CHEMISTRY
A EUROPEAN JOURNAL

ChemPubSoc Europe

DOI: 10.1002/chem.201202004

Gold Catalysis: Catalyst Oxidation State Dependent Dichotomy in the Cyclization of Furan–Yne Systems with Aromatic Tethers

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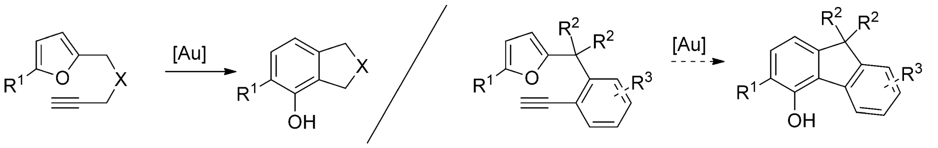
Abstract: Four different synthetic strategies led to a variety of furan–yne systems that contained an aryl system in the tether. Due to the short routes to these systems (four steps or less), a small library of substrates could easily be prepared. These were treated with $AuCl_3$ or with the Gagosz's catalyst $Ph_3PAuNTf_2$ complex. The $AuCl_3$-catalyzed reactions delivered highly substituted fluorene derivatives, a class of compounds of great importance as precursors for luminophores with extraordinary abilities. Conversely, a different mechanistic pathway was observed with the cationic gold(I) catalyst. In the latter case, a mechanistically interesting reaction cascade initiated a formal alkyne insertion into the furyl-sp^3-C bond, which gave indene derivatives as the final products. This new reaction pathway depends on the aromatic moiety in the tether, which stabilizes a crucial cationic intermediate as a benzylic cation.

Keywords: acids · alkynes · gold · insertion · oxygen heterocycles

Introduction

In the field of transition-metal-catalyzed transformations, gold catalysis has emerged from being a rarity at the end of the last millennium to one of the most frequently investigated and applied synthetic tools. This has been summarized in numerous reports on highly diverse reactions.[1]

Most of these reactions can be performed under very mild conditions without precautions[2] and in a highly atom-economic[3] fashion. Of these reports, substrates with an en–yne substructure offer a huge number of possible rearrangements that lead to highly complex target molecules. The high increase in molecular complexity[4] in these reactions has inspired organic chemists working in total synthesis and thus the application of gold in natural-product synthesis is also an emerging field.[5] Our group reported the synthesis of various benzo-annelated heterocycles by reaction of different furan–yne systems that have a terminal alkyne moiety (Scheme 1, left).[6] Furthermore, by using alkynyl ethers and ynamides, even nonterminal alkynes could be converted and new mechanistic pathways were opened with these substrates.[7]



Scheme 1. Based on the phenol synthesis (left), fluorene formation should be easy (right).

Herein we focus on the exploration of terminal furan–yne systems that have aromatic tethers, which could be useful precursors for the synthesis of substituted fluorenes (Scheme 1, right).

Fluorenes represent an extremely important class of substrates because fluorene-based polymers and oligomers and their application in organic light-emitting diodes and organic photovoltaic cells is of considerable interest.[8] Most of the synthetic strategies for substituted fluorenes are based on functionalization of the existing fluorene core. The advantage of furans as a starting material is based on the ease of chemical modification of the furan core[9] and on the opportunity to synthesize unsymmetric fluorene substructures. Furthermore, depending on the retrosynthetic disconnection

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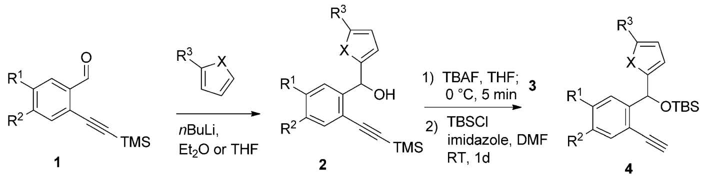
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202004.

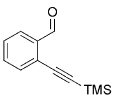
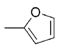
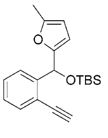
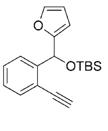
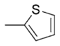
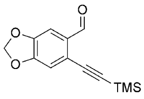
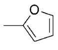
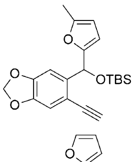
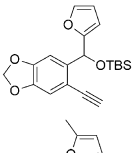
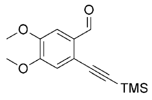
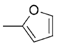
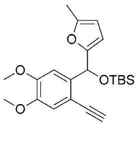
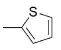
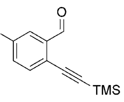
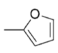
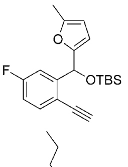
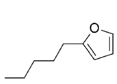
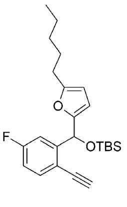
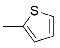
of the furan–yne precursors, an easy modification at the decisive 9-position of the fluorene moiety would become feasible.[10] However, it must be noted that similar substrates with a substituted alkyne give naphtols,[11] thus the observation of fluorenes would represent a new reaction pathway for that type of furan–yne.

Results and Discussion

Our synthesis of the substrates started from commercially available 2-bromobenzaldehydes, which were easily converted to the corresponding alkynylbenzaldehydes **1** by Sonogashira reactions with TMS-acetylene (TMS = trimethylsilyl). The reactions gave high yields at room temperature when using the common and simple $(PPh_3)_2PdCl_2/CuI$ catalyst system. The next step is a nucleophilic addition of a metalated arene moiety, which gave alkynylbenzylic alcohols **2** in high yields. By using this strategy, we could not only incorporate furan and substituted furan moieties (Table 1, entries 1, 2, 5, 6, 7, 9, 10) but also thiophene substituents (Table 1, entries 3, 8, 11) and a phenyl moiety (Table 1, entry 4). The latter substrates represent valuable precursors for the installation of two aromatic moieties at the benzylic position, and their further conversion will be discussed later. All the furan substrates were then deprotected by using TBAF (TBAF = tetrabutylammonium fluoride) in THF. The protecting group could easily be cleaved within a short reaction time, and yields were excellent in most cases. To avoid a competing attack of the alcohol nucleophile in the gold-catalyzed step, the benzylic oxygen was subsequently protected with TBSCl (TBSCl = *tert*-butyldimethylsilyl chloride), a protecting group that is known to be stable under gold-catalysis conditions.[12] Unfortunately, the yields proved to be only moderate for this reaction step. One reason might be a competing Reppe-type vinylation,[13] which would lead to methylene dihydroisobenzofuran compounds. These are sensitive and polymerize easily. Thanks to the comment of one referee, we also tested TBSOTf at 0 °C for one substrate and yields could indeed be significantly improved by using this procedure (Table 1, entry 2, compound **4b**). Nevertheless, all fluorene precursors **4** were available in an efficient three-step procedure from alkynyl benzaldehydes **1**.

Table 1. Synthesis of protected furylbenzyl alcohols **4**.

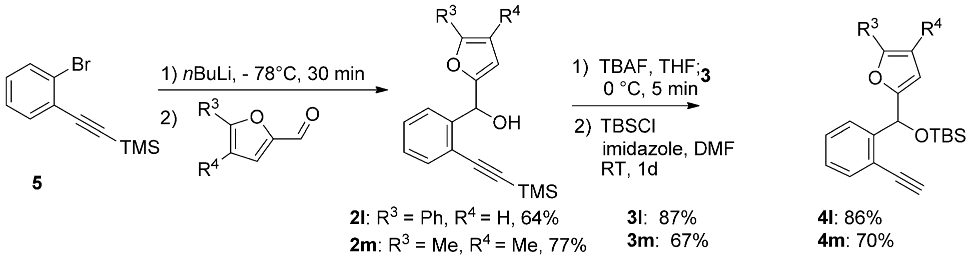


Entry	Aldehyde **1**	Nucleophile	Time [h]	Yield of **2** [%]	Yield of **3** [%]	Product **4**	Yield [%]
1			1	**2a**, 98	**3a**, > 99[a]		47
2	**1a**		3	**2b**, 86	**3b**, > 99		45/ **69**[b]
3	**1a**		3	**2c**, 93	–	–	–
4	**1a**		2	**2d**, 72[c]	–	–	–
5			3	**2e**, 50	**3e**, 89		48
6	**1b**		5	**2f**, 52	**3f**, 90		34
7			6	**2g**, 88	**3g**, 96		61
8	**1c**		3	**2h**, 63	–	–	–
9			3 d	**2i**, 84	**3i**, 58		47
10	**1d**		3 d	**2j**, 64	**3j**, 88		70
11	**1d**		1	**2k**, 88	–	–	–

[a] KF was used as a deprotecting reagent. [b] Obtained by using TBSOTf at 0 °C. [c] Phenylmagnesium bromide was used as a nucleophile.

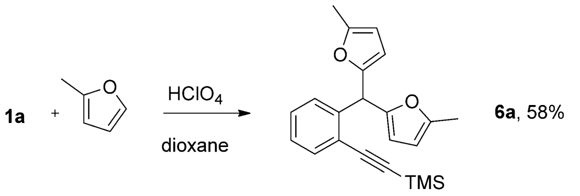
Due to the easy availability of furfurals from renewable feedstocks,[14] a different disconnection of furylbenzyl alcohols **2** was also explored. For this approach, *ortho*-alkynyl bromobenzene **5** was lithiated by using a metal halogen exchange. The resulting nucleophile reacted successfully with the furfural part in good yield. In analogy to the other arylbenzyl alcohols **2a–j**, alcohols **2l** and **2m** were transformed to the desired substrates **4l**/**4m** through a simple deprotection/reprotection strategy in good overall yields (Scheme 2).

In addition to protected benzylic alcohols, substrates with two aromatic substituents at the benzylic position were also investigated. The direct preparation of substrates with sym-



Scheme 2. Synthetic approach using furfural derivatives as starting materials.

metrically substituted benzylic positions was possible from aryl benzaldehyde **1a**, in analogy to a procedure of Butin et al.[15] This addition of aromatic nucleophiles to aldehydes, catalyzed by using perchloric acid, gave desired product **6a** in moderate yield (Scheme 3). After deprotection with TBAF, starting material **7a** was accessible. Both compounds gave crystals suitable for X-ray crystal structure analysis (Figure 1).[16] The two structures nicely document the loss of conformational freedom caused by the (*Z*)-like double bond of the aromatic system in the tether, which brings the reacting centers close together.



Scheme 3. Acid-catalyzed difurylation of benzaldehyde **1a**.

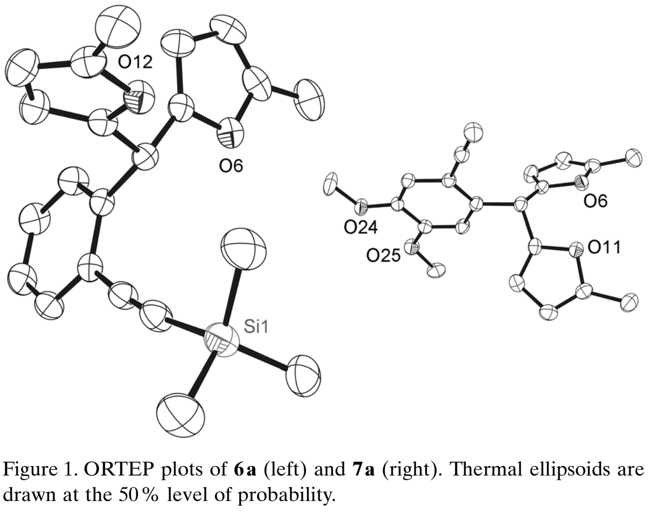
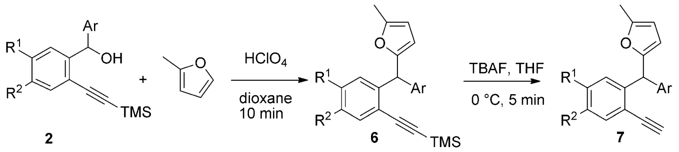


Figure 1. ORTEP plots of **6a** (left) and **7a** (right). Thermal ellipsoids are drawn at the 50% level of probability.

Unfortunately, substituted benzaldehydes **1b** and **1c** decomposed. Thus, we considered a two-step procedure that turned out to be much more successful (e.g., 85% over two steps vs. 58% for the one-step synthesis of **6a**). In these cases we started from aryl/heteroaryl benzylalcohols **2**. In a subsequent reaction step, an addition of 2-methyl furan, catalyzed by using perchloric acid, gave protected triarylmethane derivatives **6** (Table 2). By using this two-step procedure, two different aryl moieties could easily be installed at the benzylic position, which provided the opportunity to create a small library of substrates. Yields for the addition step were all high and, as in the above cases, TBAF deprotection smoothly delivered the desired compounds in excellent efficiency.

With these substrates in hand, we explored their reactivity by using simple gold(III) chloride as a pre-catalyst. Table 3 summarizes the results obtained with protected furyl alcohols **4**. To our delight, substrate **4a** displayed significant reactivity and substituted fluorenol **8a** was obtained in reasonable yields (Table 3, entry 1). The high reactivity of this system (the reaction was complete within minutes at room temperature!) probably resulted from the fixed geometry of the incorporated aryl bond, which led to a lower degree of conformational freedom compared with the substrates with aliphatic side chains (see also Figure 1). Next, we investigated monosubstituted furan–yne system **4b** (Table 3, entry 2). Aliphatic side chains were used to deliver regioisomeric phenol systems in these cases,[6a] but only one product was formed in the case of the aryl-containing tether. The structure, which contained the hydroxy moiety in the 4-position of the fluorene system, was unambiguously proven by an X-ray crystal structure analysis (Figure 2, left).[16] The reason for the high selectivity can be explained by a selective ring opening of the intermediate arene oxides;[17] a regioselective ring opening exclusively delivers a carbocation that is complimentarily stabilized by the aromatic ring in the tether (Scheme 4).[18] A comparable effect was previously observed in the conversions of furan–yne systems that contained terminal ynamides and alkynylethers, which were also able to stabilize the cationic intermediates through the heteroatom effect.[6f] Next, we investigated the functional-group tolerance towards different substitutents at the aromatic moiety in the tether. Higher yields were obtained with the electron-rich protected catechol derivative **4e** than with the benzene derivatives (Table 3, entry 3). Most unfortunately, this effect was not observed with monosubstituted furan **4f** and the yield was in the range of the benzene substrate (Table 3, entry 4). By switching to even more electron-donating me-

Table 2. Two-step synthesis of triarylmethane derivatives **7**.



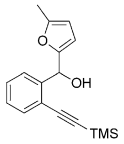
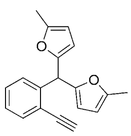
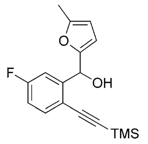
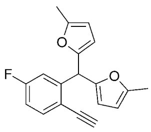
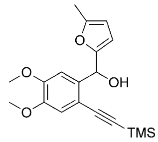
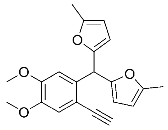
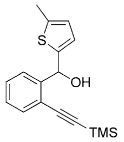
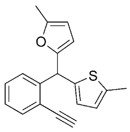
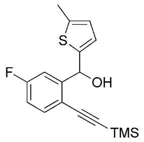
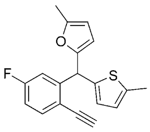
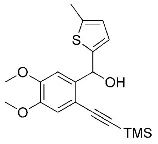
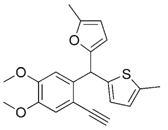
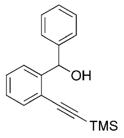
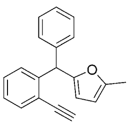
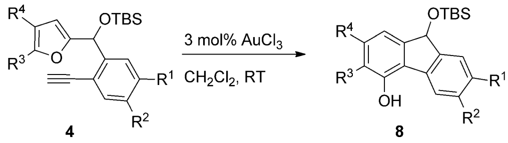
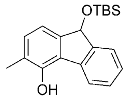
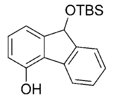
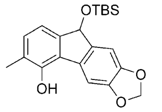
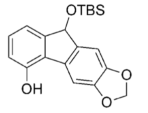
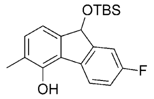
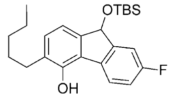
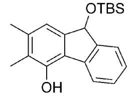
Entry	**2**	Yield of **6** [%]	Product **7**	Yield of **7** [%]
1		**6a**, 87		97
2		**6b**, 84		99
3		**6c**, 83		97
4		**6d**, 94		98
5		**6e**, 69		92
6		**6f**, 93		97
7		**6g**, 68		81

Table 3. Gold(III)-catalyzed conversion of furan–yne systems **4**.



Entry	Starting material	Time [min]	Product **8**	Yield of **8** [%]
1	**4a**	10		60
2	**4b**	5		51
3	**4e**	5		74
4	**4f**	5		50
5	**4g**	5	decomposition	–
6	**4i**	10		38
7	**4j**	10		50
8	**4l**	5	decomposition	–
9	**4m**	10 min		24

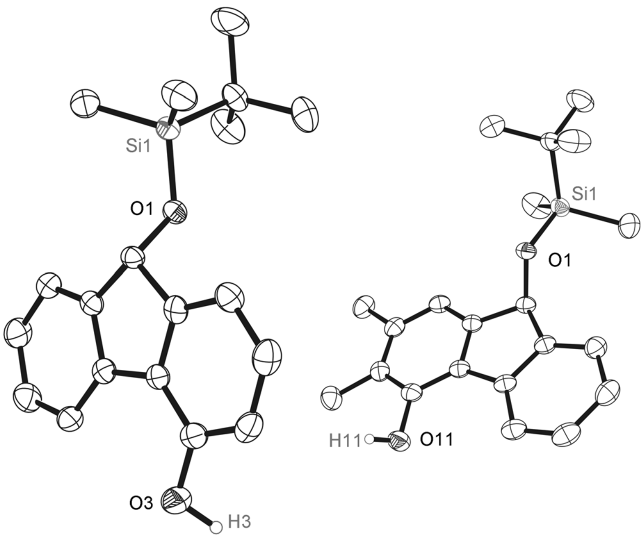
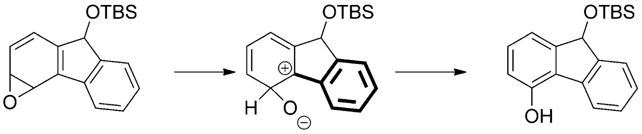


Figure 2. Solid-state molecular structures of **8b** (left) and **8m** (right). Thermal ellipsoids are drawn at the 50 % level of probability.

thoxy groups in catechol derivative **4g**, an unselective reaction was observed and a complex mixture was obtained even in the case of the substituted furan system (Table 3, entry 5). In full agreement with these observations, substrate **4i** with electron-deficient *m*-fluorobenzene in the tether led to an explicit decrease in yield (Table 3, entry 6). Interestingly, switching the chain length of the substituent on the furan system from a methyl to a pentyl group re-established an acceptable yield for these systems (Table 3, entry 7). To further explore the influence of the furan substituent, substrate **4l**, which has an aryl group, was converted. However, only decomposition was observed, even at 0 °C, after short reaction times. This is in contradiction to the previous studies,[6e] but here the protected hydroxyl moiety in the strongly activated furyl position might open degradation pathways via cationic intermediates. In the case of tri-substituted

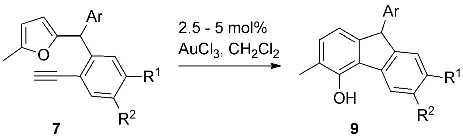


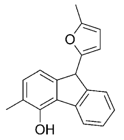
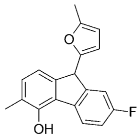
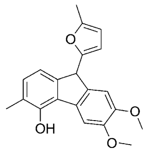
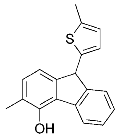
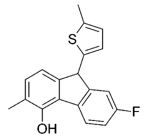
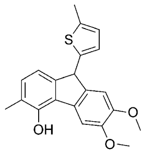
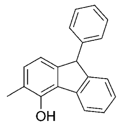
Scheme 4. Regioselective ring-opening pathway via benzyl stabilized cations.

furan system **4m**, only a low yield of the expected product was isolated and, as in previous reports on this substitution pattern, byproducts were detectable by TLC but were not stable upon isolation.[18] Nevertheless, crystals suitable for X-ray analysis were obtained that prove the positioning of the methyl groups in the 2- and 3-positions of the newly formed fluorene core (Figure 2, right).[16]

Encouraged by these findings, we also explored the reactivity of triarylmethane derivatives **7**. As in the previous case, they were converted by simple $AuCl_3$ in CH_2Cl_2. The results are summarized in Table 4. Similarly to the corresponding furylalcohol derivative **4a**, a fast conversion was observed for substrate **7a** even at 0 °C (Table 4, entry 1). Furthermore, the yield was significantly higher in this case. Because some experiments for the conversion of diaryl substrates showed a tendency for polymerization as well as catalyst deactivation even at 0 °C, the other **7b–g** systems were all converted at much lower temperatures (−60 °C). Even under these remarkably mild reaction conditions, difuryl-substituted **7b** and **7c** were converted regardless of whether electron-deficient (**7b**, Table 4, entry 2) or electron-donating substituents (**7c**, Table 4, entry 3) were attached to the aromatic core. The discrepancy in yield is not based on the intrinsic reactivity of these systems, but on the instability of some of the compounds during isolation processes (all of the reactions showed complete and selective conversion that could be monitored by TLC). Switching to thiophene-containing substrates **7d–f** (Table 4, entries 4–6**)** revealed the same picture. In all of these substrates, only the furan moiety served as a nucleophile and no competing pathways via an attack of the thiophene moiety were observed. Yields for these substrates were comparable with the furan systems and in addition to test substrate **7d** with a nonsubstituted aromatic system (Table 4, entry 4), both electron-deficient (Table 4, entry 5) and electron-donating groups (Table 4, entry 6) delivered acceptable yields even under these remarkably mild reaction conditions. Finally, we explored the reactivity of phenyl-substituted precursor **7g**. In this case selective fluorene formation also took place, but slightly slower reaction rates were monitored (Table 4, entry 7).

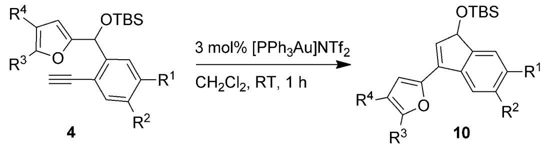
Table 4. Gold(III)-catalyzed conversion of furan–yne systems **7**.

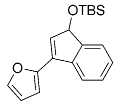
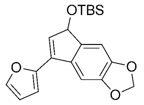
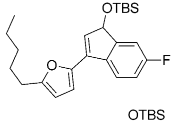
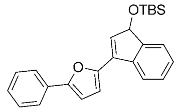


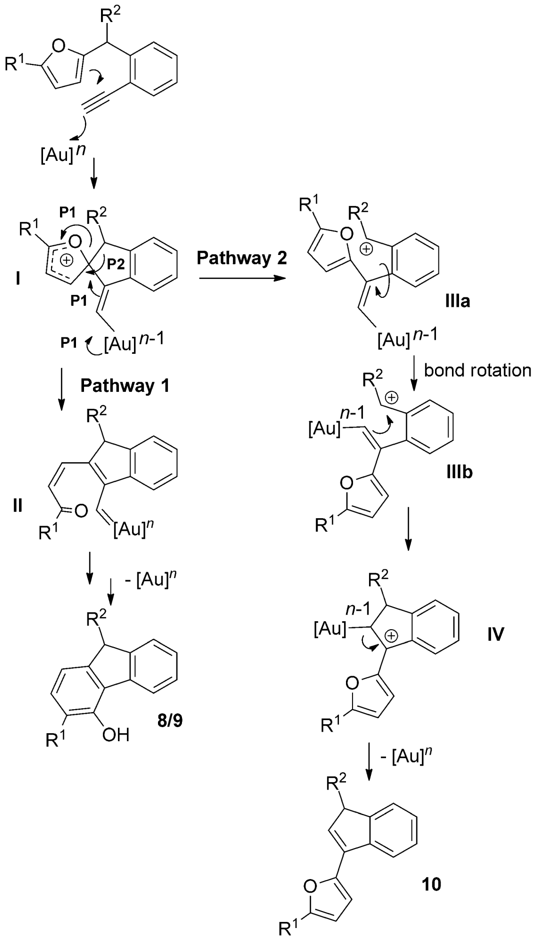
Entry	Starting material	Time	T [°C]	Product **9**	Yield of **9** [%]
1	**7a**	10 min	0		79
2	**7b**	40 min	−30		69
3	**7c**	2 h	−60		51
4	**7d**	3 h	−40		68
5	**7e**	45 min	−30		65
6	**7f**	2 h	−40		55
7	**7g**	6 h	−60		57

Because gold(I) sources are increasingly dominating the field of homogeneous gold catalysis, we tested several of our substrates with the air-stable and storable Gagosz catalyst $Ph_3PAuNTf_2$.[19] Table 5 summarizes the results. To our surprise, the conversion of starting material **4b** under gold(I) conditions did not deliver the expected fluorene substrate **8b**, although a selective transformation to an unpolar compound was observed. Most unfortunately, this compound was not stable for a prolonged time and attempts to isolate it by using column chromatography failed (with both silica and even basic alumina oxide). Finally, we succeeded in stabilizing this compound by simple filtration of the catalyst over a pad of Celite, and obtained a stable compound in pure form. NMR spectroscopy data of this compound indicate that the substructure of the monosubstituted furan moiety is still present in the product (characteristic J values of 3.4 and 1.7 Hz for the furan couplings). Furthermore, the alkyne moiety is transformed into a trisubstituted double bond and the protected benzyl alcohol moiety is also still present (assigned by a doublet at $\delta = 5.39$ ppm in the ^1H NMR spectrum and the corresponding tertiary carbon at $\delta = 78.8$ ppm in the ^{13}C NMR spectrum). In combination with additional 2D NMR experiments, the substructure of a

Table 5. Gold(I)-catalyzed synthesis of indenes.



Entry	Starting material	Product **10**	Yield of **10** [%]
1	**4b**		70
2	**4f**		>99
3	**4g**	complex mixture	–
4	**4j**		>99
5	**4l**		80
6	**4m**	complex mixture	–



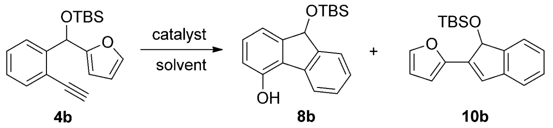
Scheme 5. Proposed mechanism, with the chemoselectivity-determining step after intermediate **I**.

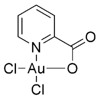
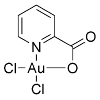
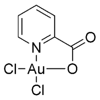
3-furyl-substituted indene with a protected hydroxy function in the 1-position could be assigned (Table 4, entry 1, **10b**). To explore the generality of this reaction pathway, different benzyl furyl alcohols were converted by using the gold(I) catalyst. Owing to the styrene analogue system in the products, only filtration from the catalyst over celite was possible as a purification step, but no side products were visible except for substrates **4g** and **4m** (Table 4, entries 3, 6), which delivered complex mixtures most probably based on polymerization of the resulting electron-rich styrene-like products. All of the starting materials were completely consumed after 1 h, regardless of whether electronically neutral (Table 4, entries 1, 5, 6), electron-rich (Table 4, entries 2, 3), or electron-deficient (Table 4, entry 4) arenes were incorporated in the tether. Interestingly, even substrate **4l**, which reacted unselectively during fluorene formation, selectively delivered the indene product in high yields (Table 4, entry 5). Possibly this substrate partly reacts via the indene pathway even with gold(III) catalysts, and the resulting product is not stable under the stronger Lewis-acidic conditions of the gold(III) catalyst. Further studies concerning these two possible reaction pathways involving diarylmethane derivatives **7** are underway and will be published elsewhere.

A possible mechanistic rationale is summarized in Scheme 5. The initial step of the reaction cascade for both pathways consists of a *5-exo-dig* cyclization of the enyne system, which delivers stabilized cationic intermediate **I**.[20] From here two mechanistic pathways are conceivable. Based on the donation of charge from the gold catalyst, a subsequent ring opening of the furan takes place (cleavage of the carbon–oxygen bond) and gold carbenoid **II** is formed (Pathway 1). Nucleophilic attack of the carbonyl oxygen onto the carbenoid carbon followed by rearrangement of the resulting oxepine/arenoxide tautomers finally delivers fluorene derivatives **I/H** by the known phenol pathway. From cationic intermediate **I**, Pathway 2 is initiated by cleavage of a carbon–carbon bond. This mechanistic pathway becomes attractive due to the stabilization of the resulting benzylic cation by the electron-donating group in substrates **4**. In addition, rearomatization of the furan system is achieved. Intermediate **III** then can be cyclized through attack of the double bond of the vinyl–gold moiety. In the last step of the cascade, cyclic intermediate **IV** liberates the catalyst through formation of the styrene-like double bond in products **J**. Considering this mechanistic puzzle, the trigger for a particular pathway might be the ability for back donation of the gold catalyst in intermediate **I**. If one starts with the neutral $AuCl_3$ catalyst (compared with the positively charged Au^I salt), a stronger back donation of the formally -1 charged Au catalyst becomes obvious.

To verify this assumption, we performed the conversion of substrate **4b** and analyzed the selectivity depending on the nature of the catalyst (Table 6). In fact, a clean formation of

Table 6. Reactions of **4b** with different gold(I) and gold(III) catalysts.[a]



Entry	Catalyst [3 mol %]	Solvent	Selectivity
1	IPrAuNTf$_2$	CD_2Cl_2	only **10b**
2	IPrAuCl$_3$	CD_2Cl_2	only **8b**
3		CD_2Cl_2	only **8b**
4	 + $AgNTf_2$ (1:1)	CD_2Cl_2	only **8b**
5	 + $AgNTf_2$ (1:2)	CD_2Cl_2	only **8b**
6	AuCl	CD_2Cl_2/CD_3CN	only **8b**
7	AuCl + $AgNTf_2$ (1:1)	CD_2Cl_2/CD_3CN	decomposition
8	$AuCl_3$ + AgOTf (1:1)	CD_2Cl_2/CD_3CN	decomposition
9	$AuCl_3$ + AgOTf (1:3)	CD_2Cl_2/CD_3CN	decomposition

[a] All reactions were monitored by using NMR spectroscopy with hexamethylbenzene as the internal standard.

product **10b** was also detected when using a charged cationic gold(I) complex with a carbene ligand (Table 6, entry 1). For the corresponding gold(III) carbene complex, no activation by a silver salt was necessary (Table 6, entry 2). If one considers the square-planar nature of the precatalyst, it becomes obvious that a halogen should dissociate before substrate activation can take place. Therefore, the active catalyst should be a cationic species as well, but nevertheless fluorene **8b** was formed exclusively. Pyridine carboxylate as the ligand on the gold(III) center showed the same result (Table 6, entry 3), even if additional silver additives were added as halide scavengers (Table 6, entries 4, 5). In contrast, gold(I) chloride in the absence of a silver source turned out to be the exception (Table 6, entry 6). Even with the gold(I) oxidation state, only compound **8b** was formed. This indicates that charge might also play a role for the reaction selectivity, but one could also consider a disproportionation of the less-stabilized gold(I) precursor into gold(III) and gold(0). Attempts to generate cationic complexes by mixing gold(I) or gold(III) chloride with silver additives delivered only complex mixtures (Table 6, entries 7–9). In conclusion, these are strong indications that the oxidation state of the gold catalyst triggers the different reaction pathways.

Conclusion

In our study of the gold-catalyzed cycloisomerization of furan–yne systems with aromatic tethers, we demonstrated that these substrates are extremely useful precursors for the synthesis of fluorene derivatives with a high degree of substitution. Because these systems could be useful precursors for optically active materials, the variability of the starting materials and their easy accessibility makes this route extremely attractive. As well as possible variations at the furan core, substitutions at the important 9-position of the resulting fluorene core can be easily achieved through simple and convergent synthetic approaches to the starting materials. Herein we investigated two different subclasses of fluorene derivatives and further variations are under investigation in our group.

Based on the ability to stabilize cationic intermediates through the benzylic positions of the incorporated aromatic system in the tether, a new reaction pathway was opened by using cationic gold(I) complexes for the conversions. Here, a new cleavage of the carbon–carbon bond instead of a cleavage of the carbon–oxygen bond (the usual pathway to open the furan system) took place and an astonishing reaction cascade finally delivered indene derivatives by a formal insertion of the terminal alkyne into a furyl−C bond.

Acknowledgements

The authors thank Umicore AG & Co. KG for the generous donation of gold salts.

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Received: June 6, 2012
Revised: September 26, 2012