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Gold-Catalyzed Synthesis of Bicyclo[4.3.0]nonadiene Derivatives via Tandem 6-*endo*-*dig*/Nazarov Cyclization of 1,6-Allenynes

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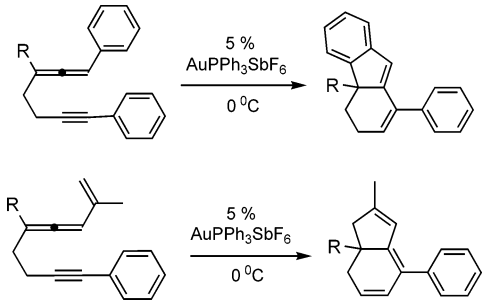
Received April 16, 2007



Catalytic cyclization of 1,6-allenynes was achieved by $AuPPh_3SbF_6$ (5 mol %) in cold CH_2Cl_2 (0 °C, 0.5−4 h) to form bicyclo[4.3.0]nonadiene products; this cyclization proceeded more efficiently for a substrate bearing R = alkyl (yields >70%). We propose a reaction mechanism involving a 6-*endo*-*dig* cyclization of Au(I)-π-alkyne, followed by Nazarov cyclization.

Introduction

Metal-catalyzed transformation of acyclic molecules into bicyclic carbocyclic species is synthetically useful because bioactive compounds typically comprise polycyclic structural frameworks.[1] Transition metal-catalyzed cycloisomerization of allenynes provides rapid and efficient access to carbocyclic compounds. Although considerable interest has been growing rapidly in this area,[2−5] literature reports focused exclusively on formation of products bearing one carbocyclic ring.[2−3] Malacria[2] and Brummond[3] reported metal-catalyzed Alder-ene reaction of allenynes via metallacyclopentene intermediates to give cyclohexenyl compounds (eq 1). Only a limited number of reports are related to the synthesis of bicyclic carbocyclic products.[4,5] Cycloisomerization of allenynes is also catalyzed by platinum and gold complexes, via nucleophilic attack of the central allene carbon at the π-alkyne functionality.[6] 1,7-Allenyne substrates containing geminal dialkyl groups were cyclized with $PtCl_2$ or $AuCl_3$ catalysts to form bicyclo[4.3.0]nonadienes (eq 2); this interesting cyclization is restricted to terminal alkynes.[5a,b] Murakami reported[5c] that 1,6-allenynes underwent $PtCl_2$-catalyzed intramolecular [2+2]-cycloaddition to form bicyclo-[3.2.0]heptadienes; the initial intermediate involves a six-membered platinum carbene as depicted in eq 3. Herein, we report a new gold-catalyzed cyclization of 1,6-allenynes bearing internal alkynes, which provides new bicyclic carbocyclic compounds at 0 °C in a one-pot operation.

Results and Discussion

Before this investigation, Au(I)- and Pt(II)-catalyzed synthesis of bicyclo[4.3.0]nonadienes was restricted to *6-exo-dig*-cycliza-

(1) For selected examples, see: (a) Kusama, H.; Hara, R.; Kawahara, S.; Nishimori, T.; Kashima, H.; Nakamura, N.; Morihira, K.; Kuwajima, I. *J. Am. Chem. Soc*. **2000**, *122*, 3811. (b) Vázquez, A.; Williams, R. M. *J. Org. Chem*. **2000**, *65*, 7865. (c) Fuwa, H.; Ebine, M.; Bourdelais, A. J.; Baden, D. G.; Sasaki, M. *J. Am. Chem. Soc*. **2006**, *128*, 16989. (d) Artman, G. D.; Grubbs, A. W.; Williams, R. M. *J. Am. Chem. Soc*. **2007**, *129*, 6336.

(2) (a) Petit, M.; Aubert, C.; Malacria, M. *Tetrahedron* **2006**, *62*, 10582. (b) Petit, M.; Aubert, C.; Malacria, M. *Org. Lett*. **2004**, *6*, 3937. (c) Llerena, D.; Buisine, O.; Aubert, C.; Malacria, M. *Tetrahedron* **1998**, *54*, 9373. (d) Llerena, D.; Aubert, C.; Malacria, M. *Tetrahedron Lett.* **1996**, *37*, 7027. (e) Aubert, C.; Llerena, D.; Malacria, M. *Tetrahedron Lett.* **1994**, *35*, 2341.

(3) (a) Brummond, K. M.; Painter, T. O.; Probst, D. A.; Mitasev, B. *Org. Lett.* **2007**, *9*, 347. (b) Bayden, A. S.; Brummond, K. M.; Jordan, K. D. *Organometallics* **2006**, *25*, 5204. (c) Brummond, K. M.; Curran, D. P.; Mitasev, B.; Fischer, S. *J. Org. Chem.* **2005**, *70*, 1745. (d) Brummond, K. M.; Mitasev, B. *Org. Lett*. **2004**, *6*, 2245. (e) Brummond, K. M.; Chen, H.; Mitasev, B.; Casarez, A. D. *Org. Lett*. **2004**, *6*, 2161.

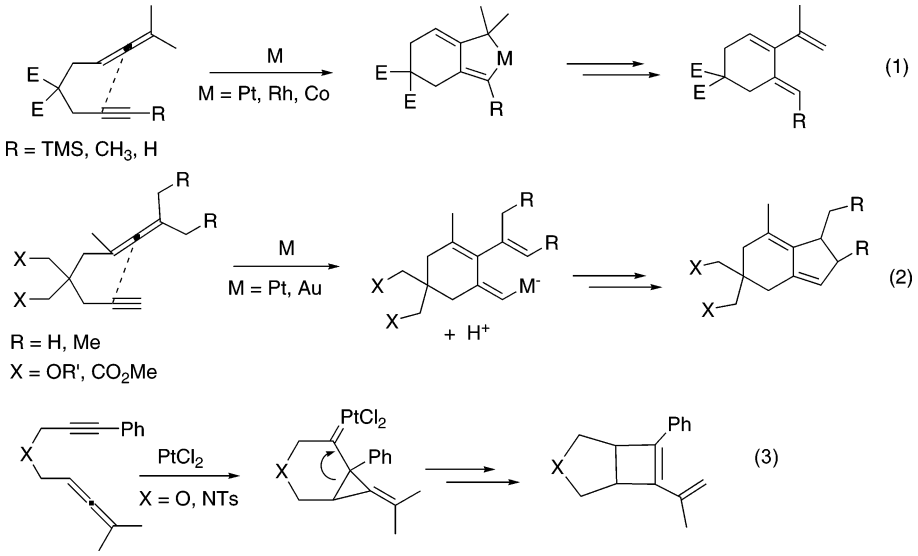
(4) Lee, S. I.; Sim, S. H.; Kim, S. M.; Kim, K.; Chung, Y. K. *J. Org. Chem.* **2006**, *71*, 7120.

(5) (a) Cadran, N.; Cariou, K.; Hervé, G.; Aubert, C.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *J. Am. Chem. Soc*. **2004**, *126*, 3408. (b) Lemiére, G.; Gandon, V.; Agenet, N.; Goddard, J.; de Kozak, A.; Aubert, C.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7596. (c) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Synlett* **2006**, 575.

(6) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *112*, 3737.

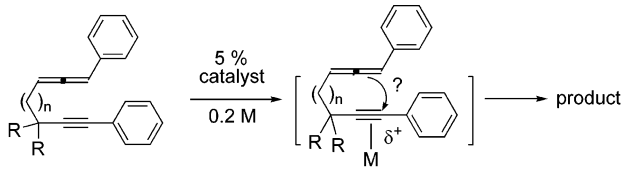
10.1021/jo0707939 CCC: $37.00
Published on Web 08/03/2007

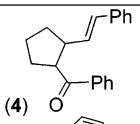
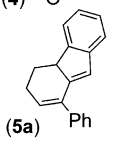
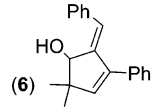
SCHEME 1



tion of 1,7-allenynes bearing a terminal alkyne (eq 2).[4,5] We sought to achieve catalytic cyclization of 1,*n*-allenynes ($n = 5$, 6, 7) via a distinct *n-endo-dig* cyclization of π-alkyne intermediates. We prepared three different 1,*n*-allenynes **1**, **2a**, and **3** to examine the chemoselectivity of this Au(I)-catalyzed cyclization reaction;[7] these substrates contain a phenylacetylene group because we envisage that the π-alkyne intermediate forms a hypothetical vinyl cation to direct the desired *n-endo-dig* cyclization,[8,9] as depicted in Table 1. Treatment of 1,7-allenyne **1** (0.2 M, entry 1) with $AuPPh_3OTf$ (5%) in wet dioxane at 100 °C gave cyclized ketone product **4** (trans/cis = 5.1) in 73% yield; we observed no reaction with 5% $AuPPh_3SbF_6$ catalyst in dry or wet CH_2Cl_2 (23 °C). In the case of 1,6-allenyne **2a** (entry 2), its $AuPPh_3SbF_6$-catalyzed cyclization in CH_2Cl_2 at 0 °C gave bicyclic product **5a** in 43% yield. The structure of compound **5a** was elucidated by ^1H NOE spectroscopy.[10] Treatment of 1,5-allenyne **3** (entry 3) with 5% $AuPPh_3OTf$ in wet CH_2Cl_2 at 23 °C gave cyclopentenol product **6** in 52% without formation of the desired bicyclo[3.3.0]octadiene. Formation of oxygen-containing compounds **4** and **6** requires water in an equimolar proportion, which is incompatible with the $AuPPh_3SbF_6$ catalyst because of its great sensitivity toward water.[7,11]

TABLE 1. Chemoselectivity for Gold-Catalyzed Cyclization of 1,*n*-Allenynes



entry	substrates	catalyst	condition	product	yield %[a]
1	n =2 R = H (**1**)	$AuClPPh_3$ AgOTf	dioxane (wet) 100°C, 36 h	 (**4**)	73[b]
2	n = 1 R = H (**2a**)	$AuClPPh_3$ $AgSbF_6$	CH_2Cl_2 0°C, 1.0 h	 (**5a**)	43
3	n = 0 R = Me (**3**)	$AuClPPh_3$ AgOTf	CH_2Cl_2 (wet) r.t.,12 h	 (**6**)	52

[a] Yields are reported after separation from a silica column. [b] Trans/cis ratio = 5.1

To optimize the condition given in entry 2 (Table 1), we tested the reactivity of 1,6-allenyne **2a** in the presence of various catalysts as depicted in Table 2. No reaction occurred in the presence of AuCl, $AuCl_3$, $AuClPPh_3$, and $AgSbF_6$ (5 mol % each) in CH_2Cl_2 at 23 °C (entries 1−4). The best results were observed by using $AuClPPh_3/AgSbF_6$ (5 mol %) with a dilute substrate concentration (0.02 M) at 0 °C to minimize the allenyne polymerization; the yield of desired compound **5a** was increased to 61% (entry 5). The use of $AuClPPh_3$/AgOTf (5 mol %) and $PtCl_2$ (10 mol %) in dioxane or toluene at 23 °C showed no trace of the desired reaction, but produced a mixture

(7) For selected examples to use PPh_3AuSbF_6 as catalysts see: (a) Genin, E.; Toullec, P. Y.; Antoniotti, S.; Brancour, C.; Genêt, J.-P.; Michelet, V. *J. Am. Chem. Soc*. **2006**, *128*, 3112. (b) Wang, S.; Zhang, L. *J. Am. Chem. Soc*. **2006**, *128*, 14274. (c) Mézailles, N.; Ricard, L.; Gagosz, F. *Org. Lett*. **2005**, *7*, 4133. (d) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402. (e) Luzung, M. R.; Markham, J. P.; Toste, F. D. *J. Am. Chem. Soc*. **2004**, *126*, 10858. (f) Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc*. **2004**, *126*, 15978. (g) Lin, C.-C.; Deng, T.-M.; Odedra, A.; Liu, R.-S. *J. Am. Chem. Soc.* **2007**, *129*, 3798.

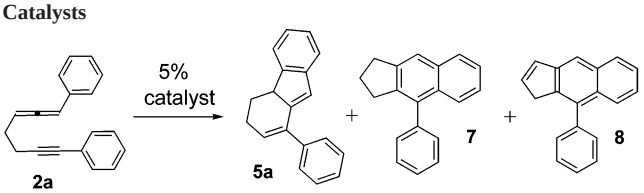
(8) For 5- or 6-*endo-dig* catalytic cyclization triggered by a π-phenylacetylene intermediate, see selected examples: (a) Harrison, T. J.; Patrick, B. O.; Dake, G. R. *Org. Lett*. **2007**, *9*, 367. (b) Zhao, J.; Hughes, C. O.; Toste, D. F. *J. Am. Chem. Soc.* **2006**, *128*, 7436. (c) Zhang, J.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 6704. (d) Zhang, L.; Kozmin, S. *J. Am. Chem. Soc.* **2005**, *127*, 6962. (e) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc*. **2003**, *125*, 10921. (f) Lian, J.-J.; Chen, P.-C.; Lin, Y.-P.; Ting, H.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2006**, *128*, 11372.

(9) Recent review for gold catalysis: (a) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (b) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6990. (c) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896. (d) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333. (e) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal*. **2006**, *348*, 2271.

(10) ^1H NOE map of key compounds and X-ray data of compound **5j** are provided in the Supporting Information.

(11) (a) Dubé, P.; Toste, F. D. *J. Am. Chem. Soc*. **2006**, *128*, 12062. (b) Lin, M.-Y.; Das, A.; Liu, R.-S. *J. Am. Chem. Soc*. **2006**, *128*, 9340.

TABLE 2. Catalytic Activity over Various Gold and Platinum Catalysts



entry	catalyst[a]	condition [alleneyne] = 0.2 M	5a	yield 7	8
1	AuCl[a]	CH_2Cl_2, 23 °C, 12 h		N.R.[e]	
2	$AuCl_3$[a]	CH_2Cl_2, 23 °C, 12 h		N.R.	
3	$AuClPPh_3$[a]	CH_2Cl_2, 23 °C, 12 h		N.R.	
4	$AgSbF_6$[a]	CH_2Cl_2, 23 °C, 12 h		N.R.	
5	$AuClPPh_3/AgSbF_6$[b]	CH_2Cl_2, 0 °C, 4.0 h[d]	61%	–	–
6	$AuClPPh_3/AgOTf$[b]	dioxane, 100 °C, 12 h	–	30%	5%
7	$PtCl_2$[c]	toluene, 100 °C, 2 h	–	25%	25%
8	$PtCl_2/CO$[c]	toluene, 100 °C, 2 h	24%	24%	12%

[a] 5 mol % catalyst. [b] 5 mol % Au and 5 mol % Ag catalysts. [c] 10 mol % $PtCl_2$. [d] [allenyne] = 0.02 M. [e] N.R. = no reaction.

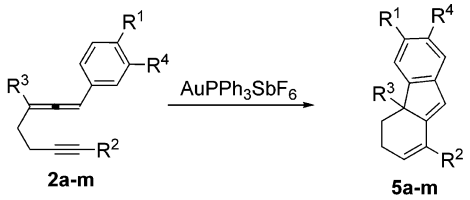
of [4+2]-cycloadduct **7** and its dehydrogenation derivative **8** in hot dioxane or toluene (entries 6 and 7). Structural elucidation of [4+2]-cycloadduct **8** relies on ^{1}H NOE spectroscopy.[10] The reaction with $PtCl_2$/CO in hot toluene (10 mol %, 100 °C) gave [4+2]-cycloadducts **7** (24%) and its dehydrogenated form **8** (12%) in addition to desired product **5a** (24%).

With optimal conditions (5% PPh_3AuSbF_6, 0.02 M substrate, CH_2Cl_2, 0 °C), the scope of this reaction was studied thoroughly. Table 3 shows the results with various 1,6-allenynes (**2b**−**m**) via alteration of the alkynyl phenyl R^2, and the allenyl R^1, R^3, and R^4 substituents. Entries 1−5 show 1,6-allenynes **2b**−**f** with their alkynyl and allenyl groups bearing phenyl, 4-methylphenyl, 4-fluorophenyl, and naphthyl substituents; the resulting bicyclo-[4.3.0]nonadienes **5a**−**f** were obtained in reasonable yields (52−65%). However, when the alkyne contained an electron-rich 4-methoxyphenyl or when both the terminal allene and alkyne groups contained a 4-fluorophenyl group as in compounds **2g** and **2h**, respectively, the corresponding cyclized products **5g** and **5h** were obtained in low yields (26−42%). The allenyl C(3)-substituent R^3 plays an important role for the reaction; a methyl or butyl group not only maintained the good yields (70−81%), but also reduced the duration of reaction (0.5 h, entries 8−12). When a 3-methoxyphenyl group was introduced at the C(1)-allene carbon of compound **2m** (entry 12), an 81% yield was obtained. An X-ray diffraction study of product **5j** has been performed to confirm the bicyclo[4.3.0]nonadiene framework (see the Supporting Information).

The synthetic utility of this new cyclization is also manifested by its applicability to 1,6-allenynes **2n**−**o** bearing an alkenyl group at the allenyl C(1)-carbon. The gold-catalyzed cyclization of these two allenynes at 0 °C proceeded smoothly to give bicyclo[4.3.0]nonatrienes **5n** and **5o** in 65% and 61% yields, respectively.

We performed deuterium-labeling experiments to elucidate the reaction mechanism (Scheme 3). Cyclization of **d_5-2a** bearing a C_6D_5 group with $AuPPh_3SbF_6$ (5 mol %) produced the desired **d_4-5a** with its vinyl deuterium content X = 0.61 D;

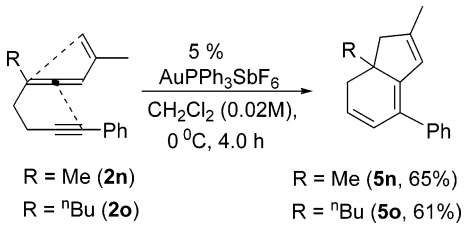
TABLE 3. Au(I)-Catalyzed Cyclization of 1,6-allenynes



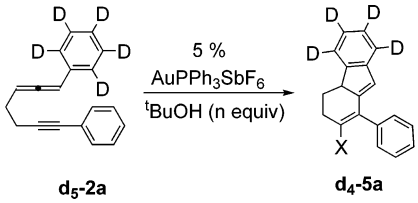
entry	allenynes[a]	R^1	R^2	R^3	R^4	products (%[b])
1	**2b**	H	4-MeC_6H_4	H	H	**5b** (57)
2	**2c**	H	4-FC_6H_4	H	H	**5c** (60)
3	**2d**	H		H	H	**5d** (52)
4	**2e**	Me	Ph	H	H	**5e** (61)
5	**2f**	Me	4-MeC_6H_4	H	H	**5f** (62)
6	**2g**	H	4-$MeOC_6H_4$	H	H	**5g** (26)
7	**2h**	F	4-FC_6H_4	H	H	**5h** (42)
8	**2i**	H	Ph	Me	H	**5i** (73)
9	**2j**	F	Ph	Me	H	**5j** (72)
10	**2k**	OMe	Ph	Me	H	**5k** (70)
11	**2l**	H	Ph	Bu	H	**5l** (71)
12	**2m**	H	Ph	Me	OMe	**5m** (81)

[a] 5.0% $AuClPPh_3$, 5.0% $AgSbF_6$, CH_2Cl_2 (0.02 M, 0 °C), 4 h for entries 1−7 and 0.5 h for entries 8−12. [b] Isolated yields are given after column chromatography.

SCHEME 2



SCHEME 3

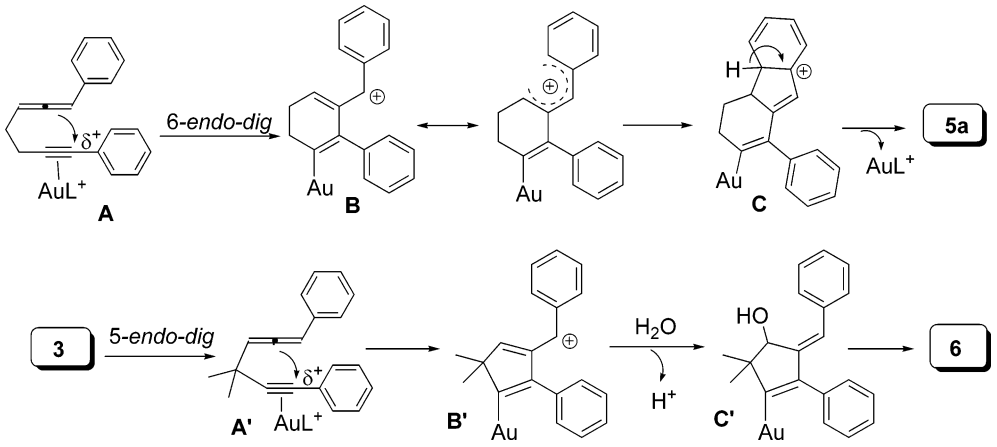


^{t}BuOH	d_4-5a
n = 0	X = 0.61 D
n = 1	X = 0.35 D

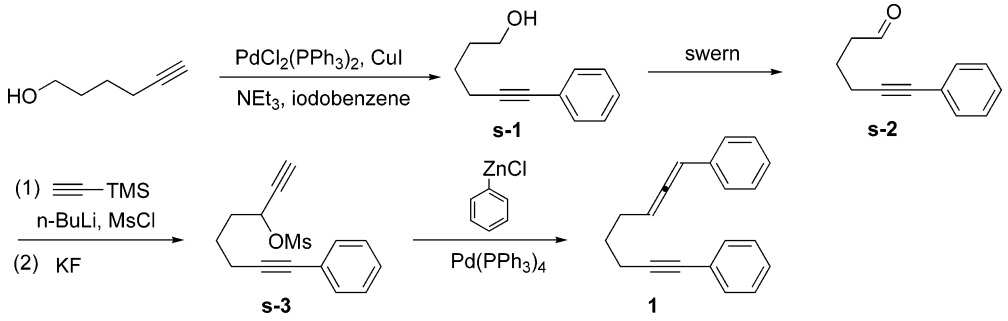
in the presence of ^{t}BuOH, this deuterium content is decreased to 0.35 D. This information indicates that a protodeauration is likely to occur at this vinyl carbon.

Scheme 4 shows a proposed mechanism to account for the chemoselectivity in the formation of bicyclo[4.3.0]nonadiene **5a** and cyclopentol **6**. We envisage that these two products arise from π-alkyne intermediates **A**, in which a partial positive character resides at the ≡*C*Ph carbon to induce a 6-*endo*-*dig* attack of the allene group to form allyl cation **B**. An extensive delocalization of species **B** is highly suitable for Nazarov

SCHEME 4



SCHEME 5



cyclization,[12,13] and leads ultimately to observed bicyclo[4.3.0]-nonadiene **5a**. This hypothetical mechanism is supported not only by our deuterium-labeling experiments, but also by the formation of cyclopentenol **6**, which follows a similar pathway to form allyl cation **B′**. Nazarov cyclization of species **B′** encounters difficulty because the expected bicyclo[3.3.0]-octadiene framework is too strained to form.[14,15]

In summary, we have reported a new efficient PPh_3AuSbF_6-catalyzed cyclization of 1,6-allenynes to generate bicyclo[4.3.0]-nonadienes chemoselectively under 0 °C. The mechanism of this new cyclization has been investigated,[16] and is proposed to proceed through a tendem 6-*endo-dig*/Nazarov cyclization of Au(I)-π-alkyne intermediates. The utility of this reaction is manifested by its applicability to various 1,6-allenynes, and the utilization of this synthetic method toward bioactive molecules is under current investigation.

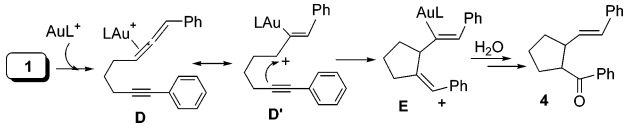
Experimental Section

(I) Experimental procedures for synthesis of the substrates. (1) Synthesis of 1,8-Diphenyl-1,2-octadien-7-yne. (a) Synthesis of 6-Phenylhex-5-yn-1-ol (s-1). To a triethylamine solution (30 mL) of iodobenzene (2.49 g, 12.2 mmol) was added $Pd(PPh_3)_2Cl_2$ (71.7 mg, 0.10 mmol) and CuI (38.0 mg, 0.2 mmol) at 28 °C, and the mixture was stirred for 5 min before addition of hex-5-yn-1-ol (1.00 g, 10.2 mmol). The resulting mixture was stirred for 12 h, and the solvent was removed in vacuo and treated with a saturated $NaHCO_3$ solution. The solution was extracted with ethyl acetate, washed with a saturated NaCl solution, and dried over anhydrous $MgSO_4$. The residues were chromatographed through a silica gel column (hexane: ethyl acetate/4:1) to afford compound **s-1** (1.37 g, 7.9 mmol, 77%) as a yellow oil.

(12) Nazarov, I. N.; Torgov, I. B.; Terekhova, L. N. *Izv. Akad. Nauk. SSSR Otd. Khim. Nauk* **1942**, 200.

(13) (a) Janka, M.; He, W.; Haedicke, I. E.; Fronczek, F. R.; Frontier, A. J.; Eisenberg, R. *J. Am. Chem. Soc.* **2006**, *128*, 5312−5313. (b) Malona, J. A.; Colbourne, J. M.; Frontier, A. J. *Org. Lett.* **2006**, *8*, 5661−5664.

(14) Formation of cyclopentyl phenyl ketone **4** is thought to arise from Au(I)-π-allene intermediate, which initiates a 5-*exo-trig* cyclization to form vinyl cation **E**, and ultimately producing desired ketone **4** upon water attack. The uncommon feature of this cyclization is the nature of the Au(I)-π-allene intermediate, which is characterized also by resonance structure **D′** such that an intramolecular attack occurs at the terminal allene carbon



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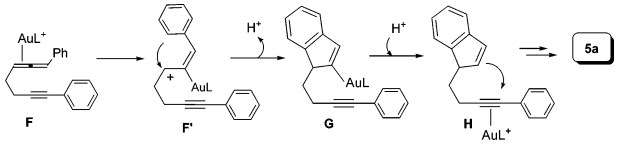
(15) For catalytic cyclization via a π-allene intermediate, see: (a) Lee, J. H.; Toste, F. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 912. (b) Funami, H.; Kusama, H.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 909. (c) Nishina, N.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3314. (d) Gockel, B.; Krause, N. *Org. Lett.* **2006**, *8*, 4485. (e) Wang, S.; Zhang, L. *Org. Lett.* **2006**, *8*, 4585. (f) Hashmi, A. S. K.; Schwartz, L.; Choi, J.-H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2285. (g) Hashmi, A. S. K.; Blanco, M. C.; Fischer, D.; Bats, J. W. *Eur. J. Org. Chem.* **2006**, 1387.

(16) According to recent Au(I)-π-allene chemistry,[15] one alternative mechanism involves initial Nazarov cyclization, followed by *6-endo-dig* cyclization of π-alkyne **H** as depicted below; the initial intermediate is Au-(I)-π-allene intermediate **F′**, which activates indene formation to give species **G**. After protodeauration, a subsequent 6-*endo-dig* cyclization of alkyne intermediate **H** provides the desired bicyclo[4.3.0]nonadiene **5a**. This pathway, however, is opposed by formation of cyclopentol **6**, which indicates initial formation of a cyclopentene ring rather than the indene ring.

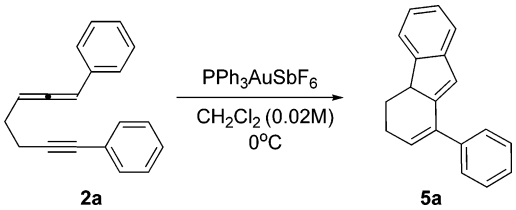


(b) Synthesis of 6-Phenylhex-5-ynal (s-2). To a dichloromethane solution of oxalyl chloride (1.50 g, 11.8 mmol) was carefully added DMSO (1.84 g, 23.6 mmol) at −78 °C. After 30 min, a dichloromethane solution of compound **s-1** (1.71 g, 9.8 mmol) was injected, and the reaction mixture was stirred for 1 h before addition of triethylamine (5.00 g, 49 mmol). The reaction mixture was warmed to room temperature, and the solution was extracted with dichloromethane, washed with water, dried over $MgSO_4$, and concentrated under reduced pressure. The residues were purified by passing through a short silica pad to afford compound **s-2** (1.57 g, 9.1 mmol, 93%) as a yellow oil.

(c) 1-(1-Ethynyl)-6-phenyl-5-hexynyl Methanesulfonate (s-3). To a mixture of trimethylsilyl acetylene (1.14 g, 11.6 mmol) and THF (20 mL) was added n-BuLi (2.5 M in hexanes, 3.0 mL, 7.5 mmol) dropwise at −78 °C, and the mixture was stirred for 30 min before addition of compound **s-2** (1.00 g, 5.8 mmol). After 3 h at room temperature, this solution was treated with MsCl (2.00 g, 17.4 mmol), and the mixture was stirred for 1 h before addition of a methanol solution of KF (461 mg, 7.95 mmol). The resulting mixture was stirred for 1.0 h, quenched by addition of water, and extracted with ethyl acetate. The extract was washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residues were chromatographed through a silica gel column (hexane:ethyl acetate/10:1) to afford compound **s-3** (1.86 g, 4.77 mmol, 82%) as colorless oil.

(d) Synthesis of 1,8-Diphenylocta-1,2-dien-7-yne (1). To a THF solution of phenylmagnesium bromide (181 mg, 1.0 mmol) was added $ZnCl_2$ (1.0 M in THF, 1.0 mL, 1.0 mmol) dropwise at 0 °C, and the resulting mixture was stirred for 1.0 h before adding $Pd(PPh_3)_4$ (4.6 mg, 0.004 mmol) and compound **s-3** (312 mg, 0.8 mmol). The resulting mixture was then stirred for 1.0 h before being warmed to room temperature, and the solvent was removed in vacuo and treated with a saturated $NaHCO_3$ solution. The solution was extracted with diethyl ether, washed with a saturated NaCl solution, and dried over anhydrous $MgSO_4$. The residues were chromatographed through a silica gel column (hexane) to afford compound **1** (155 mg, 0.6 mmol, 75%) as a colorless oil. IR (neat, cm^{-1}) 3082 (m), 2210 (w), 1963 (s), 1598 (m), 1495 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.35 (m, 2H), 7.29 (t, J = 8.0 Hz, 4H), 7.27−7.24 (m, 3H), 7.18 (t, J = 8.0 Hz, 1H), 6.17−6.15 (m, 1H), 5.60 (q, J = 6.4 Hz, 1H), 2.48 (t, J = 7.2 Hz, 2H), 2.34−2.28 (m, 2H), 1.83−1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 134.9, 131.5 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 127.5, 126.7, 126.6 (2 × CH), 123.9, 95.0, 94.2, 89.6, 81.0, 28.0, 27.8, 18.9; HRMS calcd for $C_{20}H_{18}$ 258.1409, found 258.1410.

(II) A Procedure for Catalytic Cyclization of 1,7-Diphenyhepta-1,2-dien-6-yne. (a) Synthesis of 1-Phenyl-4,4a-dihydro-*3H*-fluorene (5a). A solution of PPh_3AuSbF_6 (5 mol %) was



prepared by mixing PPh_3AuCl (9.9 mg, 0.02 mmol) and $AgSbF_6$ (6.9 mg, 0.02 mmol) in dichloromethane (2.0 mL). The mixture was stirred for 10 min before addition of excess dichloromethane (18 mL). To the resulting mixture was added compound **2a** (100 mg, 0.41 mmol) dropwise at 0 °C and the solution was stirred for 4.0 h before warming to room temperature. The resulting solution was filtered through a celite bed and eluted through a silica gel column (hexane) to give compound **5a** (56 mg, 0.23 mmol, 61%) as a colorless oil. IR (neat, cm^{-1}) 2875 (s), 1648 (w), 1522 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48−7.43 (m, 3H), 7.38 (t, J = 6.8 Hz, 2H), 7.34−7.28 (m, 2H), 7.26−7.22 (m, 1H), 7.17 (t, J = 7.2 Hz, 1H), 6.55 (s, 1H), 6.00−5.98 (m, 1H), 3.49 (dd, J = 13.8 Hz, 4.0 Hz, 1H), 2.63−2.54 (m, 3H), 1.45−1.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.5, 145.0, 140.2, 136.8, 128.8, 128.3 (2 × CH), 127.9 (2 × CH), 127.3, 126.8, 124.4, 124.2, 122.6, 121.0, 48.6, 27.7, 27.5; HRMS calcd for $C_{19}H_{16}$ 244.1252, found 244.1253.

Acknowledgment. The authors wish to thank the National Science Council, Taiwan for supporting this work.

Supporting Information Available: Experimental procedures including synthesis of allenyne **3**, spectra data for compounds **1**−**8**, **2a**−**o**, and **5a**−**o**, and X-ray data for compound **5j**; copies of ^1H and ^{13}C NMR spectra for compounds **1**−**8**, **2a**−**o**, and **5a**−**o**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0707939