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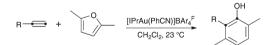
Intermolecular reactions of gold(1)-carbenes with furans by related mechanisms†‡

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The intermolecular gold(i)-catalyzed reactions of propargyl carboxylates, 1,6-enynes, or 7-substituted 1,3,5-cycloheptatrienes with furans afford cyclopentenones, polyenes or polycyclic compounds by related mechanisms initiated by the electrophilic addition of gold(i) carbenes to furans followed by ring-opening.

Gold-catalyzed intramolecular cycloisomerization reactions of 1,*n*-enynes have been widely studied and applied in synthesis, ^{1,2} following the pioneering work on similar transformations catalyzed by other late transition metals. However, the development of mechanistically related intermolecular cyclizations of alkynes with alkenes or other substrates has been more challenging. ⁴

An important transformation in this area is the cyclization of alkynylfurans, which was discovered using gold⁵ or platinum⁶ catalysts. This transformation leads to substituted phenols in a rather straightforward manner. Only one example of the corresponding gold-catalyzed intermolecular reaction of a furan with an alkyne had initially been reported using the binuclear gold(1) complex $[(Ph_3PAu)_2Cl]BF_4$, although we recently found that phenols can be obtained using air-stable $[IPrAu(PhCN)]BAr_4^F$ (A) $(BAr_4^F = 3,5$ -bis(trifluoromethyl)phenylborate) as the catalyst (Scheme 1).



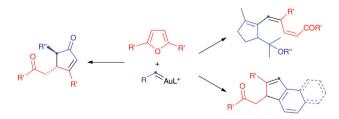
Scheme 1 Gold(i)-catalyzed intermolecular reaction of alkynes with furans.

§ D. L. and M. G. contributed equally to this work.

We have now found that propargyl carboxylates react differently with furans in the presence of gold(i) catalysts to give functionalized cyclopentenones or cyclopentadienyl carboxylates, which had not been reported before by related procedures (Scheme 2). Aryl gold(i) carbenes generated in enyne cyclizations^{1n,2,8} or by retro-Buchner reaction^{9,10} of 7-substituted 1,3,5-cycloheptatrienes also react with furans to give rise to polycyclic compounds.

The extent of stabilization of a carbocation by gold(i) has been the subject of discussion, $^{11-13}$ although, according to theoretical calculations, a carbene-like structure is favored when gold(i) is coordinated to strongly donating ligands such as N-heterocyclic carbenes and phosphines.

We first examined the reaction of propargylic acetate 1a with 2,5-dimethylfuran 2a in the presence of gold(i) catalysts, which in all cases gave rise diastereoselectively to cyclopentenone 3a (Table 1). The best yield of 3a was obtained using a cationic gold(i) catalyst [IPrAu(PhCN)]BAr $_4^F$ (A) (Table 1, entry 1). Related IPr gold(i) complex B with hexafluoroantimonate anions gave slightly lower yield after 30 min (Table 1, entry 2), whereas neutral complex C and cationic IMes derivatives required longer reaction times (Table 1, entries 3 and 4). Phosphine and phosphite gold(i) catalysts were less reactive in this transformation (Table 1, entries 5–8). Poor results were obtained with $AuCl_3$ or $PtCl_2$ (Table 1, entries 9 and 10).



Scheme 2 Intermolecular reactions of gold(i) carbenes with furans.

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[†]We dedicate this work to our colleague and friend Prof. Max Malacria on the occasion of his 65th birthday.

[‡]Electronic supplementary information (ESI) available: A text file of all computed molecule Cartesian coordinates in .xyz format. CCDC 1000511 and 1000512. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4q000130c

Table 1 Reaction between propargylic acetate 1a and furan 2a

Entry	Catalyst	Time (h)	Yield ^a (%)
1	A	0.5	57
2	В	0.5	48
3	C	3	45
4	D	24	20^b
5	E	5	44
6	F	5	27^{b}
7	G	5	30^b
8	[AuCl(PPh ₃]/AgSbF ₆	14	20^b
9	AuCl ₃	10	_
10	$PtCl_2$	16	11^b

^a Isolated yields. ^b Determined by ¹H NMR (1,4-diacetylbenzene as an internal standard).

Interestingly, when the reaction of furan 2a was performed with benzoate ester 1b and catalyst A, cyclopentadienyl benzoate 4a was isolated as the major product in 63% yield (Table 2, entry 2). Similarly, while acetates 1c, 1e, 1g, and 1h gave cyclopentenones 3b-e (Table 2, entries 3, 5, 7, and 8), benzoates 1d and 1f gave cyclopentadienes 4b and 4c as the major products (Table 2, entries 4 and 6). However, 1-cyclopropylprop-2-yn-1-yl acetate (1i) and benzoate (1j) react similarly to form 3f (Table 2, entries 9 and 10). The reaction of 2,5-diphenylfuran (2b) with benzoate 1b afforded cyclopentadienyl benzoate 4d (Table 2, entry 11). The structure of 4d was confirmed by X-ray diffraction (Fig. 1).14 Cyclopentenones were obtained in lower yields (<30%) when 2-substituted furans were used as substrates.

Unsymmetrically substituted furans 2c-d reacted with 1a and catalyst A to give a mixture of cyclopentenones 3i-j/3i'-j' favoring formation of the regioisomer with the less sterically hindered group at C-3 of the cyclopentenone (Scheme 3).

We propose a mechanism for the formation of the cyclopentenones and cyclopentadienyl esters initiated by the 1,2acyloxy migration of η^2 -alkyne-gold(I) complex 5, 15 followed by the electrophilic trapping of the α,β-unsaturated gold(1) carbene 6 by furan 2 (Scheme 4). The resulting intermediate 7 may lead to the cyclopropanation product 8, which could open

Table 2 Gold(i)-catalyzed reaction between propargylic carboxylates 1a-i with furans 2a-b

1 Ph H Ac Me 3a (57) — 2 Ph H Bz Me 3a (15) 4a (6 3 p-BrC ₆ H ₄ H Ac Me 3b (65) — 4 p-BrC ₆ H ₄ H Bz Me 3b (20) 4b (4 5 p-MeOC ₆ H ₄ H Ac Me 3c (36) —	eld %) ^a
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5 $p\text{-MeOC}_6H_4$ H Ac Me $3\mathbf{c}$ (36) —	14)
5 24 OCH H P M (24)	,
6 $p\text{-MeOC}_6H_4$ H Bz Me 3c (31) 4c (4	.8)
7 Me Me Ac Me 3d (61) —	
8 $-(CH_2)_5$ Ac Me $3e(63)$ —	
9 $c - C_3 H_5$ H Ac Me $3f (61)^b$ —	
10 c -C ₃ H ₅ H Bz Me $3f(60)^c$ —	
11 Ph H Bz Ph — 4d (75)

^a Isolated yields. ^b 2.5:1 trans/cis. ^c 5:1 trans/cis.

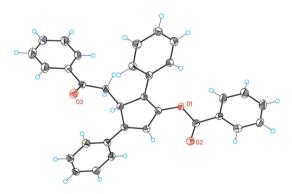


Fig. 1 ORTEP plot (50% thermal ellipsoids) of the crystal structure of cyclopentadienyl benzoate 4d.

Scheme 3 Intermolecular reaction of gold(i) carbenes with furans.

Scheme 4 Proposed mechanism for the formation of adducts 3 and 4 by gold(i)-catalyzed reaction of propargylic carboxylates with furans.

to form 9. Intermediate 9 could also be formed directly from 7 by 1,2-elimination. A Mukaiyama-Michael-type cyclization would then form 10, which leads to cyclopentenones 3 or cyclopentadienyl benzoates 4. The observed trans-stereoselectivity is presumably derived to the preferred Z-configuration of the vinyl gold(I) carbenes. 16 In the case of unsymmetrically substituted furans 2c-d, the major regioisomers are formed by the attack of the less substituted site of the furan to intermediate 6.

Formation of open chain products derived from intermediates similar to 9 has been reported before for Ru(II), Pt(II), 17,18 and, in one case, for Au(1)-19,20 catalyzed reactions of furans. A similar reactivity was observed in the reaction of furans with gold(1) carbenes generated by the ring opening of cyclopropenes.²¹ It is interesting that in our case, 2,5-disubstituted furans react preferentially at C-2, instead of at C3 as it is observed with Ru(II) as a catalyst. 17

1,6-Enynes 11a-b reacted with mono- and disubstituted furans 2a-j in the presence of gold(1) catalysts to form ketones or carboxylic acid derivatives 12a-i featuring a triene moiety with a (Z,Z)-configuration (Table 3).²²

This transformation is mechanistically interesting as it features a gold(I)-catalyzed cyclization/1,5-OR migration via intermediates 13 and 14 to form α,β -unsaturated gold(1) carbenes 15,8 which react with electron-rich furans to form 16 (Scheme 5). A similar elimination to that proposed before in the elimination of 7 (Scheme 4) gives 12a or 12d after hydrolytic cleavage of the trimethylsilyl ester.

We also examined the reaction of furans with gold(i) carbenes generated by the retro-Buchner reaction of 7-substituted 1,3,5-cycloheptatrienes (17), which proceeds by retrocyclopropanation of norcaradienes 18 (Scheme 6).9 The resulting gold(1) carbenes can be trapped with alkenes to form cyclopropanes, 9a,c or indenes. 9b These gold(1) carbenes also react intramolecularly with arenes in Friedel-Crafts-type reactions. 9b

Table 3 Gold(i)-catalyzed reaction between enynes 11a-b with furans 2a−j

11a:
$$R = Me$$
11b: $R = PNP$
2a: $R^2 = R^4 = Me$, $R^3 = H$
2b: $R^2 = R^4 = Ph$, $R^3 = H$
2c: $R^2 = OTMS$, $R^3 = R^4 = H$
2f: $R^2 = GMe$, $R^3 = R^4 = H$
2h: $R^2 = GMe$, $R^3 = R^4 = H$
2h: $R^2 = Bu$, $R^3 = R^4 = H$
2h: $R^2 = Bu$, $R^3 = R^4 = H$
2h: $R^2 = Bu$, $R^3 = R^4 = H$
2h: $R^2 = R^3 = Me$, $R^4 = H$
2i: $R^2 = R^3 = Me$, $R^4 = H$
2i: $R^2 = R^3 = Me$, $R^4 = H$

Entry	Enyne	Furan	Catalyst	12 (Yield %) ^a
1	11a	2e	A	12a (36) ^b
2	11b	2a	В	12b (32)
2	11b	2b	E	12c (42)
3	11b	2e	F	12d $(82)^b$
4	11b	2 f	E	12e (57)
5	11b	2g	F	12f (56)
6	11b	2h	E	12g (62)
7	11b	2i	E	12h (59)
8	11b	2j	E	12i (88)

^a Isolated yields. ^b The carboxylic acid was obtained. PNP = p-nitrophenyl.

Scheme 5 Proposed mechanism for the reaction of 1,6-enynes 11a-b with furans 2a-i.

Scheme 6 Generation of gold(i) carbenes by retro-Buchner reaction.

The reaction of 1-naphthyl cycloheptatriene 17a with 2,5disubstituted furans 2a-b in the presence of catalyst E in 1,2dichloroethane (DCE) at 120 °C gave 3H-cyclopenta[a]naphthalenes 19a-b (Scheme 7). In the former case, 19a was obtained along with a minor isomer with a tetrasubstituted double bond. The reaction of 17a-b with 2-substituted furans 2i and 2k leads to 1,5-diarylpenta-2,4-dien-1-ones 20a-c. On the other hand, the reaction of 17a with 1,3-diphenylisobenzofuran (21)

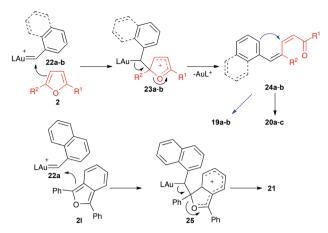
Scheme 7 Reaction of furans with gold(i) carbenes generated by retro-Buchner reaction.

Fig. 2 ORTEP plot (50% thermal ellipsoids) of the crystal structure of 21.

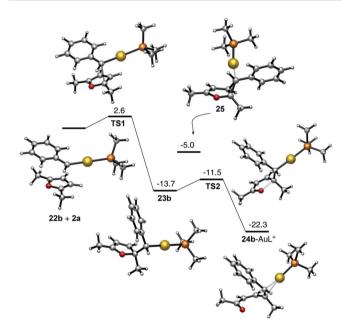
gave 21 in 56% yield. The Z configuration of 21 was determined by X-ray diffraction (Fig. 2).²³

Mechanistically, the reaction of 17a-b with catalyst E leads to aryl gold(i) carbenes 22a-b, which react with furans by pathways similar to those observed before for other gold(i) carbenes (Scheme 8). Thus, the Friedel–Crafts-type reaction would lead to intermediates such as 23 or 25, which affords open chain derivatives 24 or 21. In the former case, the initially formed 25 affords 20a-c by Z to E isomerization or 19a-b by a Michael-type ring closing.

The mechanistic proposal outlined in Scheme 8 is supported by DFT calculations (M06 level, 1,2-dichloroethane, PMe₃ as the phosphine ligand) (Scheme 9). Accordingly, the reaction between carbene 22b, resulting from the retro-Buchner reaction of 7-phenyl-1,3,5-cycloheptatriene (17b),⁹ and furan 2b through TS1 leads to intermediate 23b, which



Scheme 8 Proposed mechanism for the reaction of furans with gold(i) carbenes generated by retro-Buchner reaction.



Scheme 9 Mechanism for the reaction of carbene 22b with furan 2a based on DFT calculations. Free energies in kcal mol^{-1} .

smoothly opens up to form **24b**–AuL⁺ complex.²⁴ The intermediate cyclopropane **25**, corner-coordinated to AuL⁺, was also located as an intermediate, although its energy is higher than that of intermediate **23b**.

In summary, we have found that three very different types of substrates react with furans and gold(i) catalysts under different reaction conditions by mechanistically related pathways. This is best rationalized if similar gold(i) carbenes are involved as intermediates in all these processes, which is also supported by DFT calculations. The fact that similar reactions are observed in transformations proceeding via ruthenium(II) or platinum(II) carbenes¹⁷ further supports the involvement of closely similar species using gold(i) catalysts. These reactions of furans lead to rather elaborated products from readily available substrates under mild conditions. Further applications of

the trapping of reactive gold(I) carbenes with other types of nucleophiles are being explored.

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- 20 For gold(i)-catalyzed [4 + 3]-cycloaddition of propargyl esters with furans: (a) W. Gung, D. T. Craft, L. N. Bailey and K. Kirschbaum, Chem. Eur. J., 2010, 16, 639–644; (b) B. Gung, R. Conyers and J. Wonser, Synlett, 2013, 1238–1248.
- 21 M. S. Hadfield and A.-L. Lee, *Chem. Commun.*, 2011, 47, 1333–1335.
- 22 (*a*) See ESI‡ for additional results on the screening of other migrating groups and catalysts (*b*) Traces of minor isomers (presumably with the *E,E* configuration) were also detected in the ¹H NMR spectra.
- 23 X-Ray crystal structure of 21: CCDC 1000512.
- 24 Another pathway (*exo*-type) was also found with very similar energies for the first step ($\Delta G^{\ddagger} = 2.6 \text{ kcal mol}^{-1}$) ($\Delta G = -13.7 \text{ kcal mol}^{-1}$) although the activation energy for the second step was significantly higher ($\Delta G^{\ddagger} = 6.1 \text{ vs.} 2.2 \text{ kcal mol}^{-1}$).