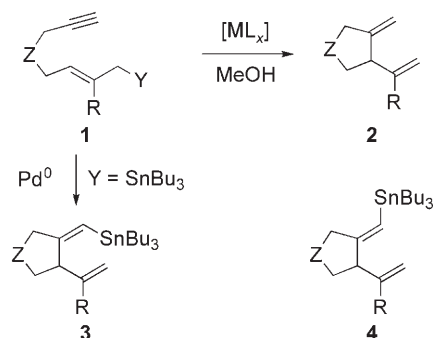


Intramolecular Carbostannylation of Alkynes Catalyzed by Silver(I) Species**

Susana Porcel and Antonio M. Echavarren*

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



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 = SiMe₃, SnBu₃; Z = C(CO₂Me)₂, C(SO₂Ph)₂, C(CH₂OR)₂.

best results were obtained by using PtCl₂ or [Pt(MeCN)₂Cl₂] 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 = SnBu₃) 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 Pd⁰.^[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 Bu₃SnH (10 mol %).^[5] Conversely, when the reaction of **1** was promoted by GaCl₃ (1 equiv), products **2** were obtained exclusively, whereas a similar reaction with InCl₃ (1 equiv) led to **2** as the major products along with mixtures of **3** and **4** in very low yields.^[6–8]

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, AgBF₄, or AgSbF₆ (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 AgBF₄ led to **4a** and dimer **5** in low yield, whereas complex **6** was ineffective (Table 1, entries 2 and 3). Remarkably, AgSbF₆ or AgSbF₆/PPh₃ 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 = PPh₃, (*o*-tolyl)₃P, (naphthyl)₃P, 2-biphenyldicyclohexylphosphine) or [(AgOTf)₂(L–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)(PPh₃)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.

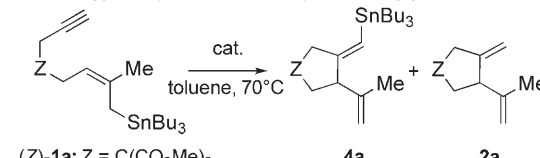
The reaction of substrates similar to **1a** proceeds satisfactorily regardless of their *E/Z* configuration. For example, (*E*)-**1a** (Table 2, entry 1) reacts similarly to (*Z*)-**1a**, and both (*E*)- and (*Z*)-**1d** gave **4d** in 90–91 % yields after 30 minutes (Table 2, entries 4 and 5). This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

[*] S. Porcel, Prof. Dr. A. M. Echavarren
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
and
Department of Organic Chemistry
Universidad Autónoma de Madrid
Cantoblanco, 28049 Madrid (Spain)
Fax: (+34) 97-792-0225
E-mail: aechavarren@iciq.es

[**] 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**.

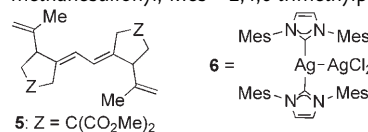
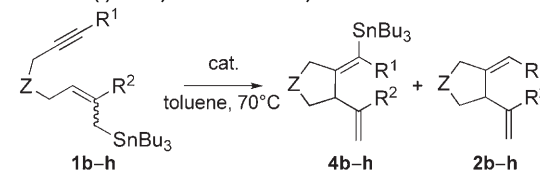
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Table 1: Silver(I)-catalyzed carbostannylation of (Z)-**1a**.



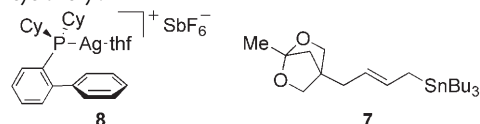
Entry	Cat. (mol %)	t	Yield of 4a [%]	Yield of 2a [%]
1 ^[a]	AgOTf (10)	12 h	29	24
2 ^[a]	AgBF ₄ (10)	12 h	29	— ^[b]
3	6 (5)	12 h	—	—
4	AgSbF ₆ (10)	1 min	83	12
5	AgSbF ₆ (10) + PPh ₃ (10)	1 min	83	5
6	[Ag OTf(PPh ₃) ₃] (3)	30 min	90	—

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


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


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

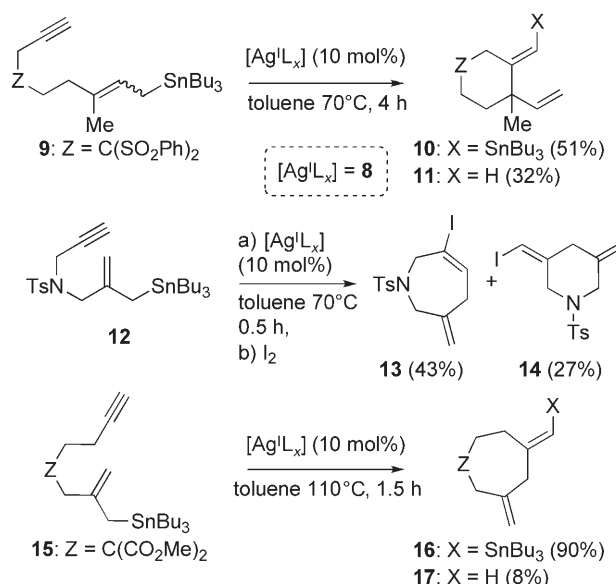
[a] Reaction with [AgOTf(PPh₃)₃] (3 mol %) in toluene at 70 °C. [b] Reaction carried out with catalyst **8** (10 mol %) in toluene at 90 °C. Cy = cyclohexyl.



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)]SbF₆ (**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 DCI in CD₃OD.^[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


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

(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 I₂. A seven-membered ring **16** was also obtained in the 7-exo-dig cyclization of **15**.

Although sterically hindered, the alkenylstannanes **4a** and **4d** undergo Stille reactions with iodobenzene in the presence of [Pd(PPh₃)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**.

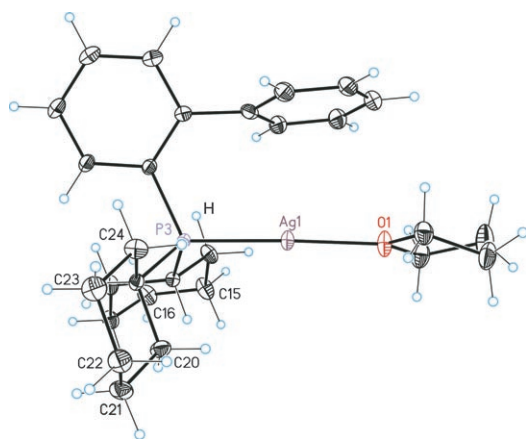
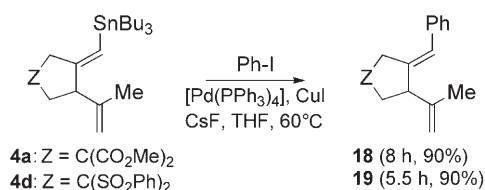


Figure 1. X-ray crystal structure of the cation of silver(I) complex **8**.



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 $[\text{AuCl}(\text{PPh}_3)]$ (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 $[\text{Au}[\text{P}[\text{C}_6\text{H}_4(o\text{-Ph})](\text{tBu})_2]\text{SbF}_6$ ^[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_2AlCl 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 $[(\text{AgOTf})_2(\text{L-L})]$ with chiral bidentate ligands.^[25] Bidentate ligands such as (+)-(2*S*,3*S*)-bis-(diphenylphosphino)bicyclo[2.2.1]hept-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)-1-benzyl-3,4-bis-(diphenylphosphino)pyrrolidine ((R,R)-deguphos), (2*S*,4*S*)-*N*-tert-butoxycarbonyl-4-diphenylphosphanyl-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 $[(\text{AgOTf})_2(\text{R})\text{-binap}]$ or $[(\text{AgOTf})_2(\text{R})\text{-Tol-binap}]$ ^[16b] were employed (Table 3). The nature of the counteranion plays a crucial role; for example, no enantioselectivity was achieved with complex $[(\text{AgSbF}_6)_2(\text{R})\text{-Tol-binap}]$ (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

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

Entry	Catalyst	T [°C]	Yield [%]	e.r. ^[b]
1	$[(\text{AgSbF}_6)_2\text{Tol-binap}]$	30	57	50:50
2	$[(\text{AgOTf})_2\text{binap}]$	70	87	86:13
3	$[(\text{AgOTf})_2\text{Tol-binap}]$	70	87	87:12
4	$[(\text{AgOTf})_2\text{Tol-binap}]$	50	91	89:11
5 ^[c]	$[(\text{AgOTf})_2\text{Tol-binap}]$	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)-1,1'-binaphthyl.

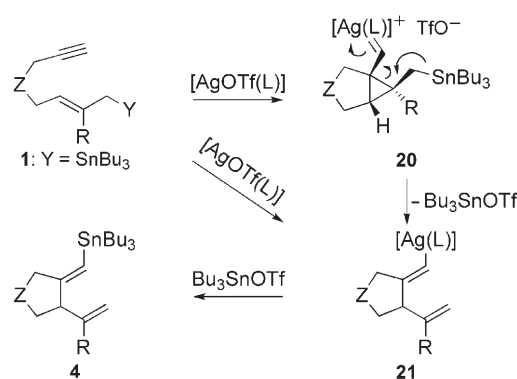
product **2a** was obtained. Reaction of (*Z*)-**1d** under the same conditions as in entry 4 led to stannane **4d** with 80:19 e.r.

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 $[\text{Pd}_2(\text{dba})_3\text{dba}]$ (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.

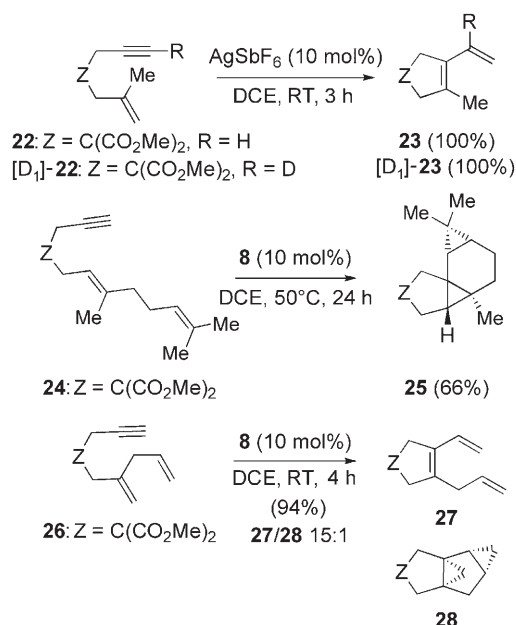
The formation of silver(I)–acetylide complexes is not a major pathway under these reaction conditions.^[26] Instead, the isolation of the products **4** is consistent with a mechanism in which the silver(I) complex selectively activates the alkyne of **1** to form the cyclopropyl carbene–silver(I) complex **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_3SnOTf (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 $[\text{D}_1]\text{-22}$ to give $[\text{D}_1]\text{-23}$.^[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
Published online: March 6, 2007

Keywords: cyclization · enantioselectivity · enynes · silver · stannanes

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