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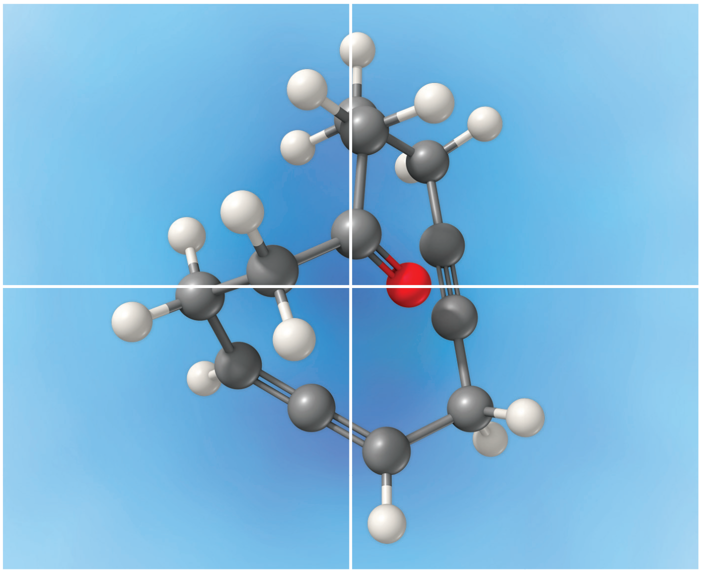

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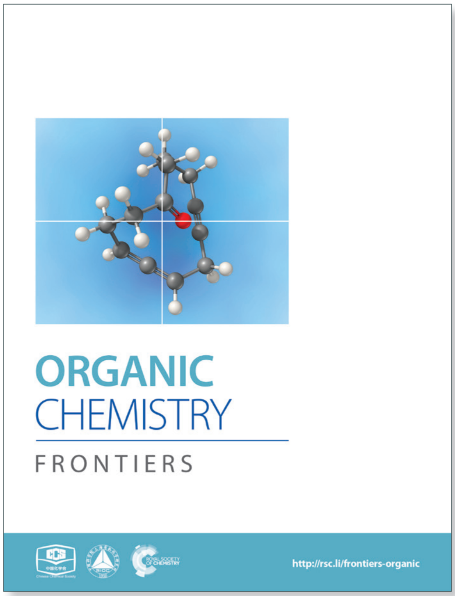

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ARTICLE TYPE

Intermolecular Reactions of Gold(I)-Carbenes with Furans by Related Mechanisms†‡

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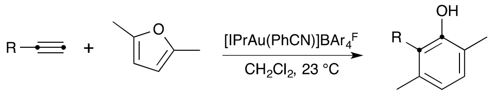
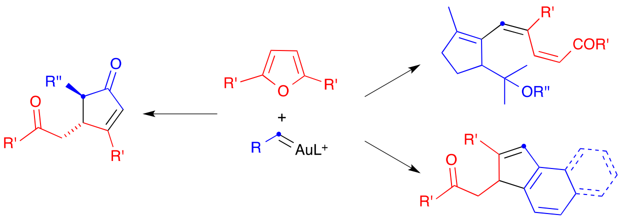
The intermolecular gold(I)-catalyzed reactions of propargyl carboxylates, 1,6-enynes, or 7-substituted 1,3,5-cycloheptatrienes with furans afford cyclopentenones, polyenes or polycyclic compounds by related mechanisms initiated by the electrophilic addition of gold(I) carbenes to furans followed by ring-opening.

Gold-catalyzed intramolecular cycloisomerization reactions of 1,n-enynes have been widely studied and applied in synthesis,[1,2] following pioneering work on similar transformations catalyzed by other late transition metals.[3] 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 gold[5] or platinum[6] 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(I) complex $[(Ph_3PAu)_2Cl]BF_4$,[5f] 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 catalyst (Scheme 1).[7]



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

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[1o,2,8] or by retro-Buchner reaction[9,10] of 7-substituted 1,3,5-cycloheptatrienes also react with furans to give polycyclic rise to compounds.

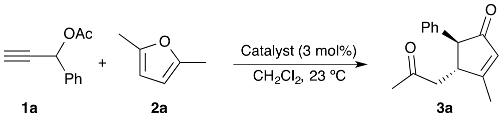


Scheme 2 Intermolecular reactions of gold(I) carbenes with furans.

The extent of stabilization of a carbocation by gold(I) has been the subject of discussion,[11,12,13] although, according to theoretical calculations, a carbene-like structure is favored when gold(I) is coordinated to strongly donating ligands such a 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 stereoselectively to cyclopentenone **3a** (Table 1). The best yield of **3a** was obtained using cationic gold(I) catalyst $[IPrAu(PhCN)]BAr_4^F$ (**A**) (Table 1, entry 1). Related IPr gold(I) complex **B** with hexafluoroantimonate anion gave slightly lower yield after 30 min (Table 1, entry 2), whereas neutral complex **C** and cationic IMs derivative 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).

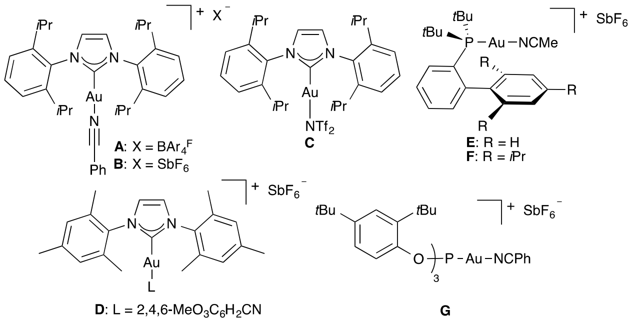
Table 1 Reaction between propargylic acetate **1a** and furan **2a**.



1a **2a** **3a**

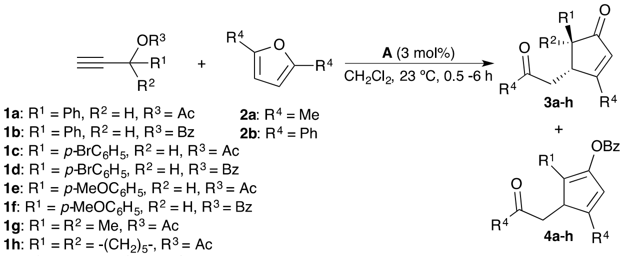
entry	Catalyst	Time (h)	Yield (%)[a]
1	**A**	0.5	57
2	**B**	0.5	48
3	**C**	3	45
4	**D**	24	20[b]
5	**E**	5	44
6	**F**	5	27[b]
7	**G**	5	30[b]
8	$[AuCl(PPh_3)] / AgSbF_6$	14	20[b]
9	$AuCl_3$	10	-
10	$PtCl_2$	16	11[b]

[a] Isolated yileds. [b] Determined by ^1H NMR (1,4-diacetylbenzene as internal standard).



Interestingly, when the reaction of furan **2a** was performed with benzoate ester **1b** and catalyst **A**, cyclopentadienyl benzoate **4a** was isolated as 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** led to 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). 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 (Figure 1).[14] Cyclopentenones were obtained in lower yields (<30%) when 2-substituted furans were used as substrates.

Table 2 Gold(I)-catalyzed reaction between propargylic carboxylates **1a-j** with furans **2a-b**.



1a: R^1 = Ph, R^2 = H, R^3 = Ac
1b: R^1 = Ph, R^2 = H, R^3 = Bz
1c: R^1 = *p*-BrC$_6$H$_5$, R^2 = H, R^3 = Ac
1d: R^1 = *p*-BrC$_6$H$_5$, R^2 = H, R^3 = Bz
1e: R^1 = *p*-MeOC$_6$H$_5$, R^2 = H, R^3 = Ac
1f: R^1 = *p*-MeOC$_6$H$_5$, R^2 = H, R^3 = Bz
1g: R^1 = R^2 = Me, R^3 = Ac
1h: R^1 = R^2 = -(CH$_2$)$_5$-, R^3 = Ac
1i: R^1 = *c*-C$_3$H$_5$, R^2 = H, R^3 = Ac
1j: R^1 = *c*-C$_3$H$_5$, R^2 = H, R^3 = Bz

2a: R^4 = Me
2b: R^4 = Ph

entry	R^1	R^2	R^3	R^4	**3** (yield %)[a]	**4** (yield %)[a]
1	Ph	H	Ac	Me	**3a** (57)	-
2	Ph	H	Bz	Me	**3a** (15)	**4a** (63)
3	*p*-BrC$_6$H$_4$	H	Ac	Me	**3b** (65)	-
4	*p*-BrC$_6$H$_4$	H	Bz	Me	**3b** (20)	**4b** (44)
5	*p*-MeOC$_6$H$_4$	H	Ac	Me	**3c** (36)	-
6	*p*-MeOC$_6$H$_4$	H	Bz	Me	**3c** (31)	**4c** (48)
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*. [b] 5:1 *trans*/*cis*.

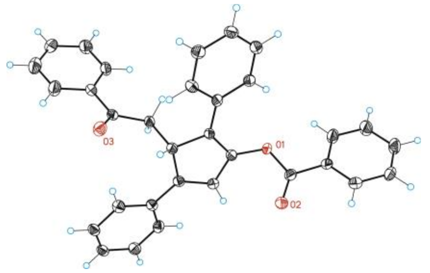
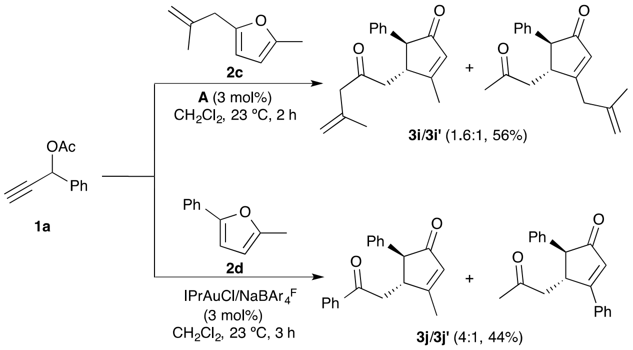


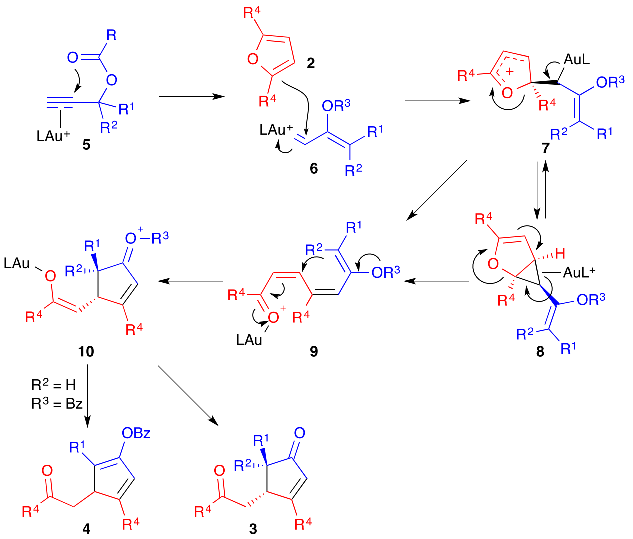
Figure 1 ORTEP plot (50% thermal ellipsoids) of the crystal structure of cyclopentadienyl benzoate **4d**.

Unsymmetrically substituted furans **2c-d** reacted with **1a** and catalyst **A** to give a mixtures 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).



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

We propose a mechanism for the formation of the cyclopentenones and cyclopentadienyl esters initiated by the 1,2-acyloxy migration of η^2-alkyne-gold(I) complex **5**,[15] followed by the electrophilic trapping of the α,β-unsaturated gold(I) carbene **6** by furan **2** (Scheme 4). The resulting intermediate **7** may lead to the product of cyclopropanation **8**, which could open to form **9**. Intermediate **9** could also be formed directly from **7** by 1,2-elimination. A Mukaiyama-Michael-type cyclization would then forms **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 less substituted site of the furan to intermediate **6**.

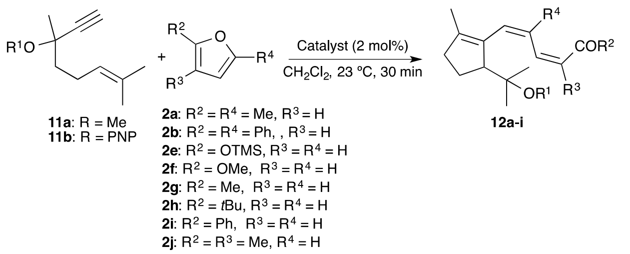


Scheme 4 Proposed mechanism for the formation of adducts **3** and **4** by gold(I)-catalyzed reaction of propargylic carboxylates with furans.

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

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

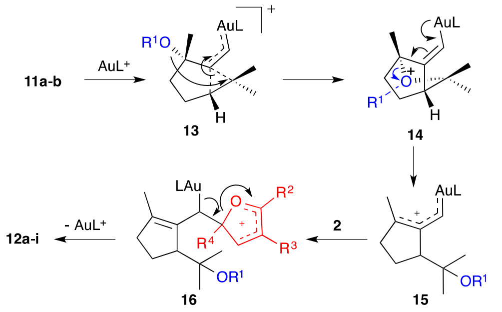
Table 3 Gold(I)-catalyzed reaction between enynes **11a-b** with furans **2a-ji**.



entry	enyne	furan	catalyst	**12** (yield %)[a]
1	**11a**	**2e**	**A**	**12a** (36)[b]
2	**11b**	**2a**	**B**	**12b** (32)
2	**11b**	**2b**	**E**	**12c** (42)
3	**11b**	**2e**	**F**	**12d** (82)[b]
4	**11b**	**2f**	**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)

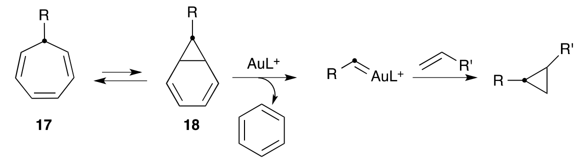
[a] Isolated yields. [b] The carboxylic acid was obtained. PNP = *p*-nitrophenyl.

This transformation is mechanistically interesting as it features a gold(I)-catalyzed cyclization/1,5-OR migration via intermediates **13** and **14** to form a α,β-unsaturated gold(I) 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.



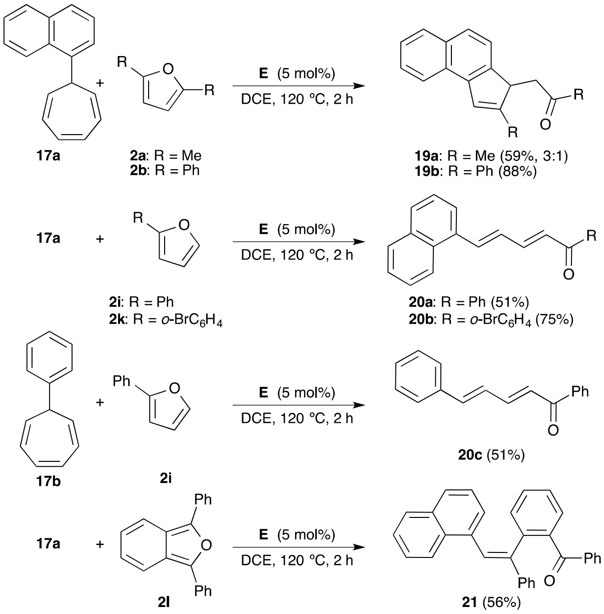
Scheme 5 Proposed mechanism for the reaction of 1,6-enynes **11a-b** with furans **2a-j**.

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



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

Reaction of 1-napthtyl cycloheptatriene **17a** with 2,5-disubstituted furans **2a-b** in the presence of catalyst **E** in 1,2-dichloroethane (DCE) at 120 °C gave 3*H*-cyclopenta[*a*]naphthalenes **18a-b** (Scheme 7). In the former case, **18a** was obtained along with a minor isomer with a tetrasubstituted double bond. 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, reaction of **17a** with 1,3-diphenylisobenzofuran (**2l**) gave **21** in 56% yield. The Z configuration of **22** was determined by X-ray diffraction (Figure 2).[23]



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

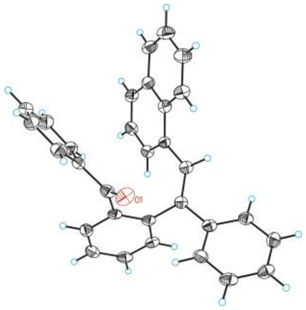
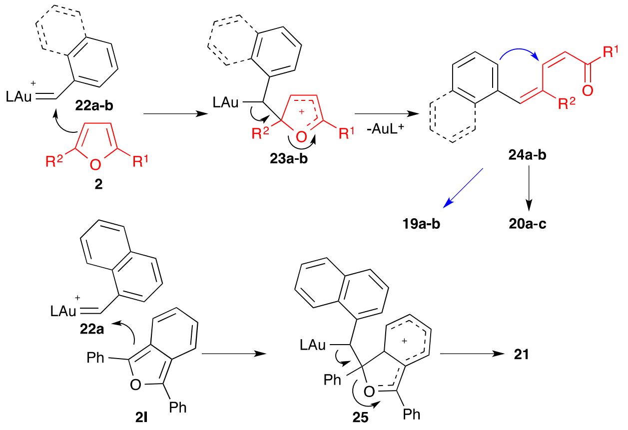


Figure 2 ORTEP plot (50% thermal ellipsoids) of the crystal structure of **21**.

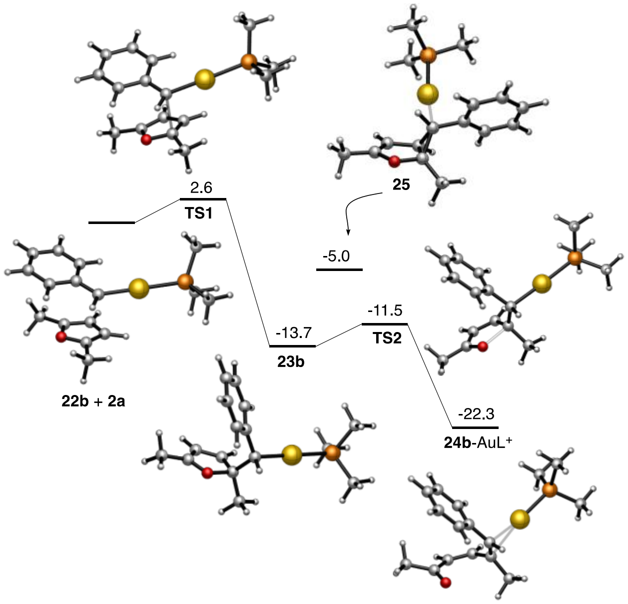
Mechanistically, the reaction **17a-b** with catalyst **E** leads to aryl gold(I) carbenes **22a-b**,[9] which react with furans by pathways similar to those observed before for other gold(I) carbenes (Scheme 8). Thus, the Friedel-Crafts-type reaction would lead to intermediates such as **23** or **25**, which give open chain derivatives

24 or **21**. In the former case, the initially formed **25** affords **19a-c** by Z to E isomerization or **20a-b** by a Michael-type ring closing.



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

The mechanistic proposal outlined in Scheme 8 is supported by DFT calculations (M06 level, 1,2-dichloroethane, PMe_3 as the phosphine ligand) (Scheme 9). Accordingly, the reaction between carbene **22b**, resulting by the retro-Buchner reaction of 7-phenyl-1,3,5-cycloheptatriene (**17b**),[9] with furan **2b** through **TS1** leads to intermediate **23b**, which 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**.



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

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) carbenes[17] 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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Notes and references

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[†] Electronic supplementary information (ESI) available. A text file of all computed molecule Cartesian coordinates in .xyz format. CCDC 1000511– CCDC 1000512.

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

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