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Homogeneous Catalysis

Silver-Free Activation of Ligated Gold(I) Chlorides: The Use of $[Me_3NB_{12}Cl_{11}]^-$ as a Weakly Coordinating Anion in Homogeneous Gold Catalysis

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Abstract: Phosphane and N-heterocyclic carbene ligated gold(I) chlorides can be effectively activated by $Na[Me_3NB_{12}Cl_{11}]$ (**1**) under silver-free conditions. This activation method with a weakly coordinating *closo*-dodecaborate anion was shown to be suitable for a large variety of reactions known to be catalyzed by homogeneous gold species, ranging from carbocyclizations to heterocyclizations. Additionally, the capability of **1** in a previously unknown conversion of 5-silyloxy-1,6-allenynes was demonstrated.

Introduction

Homogeneous gold catalysis as a means for activating multiple bonds to effect complex transformations of small molecules is of ever-growing importance in organic synthesis.[1] As a result, recent reports on previously unsuspected complications that arise from the commonly used activation of gold(I) chloride complexes by silver salts are of major significance.[2] It was shown that, in many cases with silver activation, the success of gold-catalyzed reactions strongly depends on subtle changes in the reaction conditions, particularly with regard to handling of the gold precatalyst and the silver salt. Other, more obvious downsides of silver salts as activating reagents (e.g., light sensitivity, solubility) have spurred the desire for alternative, silver-free methods for quite some time now,[3] and in light of these recent revelations, interest is rapidly increasing.

Gagosz and co-workers introduced the widely used gold(I) bis(trifluoromethanesulfonyl)imidates as stable, highly reactive catalysts that can be isolated free of silver.[4] Stable cationic nitrile complexes, which were applied by Echavarren and co-workers, among others, had a similar impact.[5] On the other hand, a variety of concepts for silver-free in situ generation of active gold(I) catalysts from stable gold(I) precatalysts have also been introduced. For instance, since the pioneering work by Teles et al., it is known that treatment of methyl gold complexes with a Brønsted acid generates catalytically active cationic species with release of methane.[6] Following a similar concept, Nolan and co-workers developed an N-heterocyclic carbene (NHC) gold(I) hydroxide precatalyst that can also be activated under acidic conditions.[7] In addition, there has been evidence for the catalytic activity of $(Ph_3P)AuCl$ in the presence of TfOH.[8] Non-silver-containing Lewis acids have successfully been used as activating reagents for gold(I) sulfonate or acetate precatalysts,[9] and in particular the combination of gold(I) chloride complexes with $Cu(OTf)_2$ appears to give an effective catalyst system.[10] The generation of active catalysts from gold(I) chloride complexes and alkali metal salts of borates such as $B(C_6F_5)_4^-$ (extensively used by Bertrand and co-workers to activate gold(I) NHC complexes) is also well-documented.[11] Recently, Echavarren and co-workers demonstrated that, in a series of gold(I) complexes with different counterions, those with the bulky and poorly coordinating $BAr^F{}_4^-$ ($= B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$) ion are particularly efficient in substantially raising the yields of intermolecular reactions.[12] However, studies on the general applicability of the $BAr^F{}_4^-$ counterion through the experimentally quite simple in situ activation of gold(I) chlorides are somewhat scarce.[13]

Due to their broad availability, gold(I) chloride precatalysts remain the prominent gold source for all types of homogeneous gold catalysis. Therefore, a general method for their activation, apart from the classical silver activation, would be of great significance. We now report the application of the sodium salt of an anionic boron cluster to activate a range of widely used gold(I) chloride precatalysts. The active gold species with the weakly coordinating counterion are formed in situ under experimentally simple, silver-free conditions. The efficiency of this new method is demonstrated by a broad spectrum of known reactions and an unprecedented cascade reaction of 1,6-allenynes.

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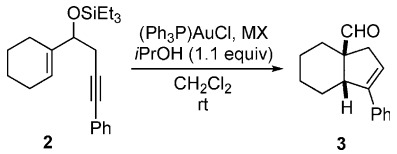
Results and Discussion

Inspired by the ongoing investigation of halogenated icosahedral borates as weakly coordinating anions for access to reactive cations,[14] we envisaged the application of such borates as a means to generate catalytically active, cationic gold(I) complexes from the corresponding gold(I) chlorides. These boron clusters are very robust, only weakly basic, and can be prepared and used as their alkali metal salts. During our studies (see below), $Na[Me_3NB_{12}Cl_{11}]$ (**1**) emerged as the reagent of choice. The singly charged anion has been prepared as its sodium salt by a simple two-step procedure: The reaction of $[H_3NB_{12}H_{11}]^-$ with an excess of $SbCl_5$ as the chlorinating agent gives the perchlorinated $[H_3NB_{12}Cl_{11}]^-$ anion. In the second step, this anion is methylated by methyl iodide to yield $[Me_3NB_{12}Cl_{11}]^-$.[14i]

Carbocyclization reactions of enynes

Our initial studies focused on the pinacol-terminated cyclization of 1,5-enyne **2** to generate bicyclic aldehyde **3** (Table 1).[15] $(Ph_3P)AuCl$ shows no catalytic reactivity in this reaction, unless it is activated with a suitable silver salt (Table 1, entries 1 and 2), in which case the removal of silver salts by filtration through Celite before addition of the catalyst is essential, since they cause decomposition of the starting material.[15a] We then replaced the silver salt with a variety of *closo*-dodecaborates $[B_{12}X_{12}]^{2-}$. In initial screening, different alkali metal salts of the clusters and $(Ph_3P)AuCl$ were directly added to the substrate solution to trigger the conversion of enyne **2** to aldehyde **3**.

Table 1. Cascade reaction of **2** in the presence of dodecaborates.



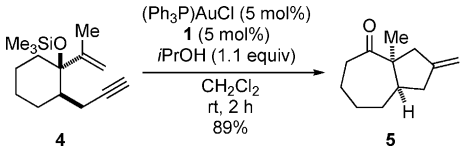
2 **3**

Entry	MX	*t* [h]	**3** [%][a]	**2** [%][a]
1[b]	–	24	0	>95
2[b]	$AgSbF_6$	<1	93	0
3[c]	$Na_2[B_{12}H_{12}]$	24	11	71
4[c]	$Na_2[B_{12}F_{12}]$	24	0	100
5[c]	$Na_2[B_{12}Cl_{12}]$	3	66	–
6[c]	$Na_2[B_{12}Br_{12}]$	24	50	31
7[c]	$Na_2[B_{12}I_{12}]$	24	28	39
8[c]	$Li_2[B_{12}Cl_{12}]$	48	43	37
9[c]	$K_2[B_{12}Cl_{12}]$	48	37	48
10[c]	$Cs_2[B_{12}Cl_{12}]$	24	0	100
11[d]	**1**	1	92	–
12[c]	$Na[BAr^F{}_4]$	24	90	–

[a] Yield of isolated product after column chromatography. $(Ph_3P)AuCl$ and MX were directly added to a solution of substrate unless stated otherwise. [b] Entry 1: gold catalyst (5 mol%) was directly added to the solution. Entry 2: gold catalyst (10 mol%) was preactivated by silver catalyst (5 mol%) and filtered through Celite; see ref. [15a,b]. [c] 10 mol% $(Ph_3P)AuCl$, 5 mol% MX. For the synthesis of the borates, see ref. [16]. [d] 5 mol% $(Ph_3P)AuCl$, 5 mol% **1**.

Most of the salts generated catalytically active species, albeit with varying reactivity. The boron hydride cluster (Table 1, entry 3) and its perfluorinated analogue (Table 1, entry 4) effected hardly any or no conversion after 24 h. Of the remaining dianionic clusters, the chlorinated cluster proved to be the most effective, giving complete conversion after 3 h and a yield of 66% (Table 1, entry 5). The reactivity decreased significantly when the brominated and iodinated clusters were used (Table 1, entries 6 and 7). Employing different alkali metal salts of the chlorinated cluster (Table 1, entries 8 to 10) also did not bring any improvement either, most likely due to solubility issues.

In contrast, **1**, which is the sodium salt of a monoanionic cluster, gave the desired product **3** in 92% yield after only 1 h, which matches our best results so far using silver-salt activation.[15] This silver-free activation mode seemed to be of general value, since it proved to be equally effective when applied to 1,6-enyne **4**, which gave the expected product **5** in excellent yield [Eq. (1)].[17]



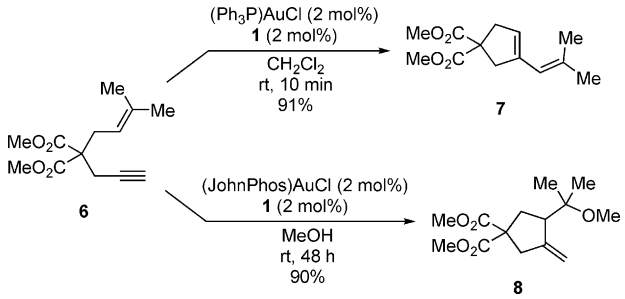
4 **5** (1)

In the context of these silver-sensitive reactions **2**→**3** and **4**→**5**, we were thus able to adjust the reaction conditions in a way that would be impossible with the in situ use of silver salts. Preactivation of the catalyst, notably in the absence of the substrate, and subsequent filtration to remove the silver are no longer necessary; instead, gold(I) catalyst and **1** are both simply added directly to the substrate solution.

The commercially available $Na[BAr^F{}_4]$ is also a potent additive for the in situ activation of $(Ph_3P)AuCl$: 3-silyloxy-1,5-enyne **2** was converted to aldehyde **3** in 90% yield (Table 1, entry 12), which is comparable to the yields we obtained using $AgSbF_6$ or cluster **1**. However, under otherwise identical conditions, the conversion of 3-silyloxy-1,6-enyne **4** with $Na[BAr^F{}_4]$ instead of cluster **1** gave a significantly reduced yield of 51% of **5**. Further experiments with both additives confirmed our impression that **1** is the more reliable and robust reagent for a variety of gold-catalyzed conversions (see below).

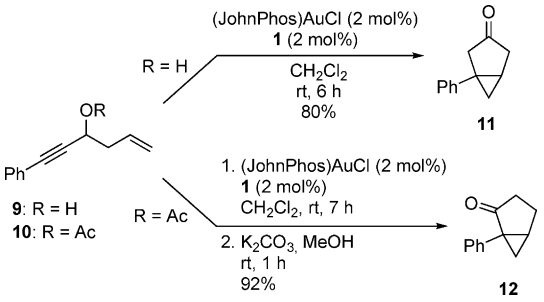
Encouraged by our results with cluster **1** in the cascade reactions of silyloxy-enynes **2** and **4**, we next tested how this activation method applies to other enyne systems that were previously converted by gold catalysis. As was generally the case with all previously described reactions herein, unless stated otherwise, no further attempt was made to optimize the reaction conditions reported in the respective literature; we simply changed the original activation method by adding **1** instead of the silver salt, without filtration or any other intermediary purification step.

We first chose the cycloisomerization of 1,6-enyne **6** to test the broad applicability of our activation method,[6d] and found that the combination of $(Ph_3P)AuCl$ and cluster **1** is indeed highly reactive in the formation of diene **7** (Scheme 1). An



Scheme 1. Carbocyclization reactions of 1,6-enyne **6**.

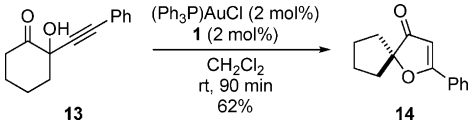
equally high yield was obtained for the methoxycyclization of **6** to **8** with (JohnPhos)AuCl (instead of the originally used (Ph_3P)AuMe/protic acid system) in methanol,[6d] although the reaction rate was considerably lower. The same catalyst was also effective in the cyclization of 1,5-enynes **9** and **10** to the two different bicyclohexanone isomers **11** and **12**, respectively (Scheme 2), whereby the high-yield two-step conversion of acetate **10** is particularly noteworthy.[18] The combination of **1** with the originally reported (Ph_3P)AuCl precatalyst gave slightly inferior yields and lower reaction rates in those cases.



Scheme 2. Cycloisomerization reactions of 1,5-enynes **9** and **10**.

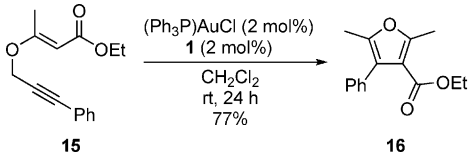
Heterocyclization reactions

We were also able to successfully perform a variety of heterocyclization reactions with cluster-activated gold(I) catalysts. For example, alkynone **13** was converted to furanone **14** in the presence of (Ph_3P)AuCl and cluster **1** [Eq. (2)].[19] Compared to the activation of the catalyst with various silver salts, this is by far the best result we could obtain with gold(I) catalysts at room temperature for this reaction, which runs more efficiently with platinum(II) catalysts at elevated temperatures.



(2)

In the case of applying the same conditions to propargyl vinyl ether **15** to effect the propargyl Claisen rearrangement and heterocyclization cascade to give furan **16** [Eq. (3)], our expectations were low, since we were never able to perform this reaction in the absence of a silver-salt catalyst.[20] Nevertheless, the desired furan **16** could indeed be obtained in 77% yield. An equally good yield was observed for the acetylenic Schmidt reaction of azide **17** to give pyrrole **18** with $(dppm)Au_2Cl_2$ (dppm = 1,1-bis(diphenylphosphino)methane) as precatalyst [Eq. (4)].[21]



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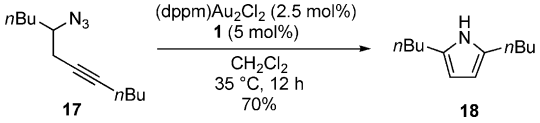
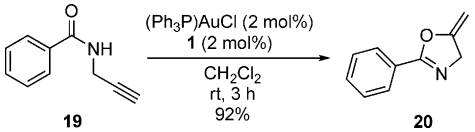


(4)

(Ph_3P)AuCl and **1** again proved to be a very effective combination in the cyclization of propargylic amide **19**, which rapidly gave oxazoline **20** in high yield [Eq. (5)].[22] The same combination, however, fell short compared to the highly reactive $(Ph_3P)AuNTf_2$ catalyst in the cyclization of propargylic *tert*-butyl carbonate **21** to dioxolanone **22** [Eq. (6)], in which case we had to use slightly elevated temperatures to force conversion.[4c]



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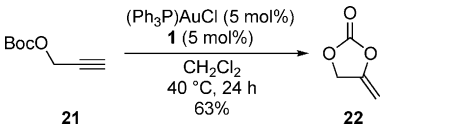
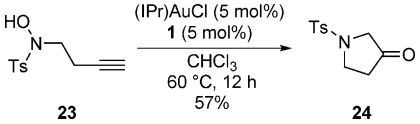


(6)

Changing the solvent from toluene to chloroform was necessary to perform the cyclization of homopropargylic hydroxylamine **23** to pyrrolidinone **24** [Eq. (7)], which we obtained in a moderate yield close to the previously reported result.[23] The use of molecular sieves described in the original procedure was not necessary when we conducted the reaction. For the formation of dihydrobenzofuran **26** from allyl ether **25**, which likely proceeds via Claisen rearrangement and subsequent cyclization, we applied slightly higher temperatures to obtain the product in 51% yield [Eq. (8)].[24] This pretty poor result sup-



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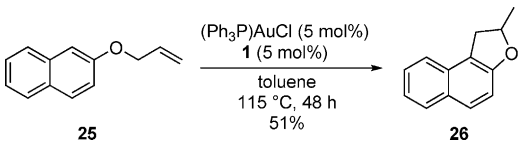
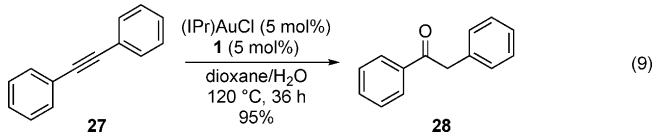


(8)

ports the original assumption that an assisting role can be attributed to the silver salt in this reaction.[2a]

Other gold(I)-catalyzed reactions

Other gold(I)-catalyzed transformations in which we applied **1** include the hydration of alkyne **27**, in which case we could successfully activate the NHC–gold precatalyst in aqueous medium and obtain ketone **28** in high yield [Eq. (9)];[25] however, we were forced to increase catalyst loading to 5 mol% compared to the reported procedure to reach full conversion. The combination of (JohnPhos)AuCl and **1** worked well in the tandem hydroamination/hydrogenation of phenylacetylene (**30**) with *N*-methylaniline (**29**) in the presence of diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (Hantzsch ester), as shown in [Eq. (10)].[26] We were able to isolate tertiary amine **31** in 72% yield, although conversion of amine **29** was not yet complete after 48 h.



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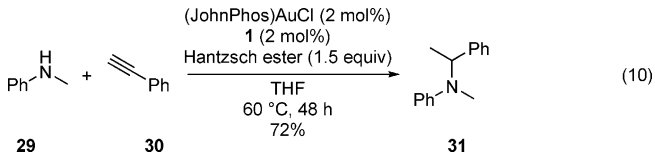
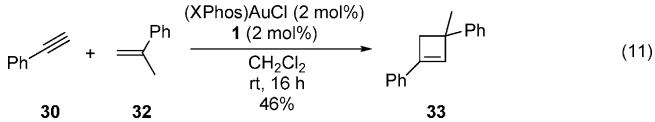


(10)

Also in case of the [2+2] cycloaddition of phenylacetylene (**30**) with α-methylstyrene (**32**) [Eq. (11)], (XPhos)AuCl activated in situ by **1** proved to be reactive, although the yield was lower than those obtained with the isolated [(XPhos)Au(NCMe)]SbF_6 catalyst.[5e] Recently, Echavarren and co-workers reported that cyclobutene **33** is formed in 95% yield when the isolated [(*t*BuXPhos)Au(MeCN)]BAr^F_4 catalyst is employed.[12,27]



(11)

Several reactions discussed above can be efficiently performed with Na[BAr^F_4] instead of cluster **1** under otherwise identical conditions. The in situ activation of gold(I) complexes with Na[BAr^F_4] gave, for example, good results for the formation of **7** (82%), **12** (94%), **20** (82%), **31** (74%), and **33** (41%), whereby the yields are in the range of those obtained with cluster **1**. In other cases, however, we found markedly reduced yields when employing Na[BAr^F_4]: **8** (42%), **11** (69%), **14** (44%), **16** (43%), **18** (36%), **26** (no product formation), and **28** (39%). We conclude that for a couple of reactions Na[BAr^F_4] and cluster **1** are equally effective for the in situ activation of gold complexes, but cluster **1** is easily prepared and shows, at least in our hands, superior performance in several reactions in which the anionic boron cluster appears to be the more efficient counterion.

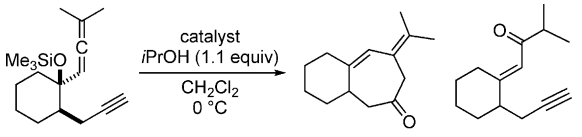
Cyclization cascade of 5-silyloxy-1,6-allenynes

Apart from the above known reactions, we also found application for this new activation method in a previously undisclosed gold(I)-catalyzed reaction of 1,6-allenynes. Although a variety of allenynes have been shown to engage in cyclization reactions similar to corresponding enyne systems in the presence of transition-metal catalysts, their reactivity has not been investigated nearly as thoroughly as that of their enyne counterparts.[1k,m,28] That fact, along with our work on cyclization reactions of silyloxy-enynes, fueled our interest in the reactivity of allenynes bearing a silyloxy group.

In various instances, 1,6-enynes in the presence of base or gold catalysts have been shown to engage in a cascade reaction consisting of a heterocyclization step followed by Claisen rearrangement to give complex and often polycyclic cycloheptenones.[17,29] We now report that 5-silyloxy-1,6-allenynes undergo a similar gold(I)-catalyzed transformation to (bi)cyclic, polyunsaturated products.

As shown in Table 2, we initially found that 1,6-allenyne **34a** in the presence of (Ph_3P)AuCl and $AgSbF_6$ gives both bicyclic ketone **35a** and the rearrangement product **36** (Table 2, entry 1). Conducting the same experiment solely with $AgSbF_6$ gave exclusively ketone **36** (Table 2, entry 2), that is, the silver salt seems to be responsible for the formation of this undesired byproduct. Indeed, preactivation and filtration of the catalyst resulted in the sole formation of ketone **35a** in 73% yield (Table 2, entry 4). Other silver salts such as AgOTf and $AgNTf_2$ proved to be less efficient than $AgSbF_6$. In an effort to dispense with silver salts altogether, we also tried to convert allenyne **34a** in the presence of (Ph_3P)AuCl and cluster **1**, in which case we were able to match the best yield of 73% obtained with silver-salt activation. Under experimentally simple conditions, the gold(I) catalyst and **1** are both added to the sub-

Table 2. Optimization of catalyst activation for the conversion of **34a**.



34a **35a** **36**

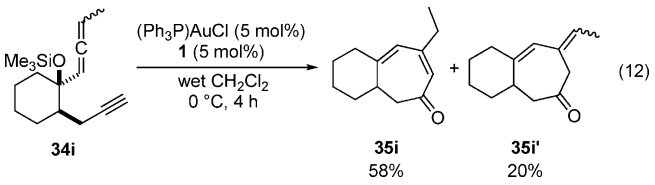
Entry	Catalyst (mol%)	*t* [h]	**35a** [%][a]	**36** [%][a]
1[b]	(Ph_3P)AuCl (5)/$AgSbF_6$ (5)	3	42[c]	32[c]
2	$AgSbF_6$ (5)	3	0	64
3	(Ph_3P)AuCl (5)	24	0[d]	0[d]
4[e]	(Ph_3P)AuCl (10)/$AgSbF_6$ (5)	1	73	0
5[e,f]	(Ph_3P)AuCl (10)/AgOTf (5)	22	60	0
6[e]	(Ph_3P)AuCl (10)/$AgNTf_2$ (5)	6	65	0
7[b]	(Ph_3P)AuCl (5)/Na[BAr^F_4] (5)	2	59	0
8[b]	(Ph_3P)AuCl (5)/**1** (5)	2	73	0
9	**1** (5)	24	0[d]	0[d]

[a] Yield of isolated product after column chromatography. [b] (Ph_3P)AuCl and activating reagent were directly added to a solution of substrate. [c] Obtained as mixture; individual yields determined by NMR spectroscopy. [d] No reaction. [e] (Ph_3P)AuCl and silver salt were stirred separately and filtered through Celite before addition to substrate. [f] Reaction was performed at rt.

strate solution. In comparison, the use of $Na[BAr^F_4]$ under the same conditions also led to complete conversion of the starting material, but gave a markedly inferior yield.

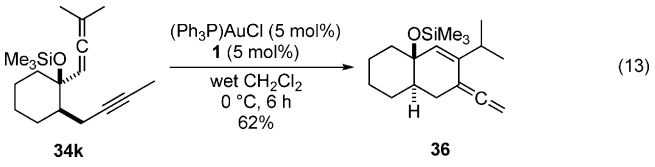
After further optimization of the reaction conditions (notably, the use of wet CH_2Cl_2 instead of *i*PrOH to effect hydrolysis of the silyl ether resulted in slightly improved yields), we next investigated the scope of the reaction. Entries 1–5 in Table 3 show that substrates with a variety of substituents on the terminal allene carbon atom, such as methyl, ethyl, and phenyl groups, were successfully converted in mostly good to high yields, with only the cyclohexylidene derivative **35e** being obtained in a moderate yield of 50% (Table 3, entry 5). In the case of unsymmetrically substituted allenes, comparison of the diastereomeric ratios of products and substrates indicate that the stereoinformation of the allene is transferred to the exocyclic double bond of the product. Furthermore, substrate **34f** featuring a five-membered ring gave the corresponding bicyclic product **35f** in good yield (Table 3, entry 6).

Whereas all of the substrates with two substituents at the terminal allene carbon atom resulted exclusively in the formation of products with one exocyclic double bond, substrate **34g**, which bears no further substituent on the allene moiety, gave α,β-unsaturated ketone **35g** with two endocyclic double bonds in very good yield (Table 3, entry 7), which suggests that, depending on the substitution pattern of the allene, slightly different mechanisms may be at work and lead to the more highly substituted double bond in each case. Allenyne **34h** gave the analogous product **35h** in moderate yield (Table 3, entry 8). Interestingly, allenyne **34i**, which has just one methyl substituent on the terminal allene carbon atom, gave both products **35i** and **35i'**, which could be isolated separately [Eq. (12)].



(12)

Although terminal alkynes readily reacted under the present conditions, internal alkynes proved to be much more difficult to engage in an analogous reaction. The conversion of phenylated alkyne **34j** to ketone **35j**, however, shows that it is generally feasible (Table 3, entry 9). We found that in this particular instance the use of *i*PrOH in dry CH_2Cl_2 improved the conversion, which was still not complete after 3 d at room temperature, and resulted in a comparatively low yield of 46%. Furthermore, the only product isolated after the reaction of methylated alkyne **34k** was the unexpected allene **36**, which is obviously formed by carbocyclization followed by a hydride shift [Eq. (13)], a reaction that has already been reported for similar substrates.[30] In addition to cyclic substrates, acyclic allenynes **34l** and **34m** were also successfully converted to cyclopentenones **35l** and **35m** in moderate and high yields, respectively (Table 3, entries 10 and 11).



(13)

On comparing the in situ activation of the gold(I) catalyst with cluster **1** to preactivation with $AgSbF_6$, we found that our silver-free method was generally equal or even superior to preactivation with a silver salt. For instance, applying the latter method to allenyne **34f** afforded ketone **35f** in only 34% yield, as opposed to 73% with cluster **1**. Even more noteworthy is the fact that internal alkyne **34j** gave only traces of the product **35j** after 4 d at room temperature when $AgSbF_6$ was used. This indicates that the catalyst formed during preactiva-

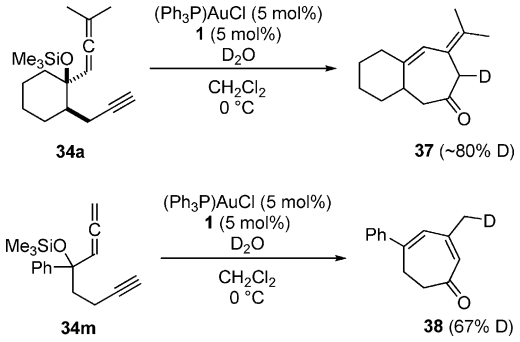
Table 3. Cascade reaction of 5-silyloxy-1,6-allenynes **34**.

Entry	Substrate	Product	Yield [%][a]
1	**34a**: $R^1=R^2=Me$	**35a**	82
2	**34b**[b]: $R^1=Me$, $R^2=Et$	**35b**	68[c]
3	**34c**: $R^1=R^2=Et$	**35c**	85
4	**34d**[d]: $R^1=Me$, $R^2=Ph$	**35d**	85[e]
5	**34e**:	**35e**:	50
6	**34f**:	**35f**:	73
7	**34g**:	**35g**:	84
8	**34h**:	**35h**:	54
9[f]	**34j**:	**35j**:	46[g]
10	**34l**: $R=C_6H_{13}$	**35l**	83
11	**34m**: R=Ph	**35m**	61

[a] Yield of isolated product after column chromatography; conditions: $(Ph_3P)AuCl$ (5 mol%), **1** (5 mol%), wet CH_2Cl_2 (0.2 M), 0 °C. [b] d.r. = 1.2:1. [c] d.r. = 1.2:1. [d] d.r. = 1.7:1. [e] d.r. = 1.5:1. [f] With *i*PrOH (1.1 equiv), rt. [g] 68% Yield based on recovered starting materials.

tion in the absence of the substrate is less reactive compared to activation with cluster **1** in the presence of the substrate. By implication, if a substrate of this nature had been chosen as a starting point to investigate the reactivity of this allenyne system, the use of common silver salts would have provided a false negative result.

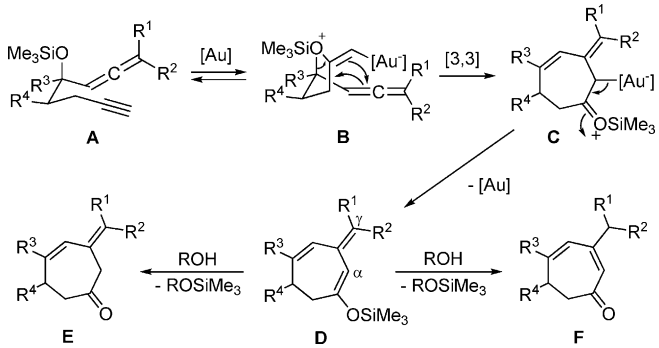
To gain a better understanding of the mechanistic details that influence the outcome of the reaction regarding the exo- or endocyclic position of the double bond in the cyclization products, we conducted deuteration experiments with allenynes **34a** and **34m** (Scheme 3). Carrying out the reaction with substrate **34m** in the presence of deuterium oxide led exclusively to the incorporation of deuterium at the methyl group of ketone **38**. In contrast, conducting the same experiment with substrate **34a** afforded product **37** deuterated at the expected α position to the ketone.



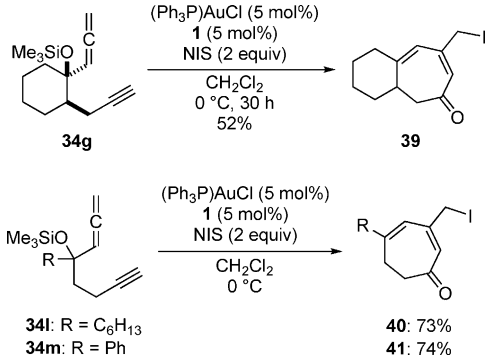
Scheme 3. Deuteration experiments with allenynes **34a** and **34m**.

A possible mechanism that is in line with these results is offered in Scheme 4. After activation of alkyne **A** by the gold catalyst towards heterocyclization, the resulting species **B** undergoes [3,3]-sigmatropic rearrangement to complex **C**, which then collapses with release of the gold catalyst to give silyl enol ether **D**. Subsequent hydrolysis of the silyl enol ether proceeds by protonation at the α or γ position leading to product **E** or **F**, respectively, depending on the steric demand of the substituents R^1 and R^2; γ protonation is favored only when $R^1 = R^2 = H$.

To further expand the scope of the reaction, we attempted to convert the intermediately formed silylenol ether in a one-pot procedure with *N*-iodosuccinimide (NIS). Consistent with the results of the deuteration experiments, we found that converting allenyne **34g** in dry CH_2Cl_2 in the presence of NIS and under otherwise standard reaction conditions led to the formation of the somewhat unusual allylic iodide **39**, which we were able to isolate in 52% yield (Scheme 5). Acyclic substrates **34l** and **34m** behaved in analogous fashion, and iodides **40** and **41** were obtained in higher yields of 73 and 74%, respectively.



Scheme 4. Probable mechanism for the cascade reaction of **A**.



Scheme 5. Synthesis of allylic iodides.

Characterization of cationic gold(I) species

To better understand the interaction of cluster **1** with gold(I) catalysts, we then isolated the activated cationic gold(I) complex. The chlorido-bridged digold complex **42** was formed on stirring equimolar amounts of $(Ph_3P)AuCl$ and **1** in CH_2Cl_2 (Figure 1). An X-ray diffraction study[31] on complex **42** revealed an A-frame structure of the cation with a short Au···Au dis-

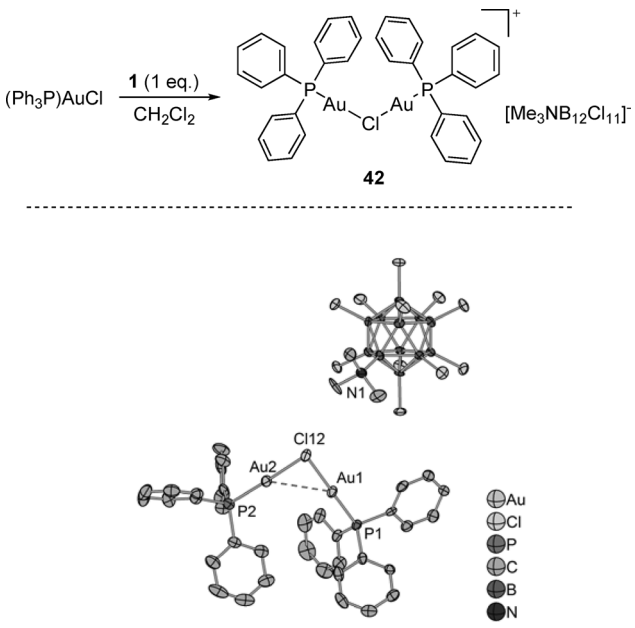
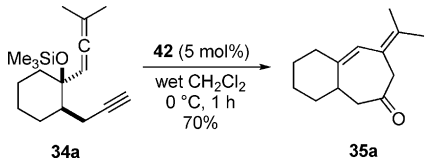


Figure 1. Formation of digold complex **42** (top). Part of the crystal structure of **42** (bottom); ellipsoids are drawn at 50% probability, and hydrogen atoms are omitted for clarity.

tance of 310.08(4) pm due to an aurophilic interaction.[31] This result, which is in accordance with previous reports on analogous dinuclear complexes generated from phosphine gold(I) halides and silver salts of different weakly coordinating anions,[2b,33] suggests that chloride abstraction from the precatalyst is not complete in the absence of a substrate or coordinating solvent. However, in our standard reaction setup, in which the precatalyst is activated in the presence of the substrate, we assume that chlorido-bridged complex **42** is not formed.

Applying the isolated digold complex **42** directly to allenyne **34a** effected the conversion to ketone **35a** almost as readily as in situ activation [Eq. (14)], which implies that this particular substrate is able to dissociate the chlorido-bridged complex to release the catalytically active species.



34a **35a** (14)

Conclusion

We have introduced a general and simple method for the activation of all types of ligated gold(I) chloride precatalysts LAuCl in which L is a phosphane or an NHC. Under silver-free conditions, the action of $Na[Me_3NB_{12}Cl_{11}]$ (**1**) produces gold species with the weakly coordinating *closo*-dodecaborate anion $[Me_3NB_{12}Cl_{11}]^-$, which were demonstrated to be highly effective catalysts for a range of literature-known conversions including carbocyclizations and heterocyclizations. Furthermore, we used this activation method to make the conversion of 5-silyloxy-1,6-allenynes into polyunsaturated cycloheptenones possible, a novel reaction that proved sensitive to silver additives. We feel that the activation of gold(I) chloride precatalysts with **1** is a general alternative to the classical usage of silver salts that will become of great value to future developments.

Experimental Section

General procedure for the Au^I-catalyzed cyclization cascade of allenynes

8-Propan-2-ylidene-3,4,4a,5,7,8-hexahydro-1*H*-benzo[7]annulen-6(2*H*)-one (35a): $(Ph_3P)AuCl$ (2.4 mg, 4.88 μmol, 5 mol%) and $Na[Me_3NB_{12}Cl_{11}]$ (2.9 mg, 4.88 μmol, 5 mol%) were added to a solution of allenyne **34a** (27.0 mg, 97.7 μmol, 1 equiv) in 0.49 mL of wet CH_2Cl_2 at 0 °C. After stirring at that temperature for 2 h, the crude mixture was mounted on silica and purified by flash chromatography (petroleum ether (PE)/EtOAc 98/2) to afford ketone **35a** (16.4 mg, 80.3 μmol, 82%) as a pale yellow oil. TLC: $R_f = 0.33$ (PE/EtOAc 90/10, [UV] [$KMnO_4$]); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.10$ (s, 1H), 3.29 (d, $J = 17.9$ Hz, 1H), 3.19 (d, $J = 17.9$ Hz, 1H), 2.67 (dd, $J = 12.2$, 9.2 Hz, 1H), 2.57 (dd, $J = 12.3$, 3.8 Hz, 1H), 2.41–2.31 (m, 1H), 2.30–2.23 (m, 1H), 2.03 (td, $J = 13.1$, 4.0 Hz, 1H), 1.85–1.72 (m, 3H), 1.76 (s, 3H), 1.70 (s, 3H), 1.45–1.35 (m, 1H), 1.35–1.26 (m, 1H), 1.26–1.17 ppm (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 211.8$, 142.5, 131.6, 123.7, 123.6, 49.1, 48.0, 40.7, 38.3, 36.0, 28.7, 26.6, 21.5, 20.6 ppm; IR (ATR): $\tilde{\nu} = 2922$, 2853, 1708, 1626, 1444, 1372, 1341, 1312, 1273, 1251, 1232, 1188, 1156, 1118, 1065, 1026, 967, 944, 878, 848, 746, 638, 586, 538, 514, 492, 450, 410 cm^{-1}; LRMS (EI): *m/z* (%): 204 (100) [M^+], 189 (14) [$M^+ - CH_3$], 171 (10), 161 (59), 147 (36), 133 (49), 119 (57), 105 (52), 91 (75), 77 (28), 67 (13), 53 (12); HRMS (ESI): *m/z* calcd for $C_{14}H_{20}ONa^+$: 227.1404; found: 227.1406 [M+Na$^+$].

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Keywords: borates · cyclization · gold · homogeneous catalysis · weakly coordinating anions

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