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Gold(I)-Catalyzed Intermolecular Addition of Carbon Nucleophiles to 1,5- and 1,6-Enynes

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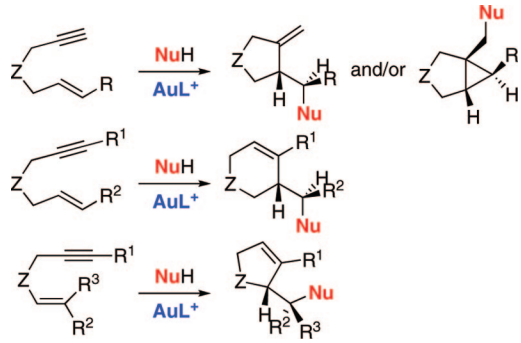

Gold(I)-catalyzed addition of carbon nucleophiles to 1,6-enynes gives two different type of products by reaction at the cyclopropane or at the carbene carbons of the intermediate cyclopropyl gold carbenes. The 5-*exo-dig* cyclization is followed by most 1,6-enynes, although those bearing internal alkynes and alkenes react by the 6-*endo-dig* pathway. The cyclopropane versus carbene site-selectivity can be controlled in some cases by the ligand on the gold catalyst. In addition to electron-rich arenes and heteroarenes, allylsilanes and 1,3-dicarbonyl compounds can be used as the nucleophiles. In the reaction of 1,5-enynes with carbon nucleophiles, the 5-*endo-dig* pathway is preferred.

Introduction

Gold salts and complexes are the most powerful catalysts for the electrophilic activation of enynes toward a variety of nucleophiles under homogeneous conditions.[1−7] Activation of the enyne **1** via the η^2-alkyne complex **2** takes place by two general pathways: a 5-*exo-dig* process via *anti*-cyclopropyl metal carbenes **3** and the relatively less common 6-*endo-dig* cyclization via metal carbenes **4** (Scheme 1).[8−10] Attack of a nucleophile NuH to intermediate **3** leads to five- or six-membered ring compounds **5** or **6** by cleavage of bonds ***a*** or ***b***, respectively. In the absence of nucleophiles, cycloisomerization by skeletal rearrangement takes place from **3**.[8−15] Intermediates **4** usually evolve by proton elimination leading to bicyclic compounds **7**,[13a,b,16−18] which are the products of an intramolecular cyclo-

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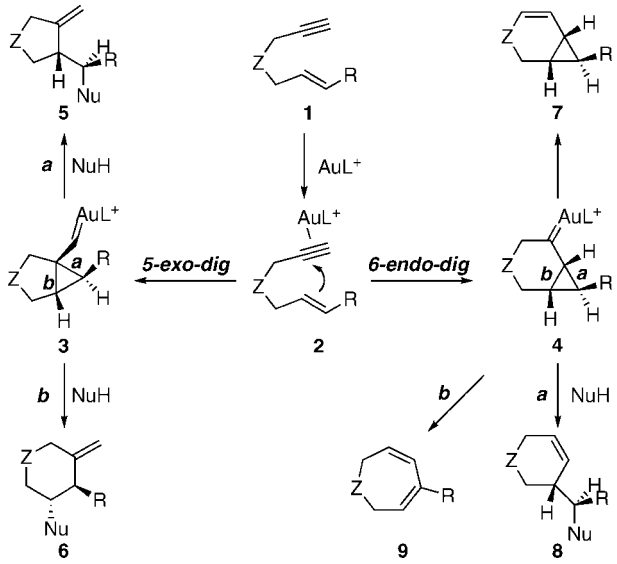
SCHEME 1



propanation of the alkene by the alkyne. Addition of heteronucleophiles at the terminal alkene carbon by cleavage of the bond labeled ***a*** in intermediate **4** has been observed using $PtCl_2$ or $AuCl_3$ as catalysts, which leads to adducts of type **8**.[19] Cleavage of the C−C bond labeled as ***b*** in intermediate **4** can give rise to cyloheptadienes **9**.[20]

The nature of intermediates of type **3** has been recently discussed, stressing their carbocationic character.[21] It is important to note, however, that although structures such as **3** and **4** are depicted in a simplified manner as cyclopropyl gold carbenes, DFT calculations reveal that these species have highly distorted structures, which are intermediate between cyclopropyl gold carbenes and gold-stabilized homoallylic carbocations.[8,10,15,17] Their carbene character becomes apparent in intra-[8,22−24] or intermolecular[25−28] cyclopropanations reactions of enynes and propargylic carboxylates with alkenes. Interestingly, a gold carbene has been recently formed in the gas phase that undergoes cyclopropanation and cross-metathesis reactions.[29]

Additions of nucleophiles to 1,6-enynes catalyzed by gold[8,9,30] or other electrophilic metal complexes[31−34] have been restricted until recently to water or alcohols. 1,5-Enynes react similarly with ROH nucleophiles in the presence of Au(I).[35−39] The intramolecular amination of 1,5-enynes with tosylamides[35] and the intermolecular addition of carbamates RO_2CNH_2 or anilines $ArNH_2$ to 1,6-enynes have also been reported.[40]

Addition of electron-rich arenes and heteroarenes to enynes has been recently reported by the group of Genêt[41] and by our group[42] using different gold(I) catalysts.[43] This addition affords adducts of type **5** by attack of the carbon nucleophile to intermediates of type **3** (Scheme 1) in a reaction that is mechanistically similar to the intramolecular reaction of arylenynes that results in a formal [4 + 2] cycloaddition reaction.[44] However, using indoles as carbon nucleophiles,[45] we found that the attack can also take place at the carbene carbon of intermediates **3**.[42] Attack at the carbene carbon of intermediates

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3 was also observed in gold-catalyzed reactions of propargyl acetates with indole.[46,47] Additions of indoles are of special importance as the resulting adducts possess skeletons that could be of interest in diversity-oriented synthesis.[43,48]

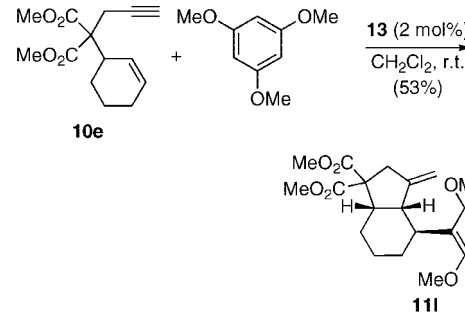
We have now found that, in addition to electron-rich arenes and heteroarenes, allylsilanes and 1,3-dicarbonyl compounds also react as nucleophiles with 1,6-enynes in the presence of electrophilic gold complexes. In these reactions the 5-*exo-dig* pathway leading to products of type **5** is usually preferred, although the C−C bond formation can take place by cleavage of bond ***b*** in an intermediates of type **3** or via endocyclic intermediates **4**, leading to adducts of type **8**. We have also found the first examples of addition of carbon nucleophiles to 1,5-enyes with gold catalysts.

Results and Discussion

Additions of Arenes and Heteroarenes to 1,6-Enynes. We explored first the reaction of indoles and electron-rich arenes with 1,6-enynes by using cationic gold complexes as catalysts. Whereas no reaction was observed between enyne **10a** and indole using AuCl or $AuCl_3$ as catalysts (Table 1, entries 1 and 2), reaction with cationic catalyst **13**[44a,49] afforded a 4:1 mixture of adducts **11a** and **12a** in 1 h at room temperature (Table 1, entry 3). A more selective transformation was found with a catalyst formed in situ from complex **14a**[44b,27] and $AgSbF_6$, which led to **11a** and **12a** in a 10:1 ratio (Table 1, entry 4). No reaction took place with neutral complex **14a** (Table 1, entry 5). However, new cationic complex **14b**, which is a stable solid at room temperature, led to **11a** and **12a** in a 5.3:1 ratio in 71% yield (Table 1, entry 6). In contrast with the relatively fast reactions (ca. 1 h) using gold complexes bearing biphenyldialkylphosphines or a bulky phosphite as ligands, additions of indole to enyne **10a** with *N*-heterocyclic carbene (NHC) gold complexes **15a**/$AgSbF_6$[44a,50] and **15b**−**e** required 17−47 h (Table 1, entries 7−11). Cationic complexes **15b**−**e** are white crystalline solids, stable at room temperature.[51] Interestingly, with the exception of complex **15e** (Table 1, entry 11), NHC−gold(I) complexes gave adduct **12a** as the major product. No reaction was observed with 5 mol % $AgSbF_6$ (Table 1, entry 12).

In general, best results for the formation of products of type **11** were obtained using 1.1 equiv of arene or indole and the catalyst formed in situ from complex **14a** and $AgSbF_6$ (see Table 1, entry 4), which was also the catalyst of choice for the formal [4 + 2] cycloaddition of arylenynes.[44b] Thus, enyne **10a** reacted with indole-5-carbonitrile, 1,3,5-trimethoxybenzene, benzodioxole, and 2,6-di-*tert*-butylphenol to give **11b**−**e** (Table 2, entries 1−4). Enynes **10b,c** with a trisubstituted double bond are prone to suffer fast gold-catalyzed skeletal rearrangements even at low temperature.[8b] Therefore, their reactions with indole, 5-methoxyindole, and 1,3,5-trimethoxybenzene with catalyst **14a**/$AgSbF_6$ were performed at −50 °C. Under these conditions, adducts **11f**−**i** were obtained in 60−78% yields (Table 2, entries 5−8). Reaction of enyne **10d** with indole and 1,3-dimethoxybenzene provided **11j** and **11k**, respectively (Table 2, entries 9 and 10). In the latter case, the reaction had to be performed at −40 °C to avoid the isomerization of the exocyclic double bond that leads to **11k′** when the reaction was carried out at room temperature (Table 2, entry 11).

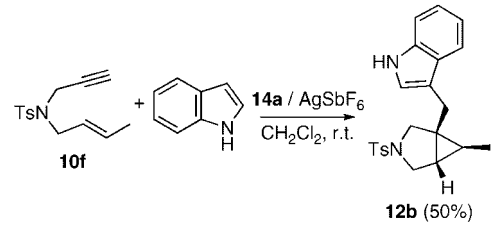
Single stereoisomers were obtained in the case of **11a**−**e** and **11j**−**k**, whose configurations were assigned on the basis of our previous work on the Pt(II) and Au(I)-hydroxy- and alkoxycyclization reactions of 1,6-enynes.[8a,9,31] To further confirm the stereoselectivity of this reaction, we performed the addition of 1,3,5-trimethoxybenzene to 1,6-enyne **10e**, which gave **11l** as a single stereoisomer (eq 1). Adduct **11l** has the same relative configuration as that of the product of the Pt(II)-catalyzed reaction of **10e** with methanol.[31b]



(1)

Formation of products **11a**−**l** can be rationalized as a result of the attack of the electron-rich arenes or indoles to intermediates of type **3** as shown in Scheme 1. Interestingly, in all these reactions we never observed significant amounts of products resulting from the direct attack of the nucleophilic arene or heteroarene to the alkyne.[45,52−57]

Enyne **10f** reacted with indole and **14a**/$AgSbF_6$ as catalyst to give cyclopropane **12b**, along with other uncharacterized products (eq 2). A slower transformation was observed with [$AuCl(PPh_3)$]/$AgSbF_6$. A more complex transformation was found in the reaction of enyne **10g** with indole and *N*-methylindole, which led to adducts **12c**−**d** (Table 3). Best yields were obtained in both cases using cationic catalysts **14b** or **15c** (Table 3, entries 2, 3, 5, and 6).



(2)

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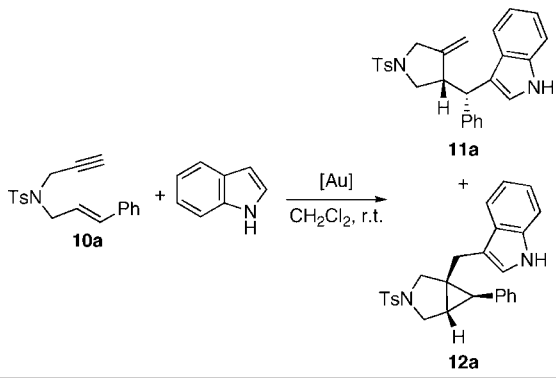
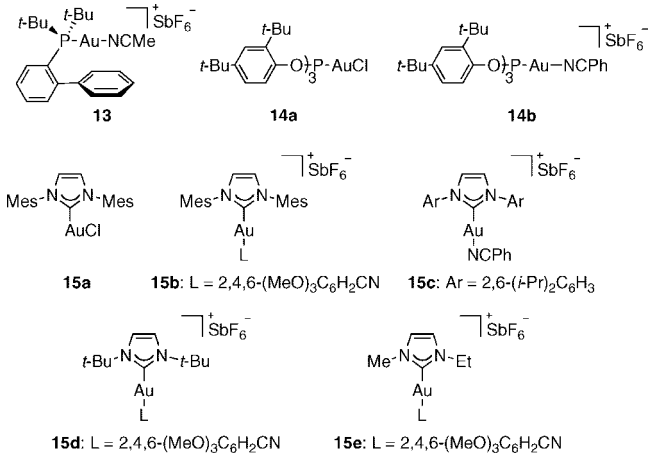
TABLE 1. Au(I)-Catalyzed Addition of Indole to 1,6-Enyne 10a[a]



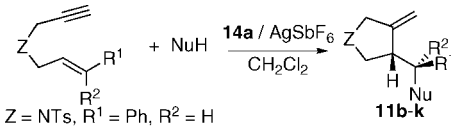
entry	[Au]	time (h)	product(s)	yield (%)
1	AuCl	192		
2	$AuCl_3$	192		
3	**13**	1	**11a** + **12a** (80:20)	74
4	**14a**/$AgSbF_6$	1	**11a** + **12a** (91:9)	68
5	**14a**	24		
6	**14b**	1	**11a** + **12a** (84:16)	71
7	**15a**/$AgSbF_6$	19	**11a** + **12a** (45:55)	72
8	**15b**	19	**11a** + **12a** (40:60)	62[b]
9	**15c**	17	**11a** + **12a** (25:75)	57[b]
10	**15d**	17	**11a** + **12a** (39:61)	68
11	**15e**	47	**11a** + **12a** (84:16)	33[b]
12	$AgSbF_6$	60		

[a] Reactions carried out at room temperature in CH_2Cl_2 with 5 mol % catalyst. [b] Determined by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.

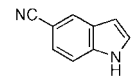
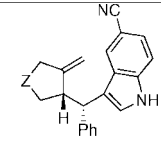
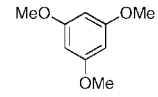
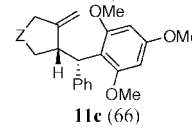
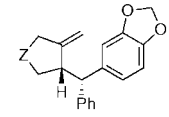
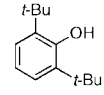
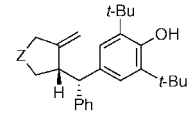
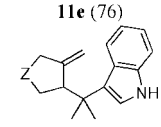
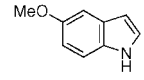
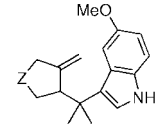
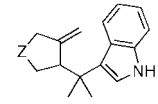
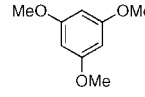
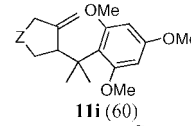
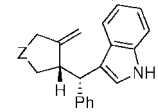
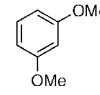
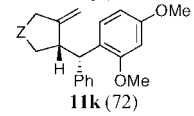
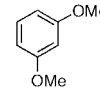
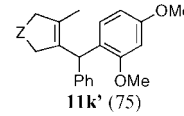


Cyclopropyl derivatives **12a**−**b** are formed by direct attack of indole at the carbene carbon of intermediates **3a**−**b** to give **16a**−**b**, which evolve by rearomatization and proto-demetalation (Scheme 2). On the other hand, in the formation of products **12c**−**d**, an isomerization of the initially formed cyclopropyl gold carbene **3c** takes place to give carbene **17**. Reaction of **17** with the indoles gives intermediates **18c**−**d**, which yield **12c**−**d** by the process shown before for **16a**−**b**. Gold(I) carbene **17**, which is the intermediate of the double cleavage skeletal rearrangement,[7−9,11,12,15] is less-sterically hindered and probably more electrophilic than **3c**, being nonconjugated with the cyclopropane. Intermediate carbene **17** had been trapped before with norbornene in an intermolecular cyclopropanation reaction.[27] We also considered a mechanism via intermediates of type **19** by cyclopropanation of the indoles by the intermediate gold carbenes such as **3c** or **17**.[58] However, *N*-methoxycarbonylindole, which affords stable cyclopropanes with metal carbenes,[59] does not react with enyne **10g** under these conditions.

TABLE 2. Au(I)-Catalyzed Addition of Electron-Rich Arenes and Indoles to 1,6-Enynes[a]

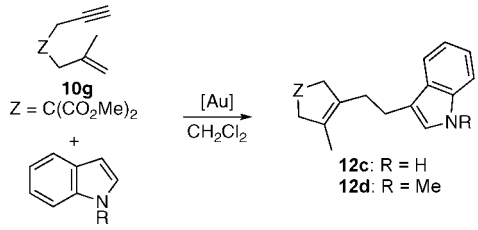


10a: Z = NTs, R^1 = Ph, R^2 = H
10b: Z = $C(CO_2Me)_2$, R^1 = R^2 = Me
10c: Z = $C(SO_2Ph)_2$, R^1 = R^2 = Me
10d: Z = $C(CO_2Me)_2$, R^1 = Ph, R^2 = H

entry	enyne	NuH	T (°C), time (h)	product (yield, %)
1	**10a**		23, 48	 **11b** (49)
2	**10a**		23, 2	 **11c** (66)
3	**10a**		-40, 4	 **11d** (74)
4	**10a**		-40, 4	 **11e** (76)
5	**10b**		-50, 5	 **11f** (78)
6	**10b**		-50, 5	 **11g** (63)
7	**10c**		-50, 1	 **11h** (78)
8	**10c**		-50, 1	 **11i** (60)
9	**10d**		23, 1	 **11j** (71)
10	**10d**		-40, 3	 **11k** (72)
11	**10d**		23, 2	 **11k'** (75)

[a] Reactions carried out in CH_2Cl_2 with 5 mol % catalyst.

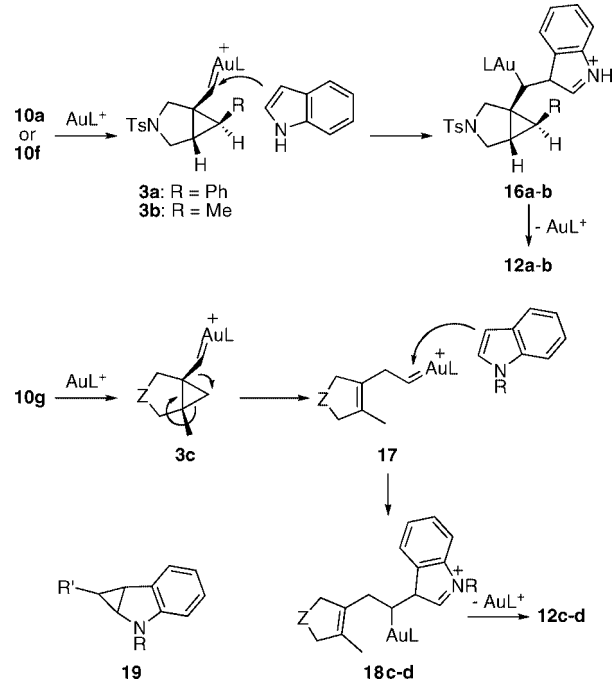
TABLE 3. Au(I)-Catalyzed Addition of Indole and *N*-Methylindole and Indoles to 1,6-Enyne 10g[a]



entry	R	[Au]	time (min)	product (yield, %)
1	H	**14a**/$AgSbF_6$	90	**12c** (56)
2	H	**14b**	30	**12c** (71)[b]
3	H	**15c**	45	**12c** (69)[b]
4	Me	**14a**/$AgSbF_6$	90	**12d** (45)
5	Me	**14b**	90	**12d** (80)[b]
6	Me	**15c**	60	**12d** (81)[b]

[a] Reactions carried out in CH_2Cl_2 with 5 mol % catalyst. [b] 3 equiv of indole was used.

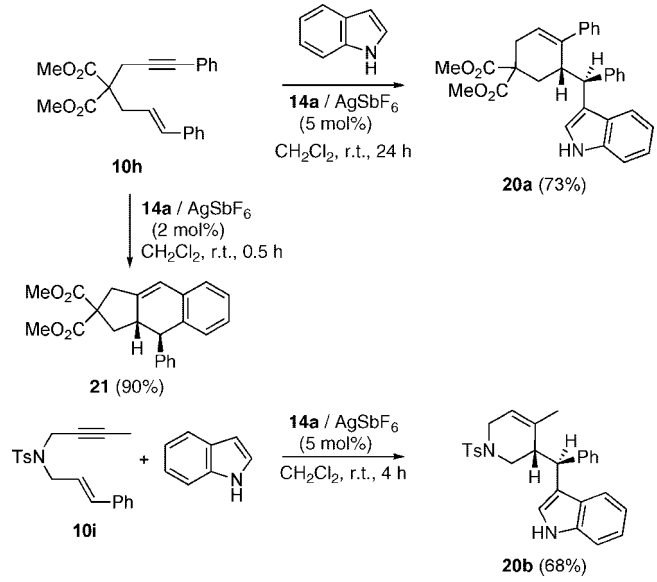
SCHEME 2



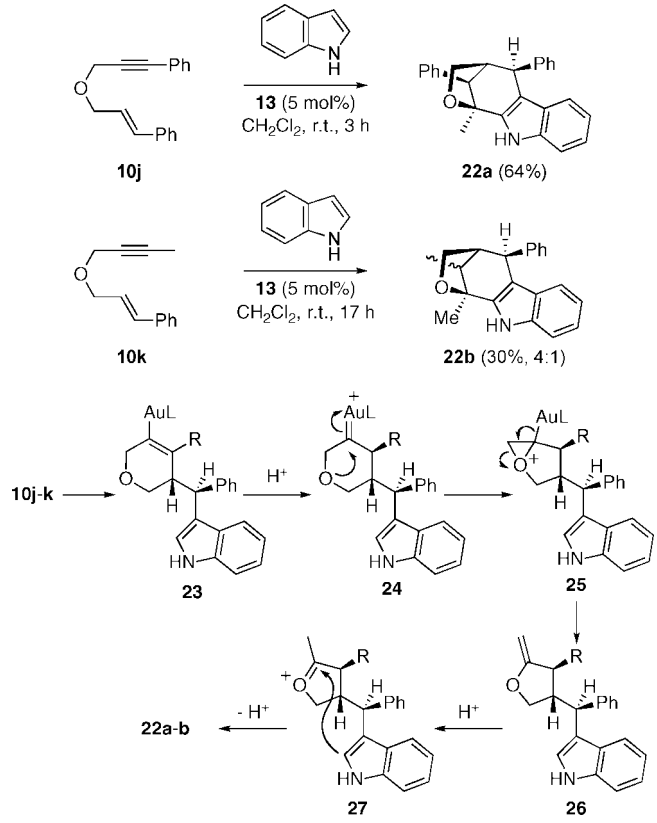
Enynes **10h**−**i** with an internal alkyne react with indole by the endocyclic pathway to give **20a**−**b** as single stereoisomers (Scheme 3), whose configuration was assigned as shown by similarity with products of alkoxycyclization of type **8** (Scheme 1).[19] The successful addition of indole to enyne **10h** is quite remarkable, since the intramolecular [4 + 2] cycloaddition of **10h** is known to give tricyclic compound **21** in good yield in just 30 min, in a reaction that proceeds by an initial 5-*exo-dig* cyclization.[44]

Enynes **10j**-**k** with an ether as the tether react with indole in the presence of catalysts **13** to give more complex products

SCHEME 3



SCHEME 4



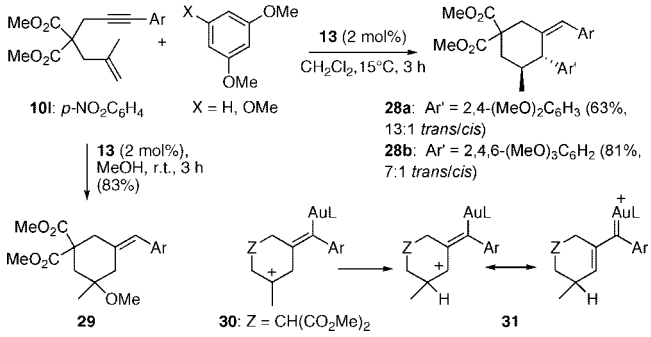
22a−**b** (Scheme 4). Tetracyclic compound **22a** was obtained as a single stereoisomer, whose structure was confirmed by X-ray diffraction,[60] whereas **22b** was a mixture of two epimers. Formation of **22a**−**b** can be rationalized as shown in Scheme 4 from intermediates **23**. Protonation of the alkenylgold moiety of **23** could give gold carbene **24**, which would react via **25** to give enol ether **26**. A final proton-catalyzed cyclization via **27** then furnish **22a**−**b**. The ring contraction (**23** to **25**) found in

(58) Padwa, A.; Austin, D. J.; Price, A. T.; Semones, M. A.; Doyle, M. P.; Protopopova, M. N.; Winchester, W. R.; Tran, A. *J. Am. Chem. Soc.* **1993**, *115*, 8669–8680.

(59) (a) Welstead, W. J.; Stauffer, H. F.; Sancillo, L. F. *J. Med. Chem.* **1974**, *17*, 544–547. (b) Wenkert, E.; Alonso, M. E.; Gottlieb, H. E.; Sanchez, E. L.; Pellicciari, R.; Cogolli, P. *J. Org. Chem.* **1977**, *42*, 3945–3949. (c) Gnad, F.; Poleschak, M.; Reiser, O. *Tetrahedron* **2004**, *45*, 4277–4280.

(60) See Supporting Information for details of the X-ray structure of **22a** and **39**.

SCHEME 5

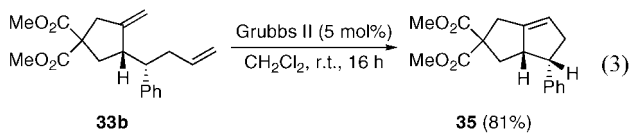


these transformations is intriguing, and might have additional applications in other contexts.

Enyne **10l** reacted with 1,3-dimethoxybenzene and 1,3,5-trimethoxybenzene in the presence of cationic catalyst **13** to provide **28a** and **28b**, respectively, with good *trans* selectivities (Scheme 5). These compounds are formed by an *exo* cyclization via intermediates of type **3** (Scheme 1), although the site of attachment of the nucleophile in the final products was unexpected. Thus, whereas the gold-catalyzed addition of methanol to **10l** gave the expected product **29** by cleavage of bond labeled ***b*** in intermediate **3**, probably via homoallylic cation **30**, isolation of **28a**−**b** shows that in these cases a 1,2-H shift occurs to form gold-stabilized allyl cation **31** prior to the attack by the nucleophile. Formation of **28a**−**b** can also be viewed as a 1,4-addition to a α,*β*-unsaturated gold carbene **31**, a type of reaction that we have found in the addition of carbon nucleophiles to related α,*β*-unsaturated gold carbenes formed by 1,2-acyl migration from propargyl carboxylates.[46]

Additions of Allylsilanes to 1,6-Enynes. Reactions between 1,6-enynes **10a**, **10d**, and **10m** and allyltrimethylsilane (**32a**) or methallyltrimethylsilane (**32b**) were carried out under different reaction conditions in the presence of additives such as *t*-BuOH, trifluoroethanol, TBAF, and water to facilitate the removal of the trimethylsilyl group in the proposed cationic intermediate. However, none of these additives led to satisfactory results. Consistent yields of adducts **33a**−**d** were obtained when the reaction was performed with nondried CH_2Cl_2 as solvent in open flasks (Table 4). The reaction of **10d** with **32a** gave **33b** along with **34** (5:1 mixture of diastereomers), which is the product of an intermolecular cyclopropanation[27] (Table 4, entry 2). The relative configuration of the major isomer of **34** was assigned based on comparison with related examples.[27]

The configuration of products **33a**−**d** was assigned by NOESY analysis of bicyclic compound **35** obtained by ring-closing metathesis of **33b** with the second generation Grubbs catalyst (eq 3). The preparation of **35** illustrates a facile, two-step synthesis of a rather strained 1,2,3,3a,4,5-hexahydropentalene.[61,62]

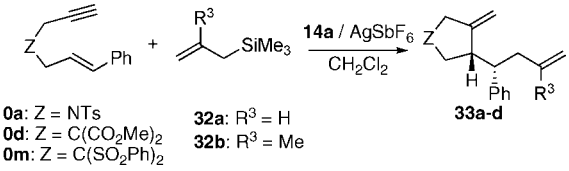


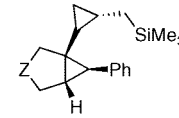
(3)

Additions of 1,3-Dicarbonyl Compounds to 1,6-Enynes. 1,3-Dicarbonyl compounds also react with 1,6-enynes in the presence of gold catalysts (Table 5). Two different types of

(61) Agosta, W. C.; Wolff, S. *J. Org. Chem.* **1975**, *40*, 1699–1701.
(62) Rogers, D. W.; McLafferty, F. J. *J. Phys. Chem. A* **2000**, *104*, 9356–9361.

TABLE 4. Au(I)-Catalyzed Addition of Allylsilanes to 1,6-Enynes[a]



entry	enyne	NuH	T (°C), time (h)	product (yield, %)
1	**10a**	**32b**	23, 90	**33a** (38)[b]
2	**10d**	**32a**	-20, 3	**33b** (44) +  **34** (28; 5:1) Z = C(CO2Me)2
3	**10m**	**32a**	23, 16	**33c** (62)
4	**10m**	**32b**	23, 16	**33d** (57)

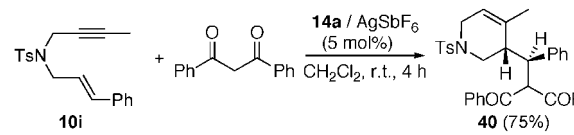
[a] Reactions carried out in CH_2Cl_2 (nondried) with 5 mol % catalyst. [b] 45% conversion.

adducts were obtained depending on the structure of the 1,3-dicarbonyl compound. Thus, open-chain 1,3-diketones afforded adducts **36a**−**d** (Table 5, entries 1−4), whereas cyclohexane-1,3-dione and 2-oxocyclohexanecarbaldehyde behave as O-nucleophiles to give adducts **37a**−**d** (Table 5, entries 5−8). Cyclopentane-1,3-dione, indane-1,3-dione, dimethyl malonate, and Meldrum acid where not suitable nucleophiles under these reaction conditions.

In the reaction of enyne **10a** with dibenzoylmethane, in addition to the expected adduct **36a**, cyclopropyl derivative **38a** was also formed (Table 6). Interestingly, site selectivity was strongly dependent on the ligands on gold. Thus, **36a** was the major product with **14a**/$AgSbF_6$ or **14b** (Table 6, entries 2−4), whereas **38a** was formed almost exclusively with the NHC-gold complexes (Table 6, entries 6−8). Enyne **10f** gave adduct **38b** with **14a**/$AgSbF_6$ (Table 6, entry 9).

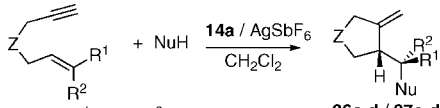
Although the reaction of enyne **10d** with dibenzoylmethane at −50 °C for just 30 min yielded **36c** (Table 5, entry 3, and Scheme 6), when the reaction mixture was warmed up to room temperature, bicyclic compound **39** was obtained as the only product. Formation of **39** from **10d** was monitored by ^1H NMR in CD_2Cl_2. After 30 min at −50 °C, **36c** had been formed as the only compound from **10d**. Upon warming to room temperature, compound **36c** slowly gave rise to **39**. Single crystals of **39** were obtained and its structure was confirmed by X-ray crystallography.[60] The molecular structure of **39** therefore allowed to establish the configuration of **36c**, which is consistent with that expected by stereospecific opening of an intermediate like **3** (see Scheme 1).

As shown before for the reaction of enynes with a nonterminal alkyne (Scheme 3), reaction of enyne **10i** with dibenzoylmethane in the presence of **14a**/$AgSbF_6$ as catalysts gave tetrahydropyridine **40**, the product of an *endo* cyclization (eq 4).



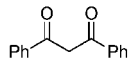
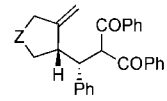
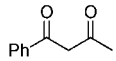
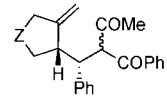
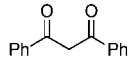
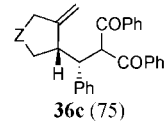
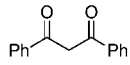
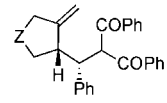
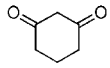
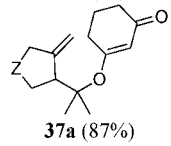
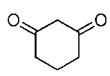
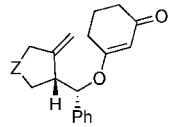
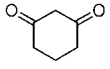
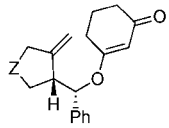
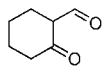
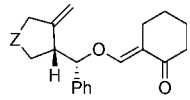
(4)

TABLE 5. Au(I)-Catalyzed Addition of 1,3-Dicarbonyl Compounds to 1,6-Enynes[a]



36a-d / 37a-d

10a: Z = NTs, R^1 = Ph, R^2 = H
10b: Z = C(CO_2Me)$_2$, R^1 = R^2 = Me
10d: Z = C(CO_2Me)$_2$, R^1 = Ph, R^2 = H
10m: Z = C(SO_2Ph)$_2$, R^1 = Ph, R^2 = H

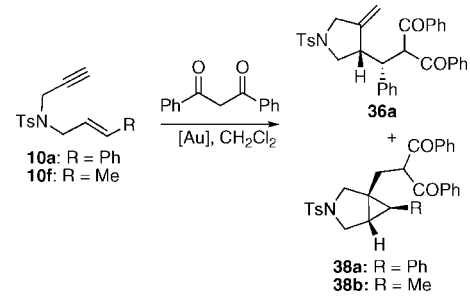
entry	enyne	NuH	T (°C), time (h)	product (yield, %)
1	**10a**		-50, 0.5	 **36a** (75)
2	**10a**		23, 1	 **36b** + **36b'** (1:1, 65%)
3	**10d**		-50, 0.5	 **36c** (75)
4	**10m**		23, 0.7	 **36d** (84)
5	**10b**		23, 2	 **37a** (87%)
6	**10d**		23, 4	 **37b** (65%)
7	**10m**		23, 4	 **37c** (85%)
8	**10m**		23, 1	 **37d** (83%)

[a] Reactions carried out in CH_2Cl_2 with 5 mol % catalyst.

1,7-Enyne **41**was readily prepared from adduct **36a** by standard propargylation of the enolate (Scheme 7). Gold-catalyzed reaction of **41** with **13** or **14a** /$AgSbF_6$ gave almost quantitatively furan **42**. This reaction presumably takes place by a gold-catalyzed attack of the ketone to the alkyne to give intermediate **43**,[63−65] followed by a debenzoylation, protodemetalation, and a final aromatization. Product **42** is the product of a formal regio- and stereoselective addition of 2-methyl-5-phenylfuran to enyne **10a**.

Derivatization of adduct **38a** was also briefly examined (Scheme 8). Thus, condensation of **38a** with hydrazine afforded pyrazole **44** in 88% yield. On the other hand, a retro-Claisen

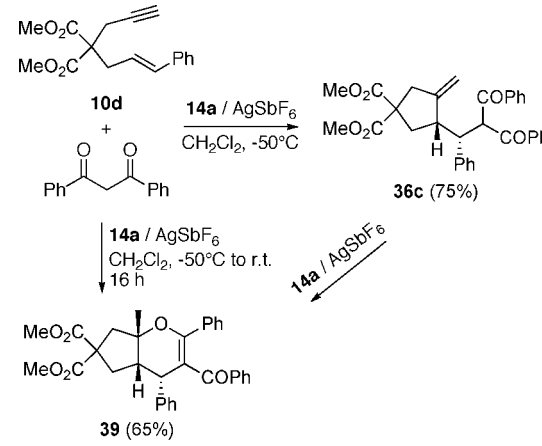
TABLE 6. Au(I)-Catalyzed Addition of 1,3-Dicarbonyl Compounds to 1,6-Enynes 10a and 10f[a]



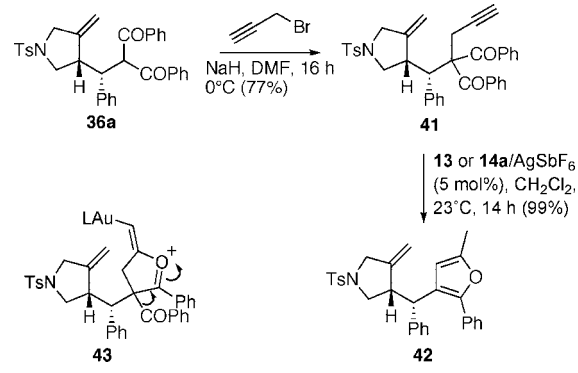
entry	enyne	[Au]	time (min)	product(s)	yield (%)
1	**10a**	**13**	30	**36a** + **38a** (33:67)	85
2[b]	**10a**	**14a**/$AgSbF_6$	30	**36a** + **38a** (95:5)	91
3	**10a**	**14a**/$AgSbF_6$	30	**36a** + **38a** (75:25)	77
4	**10a**	**14**b	20	**36a** + **38a** (77:23)	83
5	**10a**	**15a**/$AgSbF_6$	30	**36a** + **38a** (2:98)	99
6	**10a**	**15b**	20	**36a** + **38a** (<1:99)	86
7	**10a**	**15c**	20	**36a** + **38a** (<2:98)	87
8	**10a**	**15e**	30	**36a** + **38a** (4:96)	68
9[b]	**10f**	**14a**/$AgSbF_6$	120	**38b**	62

[a] Reactions carried out at room temperature in CH_2Cl_2 with 5 mol % catalyst. [b] Reaction carried out at −50 °C.

SCHEME 6



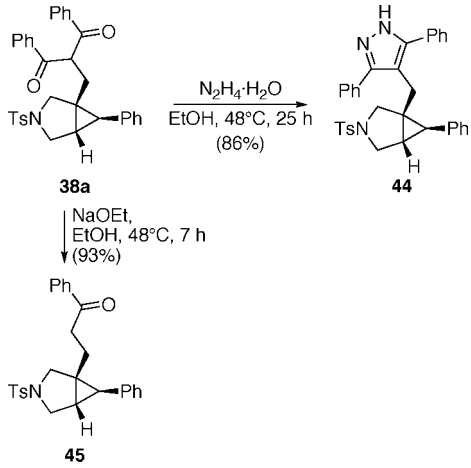
SCHEME 7



(63) (a) Hashmi, A. S. K.; Schwarz, L.; Choi, J. H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2285–2288. (b) Hashmi, A. S. K.; Sinha, P. *Adv. Synth. Catal.* **2004**, *346*, 432–438.

(64) (a) Yao, T.; Zhang, X.; Larock, R. C. *J. Am. Chem. Soc.* **2004**, *126*, 11164–1165. (b) Yao, T.; Zhang, X.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 7679–7685.

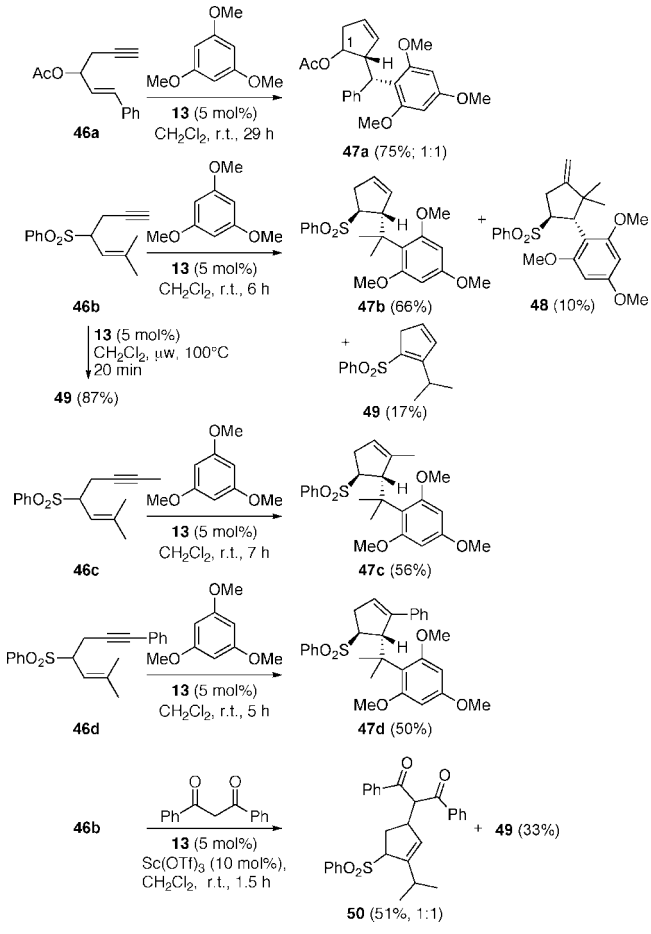
SCHEME 8



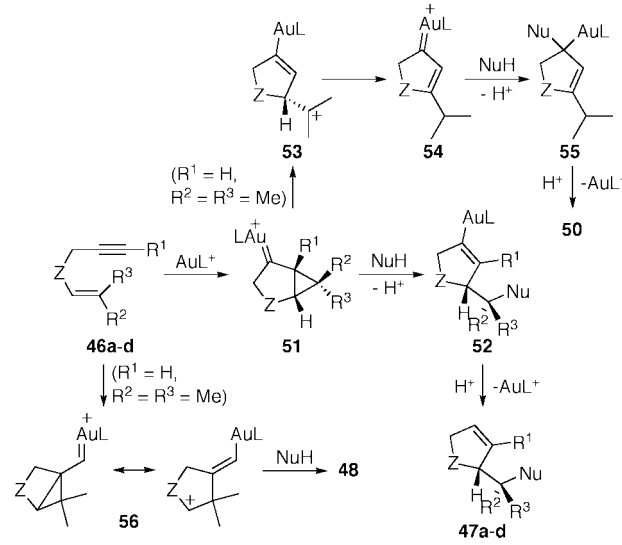
reaction on **38a** was cleanly achieved with NaOEt in EtOH to give ketone **45** in 93%.

Additions of C-Nucleophiles to 1,5-Enynes. 1,5-Enynes **46a**−**d** also react with carbon nucleophiles (Scheme 9). In these cases, cleaner reactions were obtained with cationic catalyst **13**. 5-*Endo-dig* cyclization was the major pathway in the reactions of **46a**−**d** with 1,3,5-trimethoxybenzene, which gave **47a**−**d** in 50−75% yield. Adducts **47b**−**d** were obtained as pure *trans* isomers, while **47a** was a 1:1 mixture of diastereomers. These adducts were shown to be epimers at C-1 by methanolysis (MeOH, K_2CO_3, 23 °C), which led to the selective cleavage of

SCHEME 9



SCHEME 10



the acetate of the *trans* isomer.[66] In the reaction of enyne **46b**, adduct **48**, and cyclopentadiene **49**, the product of an unexpected cycloisomerization, were also obtained as minor products. Adduct **48** is the product of a rare *exo* cyclization of a 1,5-enyne.[67] In the absence of nucleophiles, cyclopentadiene **49** was cleanly obtained from **46b**. In contrast with these results, addition of dibenzoylmethane to 1,5-enyne **46b** afforded **50** in 51% yield as a 1:1 mixture of *cis* and *trans* isomers, along with the product of cycloisomerization **49** (33% yield) (Scheme 9).

Formation of adducts **47a**−**d** can be rationalized through cyclopropyl gold carbene **51** formed in a 5-*endo-dig* cyclization.[36,68−70] Stereospecific nucleophilic attack gives alkenyl gold intermediate **52**, which is followed by protodemetalation (Scheme 10). Unexpected product **50** can arise by opening of **51** to **53**, followed by a 1,2-H shift to form **54**, an α,β-unsaturated gold carbene. Nucleophilic attack to give **55** and protodemetalation would give rise to **50**. Intermediate **54** can also explain the formation of the product of cycloisomerization **49**. We excluded the alternative formation of **50** by addition of dibenzoylmethane to cyclopentadiene **49** by performing the control experiment under the conditions of Scheme 9. Although a minor pathway, formation of **48** is interesting, and shows that an *exo* cyclization via **56** is also possible for 1,5-enynes.

Conclusions

Carbon nucleophiles, such as electron-rich arenes, heteroarenes, 1,3-dicarbonyl compounds, and allylsilanes, add to 1,6-enynes in the presence of cationic gold(I) catalysts to give products of reaction of the intermediate cyclopropyl gold carbenes at the cyclopropane or at the carbene carbons via *exo*

(65) (a) Shu, X.-Z.; Liu, X.-Y.; Xiao, H.-Q.; Ji, K.-G.; Guo, L.-N.; Qi, C.-Z.; Liang, Y.-M. *Adv. Synth. Catal.* **2007**, *349*, 2493–2498. (b) Liu, X.; Pan, Z.; Shu, X.; Duan, X.; Liang, Y. *Synlett* **2006**, 1962–1964. (c) Gold-catalyzed cyclizations of 5-hexynones and 6-heptynones: Jin, T.; Yamamoto, Y. *Org. Lett.* **2007**, *9*, 5259–5262.

(66) See Supporting Information for details.

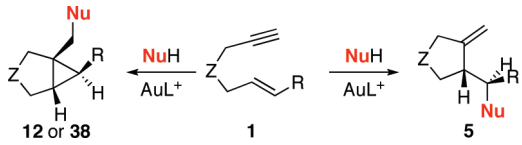
(67) Shibata, T.; Ueno, Y.; Kanda, K. *Synlett* **2006**, 411–414.

(68) Harrak, Y.; Blaszykowski, C.; Bernard, M.; Cariou, K.; Mainetti, E.; Mouriès, V.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. *J. Am. Chem. Soc.* **2004**, *126*, 8656–8657.

(69) Mamane, V.; Gress, T.; Krause, H.; Fürstner, A. *J. Am. Chem. Soc.* **2004**, *126*, 8654–8655.

(70) Luzung, M. R.; Markham, J. P.; Toste, F. D. *J. Am. Chem. Soc.* **2004**, *126*, 10858–10859.

SCHEME 11



cyclizations (Scheme 11). Whereas formation of products **5** correspond to a formal electrophilic addition of an alkyne and the nucleophile to the alkene, formation of adducts such as **12** (Table 1and eq 2) or **38** (Table 6) are more novel and further support the involvement of intermediates of type **3** in metal-catalyzed reactions of 1,6-enynes. In the examples examined in Tables 1 and 6, the regioselectivity (attack at the cyclopropane versus the carbene) depends to a certain extent on the gold catalysts, with NHC−gold complexes favoring nucleophilic attack at the carbene carbon leading to products of type **12** or **38**. However, the selection of the best catalyst for each particular enyne cyclization requires still some trial and error experimentation.

1,6-Enynes containing an internal alkyne react preferentially by the *endo* pathway, although the *exo* cyclization is followed when the alkenes is substituted at C-2. In certain cases, the cyclopropane vs carbene site-selectivity can be controlled by the ligand on gold. 1,5-Enynes react with carbon nucleophiles by the 5-*endo-dig* pathway, although an *exo* cyclization was also observed in one case as a minor process. In contrast to that found for 1,6-enynes, direct attack of the nucleophile to the carbene of the initial cyclopropyl gold carbene was not observed for 1,5-enynes. However, attack at the gold-carbene was observed on a α,β-unsaturated gold carbene formed from a 1,5-enyne.

These nucleophilic additions allow for the ready increase in molecular complexity starting from readily available starting materials under mild reaction conditions, leading to a variety of functionalized adducts, which can be useful in diversity-oriented synthesis. The new cationic gold(I) complexes **14b** and **15b−e**, which are stable solids at room temperature, are valuable catalysts that allow performing reactions of enynes in the absence of silver salts.

Experimental Section

Gold(I) Catalyst 14b. A solution of gold(I) chloro(tris(2,4-di-*tert*-butylphenyl)phosphite) (**14a**) (0.88 g, 1.00 mmol) and PhCN (0.11 mL, 1.1 mmol) in CH_2Cl_2 (11 mL) was added to a solution of $AgSbF_6$ (0.344 g, 1.00 mmol) in CH_2Cl_2 (6 mL). A white precipitate appeared immediately. After stirring for 5 min, the mixture was filtered (2 Teflon filters), evaporated and vacuum-dried (50 °C overnight). The cationic complex was obtained as a white, foamy solid (1.05 g, 88%): $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 90.88 (br s, 1P); $^1H\{^{31}P\}$ NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 7.9 Hz, 1H), 7.57 (t, J = 8.0 Hz, 2H), 7.47 (d, J = 2.5 Hz, 3H), 7.43 (d, J = 8.5 Hz, 3H), 7.27 (dd, J = 8.4, 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, PENDANT) δ 149.1 (C), 147.2 (d, J = 6.4 Hz, C), 139.3 (d, J = 7.2 Hz, C), 136.3 (CH), 134.5 (CH), 129.8 (CH), 125.9 (CH), 124.9 (CH), 120.8 (CN), 119.2 (d, J = 8.9 Hz, CH), 106.9 (C), 35.3 (C), 34.9 (C), 31.5 (CH_3), 30.7 (CH_3). Anal. Calcd for $C_{49}H_{68}AuF_6NO_3PSb \cdot 2H_2O$: C, 48.29; H, 5.95; N, 1.15. Found: C, 48.26; H, 5.63; N, 1.33.

Gold(I) Catalyst 15b. A solution of IMesAuCl (**15a**) (54.0 mg, 0.101 mmol) and 2,4,6-trimethoxybenzonitrile (19.4 mg, 0.101 mmol) in CH_2Cl_2 (1 mL) was added over solid $AgSbF_6$ (34.6 mg, 0.101 mmol) and stirred for 5 min. The mixture was filtered (HPLC Teflon filter) and the solid residue washed with CH_2Cl_2 (2 × 0.2 mL). The gold complex precipitated from the filtrate upon addition of Et_2O (5−8 mL). Filtration and air-drying furnished a bright white solid (67.2 mg, 72%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 2H), 7.07 (s, 4H), 6.10 (s, 2H), 3.90 (s, 3H), 3.87 (s, 6H), 2.39 (s, 6H), 2.13 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2 (C), 165.8 (C), 165.2 (C), 140.6 (C), 134.8 (C), 134.2 (C), 129.8 (CH), 124.1 (CH), 118.4 (C), 91.3 (CH), 78.2 (C), 56.8 (CH_3), 56.6 (CH_3), 21.3 (CH_3), 17.9 (CH_3); HRMS-ESI m/z calcd for $C_{31}H_{35}AuN_3O_3$ $[M]+$ 694.2344, found 694.2332. Anal. Calcd for $C_{31}H_{35}AuF_6N_3O_3Sb$: C, 40.02; H, 3.79; N, 4.52. Found: C, 39.89; H, 3.79; N, 4.89.

Gold(I) Catalyst 15c. A solution of IPrAuCl (497 mg, 0.800 mmol) and PhCN (0.09 mL, 0.9 mmol) in CH_2Cl_2 (10 mL) was added over a solution of $AgSbF_6$ (275 mg, 0.800 mmol) in CH_2Cl_2 (4 mL). A white precipitate appeared immediately. After stirring for 5 min, the mixture was filtered (double filter paper) and the solid was washed with CH_2Cl_2 (2 × 4 mL). The CH_2Cl_2 solution was evaporated to small volume (ca. 2 mL) and Et_2O (8 mL) was slowly added with shaking. The precipitate was decanted and washed with Et_2O (2 × 4 mL) and then vaccuum-dried. The cationic complex was obtained as a white, air-stable crystalline solid (699 mg, 94%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.82−7.77 (m, 3H), 7.60 (t, J = 7.9 Hz, 2H), 7.58 (t, J = 7.9 Hz, 2H), 7.43 (s, 2H), 7.38 (d, J = 7.8 Hz, 4H), 2.51 (septet, J = 7.0 Hz, 4H), 1.34 (d, J = 6.9 Hz, 6H), 1.27 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, PENDANT) δ 165.7 (C), 145.8 (C), 136.7 (CH), 133.9 (CH), 133.2 (C), 131.5 (CH), 130.1 (CH), 125.3 (CH), 124.8 (CH), 119.8 (C), 106.6 (C), 29.0 (CH), 24.9 (CH_3), 24.1 (CH_3). Anal. Calcd for $C_{34}H_{41}AuF_6N_3Sb$: C, 44.17; H, 4.47; N, 4.55. Found: C, 44.12; H, 4.43; N, 4.63.

General Procedure for the Addition of Arenes and Heteroarenes to 1,6-Enynes. A solution of the 1,6-enyne and the nucleophile was added to a solution of the corresponding gold catalyst in CH_2Cl_2. The reaction mixture was stirred at room temperature (unless stated otherwise) for the time indicated in Tables **1**−**3**, Schemes 3 and 4 and eq 2. The reaction mixture was filtered through silica gel with CH_2Cl_2, and the solvents were evaporated.

Dimethyl 5-((1*H*-Indol-3-yl)(phenyl)methyl)-4-phenylcyclohex-3-ene-1,1-dicarboxylate (20a). Compound **20a** was synthesized following the general procedure (Scheme 3), starting from **10h** (30 mg, 0.083 mmol) and indole (15 mg, 0.124 mmol). The residue was purified by chromatography (5:1 toluene/EtOAc) to give **20a** (29 mg, 73%) as a beige solid: mp 95−96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (br s, 1H), 7.28 (d, J = 8.4 Hz, 1H), 7.24−7.14 (m, 9H), 7.10−7.06 (m, 2H), 7.04 (dt, J = 1.7, 7.0 Hz, 1H), 6.76 (dt, J = 1.0, 7.1 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.75 (dt, J = 2.0, 6.0 Hz, 1H), 4.65 (d, J = 4.4 Hz, 1H), 3.85−3.77 (m, 1H), 3.70 (s, 3H), 3.67 (s, 3H), 2.94 (ddq, J = 1.4, 6.6, 17.1 Hz, 1H), 2.60 (ddd, J = 2.3, 3.8, 17.1 Hz, 1H), 2.41 (ddd, J = 2.7, 6.8, 13.9 Hz, 1H), 2.31 (dd, J = 10.6, 13.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 173.2 (C), 171.5 (C), 143.5 (C), 142.7 (C), 141.8 (C), 136.0 (C), 128.7 (CH), 128.3 (CH), 128.2 (CH), 126.9 (CH), 126.8 (CH), 126.1 (CH), 124.3 (CH), 122.7 (CH), 121.8 (CH), 120.4 (CH), 119.0 (CH), 114.4 (C), 110.7 (CH), 54.3 (C), 53.0 (CH_3), 52.8 (CH_3), 43.6 (CH), 41.0 (CH), 31.3 (CH_2), 30.5 (CH_2); HRMS-ESI m/z calcd for $C_{31}H_{29}NO_4Na$ $[M + Na]^+$ 502.1994, found 502.1998. Anal. Calcd for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.10; N, 2.92. Found: C, 77.46; H, 6.46; N, 2.99.

Dimethyl 3-Methylene-4-(1-phenylbut-3-enyl)cyclopentane-1,1-dicarboxylate (33b). Compound **33b** was synthesized following the general procedure (Table 4, entry 2) starting from **10d** (54 mg, 0.19 mmol) and allyltrimethylsilane (60 μL, 0.38 mmol). The residue was purified by chromatography (100:1 hexane/EtOAc) to give **33b** as a colorless oil (27 mg, 44%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.26 (m, 2H), 7.20−7.16 (m, 3H), 5.62−5.52 (m, 1H), 4.93 (dd, J = 16.9, 1.8 Hz, 1H), 4.88−4.85 (m, 2H), 4.47 (br s, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.94−2.78 (m, 4H), 2.56 (ddd, J = 13.2, 7.9, 1.6 Hz, 1H), 2.48−2.43 (m, 2H), 2.06 (dd, J = 13.1, 10.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 172.2 (C),

149.6 (C), 143.3 (C), 136.9 (CH), 128.7 (CH), 128.4 (CH), 126.5 (CH), 116.2 (CH_2), 108.9 (CH_2), 58.5 (C), 52.9 (CH_3), 49.4 (CH), 47.5 (CH), 42.3 (CH_2), 37.5 (CH_2), 36.3 (CH_2); HRMS-ESI *m/z* calcd for $C_{20}H_{24}O_4Na$ $[M + Na]^+$ 351.1572, found 351.1575. Anal. Calcd for $C_{20}H_{24}O_4 \cdot H_2O$: C, 69.34; H, 7.56. Found: C, 69.79; H, 7.71.

2-((4-Methylene-1-tosylpyrrolidin-3-yl)(phenyl)methyl)-1,3-diphenylpropane-1,3-dione (36a). Compound **36a** was synthesized following the general procedure (Table 5, entry 1), starting from **10a** (100 mg, 0.30 mmol) and dibenzoylmethane (206 mg, 0.92 mmol). The residue was purified by chromatography (10:1 hexane/EtOAc) to give **36a** (153 mg, 95%, with 5% of **38a**) as a white solid: mp 71−74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.7 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.57 (t, J = 7.7 Hz, 1H), 7.47−7.41 (m, 4H), 7.33−7.27 (m, 4H), 7.21 (d, J = 7.9 Hz, 2H), 7.07−6.99 (5H), 5.98 (d, J = 10.8 Hz, 1H), 5.01 (br s, 1H9, 4.78 (br s, 1H), 4.04 (dd, J = 4.8, 10.5 Hz, 1H), 3.57 (d, J = 13.6 Hz, 1H), 3.41−3.37 (m, 1H), 3.29−3.21 (m, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 194.7 (C), 145.7 (C), 143.6 (C), 137.4 (C), 137.2 (C), 136.8 (C), 134.1 (CH), 133.3 (CH), 132.8 (C), 129.7 (CH), 129.7 (CH), 129.2 (CH), 129.1 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 127.8 (CH), 127.3 (CH), 111.2 (CH_2), 62.4 (CH), 53.2 (CH_2), 52.2 (CH_2), 49.2 (CH), 45.5 (CH), 21.7 (CH_3); HRMS-ESI *m/z* calcd for $C_{34}H_{31}NO_4SNa$ $[M + Na]^+$ 572.1872, found 572.1871. Anal. Calcd for $C_{34}H_{31}NO_4S$: C, 74.29; H, 5.68; N, 2.55. Found: C, 74.08; H, 5.99; N, 2.60.

2-((6-Methyl-3-tosyl-3-azabicyclo[3.1.0]hexan-1-yl)methyl)-1,3-diphenylpropane-1,3-dione (38b). Compound **38b** was synthesized following the general procedure (Scheme 2) starting from **10f** (50 mg, 0.19 mmol) and dibenzoylmethane (85 mg, 0.38 mmol). The residue was purified by chromatography (10:1 hexane/EtOAc) to give **38b** (57 mg, 62%) as a white solid: mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, J = 7.3 Hz, 4H), 7.62−7.55 (m, 4H), 7.43 (dt, J = 7.5 Hz, 4H), 7.27 (t, J = 8.0 Hz, 2H), 5.20 (dd, J = 5.1, 8.1 Hz, 1H), 3.41 (d, J = 9.2 Hz, 1H), 3.37 (d, J = 9.3 Hz, 1H), 3.03 (d, J = 9.4 Hz, 1H), 2.86 (dd, J = 3.1, 9.1 Hz, 1H), 2.48 (dd, J = 8.2, 15.1 Hz, 1H), 2.43 (s, 3H), 2.21 (dd, J = 5.1, 15.1 Hz, 1H), 1.02 (d, J = 5.9 Hz, 3H), 0.89−0.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, DEPT) δ 195.7 (C), 195.4 (C), 143.5 (C), 136.3 (C), 135.9 (C), 133.9 (CH), 133.9 (CH), 133.6 (C), 129.7 (CH, 129.2 (CH), 129.1 (CH), 128.8 (CH), 128.7 (CH), 127.7 (CH), 56.5 (CH), 53.9 (CH_2), 50.3 (CH_2), 30.4 (C), 29.3 (CH), 28.68 (CH_2), 21.7 (CH_3), 19.7 (CH), 12.8 (CH_3); HRMS-ESI *m/z* calcd for $C_{29}H_{29}NO_4SNa$ $[M + Na]^+$ 510.1715, found 510.1702. Anal. Calcd for $C_{29}H_{29}NO_4S \cdot 0.5H_2O$: C, 70.14; H, 6.09; N, 2.82, S, 6.46. Found: C, 70.81; H, 6.23; N, 3.04; S, 6.14.

2-(Phenyl(2,4,6-trimethoxyphenyl)methyl)cyclopent-3-enyl Acetate (47a). Compound **47a** was synthesized following the general procedure for the reaction of 1,5-enynes with arenes, starting from **46a** (50 mg, 0.233 mmol) and 1,3,5-trimethoxybenzene (100 mg, 0.582 mmol) (Scheme 9). The residue was purified by column chromatography (6:1 hexane/EtOAc) to give **47a** (75 mg, 75% 1:0.7 *cis*/*trans*) as a yellow oil. *cis*-Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.24 (m, 2H), 7.12 (m, 1H), 6.05 (s, 2H), 5.71 (m, 1H), 5.58 (m, 1H), 5.27 (t, J = 6.5 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 4.30 (dm, J = 13.0 Hz, 1H), 3.80 (s, 6H), 3.74 (s, 3H), 2.67 (dm, J = 17.4 Hz, 1H), 2.35 (d, J = 17.4 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6 (C), 159.3 (C), 145.3 (C), 134.0 (CH), 129.0 (CH), 128.4 (CH), 127.6 (CH), 126.0 (CH), 105.6 (C), 91.6 (CH), 76.0 (CH), 55.5 (CH_3), 51.0 (CH), 41.1 (CH_2), 40.5 (CH), 21.0 (CH_3). *trans*-Diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.25 (m, 2H), 7.11 (m, 1H), 6.03 (s, 2H), 5.64 (m, 2H), 4.98 (m, 1H), 4.30 (d, J = 12.2 Hz, 1H), 4.13 (d, J = 11.3 Hz, 1H),3.74 (s, 3H), 3.73 (s, 6H), 2.80 (dm, J = 17.6 Hz, 1H), 2.22 (d, J = 17.6 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0 (C), 158.7 (C), 144.5 (C), 134.0 (CH), 129.2 (CH), 128.0 (CH), 128.0 (CH), 125.8 (CH), 113.0 (C), 91.5 (CH), 79.4 (CH), 55.9 (CH_3), 51.6 (CH), 44.2 (CH), 39.6 (CH_2), 21.4 (CH_3); HRMS-ESI *m/z* calcd for $C_{23}H_{26}O_5Na$ $[M + Na]^+$ 405.1678, found 405.1677.

1,3,5-Trimethoxy-2-(2-(2-methyl-5-(phenylsulfonyl)cyclopent-2-enyl)propan-2-yl)benzene (47c). Compound **47c** was synthesized following the general procedure for the reaction of 1,5-enynes with arenes, starting from **46c** (40 mg, 0.152 mmol) and 1,3,5-trimethoxybenzene (128 mg, 0.763mmol). The residue was purified by column chromatography (8:1 hexane/EtOAc) to give compound **47c** as a yellow solid (37.0 mg, 56%): mp 150−151 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dm, J = 7.7 Hz, 2H), 7.60 (m, 1H), 7.48 (m, 1H), 6.11 (s, 2H), 5.26 (m, 1H), 4.14 (s, 1H), 3.84 (s, 3H), 3.80 (s, 6H), 3.70 (dt, J = 8.3, 1.8 Hz, 1H), 2.78 (dm, J = 18.0 Hz, 1H), 2.69−2.61 (m, 1H), 1.45 (s, 3H), 1.44 (s, 3H), 1.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (C), 159.1 (C), 141.9 (C), 138.3 (C), 132.9 (CH), 128.7 (CH), 128.6 (CH), 124.7 (CH), 116.7 (C), 92.5 (CH), 67.1 (CH), 56.2 (CH_3), 55.7 (CH_3), 55.0 (CH), 42.7 (C), 33.6 (CH_2), 28.2 (CH_3), 27.9 (CH_3), 17.0 (CH_3); HRMS-ESI *m/z* calcd for $C_{24}H_{30}O_5NaS$ $[M + Na]^+$ 453.1712, found 453.1701.

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Supporting Information Available: Experimental details, characterization data, and X-ray diffraction data, including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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