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Cationic Gold(I)-Catalyzed Intermolecular [4+2] Cycloaddition between Dienes and Allenyl Ethers

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Abstract: Simple allenyl ethers have been shown to be efficiently activated by cationic gold(I) catalysts to form reactive dienophiles in intermolecular Diels–Alder reactions. A range of different dienes give the cycloaddition products in moderate to excellent yields and good selectivity.

Keywords: allenyl ethers; cycloaddition; homogeneous gold catalysis

Over the past decade, homogeneous gold catalysis has become a powerful tool to access unprecedented structural and mechanistic diversity.^[1] In particular, remarkable advances have been achieved in the development of Au-catalyzed intramolecular cyclizations or cycloisomerizations that, in turn, have provided impressive methods for the rapid assembly of novel cyclic and polycyclic structures. However, relatively few gold-catalyzed intermolecular cycloaddition reactions have been reported.^[2] In connection with our ongoing program of investigating novel syntheses of functionalized odorants, we became interested in developing efficient and selective Au-catalyzed transformations to provide cyclohexene derivatives which constitute an important class of substructures in fragrance chemistry.^[3] In this light we considered the possibility of adopting allenes as dienophiles in Diels-Alder reactions: they are known to be excellent substrates for gold-promoted transformations^[1] and derivatives are easily accessible. Although [4+2] cycloaddition reactions of allenes substituted with electron-withdrawing group (EWG) have been extensively studied,^[4] the poor reactivity of unactivated allenyl ethers as dienophiles has for a long time limited their use in Diels-Alder reactions.^[5] However, recent re-



Scheme 1. Ligand-controlled Au(I)-catalyzed [2+2], [4+2] and [4+3] cycloaddtion reactions of allene-dienes.

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ports show that Pt and Au complexes induce simple allene-dienes I to undergo intramolecular [2+2], [4+2] and [4+3] cycloaddition reactions (Scheme 1).^[6] A subsequently performed DFT calculation suggested that both the [4+2] and [4+3] cycloadditions proceed through an initial gold-catalyzed concerted [4+3] cycloaddition of a gold-activated allene with a diene to a carbene intermediate like III.^[7] The selectivity for either pathway depends on a preference for either 1,2-H or 1,2-alkyl shifts that the gold-stabilized intermediate III experiences. Such a mechanistic speculation was partially validated by the generation of cycloheptenone VI in the presence of an excess amount of diphenyl sulfoxide which can efficiently oxidize gold-carbene intermediates.^[6a,8]

Furthermore, it has been known for a long time that acetals of acrolein are convenient precursors of allylidene oxonium cations, which have been successfully employed as dienophiles in ionic Diels-Alder reactions.^[9] In 2007, Zhang established an intramolecular [3+2] cycloaddition of allenyl MOM ethers and enones/enals towards a cyclopentanone enol ether containing an all-carbon quaternary center. In the rationale, a selective Au(III) activation of the allenyl ether moiety to form an oxocarbenium species was proposed.^[10] A recent work by Iwasawa and co-workers has also described a novel Pt(II)-catalyzed [3+ 2]cycloaddition reaction of silyl propadienyl ethers and alkenyl ethers. Again, a π -allyl cationic intermediate was postulated to account for the reactivity of the allenes as a three-carbon unit.^[11] These results encouraged us to study the possibility of using allenyl ethers as precursors of ionic dienophiles in Au-promoted intermolecular [4+2] cycloaddition reactions.^[12] Our mechanistic working hypothesis (Scheme 2) consisted of an initial Au(I)-activation of the allenyl ether 1 to form a cationic gold-stabilized allylidene oxonium dienophile 2, which is in resonance with allyl cation 2'. We speculated that species 2 would participate in Diels-Alder cycloaddition reac-



Scheme 2. Postulated mechanaism of an Au(I)-catalyzed ionic Diels–Alder reaction of dienes with allenyl ethers.

tions with diene **3** in a standard $[{}_{\pi}4_{s}+{}_{\pi}2_{s}]$ mode. The resulting Au-substituted oxonium intermediate **4** could then undergo an elimination of a cationic Au(I) species to provide the desired six-membered carbocycles **5**.

Herein, we report a novel intermolecular [4+2] cycloaddition of allenyl ethers with dienes. This Au(I)catalyzed ionic Diels–Alder strategy shows different selectivities compared to thermal reactions and provides a convenient way to synthesize 4-(alkoxymethylidene)cyclohex-1-enes.

We initially chose the cationic complex $[(Ph_3P)Au]SbF_6$ in CH_2Cl_2 as solvent for preliminary studies of the above proposal (Table 1). Treatment of a mixture of the allenyl ether **1a** and 1,3-cyclopentadiene (**3a**) with 1 mol% $[(Ph_3P)Au]SbF_6$ (**A**) afforded the desired [4+2] cycloaddition adduct **5a** in 76% yield after 3 min at room temperature, with the (*Z*)isomer highly predominating (Table 1, entry 1). Lowering the reaction temperature to 0°C neither improved the yield nor the *Z/E* selectivity. In fact, inferi-

Table 1. Optimization of reaction conditions.^[a]



Entry	Catalyst (mol%)	Solvent	Time	Yield $[\%]^{[b]}$ $(Z:E)^{[c]}$
1 2 ^[d]	A (1) A (1)	CH ₂ Cl ₂ CH ₂ Cl ₂	3 min 30 min	76 (90:10) 60 (85:15)
3	$\mathbf{A}(1)$	Toluene	30 min	45 (80:20)
4	A (1)	CH ₃ NO ₂	3 min	60 (91:9)
5	A (1)	CH ₃ CN	3 min	48 (88:12)
6	A (1)	THF	5 min	30 (89:11)
7	B (1)	CH_2Cl_2	3 d	33 (52:48) ^[e]
8	C (1)	CH_2Cl_2	2 d	0 ^[f]
9	_	CH_2Cl_2	2 d	0 ^[e]
10	_	CH_2Cl_2	2 d	65 (22:78) ^[g]
11	D (5)	CH_2Cl_2	3 d	<5 ^[e]
12	E (5)	CH_2Cl_2	3 d	<5 ^[e]
13	F (5)	CH_2Cl_2	3 d	<5 ^[e]
14	G (5)	CH_2Cl_2	30 min	11 (20:80)

[a] Experimental conditions: a mixture of 1a (1.0 mmol), 3a (3.0 mmol) and a catalyst (0.01 mmol) in 2 mL CH₂Cl₂ in a sealed tube was stirred for the time stated.

^[b] Isolated yield of **5a**.

^[c] Z:E ratios were determined by GC and ¹H NMR.

^[d] Performed at 0 °C.

- ^[e] Starting material was recovered.
- ^[f] Decomposition.
- ^[g] Performed at 85 °C in an autoclave.

or results were obtained (Table 1, entry 2). In the solvent screen, we found that dichloromethane performed better in terms of the product yield than any of the other solvents tested (Table 1, entries 3–6). Other control experiments showed that the counter anions of the gold complexes play a vital role regarding the speed of the transformation. For example, employing 1 mol% [(Ph₃P)Au]Cl resulted in a yield of only 33% after 3 days (Table 1, entry 7).

Since the cationic complex [(Ph₃P)Au]SbF₆ was generated from [(Ph₃P)Au]Cl and AgSbF₆ in CH₂Cl₂, a control experiment using 1 mol% AgSbF₆ as the sole catalyst was performed to exclude the possibility of silver catalysis. In this case, only decomposition of the substrate allene was observed (Table 1, entry 8). It is notable that, without catalyst, no conversion occurred even after 2 days at room temperature (Table 1, entry 9). However, in the absence of any catalyst, the desired adduct 5a was also formed in a thermal reaction in 65% yield after 2 days at 85°C. Interestingly, the (E)-isomer was formed as the major isomer under these conditions (Table 1, entry 10). Other common Lewis acids showed insufficient catalytic activity (Table 1, entries 11–13). When the same reaction was conducted in the presence of 5 mol% of platinum(II) chloride, only an 11% yield of the product was achieved after 30 min, leading to the predominant formation of the (E)-isomer **5a** (Table 1, entry 14).

The scope and limitations of this cycloaddition were then investigated using cyclopentadiene **3a** and different allenyl ethers **1b–g** in the presence of 1 mol% of the cationic gold(I) complex **A** in CH_2Cl_2 . The results are shown in Table 2.

Interestingly, the electronic and steric properties of the substituents R of the allenyl ether **1** have little influence on the selectivities and yields of bicyclic products **5**. In general, the reactions proceeded smoothly with good yields to give exclusively products **5b–g** without detection of any [2+2] and [4+3] products. Notably, (–)-menthyl-substituted allene **1e** resulted in product **5e** with an outstanding Z-selectivity of the *exo*-double bond. The diastereoselectivity with regard to the configuration of the bicyclic moiety was poor (Table 2, entry 4, dr = 1:1).

To further explore the reactivities of allenyl ethers with cyclopentadienes, several mono-substituted cyclopentadienes and allenyl ethers were treated with Au(I) catalyst A under standard reaction conditions. Excellent yields were achieved with such reactive dienes and conversions were complete within 3 min (Table 3, entries 1–6). It is noteworthy that for monosubstituted cyclopentadienes only *ortho-* and *para*-regioisomers were formed with complete Z-selectivity at the *exo*-cyclic double bond. These *ortho:para* ratios were much better than those obtained in classical Lewis acid-catalyzed Diels–Alder reactions in which Table 2. Reactions of ethers 1b-g with cyclopentadiene.^[a]



Entry	Allene	R	Product	Yield $[\%]^{[b]} (Z:E)^{[c]}$
1	1b	allyl	5b	75 (88:12)
2	1c	JAN O	5c	77 (84:16)
3	1d	Me	5d	73 (77:23)
4	1e	R	5e	72 (99:1) ^[d]
5	1f	t-Bu	5f	68 (86:14)
6	1g	adamantyl	5g	62 (82:18)

 [a] Experimental conditions: a mixture of 1b-g (1.0 mmol), 3a (3.0 mmol) and catalyst A (0.01 mmol) in 2 mL CH₂Cl₂ in a sealed tube was stirred for 30 min.

^[b] Isolated yield of **5b–g**.

^[c] Z:E ratios were determined by GC and ¹H NMR.

^[d] dr = 1:1.

 Table 3. Reaction of allenyl ethers 1 with substituted cyclopentadienes.^[a]



[a] Experimental conditions: a mixture of 1 (1.0 mmol), 3 (3.0 mmol) and catalyst A (0.01 mmol) in 2 mL CH₂Cl₂ in a sealed tube was stirred for 3 min.

^[b] Z:E ratios were determined by GC and ¹H NMR.

^[c] Isolated yield of 5_o and 5_p .

substitution usually comprises the bridgehead position.^[13]

We also extended this gold-catalyzed [4+2] process to acyclic dienes (Table 4). With 2,3-dimethlybutadiene as substrate, the reaction resulted in only a 13% yield of **5n** after 20 min (Table 4, entry 1). A proTable 4. Reaction of allenyl ethers 1 with acyclic dienes.^[a]



Entry	Product	Time (min)	Yield [%] ^[b] (Z:E) ^[c]
1	5n : $R^1 = Bn$, $R^2 = R^3 = Me$, $R^4 = H$	20	13 (99:1)
2	50: $R^1 = Bn$, $R^3 = H$, $R^4 = Me$, $R^2 = 4$ -methylpent-3-enyl	12	56 (99:1)
3	5p : R^1 = allyl, R^3 = H, R^4 = Me, R^2 = 4-methylpent-3-enyl	12	41 (99:1)
4	5q : R^1 =3-MMB, R^3 =H, R^4 =Me, R^2 =4-methylpent-3-enyl	3	45 (99:1)
5	5r : $R^1 = Me$, $R^3 = H$, $R^4 = Me$, $R^2 = 4$ -methylpent-3-enyl	3	36 (99:1)

^[a] *Experimental conditions:* a mixture of 1 (1.0 mmol), 3 (3.0 mmol) and catalyst A (0.01 mmol) in 2 mL CH₂Cl₂ in a sealed tube was stirred for the time stated.

^[b] Isolated yield of **5n–r**.

^[c] Z: E ratios were determined by GC and ¹H NMR.

longed reaction time led to decomposition of the allene. However, the more reactive *homo*-myrcene participated well in the reaction to provide the cyclic adducts with nearly complete Z-selectivity, although the yields were generally low (Table 4, entries 2–5).

Recent reports have demonstrated that, under catalysis of gold or platinum complexes, furans carrying an allene group can undergo intramolecular cycloaddition reactions to give a mixture of [4+3] and [4+2] products.^[6,7] Therefore, we became interested in the behaviour of furan derivatives in the presence of allenvl ethers and cationic gold(I) catalyst A. Allenvl ether 1b was allowed to react with furan under our standard reaction conditions which furnished a Mukaiyama-Micheal type 1,4-addition product 6a in 38% yield. The treatment of 2-methylfuran did not alter the reaction pattern, and 1,4-addition product 6b was obtained in a better yield (59%). These results were comparable to those of AuCl₃-catalyzed 1,4-addition reactions between acroleins and furans (Scheme 3).^[14] These results are in accord with proposed intermediate 2 (Scheme 2) as an equivalent of an activated acrolein derivative.



Scheme 3. Au(I)-catalyzed reaction of furan and allenyl ether.

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Although our results can be rationalized by the [4+2] mechanism depicted in Scheme 2, alternative pathways through [4+3] cycloadditions of species 2' with dienes may also be suggested. In one aspect the initially formed Au-carbenoid intermediates **III**' could be formed by a concerted [4+3] cycloaddition mode followed by 1,2-alkyl shift and deauration leading to the observed [4+2] adducts (Scheme 4, route a). A different possibility could be a stepwise reaction (route b) *via* allylic cation **VII**. However, this is regarded to be the less likely option since vinylcyclobutanes **8**, formed *via* **7** by the attack of the organometallic anion at the allylic position in **VII**, have never been identified in our chemistry.

To differentiate the concerted [4+3] versus [4+2] pathways, a trapping experiment of the hypothetical Au-carbenoid intermediates **III**' was attempted (Scheme 5). Thus, when the reaction of substrates **1a** and **3a** was performed in the presence of an excess amount of diphenyl sulfoxide, which has proved to be an efficient oxidant to intercept gold-carbene intermediates in many gold-catalyzed transformations,^[6a,8] the formation of ketone **9** could not be detected (Scheme 5). This suggests that the formation of the six-membered ring compounds occurs via a favoured [4+2] pathway. However, it could be still argued that the [4+3] cycloaddition/1,2-rearrangement sequence proceeds much faster than the oxidation of intermediate **III**'.

In order to shed light on this mechanistic conundrum, the Au(I)-catalyzed intermolecular [4+2] cycloaddition reaction between **1d** and 1,3-butadiene with PMe₃ as the ancillary ligand was theoretically investigated by means of DFT calculations (Scheme 6). Our results indicate that $[(Me_3P)Au]^+$ firstly coordinates to the terminal double bond of allene **1d** to give **1dAu1**, from which the Au-stabilized allylic cation



Scheme 4. The alternative ways leading to [4+2] products.



Scheme 5. Trials to trap [4+3] Au-carbenoid intermediates.

1dAu2 was formed with an activation free-energy barrier of $3.9 \text{ kcal mol}^{-1}$. Based on the NBO (natural bond orbital) analysis, the C–O bond length is shortened from 1.374 Å in **1d** to 1.302 Å in the cation. Consistently, the charge on the oxygen atom is also reduced from -0.52844e in **1d** to -0.43860e in the

cation. These are evidences for the conjugation interaction of MeO group with the allyl cation system, indicating that the structure **1dAu3** is a significant resonance contributor.

1,3-Butadiene may react with **1dAu3** to deliver the Au-coordinated Z- and E-products through two concerted transition state structures: **1dTSconcZ** and **1dTSconcE**, respectively (Figure 1). The barrier height for the former one is $2.2 \text{ kcal mol}^{-1}$ which is smaller than that for the latter ($4.2 \text{ kcal mol}^{-1}$). These data suggest that the reaction occurs resulting in the preferential formation of the Z-product. This is just what we observed experimentally.

According to our NBO calculation results, both **1dTSconcZ** and **1dTSconcE** are clearly stabilized by the interaction between Au and C2 (the carbon atom connected with Au atom directly). On the other hand, although the **1dTSconcE** is *endo* and **1dTSconcZ** is *exo*, the stabilization energy due to the second order perturbation (SOP) of LP*C3 \rightarrow BD*C27-C28 and BD



Scheme 6. Model reaction pathway.

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Reaction Coordinate

Figure 1. DFT energy profile for [4+2] reaction of 1d/butadiene and Me₂C=C=CH₂ (1h)/butadiene initiated by Au(I) catalyst. A: 1,3-butadiene.

C27-C28 \rightarrow LP*C3 in **1dTSconcZ** is much higher than those in **1dTSconcE** (2.67 kcalmol⁻¹), which stabilizes **1dTSconcZ** to a greater degree than the *E* counterpart. This may be the main reason for the Z-product predominance (for the numbering system and the structures of the transition states, see Supporting Information).

The similar pathway for the Au(I)-catalyzed intermolecular [4+2] cycloaddition reaction of 1,3-butadiene with dimethylallene 1h was also evaluated for comparison. It has been found that the activation barrier for **1hTSconc** is considerable larger than that for the reaction of allenyl ether 1d. This difference in activation energy predicts that the same reaction with 1h will occur less feasibly. According to the SOP result, there is no similarly significant stabilization effect originated from the interaction between Au and C2 as in the 1dTSconcZ and 1dTSconcE. This may be accounted for by the less electron-donating property of methyl group than the methoxy group in 1d. The intermolecular character of our reactions and the electron-donating alkoxy group to assist the formation of oxonium cation 2 may be key factors dictating the reaction pathway.

We also located a stepwise pathway for the reaction with allenyl ether **1d**, but the free activation energy in the rate-limiting step (7.6 and 7.4 kcal mol⁻¹ for Z and E, respectively) is not favourable in comparison to the concerted one. The concerted [4+3] process followed by a 1,2-alkyl shift pathway is not located in our case.

In conclusion, we have developed a highly regioselective and stereoselective intermolecular [4+2] cycloaddition reaction of allenyl ethers and dienes mediated by a cationic Au(I) catalyst. The reactions are cationic in nature and the concept of Au-stabilized allylidene oxonium activation was applied to account for the observed unusual reactivity of allenyl ethers. This methodology represents an unprecedented strategy to access unique cyclohexene derivatives which have great synthetic value.

Experimental Section

General Procedure for the Gold-Catalyzed Diels-Alder Reaction of Allenyl Ethers and Dienes

To a solution of allenyl ether **1** (1.0 mmol) and diene **3** (3.0 mmol) in CH₂Cl₂ (10 mL) under argon atmosphere was added catalyst [(Ph₃P)Au]SbF₆ (0.01 mmol, 1.0 mL of 0.01 M solution in CH₂Cl₂) at room temperature. The reaction mixture was stirred at room temperature for the time displayed in the tables. Triethylamine was then added to quench the reaction and the reaction mixture was concentrated under reduced pressure. The crude product was purified by kugelrohr distillation or column chromatography (SiO₂, hexane:MTBE = 50:1).

The quantum mechanical study was carried out at density functional theory (DFT) level with the hybrid B3LYP functional as implemented within the Gaussian09 package.^[15] For geometry optimizations, the main group elements (C, O, P, H) were described using the 6–31G(d) basis set. The Au metal centre was described by the SDD combination of relativistic effective core potentials and valence functions.^[16] Solvation effects (dichloromethane) were evaluated through PCM calculations (with UFF atomic radii) on the gas-phase optimized geometries. Quoted energies are Gibbs free ener-

gies at 298 K and 1 atm. The energies we discussed are referred to the CH_2Cl_2 solution.

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