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# Dual Gold Catalysis: σ,π-Propyne Acetylide and Hydroxyl-Bridged Digold Complexes as Easy-to-Prepare and Easy-to-Handle Precatalysts

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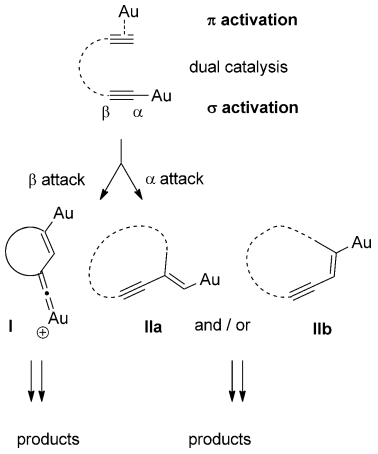
**Abstract:** A series of dinuclear gold σ,π-propyne acetylide complexes were prepared and tested for their catalytic ability in dual gold catalysis that was based on the reaction of an electrophilic π-complex of gold with a gold acetylide. The air-stable and storable catalysts can be isolated as silver-free catalysts in their activated form. These dual catalysts allow a fast initiation phase for the dual catalytic cycles without the need for additional additives for acetylide formation. Because propyne serves as a throw-away ligand, no traces of the precatalyst are generated. Based on the fast initiation process, side products are minimized and reaction rates are higher for these catalysts. A series of test reactions were used to demonstrate the general applicability of these catalysts. Lower catalyst loadings, faster reaction rates, and better selectivity, combined with the practicability of these catalysts, make them ideal catalysts for dual gold catalysis.

**Keywords:** acetylides · diynes · dual gold catalysis · gold · traceless precatalysts · vinylidenes

## Introduction

The most common reactivity in the field of gold chemistry is, without any doubt, the activation of multiple bonds towards the attack of a nucleophile by the π-coordination of a gold complex. Based on this reactivity, a manifold of different reaction patterns have been developed throughout the last decade.[1]

The use of gold acetylides as nucleophiles in gold-catalyzed reactions has only rarely been mentioned in the literature to date. The first examples were the gold-catalyzed version of the $A^3$-coupling (aldehydes, alkynes, and amines leading to propargylic amines) and related reactions that are based on a Grignard-type reactivity of a gold acetylide.[2] Recently, a new field of gold catalysis that is based on a dual activation mode by the gold catalyst has been opened (Scheme 1).[3] In these cases, the gold catalyst activates the alkyne by the known π-activation mode and, in addition, a second molecule of gold catalyst activates one alkyne by σ-coordination, which enables it to react as a nuleophile. This σ-activated alkyne can react at its α-carbon atom, leading to enyne systems **IIa/IIb**.[4] A second option comprises an attack at the β-carbon atom of the acetylide to deliver gold vinylidenes **I**, which are interesting intermediates that open up completely new reaction pathways.[5] We believe that the concept of dual activation will lead to a completely new field of gold chemistry, thus we started our efforts towards establishing a generally applicable and easy-to-handle catalyst system. So far, most of these reactions are conducted without any additives or with basic additives to induce acetylide formation. For these cases, the equilibrium depicted in Scheme 2 plays a crucial role and therefore the amount of activated catalyst (left side of the equilibrium) depends on the acidity of the alkyne and the base that is applied. The counter ion also influences the conjugated acid that is formed from the acetylide. For many substrates, these factors might lead to a quantitative acetylide formation (with respect to the gold catalyst) that would inhibit the catalytic cycle. This is underlined by recent reports on the inactivity




Scheme 1. Reaction modes for dual gold catalysis.

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[+] Crystallographic investigation

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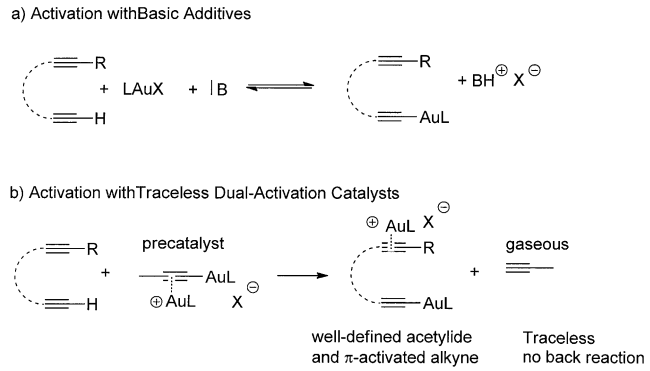



Scheme 2. a) Activation with basic additives; b) activation with a traceless dual-activation catalyst.

of gold acetylides in cycloisomerization reactions of enynes.[6]

During our investigations on the gold-catalyzed hydroarylation aromatization of terminal diynes,[5b] we provided experimental proof that the reformation of the σ-activated substrate, by catalyst transfer from an organogold intermediate onto a starting terminal alkyne, can close the catalytic cycle (release of the product and activation of new starting material). Furthermore, organogold compounds were used as suitable additives to initiate a dual-catalysis cycle without any basic additive. In the same report *geminal*-diaurated compounds (prepared from the stoichiometric reaction of a gold acetylide and one equivalent of activated catalyst) could be used as instant dual-activation catalysts. To design a generally applicable, instant catalyst system for dual gold catalysis, we had the following requirements of the catalysts:

1) preparation must be easy;
2) handling and storage even under open flask conditions should be possible;
3) a broad range of counter ions and ligands should be applicable;
4) generation of byproducts derived from components of the precatalyst should be minimized as much as possible;
5) the initiation of the dual activation cycle should be fast to avoid competing reaction pathways that lead to undesired byproducts (one example is the formation of an α-naphtalene in the hydroarylating cyclization during the initiation phase);[5b]
6) the ratio of acetylide and activated catalyst should be well-defined after the initiation phase;
7) the catalyst should be preactivated to avoid the necessity of in situ activation with silver salts;
8) the catalyst should be thermally stable.

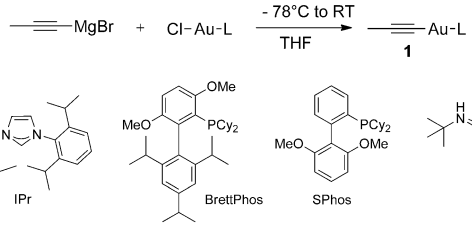
To conform to these requirements, we considered a catalyst system that is based on dinuclear gold σ,π-acetylide complexes as possible precatalysts.[7]

The advantage of σ-activation by ligand exchange, in contrast to activation by using a basic additive, is the well-defined 1:1 ratio of activated catalyst and σ-activated substrate, which should allow high reproducibility and efficiency (Scheme 2b). To circumvent a possible equilibrium of the released alkyne after substrate activation (which should matter at late reaction stages and/or for high catalyst loadings), we considered propyne precursors to be ideal because gaseous propyne is released after the exchange process. The preparation and catalytic abilities of these species are discussed within this contribution.

## Results and Discussion

**Preparation of the catalysts**: To keep the synthesis of the acetylide complexes as simple as possible, we used the commercially available propynyl Grignard as a transmetalation reagent, instead of the reported protocols that are based on the use of condensed propyne in combination with a base.[8] Starting from gold(I) chloride precursors with different ligands, a small series of propyne gold acetylides were available in good to excellent efficiency (Table 1). The differences

Table 1. Preparation of gold propyne acetylides by transmetalation.




| Entry | Ligand L | Time [h] | Compound | Yield [%] |
|---|---|---|---|---|
| 1 | IPr | 5 | **1a**[a] | 100 |
| 2 | $PPh_3$ | 6 | **1b** | 80 |
| 3 | BrettPhos | 5 | **1c** | 71 |
| 4 | SPhos | 5 | **1d** | 70 |
| 5 | **L1** | 5 | **1e** | 99 |

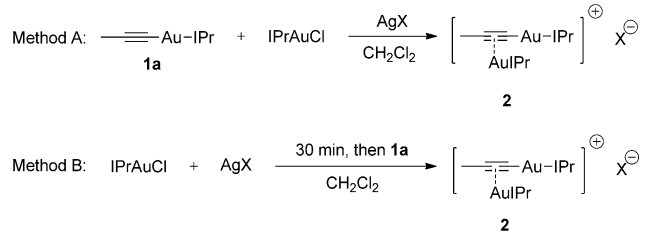
[a] See the Supporting Information for the solid-state molecular structure.[9]

in yields are based on the purification by crystallization. This turned out to be slightly more efficient for carbene complexes (Table 1, entries 1 and 5) but, nevertheless, yields for phosphane complexes were also high (Table 1, entries 2–4) and all of the products could be obtained as air-stable crystalline solids.

As the next step, we focused on the preparation of a series of σ,π-acetylide complexes. First, we prepared a set of compounds with the established IPr N-heterocyclic (NHC) ligand[10] in combination with different weakly coordinating counter ions. For preparing the complexes, two different protocols were applied (see Table 2). The most straightforward process is the direct reaction of the gold acetylide with IPrAuCl (method A). Simple addition of the corresponding silver salt and filtration over Celite delivered the desired complexes after evaporation of the solvents and washing with diethyl ether. This process delivered high yields of pure

Table 2. Preparation of σ,π-propyne acetylide complexes with the IPr ligand.

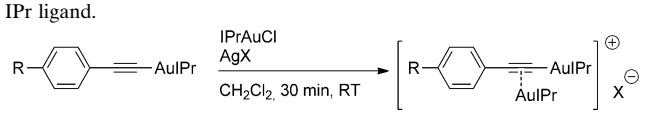



| Entry | Counter Ion | Method[a] | Time [min] | Compound | Yield [%] |
|---|---|---|---|---|---|
| 1 | $NTf_2^-$ | B | 30 | **2a** | 92 |
| 2 | $SbF_6^-$ | A | 30 | **2b** | 86 |
| 3 | $PF_6^-$ | A | 30 | **2c** | 98 |
| 4 | $PF_6^-$ | B | 30 | **2c** | 94 |
| 5 | $BF_4^-$ | A | 45 | **2d** | 97 |
| 6 | $TsO^-$ | A | 30 | **2e** | 96 |
| 7 | $TsO^-$ | B | 60 | **2e** | 89 |
| 8 | $NNf_2^-$ | A | 30 | **2f** | 74 |
| 9 | $TfO^-$ | B | 50 | **2g** | 89 |

[a] Method A: simple mixing of gold acetylide/IPrAuCl and AgX; Method B: preactivation of IPrAuCl with AgX, then addition of the acetylide

compounds for all of the applied counter ions (Table 2, entries 2, 3, 5, 6, and 8). As an alternative (method B), we performed the reaction in a sequential process. First, the corresponding silver salt and the gold chloride complexes were stirred for 30 min and then the gold acetylide was added to the preactivated gold catalyst. This was practical for the triflimide anion (Table 2, entry 1) and the triflate anion (Table 2, entry 9). In addition, we compared the two protocols and this showed no significant differences for the hexafluorophosphate anion (Table 2, entries 3 and 4) or for silver tosylate (Table 2, entries 6 and 7). Nonaflate as the anion was also suitable, but the yield for the final complex was slightly lower (Table 2, entry 8). To evaluate the effect of other acetylenes on the preparation of these catalysts, we synthesized six different phenylacetylene-derived σ,π-acetylide complexes (Table 3). Different electronic properties and counter ions were applied. Interestingly, the approach involving preformed acetylides (instead of π-coordinated alkyne complexes in the Widenhoefer protocol) delivered air-stable complex **3** as a crystalline solid in excellent yield (Table 3, entry 1), a compound that decomposed by the alternative pathway.[7d] One explanation might be the function of gold as a type of protecting group for the terminal alkyne, which might suppress side reactions due to alkyne/alkyne dimerizations.[4b] All the other derivatives were also obtained as air-stable crystalline solids in excellent yields (Table 3, entries 2–6).

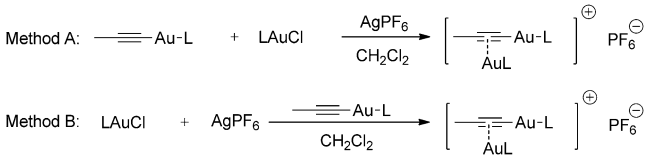
Table 3. Preparation of σ,π-phenylacetylene acetylide complexes with the IPr ligand.




| Entry | R | Counter Ion | Compound | Yield [%] |
|---|---|---|---|---|
| 1 | OMe | $SbF_6^-$ | **3** | 93 |
| 2 | $NO_2$ | $SbF_6^-$ | **4** | 93 |
| 3 | OMe | $PF_6^-$ | **5** | 96 |
| 4 | $NO_2$ | $PF_6^-$ | **6** | 97 |
| 5 | OMe | $BF_4^-$ | **7** | 89 |
| 6 | $NO_2$ | $BF_4^-$ | **8** | 98 |

Next, we installed different ligands at the σ,π-acetylide complexes (Table 4). All of the complexes were prepared with hexafluorophosphate as the counter ion under the same conditions as for the IPr complexes. Unfortunately, the reaction with $PPh_3$–acetylide **1a** and $PPh_3$–AuCl led to a decomposition of the starting material (Table 4, entry 1). The lack of stability of this compound seems to be based on the decreased steric hindrance of the phosphane ligand. By switching to the bulkier phosphane ligands BrettPhos (Table 4, entry 2) and SPhos (Table 4, entry 3), clean conversions were observed and yields were nearly quantitative. NAC–acetylide **1e** (NAC = nitrogen acyclic carbene) led to a decomposition of the starting material even if a sequential addition of silver salt was used (Table 4, entries 4 and 5). Once again, the increase in bulkiness of the NAC ligand seems to be insufficiently stabilizing the resulting species.

Table 4. Preparation of hexafluorophosphate σ,π-propyne acetylide complexes with different ligands.




| Entry | Ligand L | Method | Time [min] | Compound | Yield [%] |
|---|---|---|---|---|---|
| 1 | $PPh_3$ | A | 30 | – | –[a] |
| 2 | BrettPhos | A | 15 | **9** | 94 |
| 3 | SPhos | B | 20 | **10** | 97 |
| 4 | **L1** | A | 30 | – | –[a] |
| 5 | **L1** | B | 20 | – | –[a] |

[a] Decomposition.

**Structures of the catalysts**: During purification of the complexes, most of the IPr-ligated compounds delivered single crystals that were suitable for X-ray crystal-structure analyses.[9] Two representative solid-state molecular structures of **2b** and **3** are depicted in Figure 1. A summary of the key data is depicted in Table 5 (for comparison, the structural data of **10**[7d] is also shown). Along the $C^2$–$Au^2$-axis, the bond lengths $C^1$–$C^2$, as well as $C^1$–$Au^2$, are quite similar and nearly no effects due to the counter ion or the substituent at the alkyne are apparent. Interestingly, if at all, only small influences due to the counter ion/alkyne moiety are detected for the distances between the π-bonded gold ($Au^1$) and the $C^1/C^2/R^1$ atoms. Small variations in the values for the different complexes can be found for the $Au^1$–$Au^2$ separation, as well as for the $Au^1$-$C^1$-$Au^2$ angles. The exchange of $SbF_6^-$ with the stronger coordinating $TsO^-$ leads to a shortening of

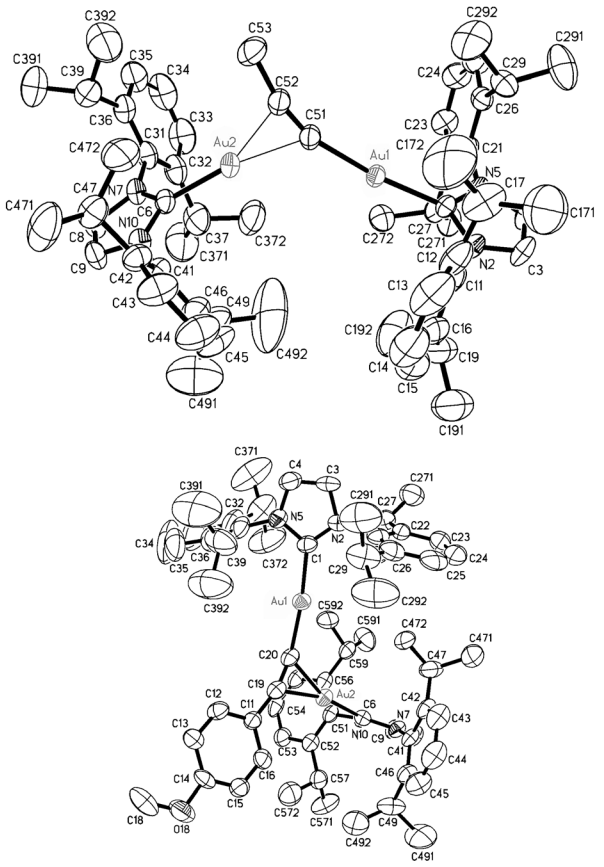
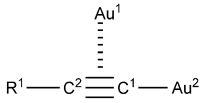



Figure 1. Solid-state molecular structures of compounds **2b** and **3**.

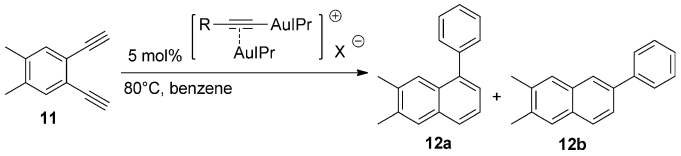
Table 5. Comparison of the structural data of the σ,π-digold species.




| Compound | **2b** | **2c** | **2e** | **2f** | **3** | **10** (Ref. [7d]) |
|---|---|---|---|---|---|---|
| counter ion | $SbF_6^-$ | $PF_6^-$ | $TsO^-$ | $NNf_2^-$ | $SbF_6^-$ | $SbF_6^-$ |
| $R^1$ = | Me | Me | Me | Me | MeO-C$_6$H$_4$- | C$_6$H$_5$- |
| R1 value [%] | 2.9 | 3.2 | 3.6 | 6.8 | 4.5 | |
| space group | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ |
| distances [Å] | | | | | | |
| $C^1$–$Au^2$ | 1.994(4) | 1.993(4) | 1.989(4) | 1.997(9) | 2.001(8) | 1.997 |
| $C^1$–$C^2$ | 1.226(5) | 1.231(5) | 1.214(6) | 1.203(11) | 1.245(10) | 1.214 |
| $C^2$–$R^1$ | 1.476(6) | 1.474(6) | 1.479(6) | 1.482(13) | 1.433(11) | 1.450 |
| $C^1$–$Au^1$ | 2.217(4) | 2.220(4) | 2.204(4) | 2.212(9) | 2.221(7) | 2.193 |
| $C^2$–$Au^1$ | 2.216(4) | 2.192(4) | 2.241(4) | 2.230(9) | 2.194(7) | 2.234 |
| $Au^1$–$R^1$ | 3.202(4) | 3.207(4) | 3.202(4) | 3.184(9) | 3.247(7) | 3.247 |
| $Au^1$–$Au^2$ | 3.716(3) | 3.690(3) | 3.547(3) | 3.677(8) | 3.745(6) | 3.624 |
| Angles [°] | | | | | | |
| $Au^1$-$C^1$-$Au^2$ | 129.8 | 122.2 | 115.5 | 121.7 | 125.0 | 119.7 |
| $Au^1$-$C^2$-$R^1$ | 118.9 | 118.9 | 117.4 | 116.7 | 125.7 | 122.2 |

the $Au^1$–$Au^2$ separation by 0.17 Å and the $Au^1$-$C^1$-$Au^2$ angle decreases from 129.8° to 115.5°. The same parameters were also affected by changing the electronic parameters of the alkyne moiety. Analogously to the report of Widenhoefer, all of the prepared complexes showed equivalent $^1H/^{13}C$ NMR shifts for the two coordinating ligands, which can be explained by a fast fluctuation of the gold fragments even at low temperatures (−90 °C). To investigate the thermal stability of the propyne catalysts, we measured a series of $^1H$ NMR spectra of compound **2a** over a period of 2 h in $C_2D_2Cl_4$ at 110 °C. The complex showed a remarkable stability and no traces of decomposition could be monitored even at this temperature.

**Tests of the catalytic properties**: As the first test reaction for the catalytic abilities of the complexes, we investigated the gold-catalyzed formation of β-phenyl naphthalenes (reaction type **I**, Scheme 1) under the previously reported reaction conditions (Scheme 3).[5b] In the first set of experiments, the




Scheme 3. Gold-catalyzed hydroarylating aromatization

propyne derived catalysts **2a**–**2g** containing the IPr ligand but different counter ions were compared. Figure 2 displays the formation of the β-product (**12b**) at different reaction times. A rather large effect due to the counter ions can be monitored. By far the best results were obtained for propyne catalyst **2c**, which contains the hexafluorophosphate ion. Complete conversions were obtained within 1 hour, four times faster than under our previously applied conditions (5 mol% $IPrAuNTf_2$, 10 mol% IPrAuPh as the additive). Even higher reaction rates were obtained with catalyst **2g**, which contains the triflate counter ion; however, complete conversion was not obtained. Slightly lower reaction rates were detected for the tetrafluoroborate anion, as well as for the nonaflate anion, both of which perform in the same range (complete conversions after 4.5 h). Although the triflimide and the tosylate anion still delivered acceptable results (complete conversions after 6 to 7 h), only slow conversion rates were detected for the hexafluoroantimonate anion. The pronounced difference of the hexafluorophosphate and the hexafluoroantimonate anion seems unusual, but there is precedence for this phenomenon in gold catalysis.[11]

Table 6 presents the α/β ratios after complete conversion for all the propyne dual catalysts and the phenylacetylene derivatives. Even though only one equivalent of the additive (acetylide), with respect to the catalyst, was available for σ-activation of the substrate, the β-selectivity for most of the counter ions was excellent. This indicates a fast ligand exchange of the acety-

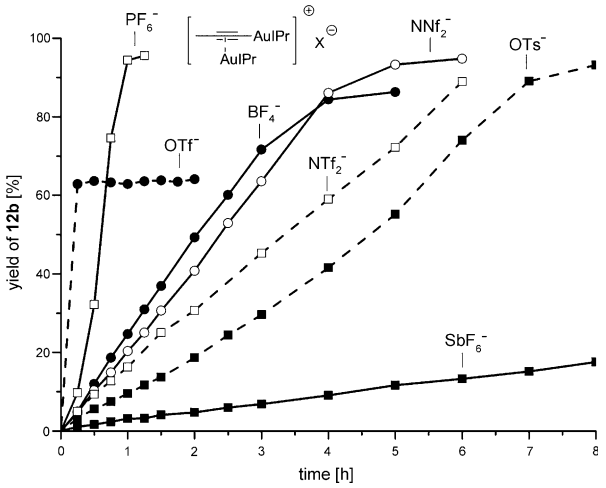



Figure 2. Yields of **12b** at different reaction times for propyne catalysts **2a**–**2g** (different counter ions)

Table 6. Yields and selectivities due to dependency of the counter ion and the alkyne moiety of the dual catalysts.

| Entry | Compound | Time [h] | Yield [%] | Ratio **12a**/**12b** |
|---|---|---|---|---|
| 1 | **2a** | 6 | 36 | 4:96 |
| 2 | **2b** | 48 | 98 | 11:89 |
| 3 | **3** | 48 | 92 | 25:75 |
| 4 | **4** | 48 | 98 | 33:67 |
| 5 | **2c** | 1 | 98 | 2:98 |
| 6[a] | **2c** | 5 | 77 | 2:98 |
| 7[a] | **5** | 8 | 69 | 4:96 |
| 8[a] | **6** | 8 | 61 | 3:97 |
| 9 | **2d** | 4 | 92 | 7:93 |
| 10 | **7** | 5 | 85 | 20:80 |
| 11 | **8** | 5 | 84 | 14:86 |
| 12 | **2e** | 7 | 97 | 4:96 |
| 13 | **2f** | 5 | 97 | 4:96 |
| 14 | **2g** | 2[b] | 66 | 4:96 |

[a] Only 1 mol% catalyst loading; [b] only 87% conversion.

lide, which circumvents the formation of α-phenylnaphtalene (**12a**; the side product that is formed if no activation of the substrate by acetylide exists).[5b] It is also worth noting that for catalyst **2c**, not only the second fastest reaction rate was observed, but also the highest β-selectivity, combined with perfect yields even for low catalyst loadings (see Table 6).

Furthermore, a strong effect of the alkyne moiety on the precatalysts was visible. For all of the three tested counter ions, poorer selectivity was obtained with phenylacetylene derivatives. Only a minor effect on the selectivity was visible for the different aromatic substituents, but a high dependency of the selectivity on the counter ion was observed. A related strong effect on the stability for diaurated aromatic species was reported by Gagné and co-workers.[12]

For a comparison of the induction phase, propyne- and phenylacetylene-derived catalysts with the hexafluoroantimonate counter ion were used. Complexes **2b**, **3**, and **4**, which contain different alkyne substituents, were tested due to their largest influence on selectivity and slow conversion rates (which allow a collection of accurate data points, even for the initiation phase). Figure 3 shows the formation of the

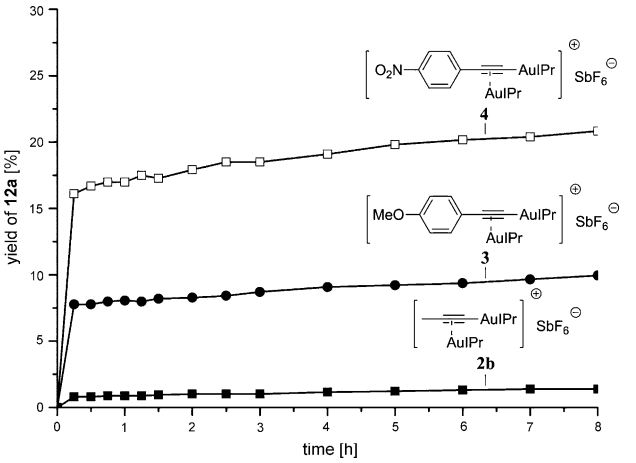



Figure 3. Yield of **12a** for different reaction times—dependency of the alkyne unit.

α-phenylnaphtalene **12a** for the different precatalysts at different reaction times. These results clearly demonstrate a much faster initiation phase for the propyne catalyst **2b**. One reason might be the release of the volatile propyne after acetylide exchange, which (in a traceless manner) avoids the possibility of a back reaction. Furthermore, the acidity seems to also play a role. Although the effect of the acidity of the aromatic systems is inconsistent (compare results in Table 6), the faster ligand exchange for less acidic alkynes seems to occur for all of the propyne catalysts. This seems reasonable as the pKa value for alkylacetylenes is approximately two units higher than for phenylacetylene derivatives.[13]

Complex **2c** is the best catalyst and thus was used in the subsequent tests, but here the kinetics were too fast for our kinetic investigation and, in accordance with our model of a short induction period leading to high selectivity, the selectivity of the reactions conducted with **2c** were so high that we failed to detect the formation of **12a**.

The faster initiation of the propyne catalyst leads to a better selectivity for the β-product **12b** at the same conversion rates. This is demonstrated in Figure 4, which displays the β/α ratios at different conversion rates for the three catalysts. It is clear that even at the early stages of the reaction, a very high selectivity for the β-product is obtained for the propyne catalyst, whereas the phenylacetylene derivatives predominantly deliver the α-product **12a** at early stages of the reaction and the β pathway becomes dominant only after significant conversion.

Next, we evaluated the efficiency of the bulky phosphane complexes **9** and **10** in comparison to the carbene ligand (Figure 5). Unfortunately, these ligands turned out to be less efficient and, as well as prolonged reaction times, unacceptable yields were obtained with both of the complexes. In ad-

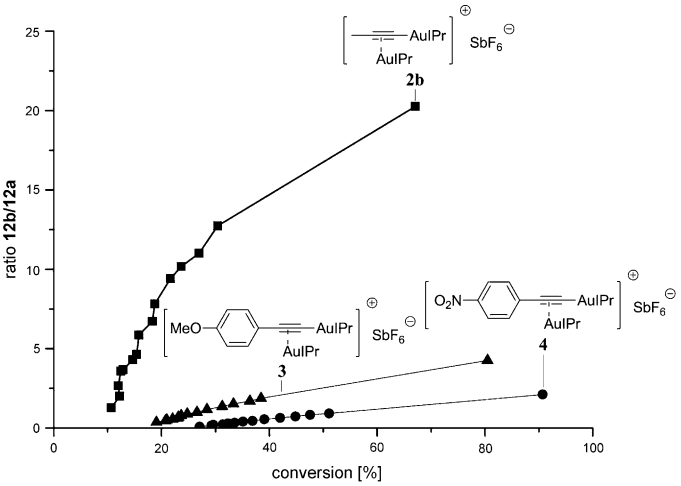



Figure 4. Dependence of selectivity on the alkyne unit of the dual catalysts.

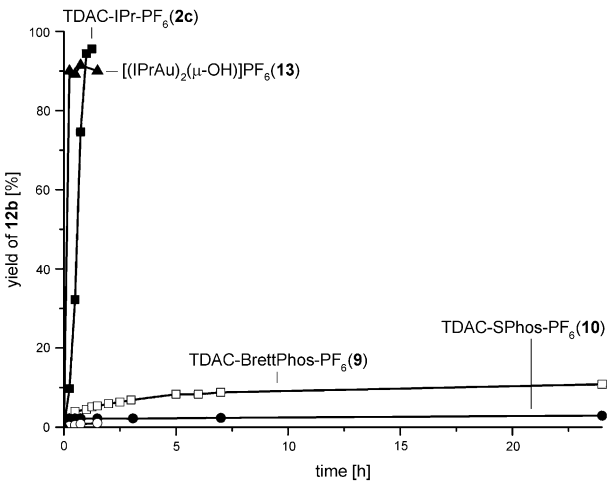
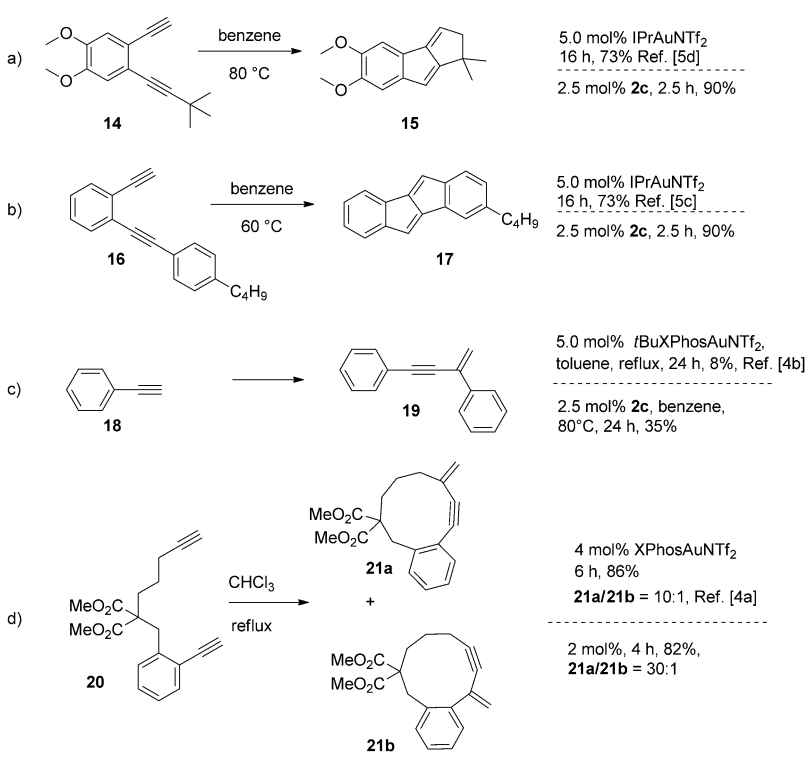



Figure 5. Yields of **12b** at different reaction times for catalysts **2c**, **9**, **10**, and **13**.

dition, we included a study of hydroxyl-bridged carbene catalyst **13**, a species which was first reported by Nolan et al.[14] This complex can also be regarded as a dual-activation catalyst, as it provides NHC-Au$^+$ and NHC-Au-OH. The latter species has been shown to directly form gold acetylides with terminal alkynes as well. However, in this process water is liberated, which could be problematic for higher catalyst loadings. The reaction rates for this class of dual-activation catalysts is similar to the propyne-based system with the same NHC ligand, but the yields obtained with **13** are slightly lower. Furthermore, no complexes of type **13** with non-NHC ligands have been reported so far, and the preparation, storage, and handling of **13** proved to be more difficult than the traceless dual-activation catalysts (TDACs). The only advantage of **13** is a slightly faster product formation.




Scheme 4. Set of test reactions for TDAC **2c**.

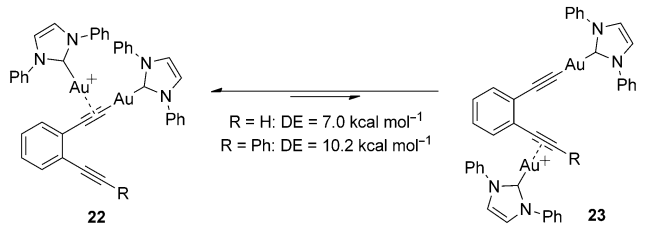
After the catalytic testing for the hydroarylating reaction, we wanted to know whether the traceless dual-activation catalysts are generally applicable for this field of gold chemistry. We used the same counter ion ($PF_6^-$) for our set of test reactions. All other reaction parameters were in accordance with the references, or were even milder. As a starting point, we used TDAC **2c** for the transformation of diyne **14** to the fulvene derivative **15** (Scheme 4, a), a transformation which also follows the reactivity pattern **I** shown in Scheme 1. With the use of 2.5 mol% of TDAC **2c**, reaction rates were faster and the isolated yield of the product could be nicely improved.[5d] Next, we tested the mechanistically related dibenzopentalene synthesis.[5c] As in the previous case, a faster reaction was observed than under the original conditions. Furthermore, better yields were obtained with the TDAC (Scheme 4, b).

The intermolecular alkyne/alkyne cross dimerization of **18**[4b] was also considered as a test reaction for our catalysts. In contrast to the previously discussed reactions, this trans-

formation is believed to proceed by reaction type **II**, shown in Scheme 1. Our tests were concentrated on the dimerization of phenylacetylene as a substrate, which delivered only marginal yields under the original conditions. Without optimization, our catalyst system allowed the reaction to be performed under slightly milder conditions (Scheme 4, c). Yields for this transformation could be significantly improved but further optimization would be necessary for a practical use of this transformation. Finally, we investigated the alkyne/alkyne macrocyclization that was reported by the Gagosz group (reaction type **II**, Scheme 1).[4a] The yield for this transformation turned out to be slightly lower for the TDAC but the selectivity of the reaction was much better (almost pure **21a** was obtained).

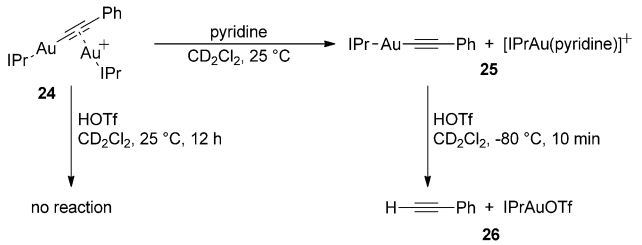
**Alkynes versus gold acetylides: Computational study on the relative affinity of [L-Au]$^+$**: The observation of the (desired) very high affinity and stability of the [L-Au]$^+$ to the aurated alkynes in the preparation of the traceless dual-activation catalysts immediately raised the question of the fate of [L-Au]$^+$ after the catalyst transfer step. This catalyst transfer step in the diyne substrates chemospecifically generates a gold acetylide at the terminal position of one of the alkynes. Because the thermodynamic affinity of the second gold, the [L-Au]$^+$, which is needed to π-activate the second triple bond (to form gold(I) vinylidene species), might be lower than the affinity for the triple bond of the gold acetylide, we conducted a computational study.

The relative stabilities of the two σ,π-acetylide complexes **22** and **23** were examined by calculations and a clear preference was found for the *geminal* digold species **22**. The geometry optimizations were carried out by using the B3LYP hybrid functional along with the correlation-consistent double-ζ basis (cc-pPDZ) for all atoms but gold.[15] For gold, a relativistic effective core potential reported by the Stoll group was used.[16] These studies revealed an enhanced stability of 7–10 kcal mol$^{-1}$ for the *geminal* σ,π-acetylide complexes **22** compared to the corresponding non-*geminal* digold complexes **23** (Scheme 5).



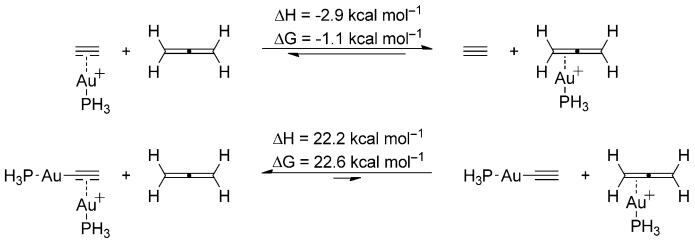

Scheme 5. Calculating the relative energies of the isomers **22** and **23**.

This energy difference between the two catalytic intermediates is in accordance with the high thermostability that was found experimentally for the dual catalyst described herein and with the earlier experimental result of Widenhoefer and co-workers.[7d] From NMR experiments in $CD_2Cl_2$, Widenhoefer found that the binding affinity of a IPrAu$^+$ moiety towards IPr–gold phenylacetylide exceeded the binding affinity towards phenyl acetylide by a factor of 80. This change in binding affinity corresponds to an energy difference of $\Delta\Delta G = 1.9$ kcal mol$^{-1}$. Furthermore, the stability of the *geminal*-digold complex of phenylacetylene was tested by exposure to triflic acid. Unlike the gold σ-acetylide, which was rapidly protodeaurated even at low temperatures, the *geminal*-digold compound showed no detectable decomposition over a period of 12 h at room temperature (see Scheme 6).




Scheme 6. Different stabilities against protodeauration for **24** and **25**.[7d]

Along the same lines, Houk, Toste, and co-workers computationally found that between a gold σ-acetylide and an allene, phosphinogold showed a strong preference towards binding to the acetylide ($\Delta\Delta G = 22.6$ kcal mol$^{-1}$).[3] In contrast, there was no great difference in the affinity towards an alkyne and an allene—the binding to the allene was favored slightly by 1.1 kcal mol$^{-1}$ (Scheme 7).




Scheme 7. Similar preference of digold–acetylides in competition with allenes.[3]

This suggests that a kinetic coordination of [L-Au]$^+$ to the non-aurated triple bond of the σ-activated substrate or, more probably, a dynamic equilibrium between **22** and **23** delivers the reactive dual-activated complex, leading to the gold vinylidene intermediates.

## Conclusion

σ,π-Acetylide complexes derived from propyne proved to be generally applicable catalysts in the new field of dual gold catalysis. Without optimization of the conditions, the catalysts delivered improved results for the small series of test reactions. Moreover, all of the complexes were air-stable

crystalline solids and the catalysts could be applied without further activation. This makes screenings of counter ions and ligands fast and effective, which was demonstrated by the successful optimization of the hydroarylating aromatization reaction. A fast initiation of the dual-catalysis cycle leads to high selectivity and fast reaction rates. In contrast to other additives, reproducibility is high and the well-defined ratio of active catalyst and acetylide guarantees efficient amounts of cationic gold. We are convinced that this class of catalysts will further enhance the developments in the field of dual gold catalysis.

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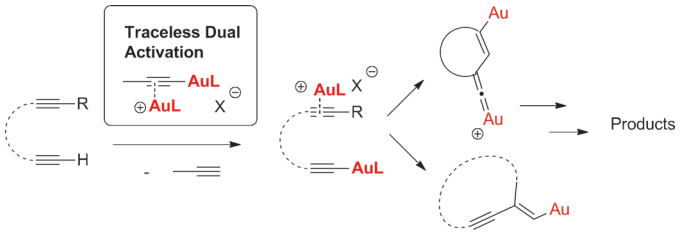


**Traceless dual-activation catalysts**: Air-stable π-coordinated propyne acetylide gold complexes proved to be powerful precatalysts for dual gold catalysis (see scheme). A fast catalyst transfer to the starting substrates initiates the catalytic cycle. Reaction yields and selectivity were improved without the need for basic additives or activation by silver salts.

**Gold**

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**Dual Gold Catalysis: σ,π-Propyne Acetylide and Hydroxyl-Bridged Digold Complexes as Easy-to-Prepare and Easy-to-Handle Precatalysts**