Cyclization

DOI: 10.1002/ange.200605041

Intramolecular Carbostannylation of Alkynes Catalyzed by Silver(I) Species**

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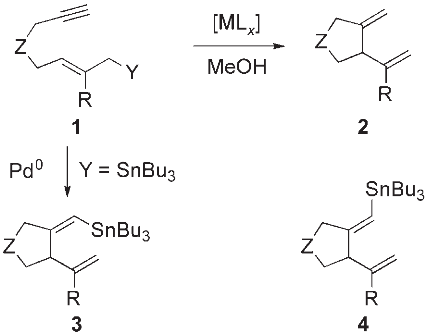
Cyclizations of α,ω-enynes catalyzed by transition- or main-group metals provide highly functionalized carbo- and heterocycles under mild conditions in atom-economical processes.[1] We have previously shown that reactions of allylsilanes or allylstannanes **1** with different metal catalysts proceed to form hetero- or carbocycles **2** (Scheme 1).[2,3] The best results were obtained by using $PtCl_2$ or $[Pt(MeCN)_2Cl_2]$ as the catalyst and methanol or acetone as the solvent. The reaction proceeds by *exo* attack of the allyl nucleophile to the alkyne to form carbocycles with five- or six-membered rings. Interestingly, when the reactions of the substrates **1** ($Y = SnBu_3$) were catalyzed by palladium(0) complexes, stannyl derivatives **3** were obtained stereoselectively in a process that involves a very different mechanism to that seen in the oxidative addition of the allylstannane to Pd^0.[4] Stannanes **4** have been obtained, along with the *Z* isomers (ca. 9:1 *E*/*Z* selectivity), in the radical cyclization of substrates **1** performed in the presence of azobisisobutyronitrile (5 mol %) and Bu_3SnH (10 mol %).[5] Conversely, when the reaction of **1** was promoted by $GaCl_3$ (1 equiv), products **2** were obtained exclusively, whereas a similar reaction with $InCl_3$ (1 equiv) led to **2** as the major products along with mixtures of **3** and **4** in very low yields.[6–8]



Scheme 1. Cyclizations of allylsilanes or allylstannanes **1** with different metal catalysts. $M = Pt^{II}, Pd^{II}, Cu^{I}, Ru^{II}, Ag^{I}, Au^{III}$; L = ligand; $Y = SiMe_3, SnBu_3$; $Z = C(CO_2Me)_2, C(SO_2Ph)_2, C(CH_2OR)_2$.

Reactions of simple 1,6-enynes with platinum(II)[9] or gold(I)[10] species have been shown to proceed through cyclopropyl metal–carbene intermediates. In many of the gold(I)-catalyzed cyclizations of enynes and other alkynes, a silver salt such as AgOTf, $AgBF_4$, or $AgSbF_6$ (Tf = trifluoromethanesulfonyl) is used to generate in situ a cationic gold(I) species from [AuCl(L)] complexes (L = phosphine or a related ligand).[10–12] The silver salt has been shown to be catalytically inert for many of these processes,[10,11] although in a few instances silver(I) species can catalyze cyclization reactions.[13] Herein we report that, in contrast to gold(I) complexes, silver(I) salts and complexes are catalytically active in the cyclization of **1** and afford stannanes **4** as the exclusive stereoisomers. We also report the first examples of skeletal rearrangements and intramolecular cyclopropanation reactions of 1,6-enynes catalyzed by silver(I) complexes, which suggest that metal–carbene intermediates are also involved in these silver(I)-catalyzed transformations.[14,15]

When the reaction of **1a** with AgOTf (10 mol %) was carried out in toluene at 70 °C, stannane **4a** was obtained in 29 % yield, along with **2a** (Table 1, entry 1). The use of $AgBF_4$ led to **4a** and dimer **5** in low yield, whereas complex **6** was ineffective (Table 1, entries 2 and 3). Remarkably, $AgSbF_6$ or $AgSbF_6/PPh_3$ led to a very fast cyclization of (*Z*)-**1a**, and yielded **4a** (83 %) and **2a** (5–12 %) (Table 1, entries 4 and 5). The reaction also proceeded satisfactorily in the presence of a variety of silver(I) complexes [Ag(OTf)L] bearing phosphines as the ligands ($L = PPh_3$, $(o\text{-tolyl})_3P$, $(\text{naphthyl})_3P$, 2-biphenyldicyclohexylphosphine) or $[(AgOTf)_2(L\text{–}L)]$ (L–L = ethane-1,2-diylbis(diphenylphosphane) (dppe), 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene (xantphos), 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl (binap)),[16,17] which gave **4a** in 85–91 % yield. Consistent results were obtained with the preformed $[\{Ag(OTf)(PPh_3)\}_3]$ complex[18] as catalyst (Table 1, entry 6). No reaction was observed when the ratio of L to Ag was higher than 1:1.

The reaction of substrates similar to **1a** proceeds satisfactorily regardless of their *E*/*Z* configuration. For example, (*E*)-**1a** (Table 2, entry 1) reacts similarly to (*Z*)-**1a**, and both (*E*)- and (*Z*)-**1d** gave **4d** in 90–91 % yields after 30 minutes (Table 2, entries 4 and 5). This silver(I)-catalyzed reaction tolerates protection of the hydroxy groups with acetate and *tert*-butyldiphenylsilyl (TBDPS) groups (Table 2, entries 6

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[**] We are grateful to the MEC (project CTQ2004-02869 and Consolider Ingenio 2010, Grant CSD2006-0003), the UAM (predoctoral fellowship to S.P.), the AGAUR (2005 SGR 00993), and the ICIQ Foundation for financial support. We also thank E. Escudero-Adán and Dr. J. Benet-Buchholz (X-ray diffraction unit, ICIQ) for the determination of the structure of complex **8**.

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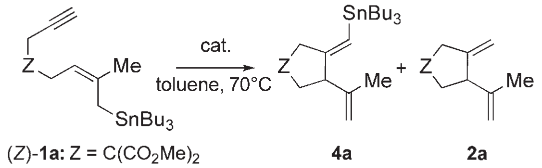
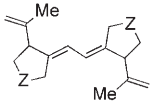
Table 1: Silver(I)-catalyzed carbostannylation of (Z)-**1a**.



Entry	Cat. (mol %)	t	Yield of **4a** [%]	Yield of **2a** [%]
1[a]	AgOTf (10)	12 h	29	24
2[a]	$AgBF_4$ (10)	12 h	29	–[b]
3	**6** (5)	12 h	–	–
4	$AgSbF_6$ (10)	1 min	83	12
5	$AgSbF_6$ (10) + PPh_3 (10)	1 min	83	5
6	[Ag OTf(PPh_3)]$_3$ (3)	30 min	90	–

[a] Conversion of 85 %. [b] Dimer **5** (7 %) was obtained. Tf = trifluoromethanesulfonyl, Mes = 2,4,6-trimethylphenyl.



5: Z = $C(CO_2Me)_2$

6 =

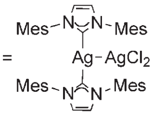
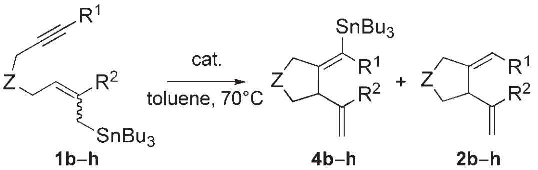
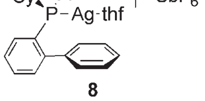


Table 2: Silver(I)-catalyzed carbostannylation of **1b–h**.[a]



Entry	Substrate	t [h]	Product(s) (yields, [%])
1	(*E*)-**1a**: Z = $C(CO_2Me)_2$, R^1 = H, R^2 = Me	0.5	**4a** (87) + **2a** (3)
2	(*E*)-**1b**: Z = $C(CO_2Me)_2$, R^1 = R^2 = H	5	**4b** (71) + **2b** (6)
3	(*Z*)-**1c**: Z = $C(SO_2Ph)_2$, R^1 = R^2 = H	3.5	**4c** (72) + **2c** (9)
4	(*E*)-**1d**: Z = $C(SO_2Ph)_2$, R^1 = H, R^2 = Me	0.5	**4d** (90)
5	(*Z*)-**1d**: Z = $C(SO_2Ph)_2$, R^1 = H, R^2 = Me	0.5	**4d** (91)
6	(*E*)-**1e**: Z = $C(CH_2OAc)_2$, R^1 = R^2 = H	2.5	**4e** (69) + **2e** (12)
7	(*E*)-**1f**: Z = $C(CH_2OTBDPS)_2$, R^1 = R^2 = H	2	**4f** (93)
8	(*E*)-**1g**: Z = $C(CH_2OH)_2$, R^1 = R^2 = H	0.2	**4g** (31) + **2g** (11) + **7** (30)
9[b]	(*E*)-**1h**: Z = $C(SO_2Ph)_2$, R^1 = Ph, R^2 = Me	3	**4h** (50) + **2h** (50)

[a] Reaction with [AgOTf(PPh_3)]$_3$ (3 mol %) in toluene at 70 °C. [b] Reaction carried out with catalyst **8** (10 mol %) in toluene at 90 °C. Cy = cyclohexyl.



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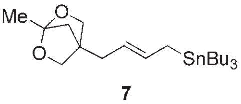

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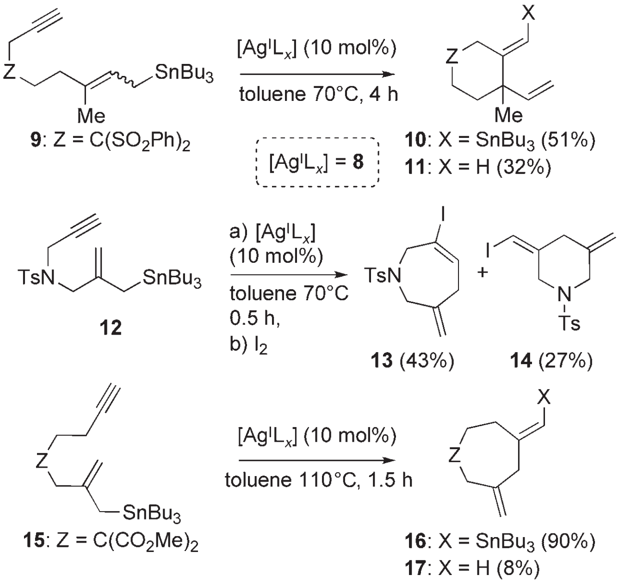
and 7). The free hydroxy groups in substrate **1g** compete in the reaction with the alkyne, leading to a 1:1 ratio of bicyclic acetal **7** and stannane **4g** (Table 2, entry 8). A similar cyclization of diols with alkynes has been reported by Genêt and co-workers with gold(I) catalysts.[19] Substrate **1h**, which is substituted at the alkyne with a phenyl group, reacted with the catalyst [Ag(2-biphenyldicyclohexylphosphine)(thf)]SbF_6 (**8**)[20] to give a 1:1 ratio of **4h** and **2h** in quantitative yield. In this case, extensive destannylation of **4h** was observed. The structure of the cationic silver(I) complex **8** is similar to the related gold(I) complexes.[10c,20,21] In contrast, the radical reaction of (*E*)-**1h** reported by Hosomi and co-workers occurred exclusively by a 6-*endo-dig* pathway.[5] Alkenyl stannanes **4a–h** were obtained as single stereoisomers, whose configuration was assigned as *E* by comparison of their NMR spectra with those of the *Z* isomers **3**[4] as well as by reaction of **4c** with DCl in CD_3OD.[22] Reaction of the analogous allylsilanes under these conditions proceeded rather sluggishly to give only products **2**.

The reaction can be extended for the preparation of six- and seven-membered-ring compounds (Scheme 2). For these cyclizations, complex **8** was found to be the best catalyst (Figure 1). Substrate **9**, which has an additional methylene group at the stannane chain, afforded the six-membered-ring derivatives **10** and **11**. A 7-*endo-dig* cyclization was the predominant pathway in the reaction of tosylamide **12,** which afforded heterocycle **13** as the major product after treatment of the mixture of stannanes with I_2. A seven-membered ring **16** was also obtained in the 7-*exo-dig* cyclization of **15**.



Scheme 2. Silver(I)-catalyzed carbostannylations for the synthesis of six- and seven-membered-ring systems. Ts = toluene-4-sulfonyl.

Although sterically hindered, the alkenylstannanes **4a** and **4d** undergo Stille reactions with iodobenzene in the presence of [Pd(PPh_3)$_4$] (10 mol %), CuI (10 mol %), and CsF (4 equiv) in THF[23] to give stereospecifically **18** and **19**, respectively (Scheme 3). Compound **19** is the *E* diastereomer of **2h** (Table 2, entry 9), thus providing further confirmation of the configuration assigned for **4a–h**.

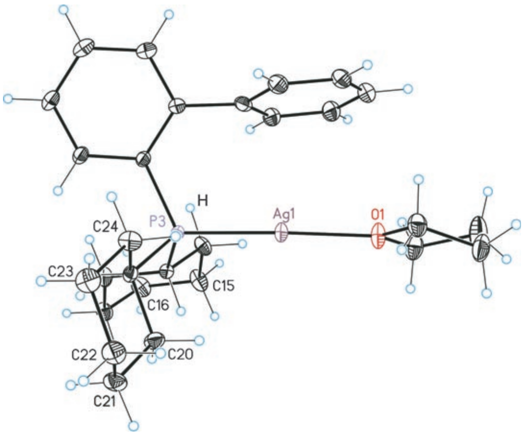
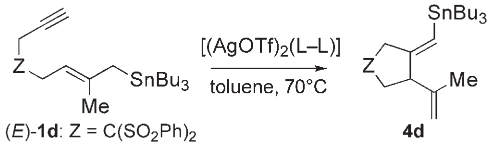


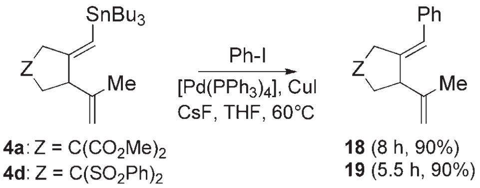
Figure 1. X-ray crystal structure of the cation of silver(I) complex **8**.

Table 3: Enantioselective cyclization of (*E*)-**1d**.[a]



Entry	Catalyst	*T* [°C]	Yield [%]	e.r.[b]
1	$[(AgSbF_6)_2$Tol-binap]	30	57	50:50
2	$[(AgOTf)_2$binap]	70	87	86:13
3	$[(AgOTf)_2$Tol-binap]	70	87	87:12
4	$[(AgOTf)_2$Tol-binap]	50	91	89:11
5[c]	$[(AgOTf)_2$Tol-binap]	30	74	89:11

[a] Reactions with 5 mol% catalyst for 30 min. [b] Determined by HPLC (Daicel Chiralpack AD column). [c] Reaction time: 100 min. Tol-binap = 2,2′-bis(di-*p*-tolylphosphanyl)-l,l′-binaphthyl.



Scheme 3. Stille coupling reactions of stannanes **4a** and **4d**.

A similar reaction of substrates **1** with gold(I) catalysts[10] led only to destannylated products **2**. For example, reaction of (*Z*)-**1c** with [AuCl(PPh$_3$)] (5 mol%) was very sluggish and led only to **2c** in around 20% yield (toluene, 70°C, 14 h). Conversely, reaction of (*Z*)-**1c** with the cationic complex $[Au\{P[C_6H_4(o\text{-}Ph)](tBu)_2\}\{NCMe\}]SbF_6$[20,21] was complete in 30 minutes at 70°C to give **2c** in 97% yield. Reaction of (*Z*)-**1a** with Lewis acids such as Et$_2$AlCl and ZrCl$_4$ (toluene, −78 to 0°C, 12–24 h) led only to the partial destannylation of the starting material.[24]

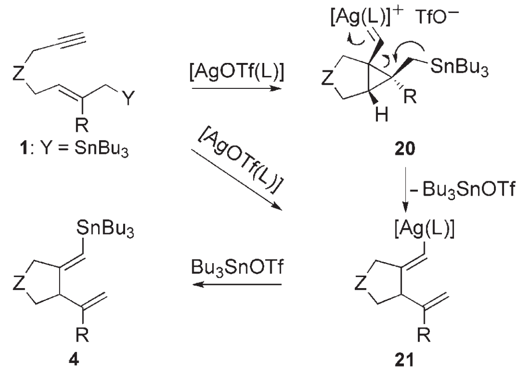
The enantioselective cyclization of allylstannanes with alkynes was examined with substrate (*E*)-**1d** using the complexes $[(AgOTf)_2$(L–L)] with chiral bidentate ligands.[25] Bidentate ligands such us (+)-(2S,3S)-bis-(diphenylphosphino)bicyclo[2,2,llhept-5-ene ((+)-(S,S)-norphos), (−)-(*R*,*R*)-*P*,*P*’-[2,2-dimethyl-1,3-dioxolane-4,5-bis(methylene)]bis(diphenylphosphane) ((−)-(*R*,*R*)-diop), (*R*,*R*)-l-benzyl-3,4-bis-(diphenylphosphino)pyrrolidine ((*R*,*R*)-deguphos), (2*S*,4*S*)-*N*-tert-butoxycarbonyl-4-diphenylphospanyl-2-diphenylphosphanylmethylpyrrolidine ((2*S*,4*S*)-bppm) in combination with AgOTf (20 mol% of AgOTf, 9% mol of ligand) gave low enantiomeric ratios (e.r.), ranging from 53:47 to 63:37. The best results were obtained when isolated complexes $[(AgOTf)_2$(*R*)-binap] or $[(AgOTf)_2$(*R*)-Tol-binap][16b] were employed (Table 3). The nature of the counteranion plays a crucial role; for example, no enantioselectivity was achieved with complex $[(AgSbF_6)_2$(*R*)-Tol-binap] (Table 3, entry 1), but use of the OTf, which is a better coordinating anion, led to a 89:11 e.r. under the same reaction conditions (Table 3, entry 5). The corresponding complex formed between (*R*)-Tol-binap and AgPF$_6$ led to lower enantioselectivity (68:32 e.r.), whereas with AgBF$_4$, only the destannylated product **2a** was obtained. Reaction of (*Z*)-**1d** under the same conditions as in entry 4 led to stannane **4d** with 80:19 e.r.

Yamamoto and co-workers have suggested that a transmetalation between the silver(I) complex and allyltrimethoxysilanes may take place.[16a–c] However, in the reactions of allylstannanes with aldehydes, the silver(I) complex was proposed to act as a chiral Lewis acid rather than forming an allyl–silver(I) species.[16d] A transmetalation of the allylstannane with silver(I) would lead to the products **3**, after insertion of the allyl–silver(I) species into the alkyne followed by reductive elimination. To exclude this pathway, we prepared the *Z* isomer of **1a** from the cyclization of (*E*)-**1d** with [Pd$_2$(dba)$_3$·dba] (dba = *trans*,*trans*-dibenzylideneacetone) as the catalyst.[4] However, no isomerization of this substrate into **4d** was observed after the substrate was heated with complex **8** (10 mol%) in toluene at 70°C for 14 h.

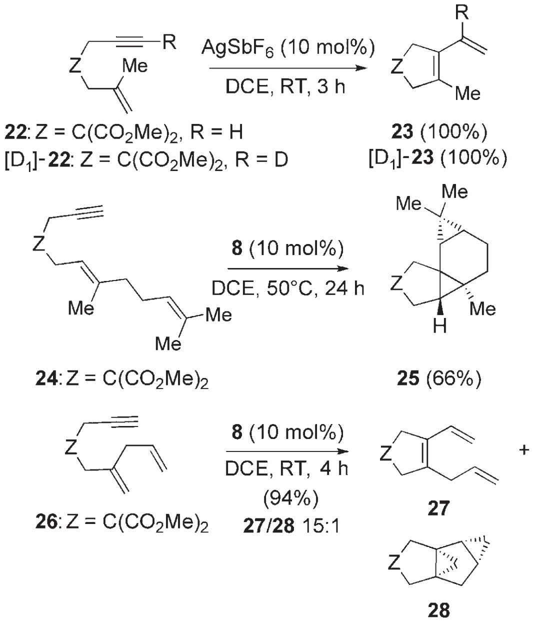
The formation of silver(I)–acetylide complexes is not a major pathway under these reaction conditions.[26] Instead, the isolation of the products **4** is consistent with a mechanism in which the silver(I) complex selectively activates the alkyne of **1** to form the cyclopropyl carbene–silver(I) complex **20**, followed by cleavage of the cyclopropane to form the alkenyl–silver(I) complex **21** (Scheme 4).[2,3,10] Reaction of **21** with Bu$_3$SnOTf (or a similar electrophile in the case of AgSbF$_6$ or catalyst **8**) gives the stannanes **4**. Alternatively, formation of **21** might take place in a single step as shown in Scheme 4.

To support the formation of silver carbenes in these cyclizations, we examined the reactions of simple enynes with silver(I) catalysts (Scheme 5). Thus, **22** afforded in quantitative yield diene **23**, the product of a skeletal rearrangement with a single cleavage, as shown in the reaction of deuterated substrate [D$_1$]-**22** to give [D$_1$]-**23**.[10c] Dienyne **24** led to **25** in 66% yield, along with the skeletal-rearrangement products as minor compounds. Tetracycle **25** is identical to that obtained before using gold(I) species as the catalyst.[10d] Conversely, **26** gave rise to a 15:1 mixture of the skeletal-rearrangement derivative **27** and the product of an intramolecular cyclopropanation **28** (94% yield, Scheme 5).[27]

In summary, we have reported the first intramolecular carbostannylation of alkynes catalyzed by silver(I) species, which gave (*E*)-alkenylstannanes stereoselectively as single isomers in a reaction that appears to be mechanistically



Scheme 4. Mechanistic hypotheses for the silver(I)-catalyzed carbostannylation of alkynes.



Scheme 5. Skeletal-rearrangement and cyclopropanation reactions catalyzed by silver(I). DCE = 1,2-dichloroethane.

similar to that of the reaction of enynes with other electrophilic transition-metal complexes. In this case, the alkenyl–silver(I) intermediate is able to react with the tin electrophile generated in situ, thus leading to stannanes of structure **4** with total control of the stereoselectivity. A 78% *ee* has been achieved by using $[(AgOTf)_2(R)$-Tol-binap] as the catalyst. We have also reported the first examples of skeletal rearrangements and intramolecular cyclopropanation reactions of 1,6-enynes catalyzed by silver(I) species, an observation that indicates that silver–carbene species are probably involved in these reactions.

Received: December 13, 2006

Keywords: cyclization · enantioselectivity · enynes · silver · stannanes

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