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Gold(I)-Catalyzed [2 + 2 + 2] Cyclotrimerization of 1,3-Diarylpropargyl Acetals

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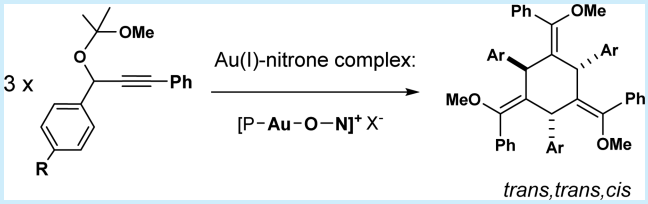
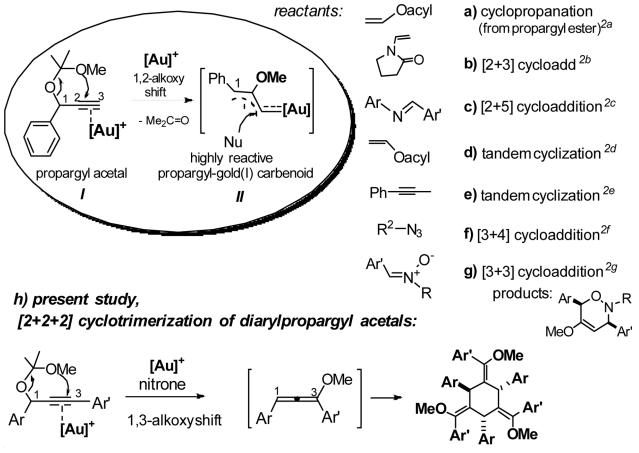
Supporting Information

ABSTRACT: A gold-nitrone catalyzed [2 + 2 + 2] cyclotrimerization of 1,3-diarylpropargyl acetals into cyclohexylidene products (up to 74% yield) is reported. The trimerization is proposed to proceed through allenic intermediates via gold-catalyzed 1,3-alkoxy rearrangement. The presence of catalytic amounts of different nitrones, tuning of the Au(I) catalyst activity, was essential for controlled regio-/chemoselective cyclotrimerization. A linear nitrone−O−Au(I)−P coordination mode was shown (X-ray analysis) for a catalytic active phosphane−gold−nitrone complex, representing a group of Au(I) catalysts with specific properties.



The propargyl ester−gold approach, based on gold-catalyzed activation of propargyl esters, has been applied in a variety of cycloaddition reactions.[1] Studies on gold(I)-catalyzed reactions of the corresponding propargyl acetals have been scarce.[1m−q] The Fiksdahl group has, however, carried out a number of studies on chemoselective gold(I)-catalyzed cycloaddition of propargyl acetals (**I**, Scheme 1b−g),[2] showing that

Scheme 1. Au(I)-Catalyzed Cycloadditions of Propargyl Substrates[2]



they are versatile substrates for a diverse range of novel Au(I)-catalyzed cycloadditions with multiple bond reactants, leading to a series of polyfunctionalized carbo- and heterocyclic products via highly reactive gold(I) carbenoid intermediates (**II**). The activating effect provided by the C2-vinylalkoxy group in the MeO-vinylgold carbenoid (**II**) facilitates the reactions and explains the high reactivity and ability of propargyl acetals to undergo cycloadditions. In the course of our recent studies on [3 + 3] cycloadditions with nitrones, giving oxazine products (Scheme 1g),[2g] a novel unusual [2 + 2 + 2] cyclotrimerization of nonterminal diarylpropargyl acetals was observed. 2,4,6-Triaryl-1,3,5-tricyclohexylidene products were selectively formed (Scheme 1h). Diarylpropargyl substrates have until recently not been applied in synthetic studies, as they have been thought to be unviable substrates, affording complex reaction mixtures.[3]

Conventional transition-metal-catalyzed alkyne [2 + 2 + 2] cyclotrimerization via metallocyclopentadiene complexes represents a useful transformation to provide highly substituted arenes.[4a] Gold nanoparticles also catalyze alkyne trimerization.[4b] However, the [2 + 2 + 2] cycloadditions suffer from regio- and chemoselectivity limitations. Allenes cyclotrimerize under metal-free conditions as well.[4c] On the basis of a different stepwise mechanism via a gold dimeric cationic intermediate, the gold-catalyzed allenamide cyclotrimerization[4d] is reported to match the outcome of alkyne [2 + 2 + 2] trimerization reactions.

To the best of our knowledge, our presently reported reaction is the first intermolecular regioselective [2 + 2 + 2] cyclotrimerization of propargyl substrates, affording densely substituted cyclohexylidene products. We hereby report the results on gold−nitrone-catalyzed transformations of diarylpropargyl acetals.

Studies on Reaction Conditions and Reactivity

Introductory studies on the Au(I)-catalyzed reactions between equimolar amounts of diarylpropargyl acetal **1a** and nitrone **2a** in DCM gave full conversion in 2 h at room temperature in the presence of 5 mol % of JohnPhos−Au(I) catalyst **I** (Table 1, entry 1). The reaction showed that the cyclotrimerization cyclohexylidene **3a** product was formed as the major product (60%) by a [2 + 2 + 2] propargyl cycloaddition. The product was formed as a mixture of three stereoisomers. Au(I) catalyst oxidation of alkynes, including propargyl substrates, is known to

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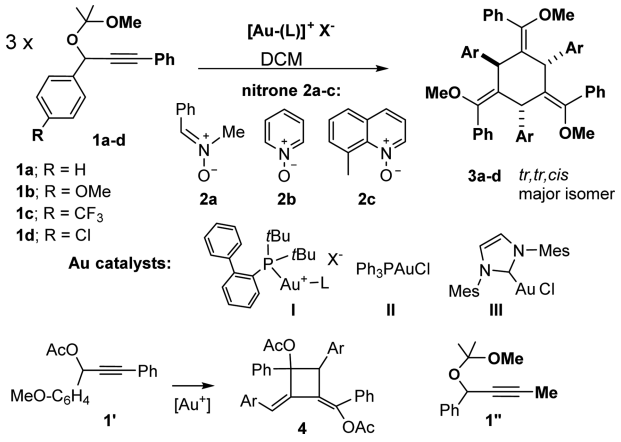
Table 1. Studies on [2 + 2 + 2] Cyclotrimerization[a]



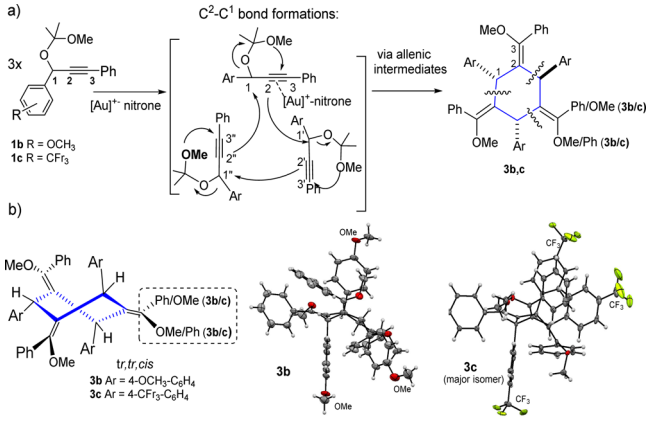
entry	catalyst [AuL]+X-	substrate + nitrone	time (full conv)	yield[b] trimer **3a-d**
1	[**I**-ACN] SbF_6^-	**1a** + **2a** (1 eq)	2h	**3a**, 60%
2	[**I**-ACN] SbF_6^-	**1a**, no nitrone	2-24h	n.d.[c]
3	[**I**-ACN] SbF_6^-	**1a** + **2a** (0.05-1 eq)	2h	**3a**, 60-65%
4	[**I**-ACN] SbF_6^-	**1b** + **2a**	2h	**3b**, 60%
	[**I**-ACN] SbF_6^-	**1c** + **2a**	24h	**3c**, 59%
	[**I**-ACN] SbF_6^-	**1d** + **2a**	2h	**3d**, 54%
5	[**I**-ACN] SbF_6^-	**1b** + **2b**	1.5h	**3b**, 64%; 67%[d]
6	[**I**-ACN] SbF_6^-	**1b** + **2c**	2h	**3b**, 67%
7	**I**-Cl + $AgNTf_2$[e]	**1b** + **2b**	2h	**3b**, 74%
8	**I**-Cl + $AgNTf_2$	**1b**, no nitrone	2h	n.d.[c]
9	**II**+ $AgSbF_6$[e]	**1b** + **2a**	20h	**3b**, 63%
10	**III** + $AgSbF_6$[e]	**1b** + **2c**	72h	n.d.[c]
11	**III**+ $AgSbF_6$[e]	**1c**, no nitrone	24h	n.d.[c]
12	$Au(III)Cl_3$	**1b**, no nitrone	72h	n.d.[c]
13	[**I**-ACN] SbF_6	**1b**[g] + **2b**	24h	**3b**, 27%
14	[**I**-ACN] SbF_6	**1b**[h] + **2b**	2.5h	**3b**, 71%
15	**I**-Cl + $AgNTf_2$[d]	**1b**[h] + **2b**	4h	**3b**, 70%
16	[**I**-ACN] SbF_6^-	**1b**, no nitrone	4h (-78 °C)	no conv.[f]
17	[**I**-ACN] SbF_6^-	**1d**, no nitrone	4h (-20 °C)	n.d.[c]
18	**II** + $AgSbF_6$[e]	**1b**, no nitrone	6h (0 °C)	n.d.[c]
19	[**I**-ACN] SbF_6^-	**1'**[i]	24h[i]	**4**, 15%[i]
20	[**I**-ACN] SbF_6^-	**1"** + **2a**	24h	n.d.[c]
21	[**I**-ACN] SbF_6^-	**1b** + Bztr[j]	24h	no conv.[f]

[a]General reactions conditions: **1a–c** (1 equiv) in DCM (approx.10 mg/mL; c = 33 mM), Au **I–III** (5 mol %), nitrone (**2a–c**, 5 mol %) were stirred at rt before being quenched with NEt_3. [b]Total yield of three isomers. [c]Full conversion into complex product mixture; trimeric product (**3**) not detected. [d]The reaction performed with crystalline Au(I)**I**–nitrone **2b** complex (5 mol %) afforded a similar yield of **3b** as when the catalyst was generated in situ. [e]Au(I) catalyst formed by counterion exchange. [f]No reaction observed. [g]Six times higher concentration of **1b**; c = 210 mM. [h]50% diluted conc. of **1b**; c = 17 mM. [i]Dimer **4** was formed in the absence of nitrone. No cyclotrimeric triacetate was formed. [j]Nitrone was replaced by benzotriazole (5 mol %).

take place with nitrone.[5,2g] However, no competing oxidation byproducts were seen in the present study. As the nitrone **2a** was not incorporated in the product, it did not seem to take part in the reaction. Unexpectedly, complex undefined product mixtures were obtained by Au(I) **I** catalyzed reaction of diarylpropargyl acetal **1a** in the absence of nitrone **2a** (Table 1, entry 2). No formation of the cyclic trimer **3a** took place. The fact that nitrone **2a** was not incorporated in the trimeric product and that complex product mixtures were obtained in the absence of nitrone **2a** would suggest that Au catalyst **I** was too active to afford selective trimerization. A relevant hypothesis would be that reduced Au catalyst activity may be due to nitrone–Au coordination, thereby allowing chemoselective trimerization to take place. The Au–nitrone hypothesis was supported by the fact that the rate and yield of the reactions were essentially unchanged by reducing the amount of nitrone **2a** from 1.0 to 0.05 equiv (60–65% yield of **3a** in 2 h, Table 1, entry 3). Hence, controlled Au(I)-catalyzed trimerization reactions of propargyl acetal **1a** only took place in the presence of (catalytic amounts of) nitrone **2a**.

Reactivity studies of acetals **1a–d** in the presence of Au(I) complexes **I–III** (0.05 equiv) and nitrones (**2a–c**, 0.1 equiv) were carried out. The Au-complex counterions (± nitrone), the substrate concentration, and the temperature (Table 1) were varied. The reactivity and reaction time of MeO-, CF_3-, and Cl-phenylpropargyl acetals **1b–d** differed, but the yields remained almost constant (54–60%, 2–24 h, entry 4). The aromatic nitrones, pyridine *N*-oxide **2b** and 8-methylquinoline 1-oxide **2c**, were likewise able to tune the activity of Au catalyst **I**, affording somewhat higher reactivity (>64% yield, entries 5 and 6) than nitrone **2a**. The isomer ratios of products **3a–d** (entries 3–6) were approximately 5:3:3, as shown by ^{1}H NMR. Selected isomers of **3b** and **3c** were isolated and fully characterized (Scheme 2b).

Scheme 2. (a) Outline of the Overall Triple C–C Bond Formation Sequence for Au(I)–nitrone Catalyzed [2 + 2 + 2] Cyclotrimerization of Propargyl Acetals 1. (b) X-ray Structure Analysis of Cyclotrimerization Products 3b and 3c



The Au(I) complex counterion slightly affected the reactivity, as the more weakly coordinating anion, NTf_2^-, gave higher yields of product **3b** than SbF_6^- (74% vs 64%, entries 7 and 5). Comparable results were obtained by the less bulky Ph_3P (**II**) to the originally used JohnPhos ligand (entries 4 and 9). The NHC–Au(I) catalyst **III** was also tested, as a less active catalyst could be expected to give controlled trimerization, even without nitrone tuning of the Au(I) catalyst. However, complex product

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mixtures were obtained both in the presence and absence of nitrone (entries 10 and 11). Likewise, Au(III)Cl_3 (entry 12) was unable to afford trimerization, giving full conversion of **1b** into a number of unidentified products.

An effect of the substrate concentration was expected for this reaction. Higher concentration would assist intermolecular reaction, such as dimer and trimer formation. However, the final intramolecular cyclization step would be favored in diluted reaction mixtures, which seemed to control the outcome of the reaction, as higher reactivity and yield were obtained by 50% substrate dilution (2 h, 71%, entry 14). Moreover, yields dropped remarkably in six times concentrated solution (27%, 24 h, entry 13; versus 64%, 1.5 h, entry 5).

Combining the positive impact of counterion (NTf_2^-, entry 7) and dilution (entries 14) did not give any additional effect on the yield of trimeric product **3b** (entry 15). An alternative strategy to control the reaction toward selective trimerization would be to compensate for the absence of nitrone by decreased temperature. However, low temperature (−78 °C) failed to provide cyclotrimerization or any conversion at all (entry 16), while reactions at 0 to −40 °C gave complex product mixtures (entries 17 and 18), showing that Au catalyst tuning may only be obtained by nitrone coordination.

The diarylpropargyl acetate **1′**, which is known to be less reactive than the corresponding acetal,[2] failed to give the corresponding cyclotrimeric triacetate. Low conversion of acetate **1′** was seen in the presence of nitrone. While full conversion was seen in the absence of a nitrone, only minor amounts of a [2 + 2] cyclodimerization cyclobutylidene product (**4**, 16%, one isomer, 24 h, entry 19) were isolated. Previous studies reported formation of both [2 + 2] regioisomers,[6a] and the dimerization was proposed to proceed through an allenic Au intermediate formed by Au(I)-catalyzed 1,3-O-acyl shift. The alkylpropargyl moiety seemed to be unsuitable for the reaction, as cyclotrimerization of methylpropargyl acetal **1″** was unsuccessful. Full conversion was observed (24 h, entry 20), but no trimeric product was detected. Benzotriazole−Au(I) catalysts have been employed in chemoselective propargyl ester transformations.[6b] However, when the original Au(I)−nitrones were replaced with a benzotriazole-coordinated JohPhosAu(I) complex, no reaction took place (24 h, entry 21).

Reaction Mechanism

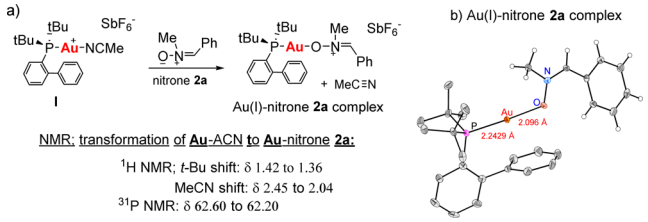
Alkyne substitution of propargyl substrates has a strong effect of their reactivity in Au-catalyzed reactions. Terminal propargyl acetals or esters tend to undergo 1,2-alkoxy or -acyloxy migration, affording gold carbenoid intermediates (**II**, Scheme 1[1g−p,2]). In contrast, nonterminal propargyl acetals/esters undergo 1,3-alkoxy shift to generate allenic intermediates, which may give rise to a series of reactions.[6] [2 + 2] cycloaddition of allenamides with alkenes[7a−d] and [2 + 2] cyclodimerizations[7e,f] are known to take place by gold catalysis. The present [2 + 2 + 2] cyclotrimerization is proposed to proceed via controlled regioselective coupling and cyclization of three propargyl units through allenic intermediates in the presence of a Au(I)−nitrone complex (Scheme 2a), in some accordance with a mechanism suggested for Au-catalyzed cyclotrimerization of allenamides.[4d] The overall regioselective trimerization reaction sequence is driven by the allene activation provided by the methoxy group. The reaction pathway is believed to be initiated by the Au-catalyzed 1,3-alkoxy shift, being the driving force for an intermolecular C2−C1′ bond formation between (gold-)allenic intermediates. The subsequent acetal cleavage and 1,3-alkoxy shift followed by C2′−C1″ bond formation is repeated twice, the last time in a C2″−C1 intramolecular manner. In total, the cyclotrimeric product **3** is afforded by ring closure, and deauration allows regeneration of the Au(I) catalyst. Previous NMR studies of 1,3-diarylpropargyl pivaloyl esters showed that Au-catalyzed 1,3-acyloxy shift and rearrangement immediately took place to give full conversion and quantitative amounts of the corresponding stable allene.[3] Subsequent allene [2 + 2] cyclodimerization seemed to be a thermal reaction, as a separate reaction afforded the trans-formation without gold activation.[3] We did not observe a corresponding simple transformation into one stable allene intermediate (^{1}H NMR). In contrast, generation of complex mixtures of intermediates was temporarily seen during Au(I)−nitrone-catalyzed conversion of acetals **1** until the selective formation of the cyclic products **3** was completed.

^{1}H NMR of stereoisomers of products **3** indicated nonsymmetrical cyclic trimeric structures, as demonstrated, e.g., by different MeO surroundings, shown by three separate MeO-signals of each isomer. X-ray analysis of isolated isomers of products **3b** and **3c** (Scheme 2b) showed a *trans,trans,cis* relationship between the 2,4,6-triarylcyclohexyl substituents, while the stereochemistry of the three vinyl groups varied.

Studies on the Au−Nitrone Catalyst

^{1}H and ^{31}P NMR analysis of an equimolar mixture of Au(I) **I** and nitrone **2a** indicated that an exchange of the acetonitrile ligand of the Au(I) catalyst **I** with nitrone **2a** took place to give a Au(I)−nitrone complex (Scheme 3a). In a previous study,[8a] a

Scheme 3. a) Formation of Au(I)−Nitrone 2a Complex, Including NMR Observations. (b) X-ray Structure Analysis of Au(I)−Nitrone 2a Complex



gold(I)−nitrone coordination has been suggested to proceed through Au(I) ligand exchange, while X-ray diffraction studies of a Au(III)Cl_3−nitrone−H^+ complex failed to show any Au−nitrone coordination through the O atom. Nitrone ligands are, however, known from Ru−heme complexes[8b] and organoboron compounds.[8c,d] X-ray analysis of our crystalline Au−nitrone **2a** complex, afforded from an equimolar mixture of Au **I** and nitrone **2a**, confirmed for the first time the O-binding of the nitrone ligand to the Au(I) center (Scheme 3b), in analogy to reported Ru−porphyrin nitrone complexes.[8b] The linear (nitrone)−*O*−*Au(I)*−*P*-(phosphane) coordination mode is clearly verified. The catalytic activity of the isolated crystalline Au−nitrone **2b** complex was tested. The trimerization reaction rate of acetal **1b** and obtained yield of trimer **3b** (67%, 5% Au−nitrone complex, 1.5 h, Table 1, entry 5) were similar to the reaction with Au−nitrone **2b** generated in situ (64%, entry 5).

Subsequent acidic hydrolysis of the enol ether moieties of trimer **3b** (10:4:3 isomer mixture) with TsOH gave the triketone product **5b** (46%, Scheme 3a) as one single isomer. Complete enolization of triketone **5b** was observed after months of storage. Compounds **3b** and **5b** were surprisingly stable

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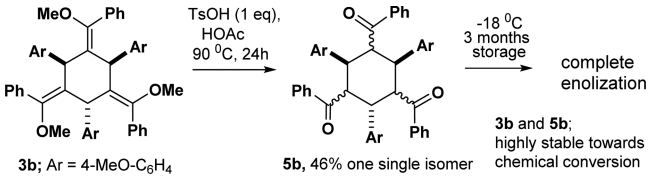
toward modifications, probably due to the densely substituted nature of the more flexible cyclohexyl(idene) ring system (Scheme 4). Several attempts to afford aromatization were

Scheme 4. Transformation of Cyclic Trimeric Compounds 3



unsuccessful. Hence, neither heating nor treatment of **3b** with NaOH (80 °C, 170h),[4c] I_2, HOAc or CH_3NO_2/Pd/C (90 °C)[9] gave any conversion at all. Likewise, dehydrogenation/oxidation of **5b** with hypervalent iodine(V)[10] failed to give any reaction.

In conclusion, we have shown that 1,3-diarylpropargyl acetals undergo regio-/chemoselective Au(I)−nitrone-catalyzed [2 + 2 + 2] cyclotrimerization to afford cyclohexylidene products (up to 74% yield). The presence of (catalytic amounts of) different nitrones was essential for successful selective cyclotrimerization. The crystalline phosphane−Au(I)−nitrone **2a** complex performed similar catalytic activity as the corresponding Au(I)−nitrone **2a** catalyst formed in situ. X-ray analysis of the Au(I)−nitrone **2a** complex confirmed the linear nitrone−O−Au(I)−P coordination mode of the crystalline catalyst. Acidic hydrolysis of the enol ether moieties of trimer **3b** afforded triketone **5b**. The [2 + 2 + 2]-cyclotrimerization approach readily allows chemoselective preparation of densely substituted and polyfunctionalized cyclohexyl(idene) products in the presence of Au(I)−nitrone complexes, which represent an interesting group of Au(I) catalysts with specific properties. Further studies on cyclotrimerizations as well as Au(I)−nitrone complexes are in progress in our laboratories.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00411.

Full experimental details, characterization of compounds (**1a−d**, **3a−d**, **4** and **5b**), and ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

Crystallographic data for Au(I)−nitrone **2a** complex and products **3b** and **3c** (CCDC nos. 1531556, 1531557, and 1531558) have been deposited with the Cambridge Crystallographic Data Centre.

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