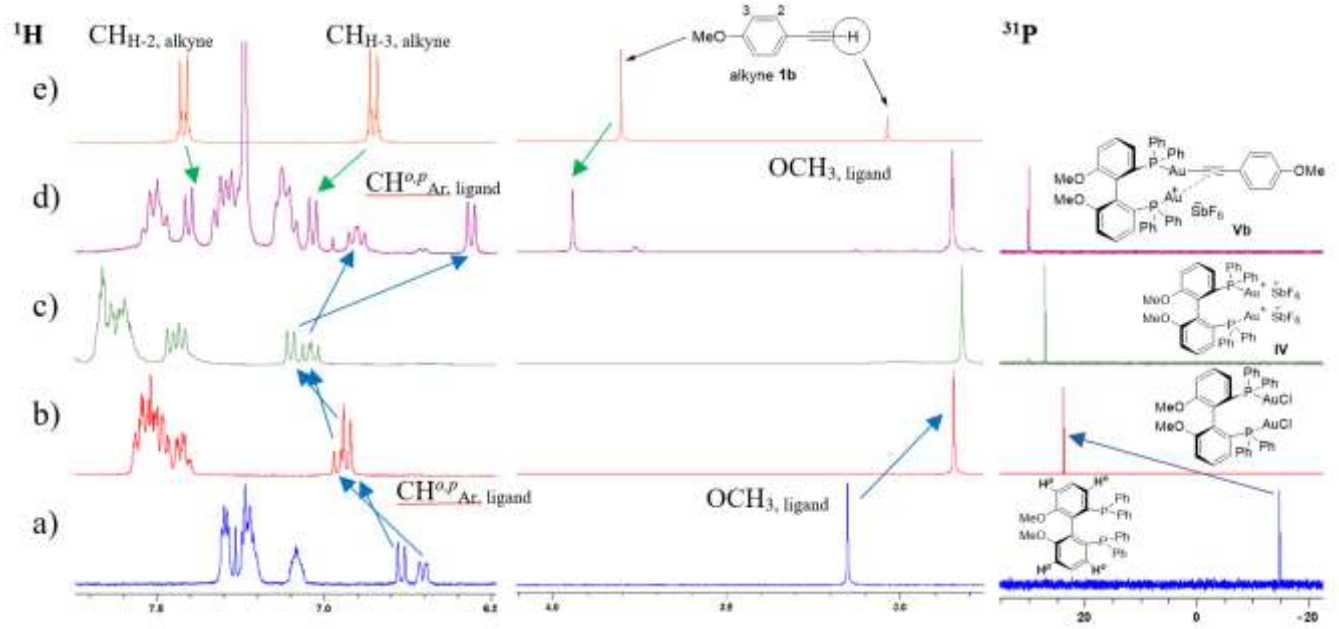


Figure 2. ^{1}H and ^{31}P NMR studies of a) the (*R*)-MeO-BIPHEP ligand through b) complexation with gold chloride, c) counter-ion exchange (**IV**) and d) formation of dual gold complex **Vb** with e) alkyne **1b**.

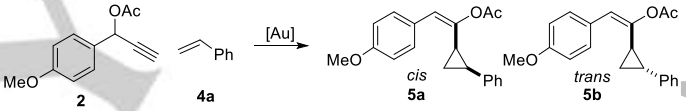
The generation of the (*R*)-MeO-BIPHEP dual gold complex **Vb** (Figure 2a-e) from the diphosphane ligand (a) by complexation with gold chloride to give the digold complex (b), subsequent exchange with a non-coordinating anion (c) and by final formation of the target dual gold complex **Vb** (d) of alkyne **1b** (e), was clearly followed by ^{1}H and ^{31}P NMR studies. The methoxy ^{1}H NMR signal from the MeO-BIPHEP ligand showed a significant shielding effect by ligand coordination to give the digold complex. Smaller changes were also observed by further transformation into the dual gold complex **Vb**. The effect on the aromatic ligand protons, particularly in biphenyl *ortho* and *para* positions, was noticeable all through the process a)-d) to give the target dual gold complex **Vb**. Also, coordination is shown by distinct ^{1}H NMR patterns of alkyne **1b**, as the methoxy signal and the aromatic H-3 protons experience a deshielding effect and move to higher shift values. As expected, the terminal alkyne proton disappears by complexation. The changes in the phosphorous environment were also seen by ^{31}P NMR. In particular, a characteristic deshielding effect was observed as a large change to a higher ^{31}P NMR shift value (from −15 ppm to 24 ppm) by initial ligand coordination to AuCl to give the digold complex. Smaller deshielding effects were also observed throughout the next steps towards the final dual complex **Vb**.

Reactivity of JohnPhos dual gold complexes I in reactions of propargylic alcohol derivatives

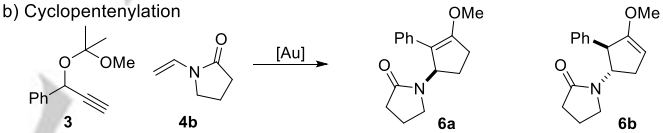
Based on our previous studies,[7] the catalytic activity of the synthesised JohnPhos dual-gold complexes **I** was tested in three gold(I)-catalysed propargyl ester and acetal reactions. The results from a) cyclopropanation,[7a] b) cyclopentenylation[7b] and c) tandem cyclisation[7c] were compared with our results obtained with JohnPhos monogold(I)-complex **VI** previously[7b, 7c] or in the current study (Table 1a-c).

Table 1. Gold(I)-catalysed propargyl test reactions; a) cyclopropanation,[7a] b) cyclopentenylation[7b] and c) tandem cyclisation reactions[7c] with known monogold complex **VI** and dual gold complexes **I**.

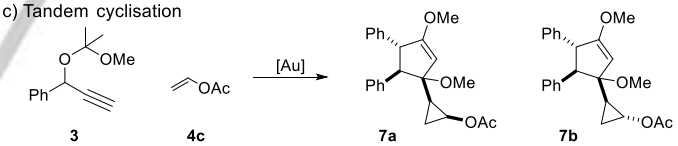
a) Cyclopropanation



b) Cyclopentenylation



c) Tandem cyclisation



Entry	Complex	Temp.	Time	Yield	Ratio
a) Cyclopropanation[a] **2+4a:**					**5a : 5b**
1	**VI**	r.t.	30 min	98%	2 : 1
2	**Ia**	r.t.	24 h	89%	8 : 1
3	**Ib**	40 °C	4 h	97%	8 : 1
4	**Ic**	40 °C	24 h	91%	9 : 1
5	**Id**	r.t.	2 h	94%	8 : 1
6	**If**	r.t.	24 h	99%	8 : 1
b) Cyclopentenylation[b] **3+4b:**					**6a : 6b**
7	**VI**[7b]	r.t.	15 min	61%	1 : 0
8	**Ia**	r.t.	2 h	66%	1 : 2
9	**Ib**	r.t.	24 h	36%	1 : 1
10	**Ic**	r.t.	2 h	68%	1 : 2.4
11	**Id**	40 °C	24 h	19%	0 : 1
12	**If**	r.t.	24 h	66%	1 : 3
c) Tandem cyclisation[c] **3+4c:**					**7a : 7b**
13	**VI**[7c]	r.t.	15 min	54%	60 : 40
14	**Ia**	r.t.	15 min	48%	55 : 45
15	**Ib**	r.t.	2 h	55%	57 : 43
16	**Ic**	r.t.	1 h	61%	56 : 44
17	**Id**	r.t.	1 h	31%	55 : 45
18	**If**	r.t.	24 h	57%	56 : 44

Reaction conditions: a) propargyl ester **2** (1 equiv.) and alkene **4a** (4 equiv.) in CH_2Cl_2 ($c \approx 50$ mM) with gold catalyst (5 mol%); b) propargyl acetal **3** (1 equiv.) and alkene **4b** (3 equiv.) in CH_2Cl_2 ($c \approx 80$ mM) with gold catalyst (5 mol%). c) propargyl acetal **3** (1 equiv.) and alkene **4c** (3 equiv.) in CH_2Cl_2 ($c \approx 80$ mM) with gold catalyst (5 mol%).

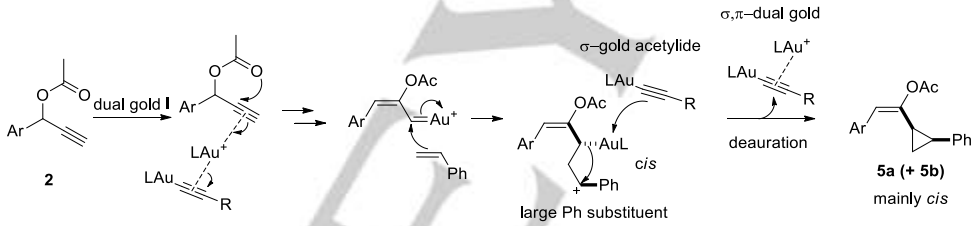
The five dual gold complexes **I** gave excellent yields in cyclopropanation of propargyl ester **2** with styrene **4a** (89-99% of **5**, Table 1a, entries 2-6), low to good yields for the cyclopentenylation of propargyl acetal **3** with 1-vinylpyrrolidin-2-one **4b** (19-68% of **6**, Table 1b, entries 8-12), and moderate yields for the tandem cyclisation reaction between propargyl acetal **3** with vinyl acetate **4c** (31-61% of **7**, Table 1c, entries 14-18). In all reactions, more than one of the new dual gold complexes gave higher yields than JohnPhos monogold complex **VI** (entries 1,7,13). In addition, higher *cis*-diastereoselectivity was obtained in cyclopropanation with all dual gold complexes (up to 80% de, entries 2-6, Table 1a). A regioselectivity shift for cyclopentenylation into the other enol ether product **6b** (up to 100%, entry 11, Table 1b) was observed, as well. The selective formation of the *trans* isomer was in accordance with previous studies.[7b]

The preferences for other isomers may generally be explained by the cyclisation deauration step, where the stereo- or regioselectivity is determined by transfer of the substrate-connected gold unit back to the σ-gold-acetylide to regenerate the σ,π-dual gold complex (Schemes 2-4). In the deauration step, favouring *cis*-cyclopropanation (Table 1a, entries 2-6), the bulky departing gold unit may prefer *cis* relation to the rigid phenyl ring in the substrate, to enable approach and coordination of the σ-gold-acetylide (Scheme 2) to regenerate the σ,π-dual gold complex.

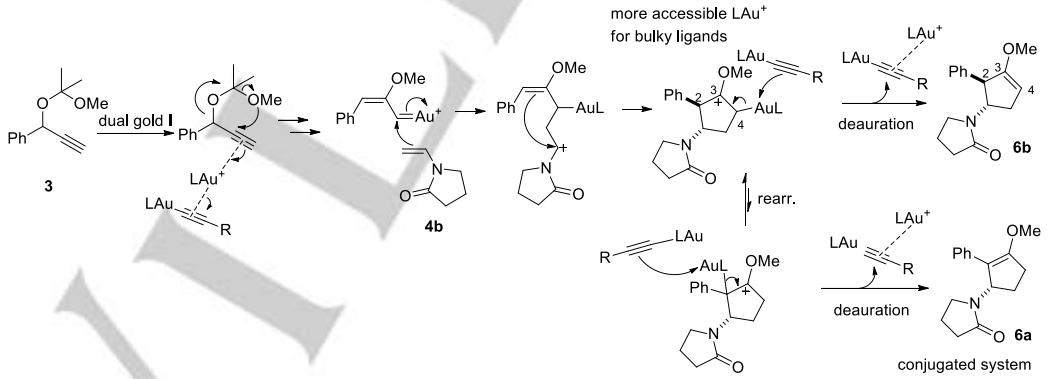
Cyclopentenylation, catalysed by the dual gold complexes **I**, with electron-withdrawing or bulky ligands, gives mainly enol ether product **6b** (up to 100% of total **6**, entries 8-12). The reaction may be rationalised by cleavage of the bulky gold unit from the most accessible 4-position of the substrate to regenerate the σ,π-dual gold complex (Scheme 3). The exclusive formation of isomer **6a** with the less bulky monogold (JohnPhos) complex **VI** (entry 7) may be enabled by formation of a stabilised conjugated system in product **6a** by rearrangement into the more crowded Au-benzylic intermediate.

No significant change in stereoselectivity was apparent for the tandem cyclisation reaction, as the smaller and more flexible acetyl group may not interfere with the incoming σ-gold-acetylide (Scheme 4) to the same extent as the more rigid and bulky phenyl group in the cyclopropanation reaction above (Scheme 2).

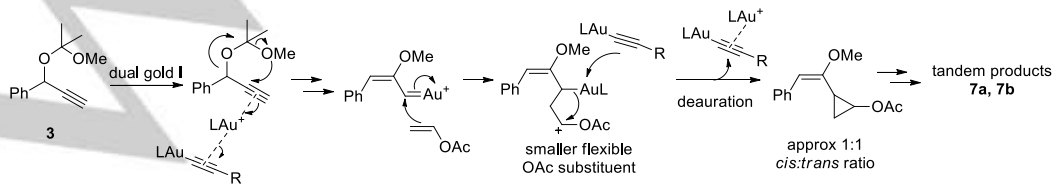
All reactions using dual gold complexes **I** required longer times or higher temperatures than the commercially available monogold complex **VI**. The lower reactivity may be caused by the necessary transfer of the π-bonded gold unit from the dual gold complex to the propargyl substrates, to act as a catalytic species (Schemes 2-4).



Scheme 2. Proposed mechanism of dual gold-catalysed cyclopropanation (Table 1a) of propargyl ester **2** and styrene, **4a**.



Scheme 3. Proposed mechanism of dual gold-catalysed cyclopentenylation (Table 1b) of propargyl acetal **3** and vinyl amide **4b.**



Scheme 4. Proposed mechanism of the cyclopropanation step of dual gold-catalysed tandem cyclisation (Table 1c) of propargyl acetal **3** and vinyl acetate, **4c**.

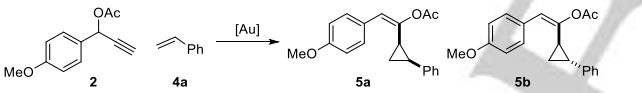
The electronic and steric properties of the substituents on alkynes **1b-f** affect the reactivity of the dual gold complexes, but the trend is not clear, as the overall reactivity is influenced by at least two opposing factors. The initial step, where the catalytic active gold unit is disconnected from the dual gold-acetylide complex and transferred to the propargyl substrate (Schemes 2-4), would likely require an energy barrier crossing. Electron-rich (e.g. complex **Id**, entries 11 and 17) or sterically non-hindered gold-acetylides may deactivate for initial disconnection and transfer of the π-bonded gold unit, but would, in contrast, activate for final deauration to regenerate the σ,π-dual gold complex by re-connection to the σ-gold-acetylide.

The chiral dual gold complex **If**, based on the chiral MeO-camphorylalkyne **1f**, did not induce any enantioselectivity in cyclopropanation or cyclopentenylation reactions (HPLC, GLC), probably due to the long distance between the chiral acetylide unit and the propargyl substrate in the stereogenerating deauration step. The proposed mechanisms (Schemes 2-4) are supported by results from our earlier trifluoromethylation study where the dual gold complex was the sole gold species observed.[3]

Reactivity of chiral (*R*)-MeO-BIPHEP *dual-gold complexes V in reactions of propargylic alcohol derivatives*

Based on our previous studies,[7c, 8] the catalytic activity and stereoselectivity of chiral dual gold complexes **V** were tested in gold(I)-catalysed reactions of propargylic alcohol derivatives (Tables 2-5 and Scheme 5). The results were compared with our corresponding results with digold complex **IV** and JohnPhos monogold-complex **VI**.[7c, 8]

Table 2. Gold(I)-catalysed propargyl cyclopropanation with monogold (**VI**) digold (**IV**) and dual gold complexes (**V**).



Entry	[Au]	Temp.	Time	Yield	**5a**:**5b**	ee[b] **5a**; *cis*	ee[b] **5b**; *trans*
1	**VI**	r.t.	15 min	98%	2:1	-	-
2	**IV**	r.t.	2 h	58%	1:0	65%	-
3	**Va**	−40 °C	6 h	0%	-	-	-
4		−40 °C to 10 °C	18 h	40%	14:1	43%	35%
5		−20 °C	24 h	40%	6:1	52%	15%
6		0 °C	3 h	66%	3:1	50%	10%
7		r.t.	2 h	36%	1:0	38%	-
8	**Vg**	0-4 °C	24 h	56%	11:1	51%	20%
9		r.t.	6 h	76%	1:0	40%	-
10	**Vb**	r.t.	24 h	40%	1:0	44%	-
11		40 °C	4 h	61%	1:0	40%	-

a) The reactions were performed with propargyl ester **2** (1 equiv.) and alkene **4a** (4 equiv.) in CH_2Cl_2 (*c* ≈ 50 mM) together with gold catalyst (5 mol%); b) % ee determined by HPLC (Chiralpak AD Column 5:95 2-propanol:hexane, 0.8 mL/min).

Fair yields of products **5** (61-76%) were obtained in cyclopropanation of propargyl ester **2** and alkene **4a** in the presence of (*R*)-MeO-BIPHEP complexes **V** (Table 2).[7a] Reaction times with digold complex **IV** and dual gold complexes **V**, were longer compared to the monogold complex **VI** (Table 2, entries 1, 2, 7, 9 and 10), as also seen for dual gold complexes **I** above (Table 1a). The reaction times to give full conversion increased with increasing electron-density of the acetylide (entries 7, 9 and 10; 2 h to 24 h at r.t.), which indicates that the rate-determining step in this reaction is the disconnection of the π-bound gold unit from the σ,π-dual gold complex.

The digold and bridged dual gold complexes **V** give exclusive *cis* diastereomer formation at r.t. (entries 2, 7, 9, 10), as seen for complexes **I**, likely for the same deauration reason as discussed above (Scheme 2). The enantioselectivity of the reactions was positively affected by temperature reduction. All the tested chiral (*R*)-MeO-BIPHEP complexes **IV** and **V** gave substantial enantioselectivity (65% ee of *cis*-**5a** with digold complex **IV**, entry 2; and up to 52% ee *cis*-**5a** with dual gold complexes **V**, entries 5, 8, 10). The lower enantioselectivity obtained with dual gold complexes than the digold complex **IV**, may be explained by a conceivable *gem*-digold intermediate,[1b, 9] which is possible for monogold complex **VI** and digold complex **IV**, but not for the bridged dual gold complexes **V** (Figure 3a).

The cyclopentenylation reaction of propargyl ester **2** and sulfonamide **4d**[8] with bridged dual gold complexes **V** (Table 3a, entries 5-9) gave selectively the vinyl acetate product **8** (up to 67%). In contrast to cyclopropanation results (Table 2), the bridged dual gold complexes **V** gave higher enantioselectivity (42-46% ee of **8** at r.t.; entries 4-9) than the digold complex **IV** (<16% ee, entries 2 and 3).

An explanation for the higher enantioselectivity of the dual gold complexes in cyclopentenylation reactions, may be seen in the cyclisation step, which determines the enantioselectivity (Figure 3b). As a larger ring is formed, the gold centers are less directly involved. Therefore, the effect of a possible *gem*-digold complex on the enantioselectivity of the reaction is reduced, and the selectivity is likely mainly dependent on the bulkiness of the overall gold complex.

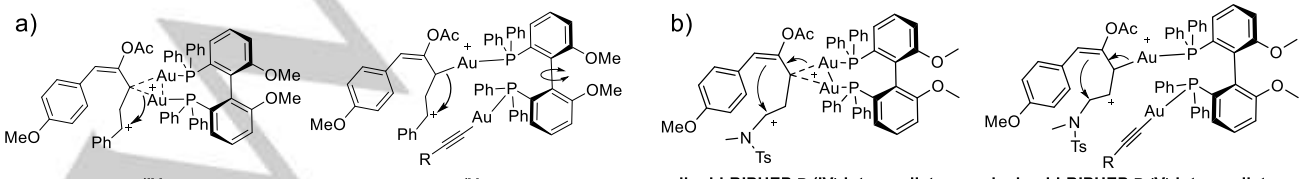
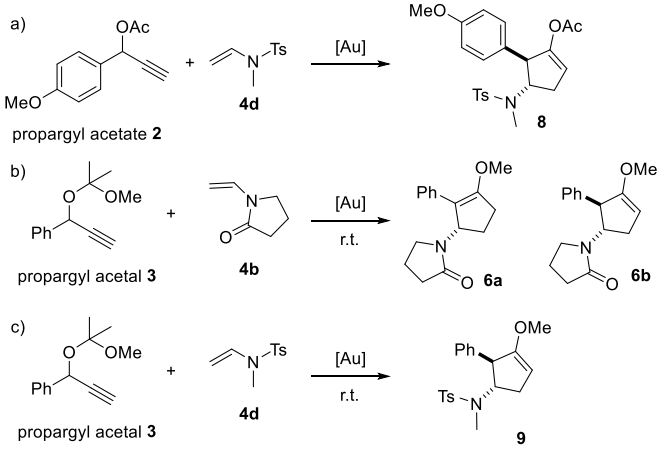


Figure 3. Possible gold-intermediates with digold complex **IV** and dual gold complexes **V** in the deauration step of the a) cyclopropanation reaction (Scheme 2) and b) cyclopentenylation reactions (Scheme 3).

Table 3. Gold(I)-catalysed propargyl cyclopentenylation with gold complexes **IV**, **VI** and **V**[a]



Entry	Au (I)	Alkene	Temp.	Time	Product yield	ee[c]
a) Propargyl acetate **2**:					**8:**	
1	**VI**	**4d**	r.t.	15 min	64%	-
2	**IV**	**4d**	r.t.	5 h	58%[b]	9%
3		**4d**	40 °C	3 h	40%[b]	16%
4	**Va**	**4d**	r.t.	5 h	19%	42%
5		**4d**	40 °C	2 h	38%[b]	36%
6	**Vg**	**4d**	r.t.	72 h	18%[b]	46%
7		**4d**	40 °C	24 h	29%	44%
8	**Vb**	**4d**	r.t.	3 h	67%[b]	44%
9		**4d**	40 °C	3 h	32%[b]	39%
b) Propargyl acetal **3**:					**6a:**	
10	**VI**	**4b**	r.t.	15 min	61%	-
11	**IV,Va,Vb**	**4b**	r.t.	48 h	5-24%[b]	-
12	**Vg**	**4b**	r.t.	48 h	31%	14%
c) Propargyl acetal **3**:					**9:**	
13	**VI**	**4d**	r.t.	15 min	54%	-
14	**IV**	**4d**	r.t.	48 h	26%	32%
15	**Va**	**4d**	r.t.	48 h	33%	32%
16	**Vg**	**4d**	r.t.	48 h	30%	36%
17	**Vb**	**4d**	r.t.	24 h	55%	38%

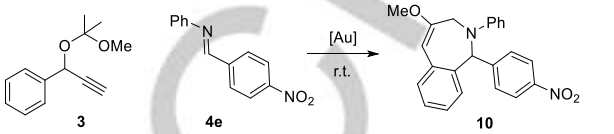
a) The reactions were performed with propargyl ester **2** (1 equiv.) and alkene **4d** (2 equiv.) in CH_2Cl_2 ($c \approx 17$ mM); or acetal **3** (1 equiv.) and alkene **4b** or **4d** (3 equiv.) in CH_2Cl_2 ($c \approx 80$ mM) in the presence of gold catalyst (5 mol%); b) yield calculated by NMR from product mixture; c) % ee of products **6**, **8** and **9** determined by HPLC (Chiralpak AD Column 10:90 2-propanol:hexane, 0.8 mL/min for product **8**; 1.0 mL/min for products **6a/6b**; 0.5 mL/min for **9**).

Corresponding cyclopentenylation reactions of the more reactive propargyl acetal **3** with vinyl amide **4b**[7b] (Table 3b, entries 10-12) were studied, as well. However, the di-/dual gold complexes **IV** and **V** performed poorly, and only low yields of product **6a**, were estimated from complex product mixtures (NMR; 5-31% yield in 48 h). Analysis of isolated enol ether **6a** (31%) indicated low enantioselectivity (14% ee, entry 12).

The reaction was further studied by replacing the electron deficient vinyl amide **4b** with the moderately deactivated vinyl sulfonamide **4d**[10] (Table 3c, entries 13-17).[7b] The effect was apparent, and higher yields and greater enantiomeric excess of the enol ether product **9** were obtained for the dual gold complexes **V** (33-55% yield of **9**, 32-38% ee), relative to the digold complex **IV** (26% yield of **9**, 32% ee), as discussed above (Table 3a and Figure 3b). Highest yield (55% of product **9**, entry 17), comparable to monogold complex **VI** (54%, entry 13), was obtained with the dual gold complex **Vb** with electron-rich acetylide (4-OMe-C_6H_4). This result may imply that the catalytic efficiency is controlled by regeneration step of the σ,π-dual gold complex in the final deauration.

The slow gold-catalysed [2+5] cycloaddition of propargyl acetal **3** and imine **4e**[11] afforded benzazepine product **10** less efficiently with di-/dual gold complexes **IV** and **V** (17-42% in 42 h, Table 4, entries 2-5) than monogold catalyst **VI** (60%, entry 1). The yields improved (from 25% to 42%, entries 3-5) with increased acetylide electron density (from 4-CF_3 to 4-OMe). Low enantioselectivity (up to 9% ee) was observed with dual gold complex **Va**.

Table 4. Gold(I)-catalysed [2+5]-cycloaddition of propargyl acetal **3** and imine **4e**.[a]

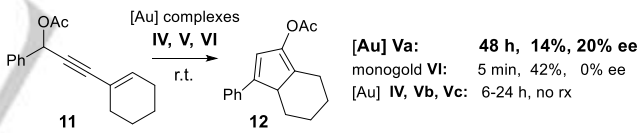


Entry	Complex	Solvent	Time	Yield	ee[b]
1	**VI**	DCM	30 min	60%	-
2	**IV**	DCM	42 h	17%	9%
3	**Va**	DCM	42 h	25%	9%
4	**Vg**	DCM	42 h	27%	8%
5	**Vb**	DCM	42 h	42%	2%

a) The reactions were performed with propargyl acetal **3** (1 equiv.) and imine **4e** (1.5 equiv.) in CH_2Cl_2 or CH_3CN ($c \approx 50$ mM) together with gold catalyst (5 mol%); b) % ee determined by HPLC (Chiralpak AD Column 10:90 2-propanol:hexane, 0.8 mL/min).

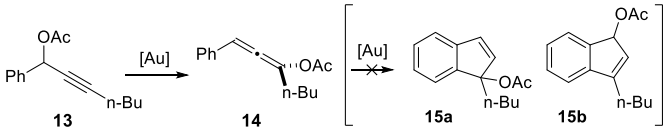
Gold-catalysed reactions of non-terminal propargyl esters were also tested (Scheme 5, Table 5). Only dual gold complex **Va** was sufficiently active to generate product **12** (14%) with some enantioselectivity (20% ee), but the reaction was slow and challenging, due to substrate and product instability. Fast cycloisomerisation of propargyl ester **11**[12] took place with monogold complex **VI** (5 min, 42%).

Scheme 5. Gold(I)-catalysed cycloisomerisation of 1,3-enyne propargyl ester **11**.



Non-terminal propargyl ester **13** was subjected to gold-catalysed acetate migration[13] to afford allene product **14**. The outcome of the reaction is in accordance with previous reports on selective allene formation with Au(I)-phosphine, whereas indene products were generated with Au(I) NHC complexes.[14] Monogold complex **VI** readily afforded high yield of allene product **14** (70%, 30 min, Table 5, entry 1). Similar yields were only obtained by very slow reactions in the presence of digold complex **IV** or the dual gold complex **Va** (65-75%, 7 days, Table 5, entries 2 and 3). No enantioselectivity was observed (HPLC). Only trace amounts of indene product **15**[15] were formed by separate gold-catalysed cyclisation of isolated allene **14** with complexes **IV** and **V.**

Table 5. Gold(I)-catalysed generation of allene by rearrangement of propargyl ester **13**.



13 **14** **15a** **15b**

Entry	Complex	Time	**13** amount	Conversion of **13** to **14** (NMR)	Yield **14**	ee[c]
1	**VI**	30 min	20 mg	-	70%	-
2	**IV**	7 d	6.0 mg	93%	65%[b]	0%
3	**Va**	7 d	6.0 mg	82%	75%[b]	0%
4	**Vg**	7 d	6.0 mg	20%	-	-
5	**Vb**	7 d	6.0 mg	7%	-	-

a) The reactions were performed with propargyl ester **13** (1 equiv.) in CH_2Cl_2 ($c \approx$ 50 mM) together with gold catalyst (5 mol%); b) isolated with starting material; yield calculated from NMR; c) % ee determined by HPLC (Chiralpak AD Column 2:98 2-propanol:hexane, 0.8 mL/min).

Conclusions

A series of new σ,π-dual gold(I)-acetylide complexes were prepared by gold coordination of selected ligands and a range of alkynes, and characterised (^{1}H, ^{19}F, ^{13}C, ^{31}P NMR; HRMS). The catalytic activity of the JohnPhos dual-gold complexes **I** and the bridged chiral MeO-BIPHEP dual-gold complexes **V** was tested in several reactions of propargylic alcohol derivatives. The results from the dual gold(I)-catalysed reactions (cyclopropanation, cyclopentenylation, tandem cyclisation, selective allene generation and cycloisomerisation of propargyl 1,3-enyne) were compared with corresponding results based on the monogold(I) phosphane (JohnPhos) complex **VI** as well as the chiral digold(I) diphosphane complex **IX**.

The JohnPhos dual gold complexes **I** gave excellent yields and high *cis*-diastereoselectivity in cyclopropanation (89-99% yield; up to 80% de). Electron-rich dual gold complexes afforded higher yields than the monogold(I) JohnPhos complex **VI** in propargyl cyclopentenylation and tandem cyclisation. The catalytic activity of bridged chiral dual gold(I) MeO-BIPHEP complexes **V** was demonstrated, as well. Both digold and bridged dual gold complexes **IV** and **V** afforded *cis*-diastereoselective (>99% de) and enantioselective (up to 65% ee) cyclopropanations. Higher yields (up to 76%) were obtained with dual gold **V** than digold **IV** complexes. The chiral dual gold complexes **V** were also catalytically active in cyclopentenylation reactions (up to 67% product yields) and were more enantioselective (up to 46% ee) than the chiral digold complex **IV** (<16% ee). Dual gold complexes **V** were not promising for tandem cyclisation, the allene generation reaction or the cycloisomerisation reaction, as very slow conversion of propargyl substrates were observed.

The present study demonstrates that dual gold complexes have different catalytic potential than the monogold **VI** or digold **IV** complexes in a variety of reactions of propargylic alcohol derivatives. The chiral dual gold(I) complexes **V** exhibit comparable catalytic activity and similar or higher enantioselectivity than the corresponding digold species **IV** in selected reactions. Mechanistic explanations are proposed for the differing regio- or stereoselective outcome of some reactions, rationalised by bulkiness or proximity effects in the deauration and product formation step.

The dual gold(I) complexes **I** and **V** appear to be less catalytically active than the monogold JohnPhos complex **VI**. However, the resulting selectivity may be useful in certain reactions to obtain specific target products, as hereby demonstrated for enantio-, diastereo- and regioselective reactions. To the best of our knowledge, the catalytic activity of bridged dual gold(I) complexes has not previously been studied. Thus, the present work contributes to new understanding of the synthesis, properties and catalytic potential of dual gold(I) complexes, including enantioselective chiral bridged dual gold(I) species.

Experimental Section

General: Commercial grade reagents were used as received. Dry solvents were collected from a solvent-purification system. All reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F254 (0.25-mm thickness) or by 1H-NMR. Flash chromatography was carried out using silica gel 60 (0.040-0.063 mm). High Throughput Flash Purification (HPFP) was performed on pre-packed cartridges. 1H and 13C NMR spectra were recorded using a 400 or 600 MHz spectrometer. Chemical shifts are reported in ppm (δ) relative to d-$CDCl_3$ or d-DCM. Coupling constants (J) are reported in Hertz (Hz). The attributions of the chemical shifts were determined using COSY, HSQC and HMBC NMR experiments and cis/trans isomers by NOESY experiments. Accurate mass determination in either positive or negative mode was performed with a "Synapt G2-S" Q-TOF instrument from Waters. Samples were ionised with an ASAP probe, and no chromatographic separation was used before the mass analysis. IR spectra were obtained using a Bruker Alpha FT-IR spectrometer using OPUS V7 software to analyse the spectra. Compounds **1a-1e**, **1g**, **4a**, **4b** and **4c** were used as received from Sigma-Aldrich. Propargyl acetates **2**,[7a] **11**[12] and **13**[14a], propargyl acetal **3**[7c] and imine **4e**[16] were synthesised from known procedures. Products **5a**, **5b**, **6a**, **7a**, **7b**, **9**, **10**, **14**, **15a** and **15b** are reported in literature.[7, 8, 11, 13] Compound **4d** is a known compound that has been previously synthesised in the Fiksdahl group, but not fully characterised. Missing spectroscopic data is included here for posterity. Compounds **1f**, **6b**, **8** and **12** are novel and are fully characterised here. Test reactions were carried out following literature procedures with any variations in conditions specified in the text. Complex **IV** (and the other chiral digold complexes) were generated following a literature procedure[5e] to obtain the dichloride salt and subsequent reaction with silver hexafluoroantimonate and filtration gave the required complex *in situ*. The syntheses of complexes **I** and **V** are described below.

Preparation of (*1R*,2*S*,4*R*)-2-ethynyl-2-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane (1f)

Compound **1f** was synthesised from (*1R*,2*S*)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol through a known procedure.[17] (*1R,4R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (541.9 mg, 3.56 mmol) was added to a solution of ethynylmagnesium bromide in THF (0.5 M, 10.0 mL, 5.00 mmol). The reaction mixture was heated under reflux for 24 h. After cooling to room temperature, the solution was quenched by the addition of H_2O (1 mL). The crude mixture was concentrated until most of the THF was removed. The residue was dissolved in Et_2O (25 mL) and sat. aq. NH4Cl (25 mL) was added. The phases were separated, and the aqueous layer was extracted with Et_2O (3 × 25 mL). The combined organic phases were washed with brine (25 mL) and dried over Na_2SO_4. After filtration and removal of the solvents in vacuo the crude product was purified by column chromatography (gradient pentane - 1:30 EtOAc:pentane - 1:4 EtOAc:pentane to give 201.9 mg of a colourless wax (ca. 60% pure (*1R,2S*)-2-ethynyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol). This product was dissolved in DMF (2 mL), cooled to 0 °C and sodium hydride (47.0 mg,

1,96 mmol) was added slowly. After stirring for 30 min at the same temperature, iodomethane (100 µl, 1.61 mmol) was added. The solution was warmed to r.t. and the DMF was extracted with ether (10 mL) and water (5 mL). The ether phase was washed with water (2 x 10 mL) and the combined aqueous washes were extracted with ether (4 x 10 mL). The combined ether extracts were concentrated in vacuo and the crude oil was chromatographed (1:10 Et_2O:pentane) to give (*1R*,*2S*,*4R*)-2-ethynyl-2-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane as a colourless volatile wax (60.4 mg, 9% yield over two steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 3.25 (s, 3H, OCH_3), 2.40 (s, 1H, ≡CH), 2.28-2.23 (m, 1H, CH_3OCCH_2), 2.02-1.95 (m, 1H, CCH_2CH_2), 1.74-1.72 (m, 1H, CH_2CHCH_2), 1.69-1.64 (m, 1H, $CHCH_2CH_2$), 1.51 (d, 1H, *J* = 13.2 Hz, (CH_3OCCH_2), 1.47-1.39 (m, 1H, CCH_2CH_2), 1.14-1.08 (m, 1H, $CHCH_2CH_2$), 0.96 (s, 3H, $CH_{3,\ bridge}$), 0.90 (s, 3H, CH_3), 0.85 (s, 3H, $CH_{3,\ bridge}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 85.0 (≡C), 83.7 (OC), 72.7 (≡CH), 54.0 (CCH_3), 50.2 (OCH_3), 48.1 ($C(CH_3)_2$), 45.5 (CH_2CHCH_2), 42.9 (CH_3OCCH_2), 32.6 (CCH_2CH_2), 26.9 ($CHCH_2CH_2$), 21.2 ($CH_{3,\ bridge}$), 20.9 ($CH_{3,\ bridge}$), 10.6 (CH_3); IR (neat, cm^{-1}) 3306, 2949, 2823, 1451, 1120, 1086, 1057, 1034, 645, 623; HRMS (ASAP+) calcd for $C_{16}H_{20}NO_2$ [M+H] 258.1494, found 258.1490.

***N*,4-Dimethyl-N-vinylbenzenesulfonamide (4d)**

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.62 (d, 2H, *J* = 8.3 Hz, CH_{Ar}), 7.28 (d, 2H, *J* = 7.9 Hz, CH_{Ar}), 6.98 (dd, 1H, *J* = 15.6/9.0 Hz, =CH), 4.31 (dd, 1H, *J* = 9.0/1.2 Hz, $=CH_2$), 4.16 (dd, 1H, *J* = 15.5/1.0 Hz, $=CH_2$), 2.84 (s, 3H, NCH_3), 2.40 (s, 3H, $PhCH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8 (CH_3C_{Ar}), 134.8 (SC_{Ar}), 133.8 (=CH), 129.7 (CH_{Ar}), 127.0 (CH_{Ar}), 93.1 ($=CH_2$), 31.2 (NCH_3), 21.5 ($PhCH_3$); HRMS (ASAP+) calcd for $C_{10}H_{14}NO_2S$ [M+H] 212.0745, found 212.0745.

1-((*1S,2R)*-3-Methoxy-2-phenylcyclopent-3-en-1-yl)pyrrolidin-2-one (6b)

Compound **6b** was synthesised from a literature procedure[7b] using propargyl acetal **3** (1 equiv.) and alkene **4b** (3 equiv.) in CH_2Cl_2 (*c* ≈ 80 mM) together with gold catalyst (5 mol%) for the required time at the required temperature. The crude mixture was purified using silica chromatography (2% MeOH/DCM) to give products **6a** and **6b** as yellow oils. **6b:** ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.29-7.26 (m, 2H, CH_{Ar}), 7.21-7.17 (m, 1H, CH_{Ar}), 7.16-7.14 (m, 2H, CH_{Ar}), 4.68-4.64 (m, 2H, =CH and NCH), 3.71 (br d, 1H, *J* = 4.3 Hz, PhCH), 3.59 (s, 3H, OCH_3), 3.46-3.34 (m, 2H, NCH_2), 2.70 (dtt, 1H, *J* = 15.5/8.1/1.9 Hz, $=CHCH_2$), 2.37-2.33 (m, 2H, $COCH_2$), 2.27-2.21 (m, 1H, $=CHCH_2$), 2.04-1.96 (m, 2H, NCH_2CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 174.5 (CO), 159.6 (C=), 140.4 (C_{Ar}), 128.6 (2C, CH_{Ar}), 127.6 (1C, CH_{Ar}), 126.9 (CH_{Ar}), 93.5 (=CH), 57.7 (NCH), 56.8 (OCH_3), 53.8 (PhCH), 43.7 (NCH_2), 31.43 and 31.40 (overlapping, 2C, $OCCH_2$ and $=CHCH_2$), 18.2 (NCH_2CH_2); IR (neat, cm^{-1}) 2933, 2855, 1676, 1645, 1419, 1284, 1250, 1231, 1161, 1024, 754, 699, 628; HRMS (ASAP+) calcd for $C_{16}H_{20}NO_2$ [M+H] 258.1494, found 258.1490.

(*4S,5R*)-4-((*N*,4-Dimethylphenyl)sulfonamido)-5-(4-methoxyphenyl)cyclopent-1-en-1-yl acetate (8)

Compound **8** was synthesised from a literature procedure[8] using propargyl ester **2** (1 equiv.) and alkene **4d** (2 equiv.) in CH_2Cl_2 (*c* ≈ 17 mM) together with gold catalyst (5 mol%) for the required time at the required temperature. The crude mixture was purified using silica chromatography (1:10 – 1:4 EtOAc:pentane) to give product **8** as a colourless oil. **8:** ^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.45-7.44 (m, 2H, $CH_{Ar,\ Ts}$), 7.13 (d, *J* =8.2 Hz, 2H, $CH_{Ar,\ Ts}$), 6.87-6.74 (m, 2H, CH_{Ar}), 6.76-6.74 (m, 2H, CH_{Ar}), 5.48-5.47 (m, 1H, =CH), 4.56 (dt, *J* = 8.5/4.6 Hz, 1H, NCH), 3.80-3.79 (m, overlapping, 1H, ArCH), 3.78 (s, 3H, OCH_3), 2.88 (s, 3H, NCH_3), 2.61 (ddt, *J* = 17.0/8.6/2.4 Hz, 1H, CH_2), 2.38 (s, 3H, $ArCH_3$), 2.15 (dm, *J* =17.0 Hz, 1H, CH_2), 1.90 (s, 3H, $COCH_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 168.4 (C=O), 158.7 ($CArOCH_3$), 150.2 (=C), 142.9 ($CArCH_3$), 136.7 (SC), 131.7 ($CArCH$), 129.5 ($CH_{Ar,\ Ts}$), 128.6 (CH_{Ar}), 127.1 ($CH_{Ar,\ Ts}$), 114.0 (CH_{Ar}), 112.8 (=CH), 63.4 (NCH), 55.2 (OCH_3), 51.9 (ArCH), 31.2 (CH_2), 29.1 (NCH_3), 21.5 ($ArCH_3$), 20.7 ($COCH_3$); IR (neat, cm^{-1}) 2929, 2837, 1753, 1511, 1337, 1244, 1203, 1178, 1155, 1088, 1032, 969, 814, 654, 569, 549; HRMS (ES+) calcd for $C_{22}H_{25}NO_5NaS$ [M+Na]$^+$ 438.1351, found 438.1353.

3-Phenyl-3a,5,6,7-tetrahydro-4H-inden-1-yl acetate (12)

The reactions were performed with propargyl ester **11** (1 equiv.) in CH_2Cl_2 (*c* ≈ 20 mM) together with gold catalyst (5 mol%) for the required time at the required temperature. The crude mixture was purified using silica chromatography (1:50 EtOAc:pentane) to give product **12** as a yellow oil. **12:** ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.39-7.38 (m, 2H, CH_{Ar}), 7.32-7-30 (m, 2H, CH_{Ar}), 7.19-7.16 (m, 1H, CH_{Ar}), 6.65 (s, 1H, =CH), 3.13 (dd, *J* = 12.7/5.8 Hz, 1H, CH), 2.70-2.66 (m, 1H, $=CCH_2$), 2.40-2.36 (m, 1H, $CHCH_2$), 2.23 (s, 3H, $COCH_3$), 2.09 (td, *J* = 13.4/5.4 Hz, 1H, $=CCH_2$), 1.96-1.92 (m, 1H, $=CCH_2CH_2$), 1.82-1.79 (m, 1H, $CHCH_2CH_2$), 1.48 (qt, *J* =13.4/3.3 Hz, 1H, $CHCH_2CH_2$), 1.28-1.16 (m, 1H, $=CCH_2CH_2$), 0.90 (qd, *J* = 12.8/3.2 Hz, 1H, $CHCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 169.0 (C=O), 147.9 (CC_{Ar}), 142.1 (=CO), 135.0 (C_{Ar}), 132.6 (OC=**C**), 128.5 (CH_{Ar}), 126.7 (CH_{Ar}), 125.6 (CH_{Ar}), 123.8 (=CH), 48.5 (CH), 33.2 ($CHCH_2$), 28.4 ($=CCH_2CH_2$), 25.6 ($CHCH_2CH_2$), 24.4 ($=CCH_2$), 20.8 ($COCH_3$); IR (neat, cm^{-1}) 2931, 2852, 1753, 1652, 1492, 1444, 1368, 1352, 1211, 1169, 1148, 1015, 889, 757, 693; HRMS (ES+) calcd for $C_{15}H_{17}O$ [(M+H_2O-$HOCOCH_3$)+H]$^+$ 213.1279, found 213.1276. The mass of the product was not observed. However, the product is unstable and previous work has identified it only by deacetylation.[18] It is proposed that in the conditions in the MS instrument the compound undergoes deacetylation to give the mass given above.

Preparation of gold complexes I and V

Complex Ia (CF_3)

Method B: Chloro[(1,1′-biphenyl-2-yl)di-tert-butylphosphine]gold(I) (41.5 mg, 1 eq) and alkyne **1a** (21.1 mg, 2 eq) were dissolved in dry DCM (5 mL) and NaH (21.1 mg, 11 eq) was added. The reaction mixture was stirred until complete conversion of the gold complex as analysed by TLC (2-7 days). The mixture was filtered through Celite and evaporated to give the gold-acetylide **VIII** as a colourless powder. The gold-acetylide (20.7 mg, 1 eq) and (acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (23.5 mg, 1 eq) were dissolved in DCM (0.5 mL) and stirred for 30 min. The mixture was evaporated to give complex **Ia** as a colourless solid (96% over two steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.89-7.84 (m, 2H, $CH_{Ar,\ ligand}$), 7.68 (d, 2H, *J* = 8.0 Hz, $CH_{Ar,\ acetylide}$), 7.57-7.51 (m, 6H, $4xCH_{Ar,\ ligand}$ and $2xCH_{Ar,\ acetylide}$), 7.30-7.27 (m, 6H, $CH_{Ar,\ ligand}$), 7.25-7.22 (m, 2H, $CH_{Ar,\ ligand}$), 7.11-7.09 (m, 4H, $CH_{Ar,\ ligand}$), 1.42 (d, 36H, *J* = 16.0Hz, *t*-Bu); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 149.1 (d, *J* = 13.8 Hz, $C_{Ar,\ ligand}$), 142.7 (d, *J* = 6.7 Hz, $C_{Ar,\ ligand}$), 133.8 (d, *J* = 1.8 Hz, $CH_{Ar,\ ligand}$), 133.3 (d, *J* = 7.7 Hz, $CH_{Ar,\ ligand}$), 132.6 ($CH_{Ar,\ acetylide}$), 131.5 (q, *J* = 33.1 Hz, CCF_3), 131.2 (br s, $CH_{Ar,\ ligand}$), 129.4 (s, $CH_{Ar,\ ligand}$), 129.1 ($CH_{Ar,\ ligand}$), 128.0 ($C_{Ar,\ acetylide}$), 127.6 (d, *J* = 6.9 Hz, $CH_{Ar,\ ligand}$), 125.7 (q, *J* = 3.5 Hz, $CH_{Ar,\ acetylide}$), 125.1 ($C_{Ar,\ ligand}$), 124.9 (d, *J* = 12.9 Hz, $C_{Ar,\ ligand}$), 124.7 (t, *J* = 80.2 Hz, AuC), 123.5 (q, *J* = 272.2 Hz, CF_3), 113.0 (t, *J* = 12.7 Hz, AuC**C**), 38.1 (d, *J* = 24.4 Hz, PC), 31.0 (d, *J* = 5.8 Hz, $PC(CH_3)_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ ppm −62.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 62.57; IR (neat, cm^{-1}) 2956, 2900, 2869, 1465, 1320, 1168, 1125, 1065, 755, 801, 654, 525, 495, 477; HRMS (ES+) calcd for $C_{49}H_{59}F_3P_2Au_2$ [M+H]$^+$ 1160.3375, found 1160.3376.

Complex Ib (OMe)

Method A: (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (43.8 mg, 1 eq) and DIPEA (10 µL, 1.0 eq) were mixed in DCM (1 mL), then alkyne **1b** (8.8 mg, 1.2 eq) in DCM (1 mL) was added. After stirring for 5 min, the mixture was filtered through Celite and precipitated with pentane to give complex **Ib** as a colourless solid (23.6 mg, 74%). The ^{1}H NMR spectrum was in accordance with reported literature.[3]

Complex Ic (MeO/Me)

Method A (1 eq alkyne): (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (40.8 mg, 1 eq) and DIPEA (10 µL, 1.1 eq) were mixed in DCM (0.5 mL), then alkyne **1c** (7.8 mg, 1.0 eq) in DCM (0.5 mL) was added. After stirring for 5 min, 2 mL DCM was added and the mixture was washed with water (5 x 2 mL), the organic phase dried over Na_2SO_4, filtered and evaporated. The resulting powder was dissolved in ca. 0.25 mL DCM and 4 mL pentane added carefully and

placed in the freezer overnight. The crystals were washed with pentane (5 x 1 mL) and dried *in vacuo* to give complex **Ic** as a colourless solid (22.0 mg, 61%).

Method A (0.5 eq alkyne): (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (20.0 mg, 1 eq) and DIPEA (5 µL, 1.1 eq) were mixed in DCM (1.0 mL), then alkyne **1c** (3.8 mg, 1.0 eq) in DCM (1.0 mL) was added. was added. After stirring for 5 min, 2 mL DCM was added and the mixture was washed with water (5 x 2 mL), the organic phase dried over Na_2SO_4, filtered and evaporated. The resulting powder was dissolved in ca. 0.25 mL DCM and 4 mL pentane added carefully and placed in the freezer overnight. The crystals were washed with pentane (5 x 1 mL) and dried *in vacuo* to give complex **Ic** as a colourless solid (13.8 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.88-7.84 (m, 2H, $CH_{Ar,\ ligand}$), 7.53-7.50 (m, 4H, $CH_{Ar,\ ligand}$), 7.38 (d, *J* = 8.3 Hz, $CH_{Ar,\ acetylide}$), 7.28-7.19 (m, 8H, $CH_{Ar,\ ligand}$), 7.08-7.05 (m, 4H, $CH_{Ar,\ ligand}$), 6.81-6.77 (m, 2H, $CH_{Ar,\ acetylide,\ ortho\ to\ OMe}$), 3.86 (s, 3H, OCH_3), 2.45 (s, 3H, CH_3), 1.39 (d, *J* = 15.6 Hz, *t*-Bu); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 161.5 (**C**OCH_3), 149.3 (d, *J* = 13.9 Hz, $C_{Ar,\ ligand}$), 144.5 (CH_3**C**$_{Ar,\ acetylide}$), 142.3 (d, *J* = 7.4 Hz, $C_{Ar,\ ligand}$), 136.0 ($CH_{Ar,\ acetylide,\ meta\ to\ OMe}$), 133.9 (br s, $CH_{Ar,\ ligand}$), 133.3 (d, *J* = 8.0 Hz, $CH_{Ar,\ ligand}$), 131.1 ($CH_{Ar,\ ligand}$), 129.3 ($CH_{Ar,\ ligand}$), 129.0 ($CH_{Ar,\ ligand}$), 128.0 ($CH_{Ar,\ ligand}$), 127.4 (d, *J* = 7.5 Hz, $CH_{Ar,\ ligand}$), 125.2 (d, C, *J* = 44.3 Hz, $C_{Ar,\ ligand}$), 123.7 (t, *J* = 69.3 Hz, AuC), 123.5 (t, *J* = 10.8 Hz, AuC**C**), 115.3 ($CH_{Ar,\ acetylide,\ ortho\ to\ OMe}$), 112.1 ($C_{Ar,\ acetylide,\ ortho\ to\ OMe}$), 111.8 ($CH_{Ar,\ acetylide}$), 55.5 ($OCH_3$), 38.1 (d, *J* = 24.7 Hz, PC), 31.0 (d, *J* = 7.5 Hz, PC**C**), 21.4 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 62.31; IR (neat, cm^{-1}) 2954, 2898, 2865, 2018, 1603, 1561, 1466, 1366, 1295, 1247, 754, 733, 699, 656, 525, 498; HRMS (ES+) calcd for $C_{50}H_{63}OP_2Au_2$ $[M]^+$ 1135.3685, found 1135.3696.

Complex Id (diOMe)

Method A: (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (40.5 mg, 1 eq) and DIPEA (10 µL, 1.1 eq) were mixed in DCM (1 mL), then alkyne **1d** (4.2 mg, 0.5 eq) in DCM (1 mL) was added. After stirring for 5 min, 2 mL DCM was added and the mixture was washed with water (5 x 2 mL), the organic phase dried over Na_2SO_4, filtered and evaporated. The resulting powder was dissolved in ca. 0.25 mL DCM and 4 mL pentane added carefully and placed in the freezer overnight. The crystals were washed with pentane (5 x 1 mL) and dried *in vacuo* to give complex **Id** as a colourless powder (32.5 mg, 45%).

^{1}H NMR (600 MHz, $CDCl_3$): δ ppm 7.87-7.85 (m, 2H, $CH_{Ar,\ ligand}$), 7.54-7.51 (m, 4H, $CH_{Ar,\ ligand}$), 7.36-7.30 (m, 6H, $CH_{Ar,\ ligand}$), 7.24-7.21 (m, 2H, $CH_{Ar,\ ligand}$), 7.11 (dd, 1H, *J* = 8.3/1.9 Hz, $CH_{Ar,\ acetylide}$), 7.09-7.07 (m, 4H, $CH_{Ar,\ ligand}$), 6.94 (dd, 1H, *J* = 8.4/1.5 Hz, $CH_{Ar,\ acetylide}$), 6.89 (d, 1H, *J* = 1.8 Hz, $CH_{Ar,\ acetylide}$), 3.95 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 1.39 (d, 36H, *J* = 15.7 Hz, t-Bu); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 151.3 ($C_{Ar,\ acetylide}$), 149.2 (d, *J* = 14.0 Hz, $C_{Ar,\ ligand}$), 148.6 ($C_{Ar,\ acetylide}$), 142.6 (d, *J* = 6.8 Hz, $C_{Ar,\ ligand}$), 133.9 (br s, $CH_{Ar,\ ligand}$), 133.3 (d, *J* = 7.7 Hz, $CH_{Ar,\ ligand}$), 131.1 (br s, $CH_{Ar,\ ligand}$), 129.3 $CH_{Ar,\ ligand}$), 129.0 $CH_{Ar,\ ligand}$), 128.0 ($CH_{Ar,\ ligand}$), 127.5 (d, *J* = 7.5 Hz, $CH_{Ar,\ ligand}$), 127.3 ($CH_{Ar,\ acetylide}$), 125.2 (d, *J* = 44.8 Hz, PC_{Ar}), 124.6 (t, *J* = 68.5 Hz, AuC), 118.2 (t, *J* = 11.4 Hz, AuC**C**), 115.3 ($CH_{Ar,\ acetylide}$), 112.5 ($C_{Ar,\ acetylide}$), 111.2 ($CH_{Ar,\ acetylide}$), 56.1 (2xOCH_3), 38.0 (d, *J* = 22.7, **C**$(CH_3)_3$), 31.0 (d, *J* = 7.0 Hz, PC(**C**$H_3)_3$); ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 62.35; IR (neat, cm^{-1}) 2947, 2899, 2865, 2017, 1592, 1508, 1463, 1263, 1136,1023, 753, 699, 655, 525; HRMS (ESI) calcd for $C_{50}H_{63}O_2P_2Au_2$ $[M]^+$ 1151.3634, found 1151.3649.

Complex If (camphorOMe)

Method A: (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (21.2 mg, 1 eq) and DIPEA (10 µL, 2.1 eq) were mixed in DCM (0.5 mL), then alkyne **1f** (5.0 mg, 0.9 eq) in DCM (0.5 mL) added. After 10 min stirring, the mixture was washed with water (5 x 1 mL), the organic phase dried over Na_2SO_4, filtered and precipitated with pentane. The solvents were evaporated and the resulting powder was washed with pentane and dried *in vacuo* to give complex **If** as a colourless powder (15.5 mg, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.90-7.86 (m, 2H, $CH_{Ar,\ ligand}$), 7.54-7.52 (m, 4H, $CH_{Ar,\ ligand}$), 7.35-7.26 (m, 6H, $CH_{Ar,\ ligand}$), 7.22-7.18 (m, 2H, $CH_{Ar,\ ligand}$), 7.13-7.08 (m, 4H, $CH_{Ar,\ ligand}$), 3.23 (s, OCH_3), 2.37-2.32 (m, 1H, CH_3OCC**H**$_2$), 1.85-1.76 (m, 3H, CC**H**$_2CH_2$ and CH_2C**H**CH_2 and CHC**H**$_2CH_2$), 1.49 (d, 1H, *J* = 13.6 Hz, CH_3OCC**H**$_2$), 1.42 (dd, 37H, *J* = 15.5/11.3 Hz, *t*-Bu and CC**H**$_2CH_2$), 1.26-1.22 (m, 1H, CHC**H**$_2CH_2$), 0.950 (s, 3H, CH_3), 0.946 (s, 3H, CH_3), 0.88 (s, 3H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ ppm 149.1 (d, *J* = 13.8 Hz, C_{Ar}), 133.8 (br s, CH_{Ar}), 133.4 (d, *J* = 7.5 Hz, CH_{Ar}), 132.1 (t, *J* = 11.8 Hz, AuC**C**), 131.2 (br s, CH_{Ar}), 129.4 (d, *J* = 5.4 Hz, CH_{Ar}), 129.3 (CH_{Ar}), 129.0 (CH_{Ar}), 127.8 (CH_{Ar}), 127.5 (d, *J* = 7.1 Hz, CH_{Ar}), 124.6 (d, *J* = 44.7 Hz, PC_{Ar}), 117.0 (t, *J* = 68.7 Hz, AuC), 85.0 (OC), 55.1 (CCH_3), 50.1 (OCH_3), 48.6 ($C(CH_3)_2$), 45.4 (CH_2**C**HCH_2), 44.0 (CH_3OC**C**H_2), 38.4 (dd, 24.4/24.4 Hz, P**C**$(CH_3)_3$), 32.8 (**C**CH_2CH_2), 31.0 (dd, *J* = 20.0/6.8 Hz, PC(**C**$H_3)_3$), 27.1 (C), 21.3 (CH_3), 20.8 (CH_3), 11.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 61.95; IR (neat, cm^{-1}) 2950, 2900, 1471, 1391, 1369, 1170, 1084, 755, 702, 655, 526, 475; HRMS (ESI) calcd for $C_{52}H_{71}OP_2Au_2$ $[M]^+$ 1167.4311, found 1167.4329.

General procedure for synthesis of Complexes V

A solution of (*R*)-(6,6'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl)bis(diphenylphosphine) (9.9 mg, 0.017 mmol) in DCM (1 mL) was added to chloro(dimethylsulfide)gold (10 mg, 0.034 mmol) in DCM (1 mL). The resulting solution was stirred for 5-10 min then silver hexafluoroantimonate (11.7 mg, 0,034 mmol) was added and the mixture filtered. A mixture of N-ethyl-N-isopropylpropan-2-amine (5 µl, 0.029 mmol) and alkyne **1a**, **1b** or **1g** (0.017 mmol) in a small amount of DCM was added. The mixture was stirred for 5-10 min then washed with water 5x1mL, dried over Na2SO4, filtered and evaporated. The residue was washed with pentane (3 x 1 mL) to give the required gold complex. The complexes tended to retain a small amount of pentane and where necessary, the yield was calculated from ^{1}H NMR.

Complex Va (BIPHEP-CF3)

Complex **Va** was synthesised according to the general procedure above using alkyne **1a** (2.9 mg, 1.0 eq) to give the desired complex as a yellow solid (20.5 mg, 87%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ ppm 7.75 (d, 2H, $CH_{Ar,\ acetylide}$), 7.60-7.56 (m, 4H, 2x$CH_{Ar,\ ligand,\ Ph}$, 2x$CH_{Ar,\ acetylide}$), 7.54-7.51 (m, 4H, $CH_{Ar,\ ligand,\ Ph}$), 7.37-7.27 (m, 6H, $CH_{Ar,\ ligand,\ Ph}$), 7.29 (dt, 2H, *J* = 8.1/2.1 Hz, $CH_{Ar,\ ligand}$), 7.20-7.17 (m, 4H, $CH_{Ar,\ ligand,\ Ph}$), 7.13 (dd, 4H, *J* = 13.3/7.5 Hz, $CH_{Ar,\ ligand,\ Ph}$), 6.93 (dd, 2H, *J* = 9.8/8.1 Hz, $CH_{Ar,\ ligand}$), 6.61 (d, 2H, *J* = 8.4 Hz, $CH_{Ar,\ ligand}$), 2.91 (s, 6H, OCH_3); ^{13}C NMR (150 MHz, CD_2Cl_2): δ ppm 159.4-159.3 (m, 2C, **C**$OCH_{3,\ ligand}$), 136.1-136.0 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 134.7-134.6 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 133.4 (s, (m, 2C, $CH_{Ar,\ acetylide}$), 133.3 (m, 2C, $CH_{Ar,\ ligand,\ Ph}$), 132.5 (m, 2C, $CH_{Ar,\ ligand,\ Ph}$), 131.0-130.9 (m, 2C, $CH_{Ar,\ ligand}$), 130.3 (dm, 2C, *J* = 62.3 Hz, $PC_{Ar,\ ligand}$), 129.75-129.68 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 129.3-129.2 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 128.3 (d, 2C, *J* = 61.4 Hz, $PC_{Ar,\ Ph}$), 128.3-128.2 (m, 2C, PC**C**$_{Ar,\ ligand}$), 126.7 (q, 1C, *J* = 3.3 Hz, **C**$HCCF_3$), 126.2 (d, 2C, *J* = 63.7 Hz, $PC_{Ar,\ Ph}$),125.2 (br s, 2C, PC**C**$H_{Ar,\ ligand}$), 123.9 (q, 1C, *J* = 272.8 Hz, CF_3), 123.8 (1C, $C_{Ar,\ acetylide}$), 117.6 (only HMBC, AuC**C**), 114.7 (s, 2C, $CH_{Ar,\ ligand}$), missing, AuC and **C**CF_3; ^{19}F NMR (376 MHz, CD_2Cl_2): δ ppm −63.34; ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm 29.29; IR (neat, cm^{-1}) 3056, 2936, 2837, 1567, 1460, 1435, 1156, 1123, 1097, 1064, 1043, 845, 743, 691, 654, 500; HRMS (ES+) calcd for $C_{47}H_{36}O_2F_3P_2Au_2$ [M+] 1145.1474, found 1145.1473.

Complex Vb (BIPHEP-OMe)

Complex **Vb** was synthesised according to the general procedure above using alkyne **1b** (2.3 mg, 1.0 eq) to give the desired complex as a yellow solid (19.4 mg, 85%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ ppm 7.58-7.52 (m, 6H, $CH_{Ar,\ ligand}$), 7.40-7.37 (m, 2H, $CH_{Ar,\ acetylide}$), 7.34-7.31 (m, 4H, $CH_{Ar,\ ligand}$), 7.29 (td, 2H, *J* = 8.3/2.5 Hz, $CH_{Ar,\ ligand}$), 7.28-7.23 (m, 2H, $CH_{Ar,\ ligand}$), 7.17-7.11 (m, 8H, $CH_{Ar,\ ligand}$), 7.03-7.01 (m, 2H, $CH_{Ar,\ acetylide}$), 6.97 (dd, 2H, *J* = 10.5/7.9 Hz, $CH_{Ar,\ ligand}$), 6.57 (d, 2H, *J* = 8.5 Hz, $CH_{Ar,\ ligand}$), 3.95 (s, 3H, $OCH_{3,\ acetylide}$), 2.87 (s, 6H, $OCH_{3,\ ligand}$); ^{13}C NMR (150 MHz, CD_2Cl_2): δ ppm 163.3 (s, 1C, **C**$OCH_{3,\ acetylide}$), 159.3-159.2 (m, 2C, **C**$OCH_{3,\ ligand}$), 136.2-136.1 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 135.8 (s, 2C, $CH_{Ar,\ acetylide}$), 134.8-134.7 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 133.0 (s, 2C, $CH_{Ar,\ ligand,\ Ph}$), 132.1 (s, 2C, $CH_{Ar,\ ligand,\ Ph}$), 130.81-130.74 (m, 2C, $CH_{Ar,\ ligand,\ Ar}$), 130.7 (dm, 2C, *J* = 63.1 Hz, PC_{Ar}), 129.44-129.37 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 129.07-128.99 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 128.4 (dm, 2C, *J* = 61.5 Hz, PC_{Ph}), 128.2-128.1 (m, 2C, PCC), 126.3 (dm, 2C, *J* = 63.2 Hz, PC_{Ph}), 125.2 (br s, 2C, $CH_{Ar,\ ligand,\ Ar}$), 119.5 (t, *J* = 72.2

Hz, AuC), 115.4 (s, 2C, $CH_{Ar,\ acetylide}$), 114.4 (s, 2C, $CH_{Ar,\ ligand,\ Ar}$), 110.9 (s, 1C, C≡C**C**), 56.3 (s, 1C, $OCH_{3,\ acetylide}$), 55.2 (s, 2C, $OCH_{3,\ ligand}$), AuC**C** not visible; ^{31}P NMR (162 MHz, CD_2Cl_2): δ ppm 29.42; IR (neat, cm^{-1}) 3053, 2936, 2837, 1998, 1597, 1435, 1255, 1167, 1156, 1086, 1042, 1025, 836, 785, 743, 653, 500; HRMS (ES+) calcd for $C_{47}H_{39}O_3P_2Au_2$ [M+] 1107.1705, found 1107.1721.

Complex Vg (BIPHEP-H)

Complex **Vg** was synthesised according to the general procedure above using alkyne **1g** (1.7 mg, 1.0 eq) to give the desired complex as a yellow solid (18.8 mg, 84%). ^{1}H NMR (600 MHz, CD_2Cl_2): δ ppm 7.64-7.61 (m, 1H, $CH_{Ar,\ acetylide}$), 7.59-7.50 (m, 9H, 2x$CH_{Ar,\ acetylide}$ and 7x$CH_{Ar,\ ligand,\ Ph}$), 7.44-7.43 (m, 2H, $CH_{Ar,\ acetylide}$), 7.34-7.32 (m, 4H, $CH_{Ar,\ ligand,\ Ph}$), 7.30-7.28 (m, 4H, 2x$CH_{Ar,\ ligand}$ and 2x$CH_{Ar,\ ligand,\ Ph}$), 7.16-7.12 (m, 7H, $CH_{Ar,\ ligand,\ Ph}$), 6.97 (dd, 2H, *J* = 10.8/8.0 Hz, $CH_{Ar,\ ligand}$), 6.58 (d, 2H, *J* = 8.3 Hz, $CH_{Ar,\ ligand}$), 2.88 (s, 6H, OCH_3); ^{13}C NMR (150 MHz, CD_2Cl_2): δ ppm 159.3-159.2 (m, 2C, **C**$OCH_{3,\ ligand}$), 136.2-136.1 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 134.8-134.7 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 133.4 (s, 2C, $CH_{Ar,\ acetylide}$), 133.1 (s, 2C, $CH_{Ar,ligand,\ Ph}$), 132.4 (s, 2C, $CH_{Ar,ligand,\ Ph}$), 132.2 (s, 1C, $CH_{Ar,\ acetylide}$), 130.9-130.8 (m, 2C, $CH_{Ar,\ ligand}$), 130.5 (dm, 2C, *J* = 62.7 Hz, PC_{Ar}), 129.8 (s, 2C, $CH_{Ar,\ acetylide}$), 129.53-129.47 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 129.07-128.99 (m, 4C, $CH_{Ar,\ ligand,\ Ph}$), 128.3 (dm, 2C, *J* = 61.4 Hz, PC_{Ph}), 128.3-128.2 (m, 2H, PC**C**), 126.3 (dm, 2C, *J* = 63.2 Hz, PC_{Ph}),125.2 (br s, 2C, $CH_{Ar,\ ligand}$), 122.9 (t, *J* = 72.2 Hz, AuC), 121.4 (t, *J* = 6.6 Hz, AuC**C**), 119.7 (s, $C_{Ar,\ acetylide}$), 114.5 (s, 2C, $CH_{Ar,ligand}$), 55.2 (s, 2C, $OCH_{3,\ ligand}$); ^{31}P NMR (12x$CH_{Ar,\ acetylide}$ and 7x$CH_{Ar,\ Ph}$), 62 MHz, $CDCl_3$): δ ppm 29.35; IR (neat, cm^{-1}) 3053, 2935, 2836, 1567, 1460, 1434, 1264, 1155, 1086, 1042, 743, 690, 653, 501; HRMS (ES+) calcd for $C_{46}H_{37}O_2P_2Au_2$ [M+] 1077.1600, found 1077.1621.

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Keywords: chiral; bridged; σ,π- dual gold(I) complexes; acetylide; propargyl; catalytic activity

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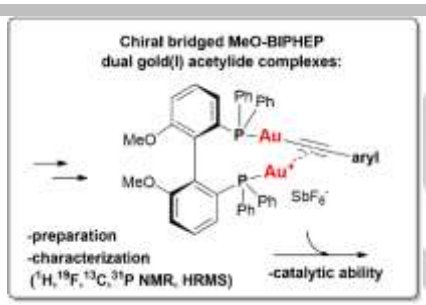
Chiral bridged σ,π-dual gold(I)-acetylide complexes were synthesised, characterised, and their catalytic activity was investigated. Dual gold(I)-catalysed reactions of propargylic alcohol derivatives show different catalytic potential than the monogold or digold complexes. Mechanistic explanations are proposed for the differing regioselectivity or the similar or higher enantioselective outcome of some reactions.



chiral bridged dual gold(I)-acetylide complexes *

Huey-San Melanie Siah

and Anne Fiksdahl*

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Preparation and catalytic activity of novel σ,π-dual gold(I)-acetylide complexes

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